

Process Economics Program

Report 31C

Advances in Adiponitrile (ADN) and Hexamethylenediamine (HMDA) Processes

By Anthony Pavone



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Abstract

Hexamethylenediamine (HMDA) and adiponitrile (ADN) are intermediate monomers used in the production of nylon 66, which is a copolymer of HMDA and adipic acid (ADA). Nylon 66 was historically used primarily to form carpet fibers used in high quality rugs for residential applications and in fibers for clothing. More recently, nylon 66 has been used as an engineering resin in demanding high-temperature automotive ‘under the hood’ applications such as linings for hydraulic brake lines, cable and wire insulation, and molded parts such as radiator housings.

Nylon 66 competes in most end-use applications with nylon 6, which is produced as a homopolymer of caprolactam. Nylon 66 has better thermal properties than nylon 6 in most end-use applications, but is perceived to be more expensive to produce than nylon 6. Adiponitrile is an intermediate product made in the integrated HMDA process, which is converted to HMDA via hydrogenation.

The three commercial manufacturing routes to HMDA are from butadiene via hydrocyanation (Invista/DuPont), from acrylonitrile via electrohydrodimerization (Ascend/Monsanto), and from adipic acid via ammoniation. All routes produce adiponitrile as an intermediate product, which is then hydrogenated to produce HMDA.

Invista, a company owned by Koch Industries that absorbed the nylon 66 business that Koch purchased from DuPont, announced new process technology in 2012 for producing HMDA and ADN, and also announced that these new technologies will be commercialized in a grassroots complex planned for China. The technologies have been commercialized at Invista’s existing plants in Texas (Orange and Victoria) via revamp. The new HMDA plant will be located in Shanghai. It will have an initial production capacity of 215 kty, and it is scheduled for commercial start-up in 2015. Invista claims the new process will produce substantially less benzene by-products than its conventional butadiene-based HMDA process, while being 30% more energy efficient.

Ascend Performance Products, which was formed from the original Monsanto nylon 66 business, produces adiponitrile via the electrohydrodimerization of acrylonitrile. Its conventional HMDA process has seen modest technology improvements as documented in the patent literature.

Rennovia (Menlo Park, California, USA) announced in 2013 a new bio-based route to HMDA. If combined with Rennovia’s existing bio-based route to adipic acid, nylon 66 can then be produced from 100% bio-based materials.

In this report we present our understanding of the current technology for producing adiponitrile and hexamethylenediamine used by Invista and Ascend, as well as the bio-based process being developed by Rennovia. This effort updates the previous IHS Chemical PEP series covering HMDA and ADN in reports 31, 31A, and 31B.

We will examine the patent and trade literature and present our understanding of the process technology commercially employed and the corresponding production economics for making HMDA and adiponitrile.

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1. Introduction

What are adiponitrile and hexamethylenediamine?

Adiponitrile (ADN) and hexamethylenediamine (HMDA) are intermediate organic monomers used primarily in the production of nylon 66, a large commercial volume polyamide.

ADN (CAS: 111-69-3) is a C₆ linear molecule with cyanide groups (CN) on each terminal carbon atom. Its molecular formula is (CH₂)₄(CN)₂ and its molecular weight is 108.14. At ambient conditions it is a clear liquid with high viscosity.

HMDA (CAS: 124-09-4) is a linear C₆ molecule with amine groups (NH₂) on both terminal carbon atoms. Its molecular formula is H₂N(CH₂)₆NH₂ and its molecular weight is 116.2. At ambient conditions, HMDA is a colorless or slightly yellow solid with a strong amine odor.

Alternate nomenclature for ADN and HMDA are presented in the table below.

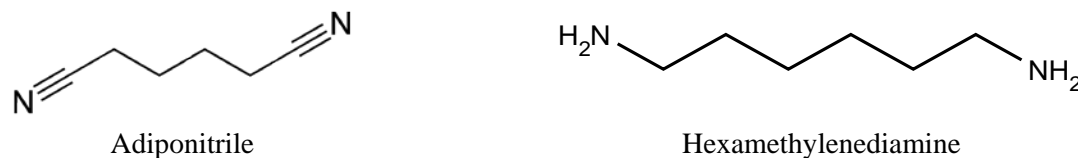
Table 1.1: Nomenclature for ADN and HMDA

Adiponitrile	Hexamethylenediamine
Adipic acid dinitrile	80HMD
Adipic acid nitrile	Advancure
Adipic dinitrile	1,6-Diaminohexane
Adipinsaeuredinitril	1,6-Diamino-n-hexane
Adipodinitrile	Hexamethylendiamin
Adiponitril	Hexamethylene diamine
Adiponitrile	Hexamethylenediamine
Adiponitrilo	Hexametilendiamina
Butane, 1,4-dicyano-	1,6-Hexanediamine
Butanedicarbonitrile	α,ω-Hexanediamine
1,4-Dicyanobutane	Hexane-1,6-diamine
Hexanedinitrile	Hexylenediamine
NSC 7617	1,6-Hexylenediamine
Tetramethylene cyanide	Hi perm
UN 2205	HMDA
	NSC 9257
	UN 1783
	UN 2280
	V 1

Molecular structure

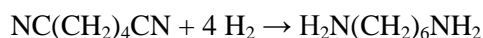
The molecular structures of ADN and HMDA are shown in the figure below. The fact that both molecules have active radical groups on both terminal carbon atoms makes it relatively easy to react these molecules with other suitable molecules to form larger monomers and polymers. Most commercial routes to HMDA produce ADN as an intermediate product. Both CN terminal groups in ADN are bonded to the adjacent carbon atoms with triple bonds. When ADN is hydrogenated, two hydrogen atoms react at the CN site to saturate the triple bond to form the amine group C-NH₂.

Figure 1.1: Molecular structure of ADN and HMDA



Hydrogenation of adiponitrile to form HMDA

ADN is produced commercially using Invista/DuPont technology via the hydrocyanation of butadiene, while ADN was originally produced commercially by Monsanto (now Ascend Performance Materials) by the electro-dimerization of acrylonitrile. ADN can also be produced from adipic acid. In both commercial cases, ADN is easily converted to HMDA via hydrogenation using cobalt, nickel, and/or iron catalysts. The reaction chemistry for hydrogenating adiponitrile to HMDA is presented below.

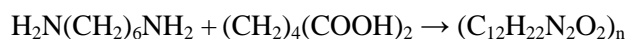


Unfortunately, the ADN hydrogenation reaction is not very selective, producing by-products 1,2-diaminocyclohexane, hexamethyleneimine, and the triamine bis(hexamethylenetriamine).

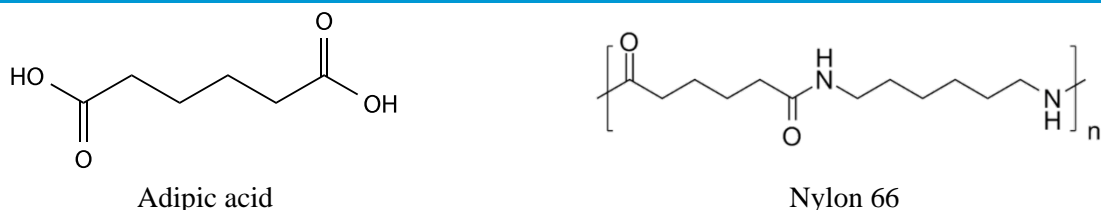
Reaction to form nylon 66

Most HMDA is consumed commercially by reaction with adipic acid to produce nylon 66. Adipic acid is a C₆ dicarboxylic acid with carboxylic acid groups on both terminal carbon atoms.

Nylon 66 [(C₁₂H₂₂N₂O₂)_n or CAS: 32131-17-2] is formed by copolymerization when the two amine (NH₂) groups on each HMDA molecule react with the two carboxylic acid groups (COOH) on adipic acid molecules to form the corresponding amide group (O=C-NH₂-), in which the oxygen atom is bonded to the carbon atom via a double bond. The reaction stoichiometry for producing nylon 66 is shown below.



The molecular structures of adipic acid and nylon 66 are presented in the figure below.

Figure 1.2: Molecular structure of adipic acid and nylon 66

Commercial uses for ADN and HMDA

Nearly all of the commercial production of ADN is consumed in nylon 66 production, with a small proportion of ADN production used as a powerful polar solvent. Small quantities of ADN are used in the following applications:

- Extraction solvent for fatty acids, oils and unsaturated hydrocarbons
- Solvent for spinning and casting and extractive distillation based on its selective miscibility with organic compounds
- Removing agent of coloring matters and aromatic alcohols
- Non-aqueous solvent for titrations and for inorganic salts
- Recrystallization of steroids
- Parent compound for organic synthesis
- Solvent or chemical intermediate in biochemistry (DNA sequencing and pesticidesynthesis)
- High-pressure liquid chromatographic analysis solvent
- Catalyst and component of transition-metal complex catalysts
- Stabilizer for chlorinated solvents
- Chemical intermediate and solvent for perfumes and pharmaceuticals

In addition to its use as comonomer in the production of nylon 66, HMDA is used as an additive in organic coatings, curing agents for epoxies, oilfield chemicals, in adhesives and inks, and also in water treatment chemicals and corrosion protection products.

In 1998, BASF developed a process and operated a large pilot plant that produced caprolactam from adiponitrile. BASF produces conventional caprolactam (from KA oil) commercially to make nylon 6. It was BASF's intent at the time to form a joint venture with DuPont to produce nylon 6 in China, for which DuPont would supply the technology and capital to produce adiponitrile from butadiene, and BASF would convert the adiponitrile to caprolactam for nylon 6 production.

Commercial uses for nylon 66

Nylon 66 was initially commercialized by DuPont in the 1930s, and soon thereafter by ICI [31C01]. Initial uses were as a fiber in clothing, military parachutes, and rope, and later as molded and extruded plastic parts for automobiles where its combination of high-temperature stability, corrosion resistance, and wear resistance were superior to steel and other thermoplastics. HMDA, as one of the two

components required to make nylon 66, was used exclusively and captively as a nylon 66 feedstock until other applications in polyurethane formulations were developed by Bayer in the 1960s.

Nylon 66 is used in both fiber and resin form. The main uses of nylon 66 fiber are for carpets, tire cord, textile yarns, and hosiery. The fiber form is produced both as a monofilament and as a bulk staple fiber. Nylon 66 is usually formed into automotive parts by injection molding, and also extruded into sheet and film. Nylon 66 is also extruded as a coating for high-temperature wire and cable.

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

Table 1.2: 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
Swimwear	Industrial machinery coatings
Auto airbags	Electric and electronic parts
	Film
	Wire and cable insulation
	Hydraulic hose linings

The 2012 global production of nylon 66, HMDA and ADN is shown in the table below.

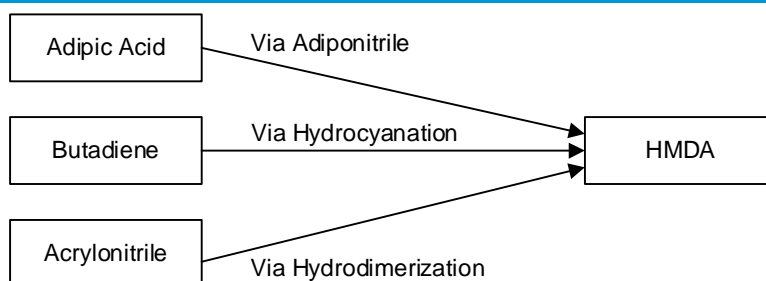
Table 1.3: Estimated 2012 production of nylon 66 and precursors

CAS number	Chemical	Kty
32131-17-2	Nylon 66	1,800
124-09-4	HMDA	1,225
111-69-3	ADN	1,245

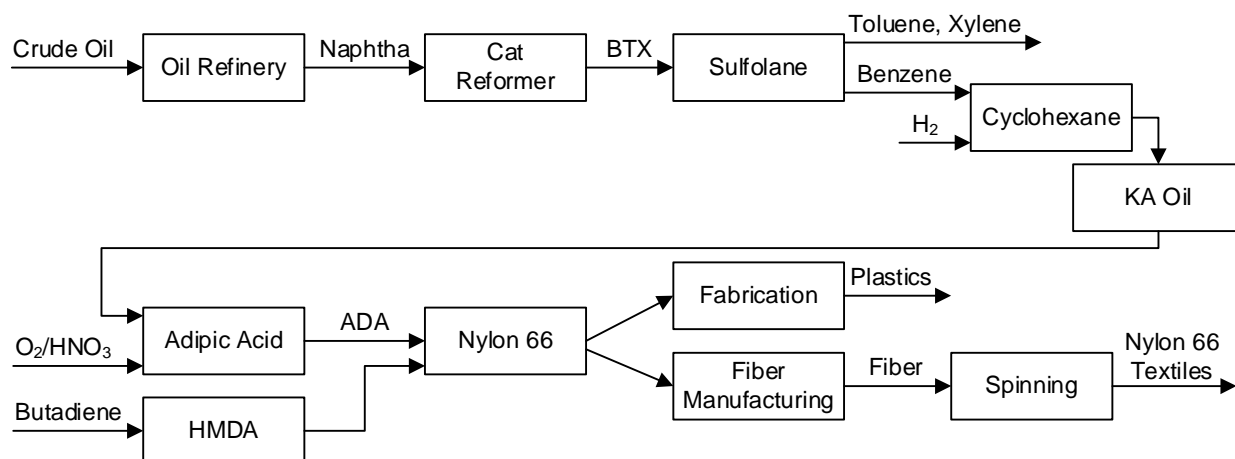
Source: IHS Chemical Economics Handbook

Nylon 66 integrated product chain diagram

The integrated product chain for both ADN and HMDA starts with petroleum crude oil. ADN is produced commercially from butadiene and from acrylonitrile, and in the past has also been produced from adipic acid. The chemical routes to HMDA are shown in the figure below.

Figure 1.3: HMDA commercial routes

The various intermediates produced along the route to nylon 66 are shown in the figure below.

Figure 1.4: Nylon 66 integrated product chain diagram

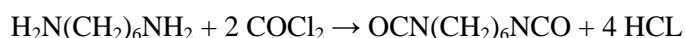
Physical properties of ADN and HMDA

ADN is a thick odorless and colorless liquid at ambient conditions. Due to its highly polar nature, ADN is soluble in polar solvents such as alcohols (methanol, ethanol), chlorinated hydrocarbons (trichloroethylene), and aromatics (benzene, toluene, xylenes). However, ADN has only slight solubility in covalent solvents like ethers, and pure aliphatic solvents (hexane, heptane). Physical properties of ADN are presented in the table below.

Table 1.4: Adiponitrile physical properties

CAS number	111-69-3
Molecular formula	C ₆ H ₈ N ₂
Physical state	Liquid at 20°C and atmospheric pressure
Color	Colorless
Odor	Odorless
Molar mass	108.14 g mol ⁻¹
Appearance	Colorless liquid
Density liquid	951 mg mL ⁻¹
Density vapor to air	3.7
Melting point	1–3°C, 274–276 K, 34–37°F
Boiling point	295°C, 568.2 K, 563°F
Solubility in water	50 g/L (20°C)
Vapor pressure	300 mPa (at 20°C)
Refractive index (nD)	1.438
Standard enthalpy of formation $\Delta_f H^\circ_{298}$	84.5–85.3 kJ mol ⁻¹
Freezing point	34°F
Solubility in water	4.50%
Lower explosion limit	1.70%
Upper explosion limit	5.00%
Flash point	163°C at atmospheric pressure
Autoignition temperature	550°C
Explosive properties	Non explosive
Self-ignition temperature	475°C at atmospheric pressure
Octanol water partition coefficient (log K _{ow})	-0.32 at 25°C
Critical temperature	507°C
Critical pressure	2.76 MPa
Viscosity	4.905 g/s ² (30°C)
Refractive index	1.4363 (20°C)
Partition coefficient, pK _{ow}	-0.32
Heat of vaporization	76.1 kJ/mol 240 Btu/lb
Heat of combustion	-4,369 kJ/mol 14,230 Btu/lb (neg)

HMDA is a solid diamine at ambient conditions, with a fish odor. When dissolved in water, HMDA is a strong base that forms strong salts in both organic acids and inorganic acids. When the acid used is adipic acid, nylon salt (called AH salt) is formed. HMDA also reacts at industrial scale with phosgene to form hexamethylene diisocyanate.

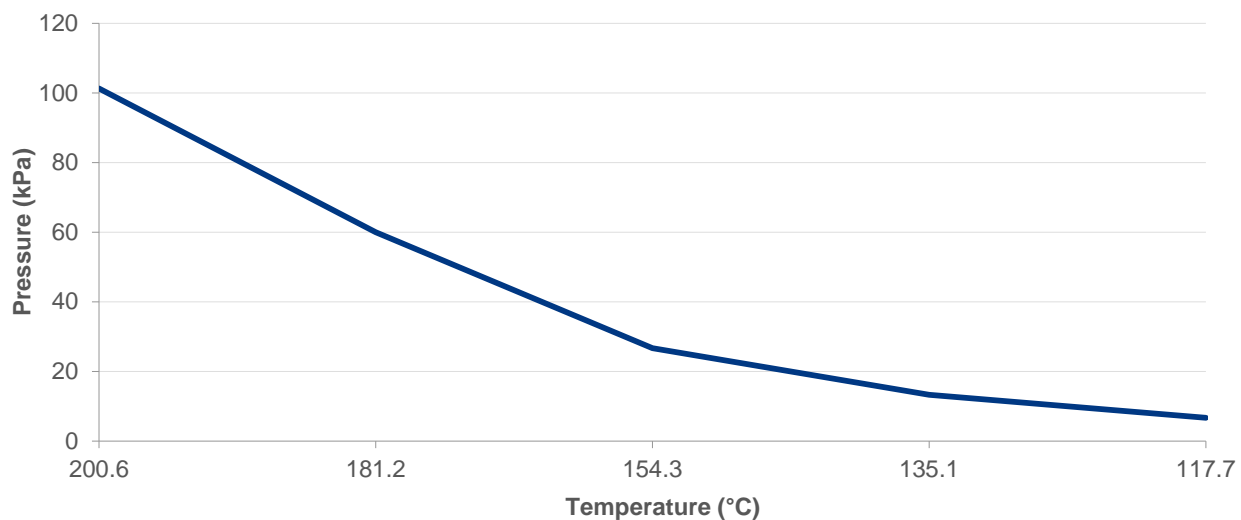


HMDA is very soluble in water and other polar solvents, and nearly insoluble in covalent solvents like aliphatic hydrocarbons and ethers. Physical properties of HMDA are shown in the table below.

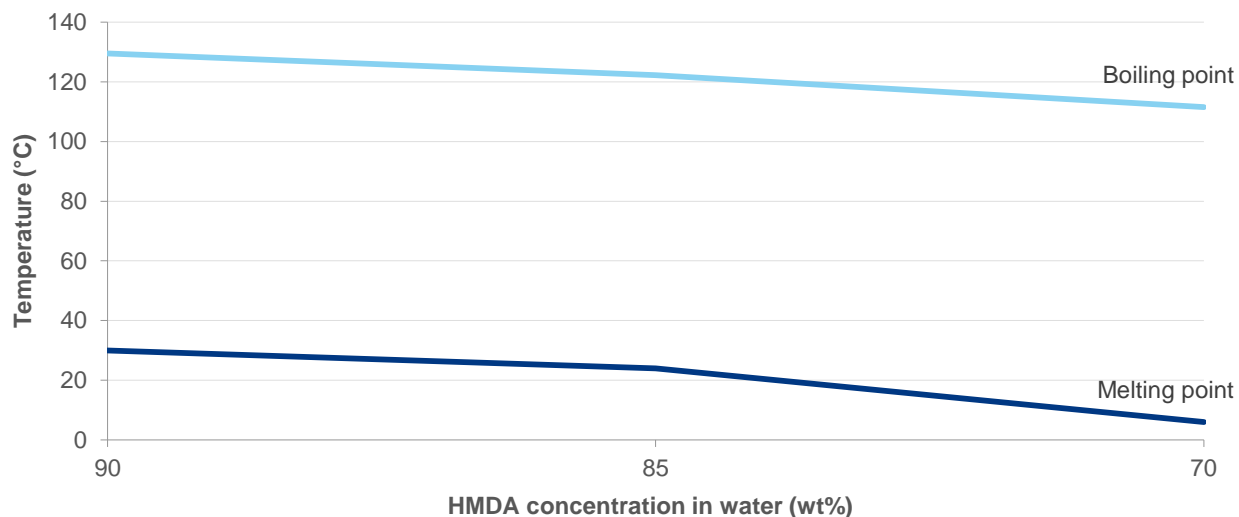
Table 1.5: Physical properties of HMDA

CAS number	124-09-4
Molecular formula	C ₆ H ₁₆ N ₂
Molar mass	116.20 g mol ⁻¹
Appearance	Colorless crystals
Density	0.84 g/mL
Melting point	39–42°C, 312–315 K, 102–108°F
Boiling point	205°C, 477.7 K, 400°F
Solubility in water	490 g L ⁻¹
Solubility in 100g H ₂ O (30°C)	960 gm
log P	0.386
Standard enthalpy of formation $\Delta_f H_{298}^\circ$	-205 kJ mol ⁻¹
Flash point	80°C
Explosive limits	0.7–6.3%
LD ₅₀	750 mg kg ⁻¹ (oral, rat) 1.11 g kg ⁻¹ (dermal, rabbit)
Autoignition temperature	550°C
Dissociation constant (water, 20°C)	
pK ₁	11.11
pK ₂	10.11
Heat of combustion (25°C)	40,208 kJ/kg
Specific heat capacity, c _p (solid)	2.85 kJ/kg-°K
Melting point of water eutectic (53% H ₂ O)	-20°C
Heat of solution in water, J/gm	
90% solution	56
85% solution	71
70% solution	112
Infinite dilution	245

As a solid at room temperature, HMDA has very low vapor pressure at standard conditions. Its vapor pressure only begins to increase appreciably above 150°C. HMDA's vapor pressure curve, as a function of temperature, is presented in the figure below.

Figure 1.5: HMDA vapor pressure curve

Aqueous solution properties (boiling point and melting point) of HMDA are presented in the figure below.

Figure 1.6: HMDA solution properties in water

Process safety

Adiponitrile and hexamethylenediamine are both organic chemical monomers, and are therefore combustible. Precautions should be taken to keep the temperature below ignition temperatures, and avoid contact with open flames or other potential sources of ignition. Pressurized vessels containing ADN or HMDA should be designed and manufactured to conform to ASME pressure code standards, and be equipped with multiple automatic pressure relief valves venting to a safe disposition such as a process flare header. ADN and HMDA should be stored in containers located in a cool and dry place, and designed to avoid direct air contact.

Adiponitrile

Although ADN is a chemically stable, low vapor pressure organic chemical, it will ignite in the presence of an open flame. Water spray, dry chemical, or CO₂ are effective for fighting ADN fires. If an ADN fire occurs, the combustion is likely to release hydrogen cyanide (HCN), which is a highly toxic gas. In this instance, firefighters should be equipped with artificial respirators, in addition to normal firefighting protective clothing. ADN is also corrosive, requiring suitable materials of construction.

ADN, being a dicyanide, is a skin and mucous membrane irritant when placed in human contact. Skin contact can often result in blistering and inflammation. Eye contact can result in reddening, watering and itching. ADN may be toxic if ingested, inhaled, or absorbed through the skin. ADN is not believed to be carcinogenic or mutagenic. ADN is toxic to blood, kidneys, lungs, and liver.

Hexamethylenediamine

HMDA is a solid at room temperature, with low potential for flammability under this condition. Its melting point is 42°C, and its boiling point is 204°C. HMDA is extremely hazardous in cases of skin or eye contact. Contact is most likely to occur from solutions of HMDA. Contact with skin, eyes, or mucous membranes is likely to cause irritation, but prolonged or high concentration exposure will cause tissue damage. Severe eye contact is likely to cause corneal damage or blindness. HMDA is not thought to be carcinogenic or mutagenic.

In liquid form, HMDA is corrosive, requiring the use of suitable materials of construction. HMDA is toxic to blood, kidneys, lungs, and liver.

Small HMDA fires should be extinguished with dry chemical powder. Large HMDA fires should be extinguished with water spray, fog, or foam. Water jets should not be used on large fires.

Hydrogen

Since large commercial production of HMDA uses chemistry that first produces ADN, which is subsequently hydrogenated to HMDA, hydrogen is present in large quantities and at high pressure in commercial HMDA production plants. Hydrogen is a stable but very light gas, with extremely high flammability and low ignition temperature.

Exposure to high concentration hydrogen can cause lung damage. Hydrogen is not known to be carcinogenic or mutagenic. Rapid depressuring of hydrogen will create unusually low temperatures that could cause cold burns (frostbite) to skin and eyes. Hydrogen also creates a risk of suffocation to persons exposed in a confined space.

The hydrogenation reactor that converts ADN to HMDA is highly exothermic, creating the potential for a runaway reaction that could lead to a high temperature over-pressure condition that can cause an explosion. The hydrogenation reactor design should be provided with multiple pressure safety valves, and temperature sensors along the axis of the reactor (both internally and on the periphery) to sense for thermal runaway conditions. In most cases, a mild temperature and pressure excursion can be mitigated by quickly depressuring the hydrogenation reactor. Snuffing steam nozzles should also be provided within the reactor for runaway conditions.

Butadiene

Butadiene is the primary feedstock for producing adiponitrile via the DuPont/Invista process. Butadiene at room temperature is a colorless gas with a gasoline odor. It is volatile, flammable, and extremely reactive. Upon contact with a source of ignition in the presence of air, butadiene is likely to cause a flash fire. Since combustion products are CO₂ and CO, combustion in a confined space is likely to form a large quantity of CO, which is toxic. Butadiene is carcinogenic. Acute or long-term exposure to butadiene is likely to cause damage to the reproductive system, mucous membranes, upper respiratory tract, skin, eyes, and central nervous system.

If a butadiene fire occurs, it should be extinguished with water spray at a safe distance. Due to the highly reactive nature of butadiene, storage vessels containing butadiene can explode if ignited. Firefighters should wear self-contained breathing apparatus.

Acrylonitrile

Acrylonitrile (ACN) is the primary feedstock for producing adiponitrile via the Ascend/Monsanto process. ACN is a liquid at room temperature with a boiling point of 77°C. ACN as a nitrile is very hazardous, and can cause permanent damage to skin or eyes. Severe exposure can cause death. ACN is a potential carcinogen, and a possible reproductive toxin with mutagenic effects. ACN may be toxic to the blood, kidneys, liver, cardiovascular system, and central nervous system.

ACN is flammable, and should be stored in a closed container free of air. If ignited, ACN fires should be fought with dry chemical powder. Large fires should be fought with alcohol foam, water spray, or fog. ACN is highly reactive, and will generate heat when reacting with oxidizing materials, acids, and alkalis.

Nylon market overview

Since ADN is used almost exclusively to produce HMDA, and HMDA is used primarily as a comonomer with adipic acid (ADA) to produce nylon 66, it is instructive to briefly address the nylon business. The nylon business, consisting of large volume polymers nylon 66 and nylon 6, has an annual global demand (in 2013) of approximately 6–7 million metric tons per year.

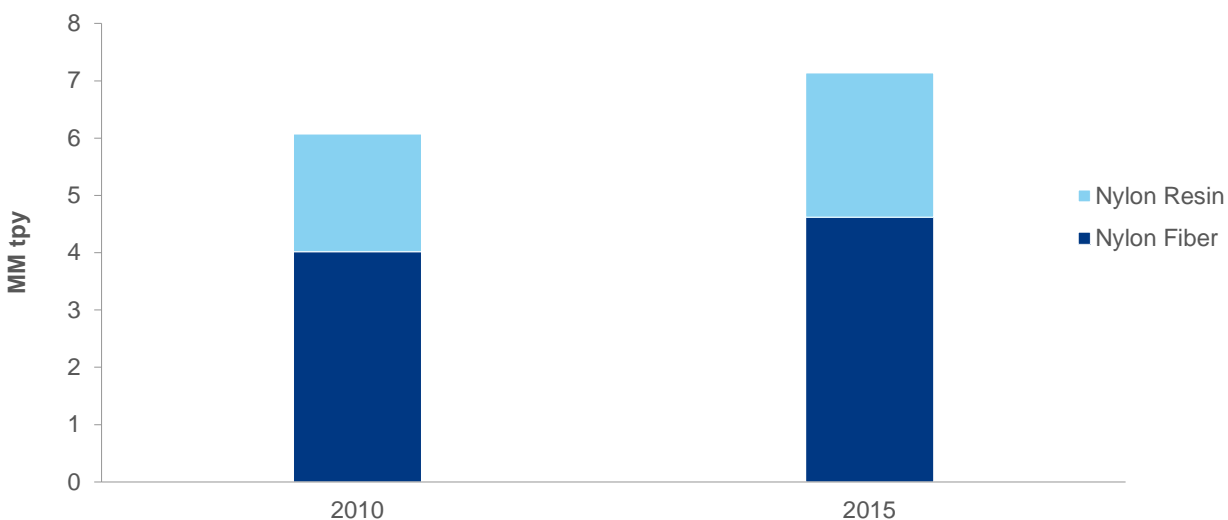
According to Solvay/Rhodia [31C02], the nylon 66 polymer derived from HMDA and ADA can be segmented into four major end-use markets, with different forecast demand growth rates. The demand growth rate of nylon for each end-use market is shown in the table below.

Table 1.6: 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 US

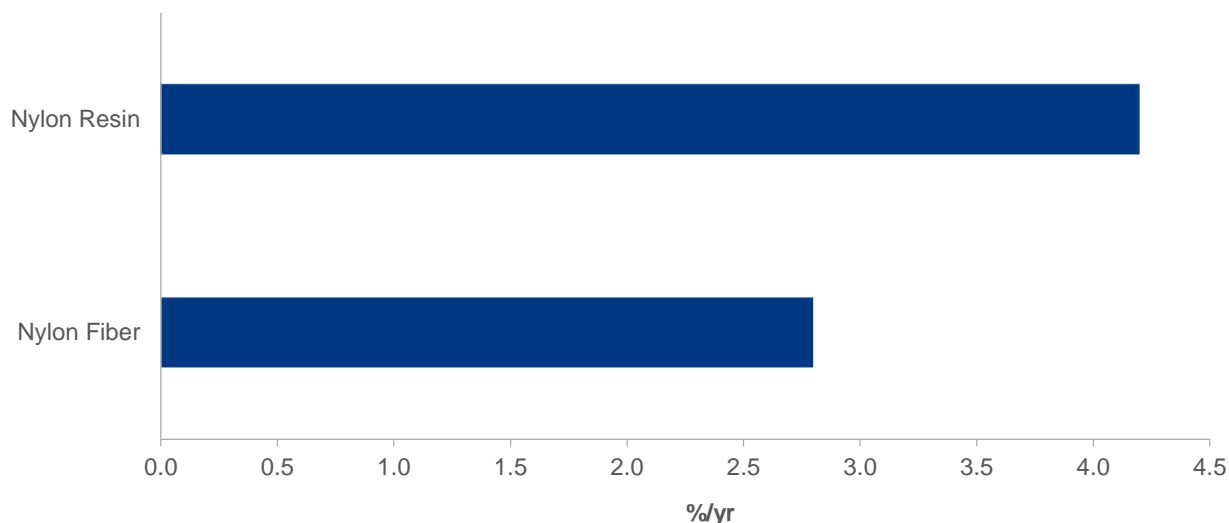
Source: Solvay/Rhodia

Nylon 66 is comprised by weight of 66% adipic acid, and 34% HMDA. The 2010 and 2015 IHS Chemical historical and forecast global demand for nylon fiber and resin is shown in the figure below.

Figure 1.7: Global nylon fiber and resin demand

Source: IHS Chemical Economics Handbook

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

Figure 1.8: Forecast nylon demand growth rate

Source: IHS Chemical Economics Handbook

ADN and HMDA production overview

ADN is currently made commercially from butadiene and acrylonitrile. In the past, it was also made from adipic acid. The butadiene route has been pioneered and developed by DuPont (now Invista), and is considered to be the lowest-cost route for high production rates. However, this route is sensitive to the price of butadiene feedstock derived from crude oil. Butadiene market prices have become erratic with the conversion of some ethylene steam crackers from liquid feeds to gas feeds, which results in significantly less by-product butadiene production. In response, several companies have announced plans to build on-

purpose butadiene production plants via butane dehydrogenation (Houdry) process technology. The DuPont/Invista technology has only been out-licensed to Butachimie, which is a 50:50 joint venture originally between DuPont and Rhodia/Solvay.

The acrylonitrile route is used by Solutia (now Ascend), BASF and Asahi Kasei. The competitiveness of this process depends primarily on the price differential between butadiene and acrylonitrile. When butadiene prices spike up due to market shortages, the acrylonitrile process becomes more cost competitive.

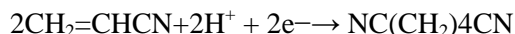
Some early ADN plants used adipic acid as feedstock but, with the exception of a small Chinese plant, this technology is no longer commercially practiced at high volume.

The hydrogenation of ADN to HMDA is carried out in a liquid-phase reactor in the presence of ammonia. Ammonia serves both to absorb the exothermic heat of reaction, and to enhance selectivity by reducing by-product make. Typical catalysts are promoted cobalt and iron oxide. Typical reactor temperatures are 100–200°C, and pressures between 28 and 41 MPa (4,000–6,000 psia). Purification is accomplished by fractional distillation. Commercial by-products are 1,2-diaminocyclohexane, hexamethyleneimine, and bis(hexamethylenetriamine).

The now obsolete process converting adipic acid to ADN begins by reacting adipic acid with ammonia at 15 psia and 300–400°C to yield adiponitrile. This process was used originally by ICI, BASF, and Rhodia/Solvay (formerly Rhone Poulenc).

The conventional DuPont/Invista process reacts butadiene with hydrogen cyanide at 100°C and 100–200 psia in the liquid phase. Adiponitrile intermediate product is separated from by-products via fractional distillation.

The Monsanto/Ascend process dimerizes acrylonitrile to adiponitrile in an electrolytic cell. Others using this technology are BASF, Rhodia, and Asahi. The reaction at the cathode is shown in the equation below.



Hydrogen is produced from water at the anode side of the electrolytic cell. The solution on the cathode side of the cell is a mixture of acrylonitrile, water and a tetraalkylammonium salt. The solution on the anode side of the cell is sulfuric acid in water. By-products include propionitrile and bis(cyanoethyl) ether.

ADN and HMDA product grades and specifications

Adiponitrile

ADN is used almost exclusively to make hexamethylenediamine (HMDA), of which 97% of commercial output is used to make nylon (polyamide) 66 fibers and resins. Most ADN production is consumed captively by HMDA and nylon 66 producers.

Invista produces and sells a single commercial grade of ADN under the trade name DYTEK™. Their product specification [31C03] is presented in the table below, which is consistent with the 99.9% purity used by most other ADN suppliers. Invista packages and offers ADN in drums (400 lbs), and in bulk rail car shipments (175,000 lbs, 79,400 kg).

Table 1.7: Invista ADN product specifications

Purity	Water content	Other organics
99.9%	< 0.05%	< 0.2%

Ascend Performance Products currently (2013) markets ADN and HMDA for commercial sale. Ascend also sells virgin and compounded nylon 66 resin grades (PA66 VydynTM) as well as the carpet and industrial fiber made from nylon 66, and trademarked nylon 66 (UltronTM) carpet.

Hexamethylenediamine

Since HMDA is a solid at room temperature, it is sold commercially either in neat liquid form at elevated temperature, or sold in liquid form as an aqueous solution. Typical commercial purity is 99.9% by weight. Invista produces HMDA at Orange and Victoria, Texas and ships it to its captive nylon 66 polymer and textile plant in Chattanooga, Tennessee in the form of 70–80% aqueous solutions [31C04]. The table below summarizes the grades of HMDA sold by Invista [31C05].

Table 1.8: Invista commercial DYTEKTM HMDA grades

	Grade					
	60%	70%	80%	85%	85–95%	100%
HMDA form	Solution	Solution	Solution	Solid	Solid	Solid

Source: Invista

A typical composition for Invista HMDA [31C05] is shown in the table below.

Table 1.9: Invista commercial DYTEKTM HMDA specification

HMDA wt%	60–100
Water wt%	0.1–40
Color, APHA	2
1,2-Diaminocyclohexane, mols per million mols	4
2-Aminomethylcyclopentylamine, mols per million mols	19
2-Methylpentamethylenediamine, mols per million mols	3
Polarographically reducible impurities, mols per million mols	8

Prior PEP reports on HMDA and ADN

Prior PEP reports pertaining to HMDA and the nylon 66 integrated product chain are listed in the table below.

Table 1.10: Prior relevant PEP reports and reviews

Report no.	Date	Title
31	1967	Hexamethylenediamine
31A	1972	Hexamethylenediamine
31B	1997	Hexamethylenediamine
54	1969	Nylon 66
54A	1980	Nylon 66
54B	1987	Nylon 66
240	2001	Strategic Business Units of Nylon 6 and Nylon 66
96-4	1998	Hexamethylenediamine and Caprolactam from Adiponitrile by Partial Hydrogenation and Cyclization of Aminocapronitrile
78-2-3	1979	Phillips Technology for Electrolytic Dimerization of Acrylonitrile

2. Summary

Physical properties and uses

Hexamethylenediamine (HMDA) and adiponitrile (ADN) are intermediate monomers that are used primarily in the production of nylon 66. They are also useful as commercial solvents, and as intermediates used to produce polyurethanes.

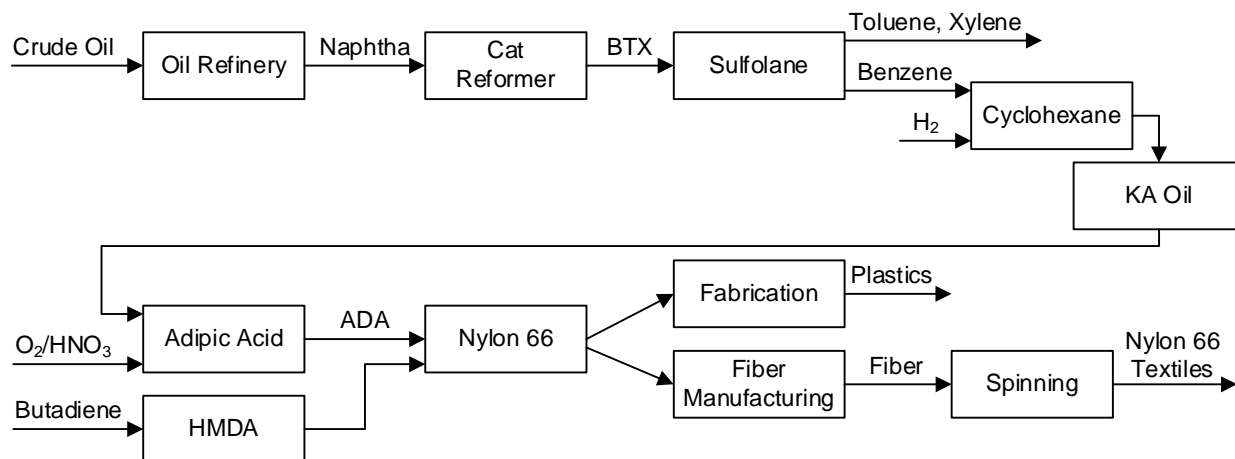
HMDA at room temperature is a solid, and is sold both in neat form as a heated liquid melt, and in grades dissolved in water so that the product is in liquid form. Physical properties of HMDA are presented in the table below.

Table 2.1: Physical properties of HMDA

CAS number	124-09-4
Molecular formula	C ₆ H ₁₆ N ₂
Molar mass	116.20 g mol ⁻¹
Appearance	Colorless crystals
Density	0.84 g/mL
Melting point	39–42°C, 312–315 K, 102–108°F
Boiling point	205°C, 477.7 K, 400°F
Solubility in water	490 g L ⁻¹
Solubility in 100g H ₂ O (30°C)	960 gm
log P	0.386
Standard enthalpy of formation $\Delta_f H^\circ_{298}$	-205 kJ mol ⁻¹
Flash point	80°C
Explosive limits	0.7–6.3%
LD ₅₀	750 mg kg ⁻¹ (oral, rat) 1.11 g kg ⁻¹ (dermal, rabbit)
Autoignition temperature	550°C
Dissociation constant (water, 20°C)	
pK ₁	11.11
pK ₂	10.11
Heat of combustion (25°C)	40,208 kJ/kg
Specific heat capacity, c _p (solid)	2.85 kJ/kg-°K
Melting point of water eutectic (53% H ₂ O)	-20°C
Heat of solution in water, J/gm	
90% solution	56
85% solution	71
70% solution	112
Infinite dilution	245

Nylon 66 is produced by the copolymerization of HMDA with adipic acid (ADA). The integrated product chain for producing nylon 66 from HMDA and adipic acid (ADA) is presented in the figure below.

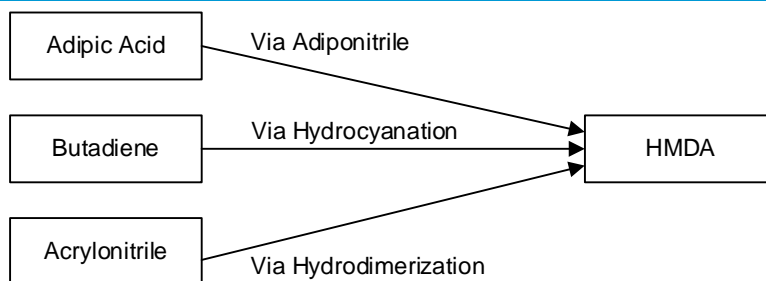
Figure 2.1: Nylon 66 integrated product chain diagram



There are three commercial feedstocks used to produce HMDA: butadiene, acrylonitrile, and adipic acid. Each feedstock is converted to adiponitrile (ADN) as an intermediate monomer, which is subsequently hydrogenated to HMDA.

Adiponitrile is one of several monomers that can be used to produce HMDA. Others are adipic acid, butadiene, and acrylonitrile. These routes from ADN to HMDA are shown in the figure below.

Figure 2.2: Adiponitrile intermediate chemical



The physical properties of adiponitrile are presented in the table below.

Table 2.2: Adiponitrile physical properties

CAS number	111-69-3
Molecular formula	C ₆ H ₈ N ₂
Physical state	Liquid at 20°C and atmospheric pressure
Color	Colorless
Odor	Odorless
Molar mass	108.14 g mol ⁻¹
Appearance	Colorless liquid
Density liquid	951 mg mL ⁻¹
Density vapor to air	3.7
Melting point	1–3°C, 274–276 K, 34–37°F
Boiling point	295°C, 568.2 K, 563°F
Solubility in water	50 g/L (20°C)
Vapor pressure	300 mPa (at 20°C)
Refractive index (nD)	1.438
Standard enthalpy of formation $\Delta_f H_{298}^\circ$	84.5–85.3 kJ mol ⁻¹
Freezing point	34°F
Solubility in water	4.50%
Lower explosion limit	1.70%
Upper explosion limit	5.00%
Flash point	163°C at atmospheric pressure
Autoignition	550°C
Explosive properties	Non explosive
Self-ignition temperature	475°C at atmospheric pressure
Octanol water partition coefficient (log K _{ow})	-0.32 at 25°C
Critical temperature	507°C
Critical pressure	2.76 MPa
Viscosity	4.905 g/s ² (30°C)
Refractive index	1.4363 (20°C)
Partition coefficient, pK _{ow}	-0.32
Heat of vaporization	76.1 kJ/mol
	240 Btu/lb
Heat of combustion	-4,369 kJ/mol
	14,230 Btu/lb (neg)

Nylon 66 competes in most end-use applications with nylon 6, which is produced by the homopolymerization of caprolactam. The major commercially relevant forms of nylon (polyamide) are presented in the table below.

Table 2.3: Major forms of nylon (polyamide)

Type	Monomer feedstocks
Nylon 6	Caprolactam
Nylon 11	Aminoundecanoic acid
Nylon 12	Aminolauric acid
Nylon 66	HMDA + ADA
Nylon 610	HMDA + sebacic acid
Nylon 612	HMDA + 1,12-dodecanedioic acid
Nylon 666	Nylon 6 + nylon 66 copolymer
Nylon 46	1,4-Diaminobutane + ADA
Amorphous nylon	Trimethylhexamethylenediamine and TPA
PPA	Any diamine and IPA and/or TPA

Source: Permeability Properties of Plastics and Elastomers [31C08]

Engineering plastics are used primarily in extruded, fiber and 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 2.4: Competing engineering plastics

Acrylonitrile–butadiene–styrene (ABS)
Polycarbonate (PC)
Specialty polyamides (PA)
Polybutylene terephthalate (PBT)
Polyethylene terephthalate (PET)
Polyphenylene oxide (PPO)
Polysulfone (PSU)
Polyetherketone (PEK)
Polyetheretherketone (PEEK)
Polyimides
Polyphenylene sulfide (PPS)
Polyoxymethylene (POM)

Process safety

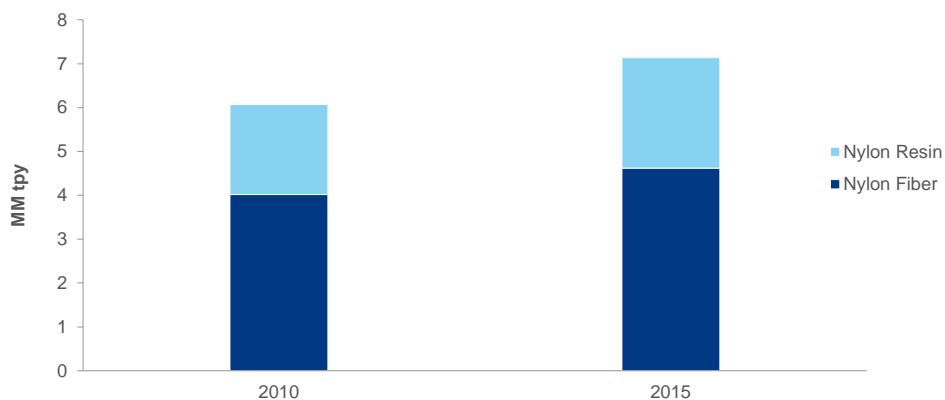
Adiponitrile and hexamethylenediamine are both organic chemical monomers, and are therefore combustible. Precautions should be taken to keep the temperature below ignition temperature, and avoid contact with open flames or other potential sources of ignition. Pressurized vessels containing ADN or HMDA should be designed and manufactured to ASME pressure code standards, and equipped with multiple automatic pressure relief valves venting to a safe disposition such as a process flare header. ADN and HMDA should be stored in dedicated containers designed to avoid direct air contact. When HMDA is handled in solid form, the area should be well ventilated and provided with dust filtration facilities, and ancillary safety facilities designed to avoid combustible dust explosions.

Supply and demand

Nylon demand

Global demand for nylon polymers in 2013, for both resin and fiber forms, was approximately 6.5 MM tpy. The 2010 and 2015 IHS Chemical historical and forecast global demand for nylon fiber and resin is shown in the figure below. The annual global consumption of nylon 66 in 2012 was 1.8 MM tpy.

Figure 2.3: Global nylon fiber and resin demand



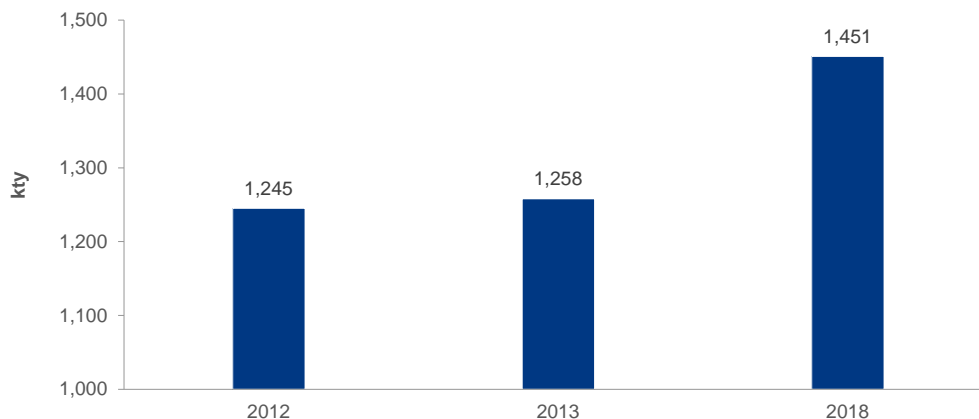
Source: IHS Chemical Economics Handbook

The anticipated annual global demand growth for nylon resin between 2012 and 2015 is estimated to be 4.3 %/year. The corresponding demand growth for nylon fiber is 2.8 %/year.

HMDA demand

IHS Chemical estimates that global demand for HMDA in 2013 was 1,258 kty, and projects it to increase by 3% annually to reach an aggregate demand of 1,451 kty by 2018. The IHS historical and forecast global demand for HMDA is shown in the figure below.

Figure 2.4: Global demand for hexamethylenediamine

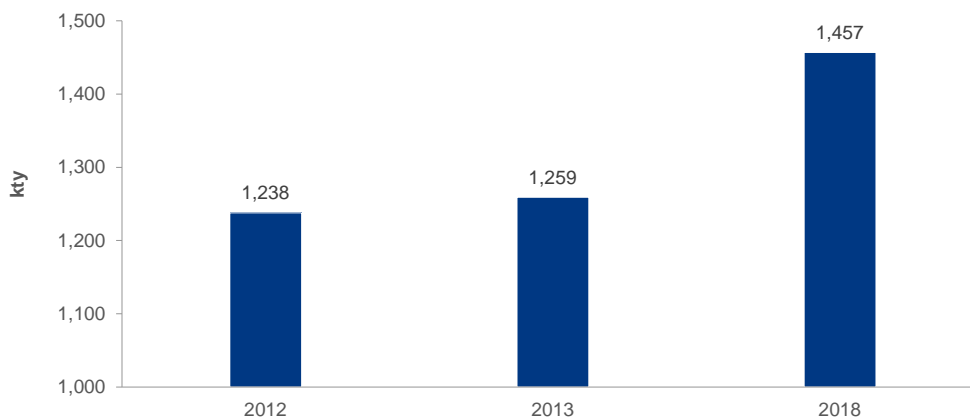


Source: IHS Chemical Economics Handbook (HMDA/ADN)

ADN demand

In 2012, ADN demand globally was approximately 1.24 MM tpy. The historical and forecast IHS global demand projection for ADN is presented in the table below. IHS projects that future ADN growth globally will average 3% per year.

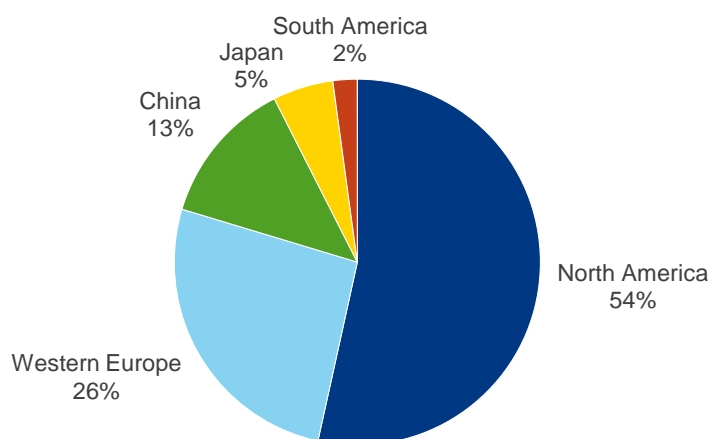
Figure 2.5: Global demand for adiponitrile



Source: IHS Chemical Economics Handbook (HMDA/ADN)

The distribution of ADN demand in 2013 by geographic region is shown in the chart below. The US demand represents all of North American demand, and over half of global demand, principally as feedstock for producing HMDA.

Figure 3.5: Regional distribution of 2013 adiponitrile demand



Source: IHS Chemical Economics Handbook (HMDA/ADN)

ADN and HMDA producers

Major producers of adiponitrile and hexamethylenediamine are listed in the table below.

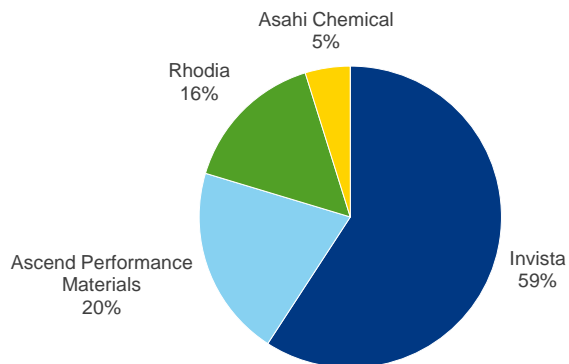
Table 2.5: Major producers of ADN and HMDA

Producer	Location	2013 HMDA capacity (kty)	2013 ADN capacity (kty)	Process
Ascend Performance Materials	Decatur, AL, USA	175	340	Acrylonitrile
	Pensacola, FL, USA	185		Adiponitrile
Invista	Orange, TX, USA	325	360	Butadiene
	Victoria, TX, USA	225	365	Butadiene
Rhodia	Paulina, Brazil	130		Adiponitrile
Butachimie	Chalampe, France	165	515	Butadiene
Rhodia	Saint-Fons, France	125		Adiponitrile
Radici Chimica SpA	Novara, Italy	40		Adiponitrile
BASF SE	Middlesbaugh, UK	120		Adiponitrile
Asahi Chemical	Nobeoka, Japan	45	80	Acrylonitrile
Guorui Chemical	Anshan, China	28		Adiponitrile
Shenma Chemical	Pingdinshan, China	150		Adiponitrile
Total		1,713	1,660	

Source: IHS Chemical Economics Handbook (HMDA)

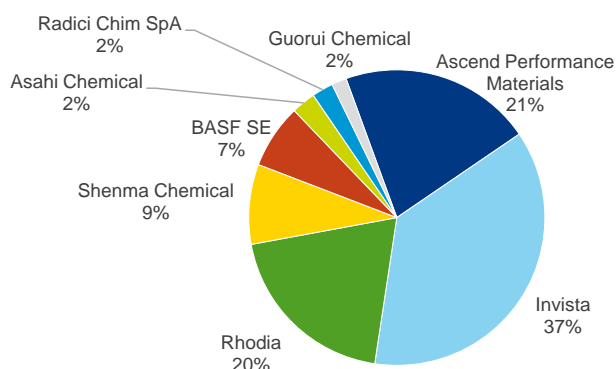
There are relatively few producers of ADN and HMDA. The figure below shows the relative market share of ADN producers.

Figure 2.6: Market share of ADN producers



Source: IHS Chemical Economics Handbook (HMDA)

As shown, well over 50% of global ADN capacity is owned by Invista. The top three producers (Invista, Ascend and Rhodia) collectively represent over 90% of global ADN capacity. The concentration of capacity is similar for HMDA. The figure below represents the global share of major HMDA producers.

Figure 2.7: Market share of HMDA producers

Source: IHS Chemical Economics Handbook (HMDA)

As with ADN, the same top three producers (Invista, Ascend, and Rhodia) dominate global HMDA capacity, although less so than for ADN.

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 2.6: 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

HMDA production economics

For this project, IHS evaluated the process design and production economics for three routes to HMDA, two of which produce ADN as an intermediate product:

- Invista/DuPont Generation-3 hydrocyanation of butadiene to ADN using homogeneous nickel ligand (multidentate phosphonite) catalyst, followed by hydrogenation of ADN to HMDA (well commercialized)
- Ascend/Monsanto electro-dimerization of acrylonitrile to ADN in an undivided cell, followed by hydrogenation of ADN to HMDA (well commercialized)
- Rennovia dehydration of high fructose corn syrup (HFCS) to 5-hydroxymethylfurfural (HMF), followed by hydrogenation of HMF to 1,6-hexanediol (HDO), followed by ammoniation of HDO to HMDA (not commercial)

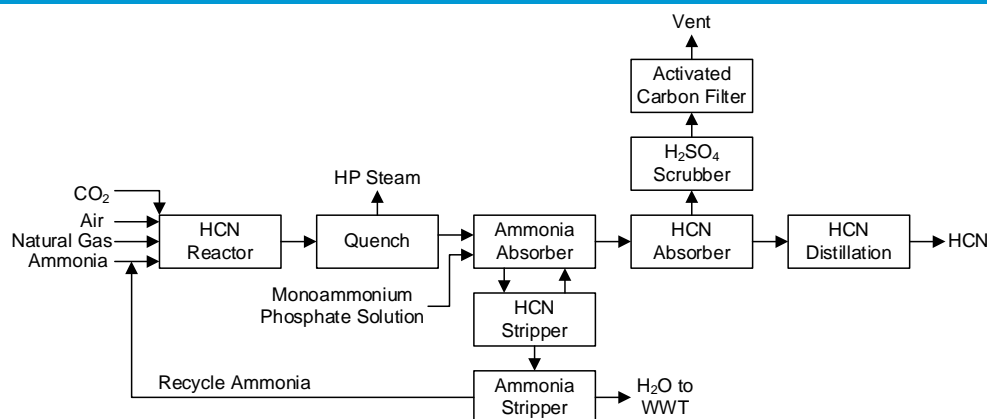
For each process evaluated, we prepared a design for a grassroots HMDA plant with a production capacity of 250 kty, a US Gulf Coast location, using a 2013 PEP COST construction cost factor of 1164.

Invista/DuPont Hydrocyanation of Butadiene to HMDA

Invista attracted significant industry attention when it announced in 2012 a 215 kty, grassroots HMDA project in Shanghai at its integrated nylon 66 manufacturing complex. Invista announced that it would utilize its 'Generation-3' process technology that had previously been commercialized at its existing nylon 66 complexes in Orange and Victoria, Texas, and announced for its joint venture Butachemie plant in France. Besides being claimed to improve raw material and energy utilization, the Gen-3 technology was also claimed to eliminate the use and potential atmospheric discharge of benzene components.

The butadiene hydrocyanation reaction consumes large quantities of hydrogen cyanide (HCN), requiring a dedicated onsite HCN plant due to its extreme toxicity. Invista utilizes the DuPont Andrussow HCN process, in which ammonia and natural gas are partially oxidized in air. A block flow diagram for the Andrussow process is presented in the figure below.

Figure 2.8: DuPont Andrussov HCN process



The Invista butadiene hydrocyanation sequence is conducted in two distinct steps. The first reaction hydrocyanates butadiene to pentenenitriles, which are subsequently purified by distillation. The second reaction further hydrocyanates pentenenitriles to adiponitrile. Intermediate 2- and 3-methyl butyl nitrile isomer by-products are selectively isomerized to pentenenitriles in a separate reactor sequence. Purified ADN is hydrogenated to HMDA using Raney cobalt catalyst at 600 psia pressure.

For our process design, we have segmented the Invista butadiene hydrocyanation process plant into the following sections:

<u>Section</u>	<u>Description</u>
100	Hydrogen Cyanide Production
200	Butadiene Hydrocyanation
300	3PN Hydrocyanation
400	Adiponitrile Hydrogenation to HMDA
500	Catalyst Purification and Recycle

Based on our design effort, we estimated a total fixed capital cost of \$556 million, segmented as \$388 million for ISBL capital, and \$168 million for OSBL capital. When combined with the material balance information, and 2013 representative unit pricing for feedstocks and products, the following production cost estimate results.

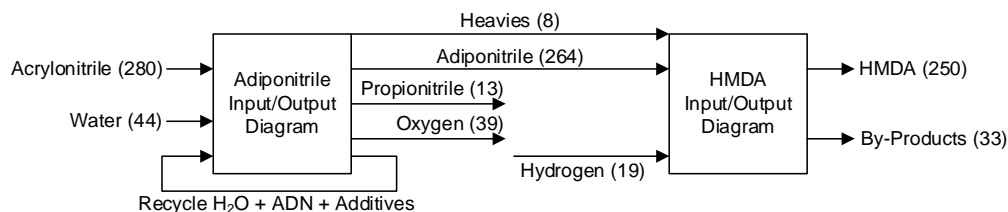
Table 2.7: Production cost estimate for Invista process (\$US/mt)

Raw materials	1148.5
Utilities	145.5
Operations & maintenance	74.7
Plant overhead	24.4
Taxes + insurance	44.4
Depreciation	222.2
Corporate SG&A	29.0
Total production cost	1,688.7

Ascend/Monsanto Electro-dimerization of Acrylonitrile to HMDA

Ascend Performance Materials is the successor company to the historical Monsanto integrated nylon 66 business. Ascend's integrated nylon 66 assets were built in the 1950s by Monsanto's Chemical Division. This business was spun off in 1996 into Solutia. After undergoing bankruptcy proceedings, Solutia sold the integrated nylon 66 business to SK Capital Partners (a venture capital firm) in 1999, which renamed this business Ascend Performance Materials.

Ascend makes ADN via the electro-dimerization of acrylonitrile, and then hydrogenates ADN to HMDA using technology very similar to that practiced by Invista/DuPont. In current practice (known as 2nd generation technology), a 2-phase emulsion of feedstock and additives is quickly pumped through an undivided electrolytic cell. The aqueous phase contains a small amount of acrylonitrile feedstock (limited by its solubility to 7% at STP) and conducting salt. The emulsion contains 15% disodium hydrogen phosphate. The oil/organic phase contains a higher concentration of acrylonitrile and product adiponitrile. Although ADN free ACN would be preferred for the organic phase of the emulsion, the resulting high concentration of ACN results in very low selectivity to ADN. In this respect, the ADN acts as an inert diluting solvent for the ACN feedstock. The overall input/output diagram for IHS's understanding of the Ascend process is presented below for a production capacity of 250 kty.

Figure 2.9: Ascend/Monsanto input/output balance (kty)

Based on our design effort, we estimated a total fixed capital cost of \$477.2 million, segmented as \$325.5 million for ISBL capital, and \$151.7 million for OSBL capital. When combined with the material balance information, and 2013 representative unit pricing for feedstocks and products, the following production cost estimate results.

Table 2.8: Production cost estimate for Ascend/Monsanto process**Capital costs (\$US-million)**

Inside battery limits	325.5
Outside battery limits	151.5
Total fixed capital	477.1

Production cost (\$US/MT)

Raw materials	2,064.6
Utilities	249.2
Operations & maintenance	54.0
Plant overhead	17.6
Taxes + insurance	38.2
Depreciation	190.8
Corporate SG&A	29.0
Total production cost	2,643.4

Rennovia HMDA process

In October 2013, Rennovia (Menlo Park, California, USA) announced [31C54] that it had produced 100% bio-based nylon 66 polymer, combining its separate technologies for producing bio-adipic acid and bio-hexamethylenediamine. The fundamental feedstock used by Rennovia is fructose purchased commercially as high fructose corn syrup (HFCS). Rennovia's key patent claims for producing HMDA from fructose are disclosed in US Patent Application 2013 0184 495 (18 July 2013), entitled 'Process for the production of hexamethylenediamine from carbohydrate containing materials and intermediates therefor'. The integrated Rennovia HMDA process contains four steps as listed below.

- 1) Dehydration of fructose in HFCS to 5-hydroxymethylfurfural (HMF) plus water using dilute hydrochloric acid as catalyst
- 2) Hydrogenation of HMF to 1,2,6-hexanetriol at elevated pressure and temperature using platinum/molybdenum catalyst on an aluminum oxide substrate

- 3) Further hydrogenation of 1,2,6-hexanetriol to 1,6-hexanediol using platinum/tungsten catalyst on zirconium oxide substrate at nearly the same process conditions as above
- 4) Ammoniation of 1,6-hexanediol to HMDA at 3,000 psia using Raney nickel catalyst

Our design for the Rennovia process uses various solvents (cyclohexane and methyl isobutyl ketone) in the HFCS dehydration reactors, in the fractional distillation trains, and also for the purification of intermediate and final products. Since the Rennovia patent application used to establish design basis conditions focused on catalyst performance and conversion/selectivity rather than optimized process patent conditions, our approach was to make design assumptions about reactor residence times, and the excess hydrogen:oil feed ratios for the hydrogenation reactions. These conditions from the Rennovia patent application resulted in large reactors (heavy-wall alloy), high capacity and horsepower hydrogen compressors, and complex vacuum distillation trains to purify intermediate products. As a result of these design conditions, our total fixed capital cost estimate is subject to a wide range of estimated values, which may be higher than one would expect if using conventional feed ratios and LHSV criteria for design. The resulting process economics are presented in the table below.

Table 2.9: Production cost estimate for Rennovia process

Capital costs (\$US-million)

Inside battery limits	532.5
Outside battery limits	253.9
Total fixed capital	786.4

Production cost (\$US/MT)

Raw materials	1,117.6
Utilities	319.3
Operations & maintenance	72.3
Plant overhead	23.1
Taxes + insurance	62.9
Depreciation	314.5
Corporate SG&A	29.0
Total production cost	1,938.7

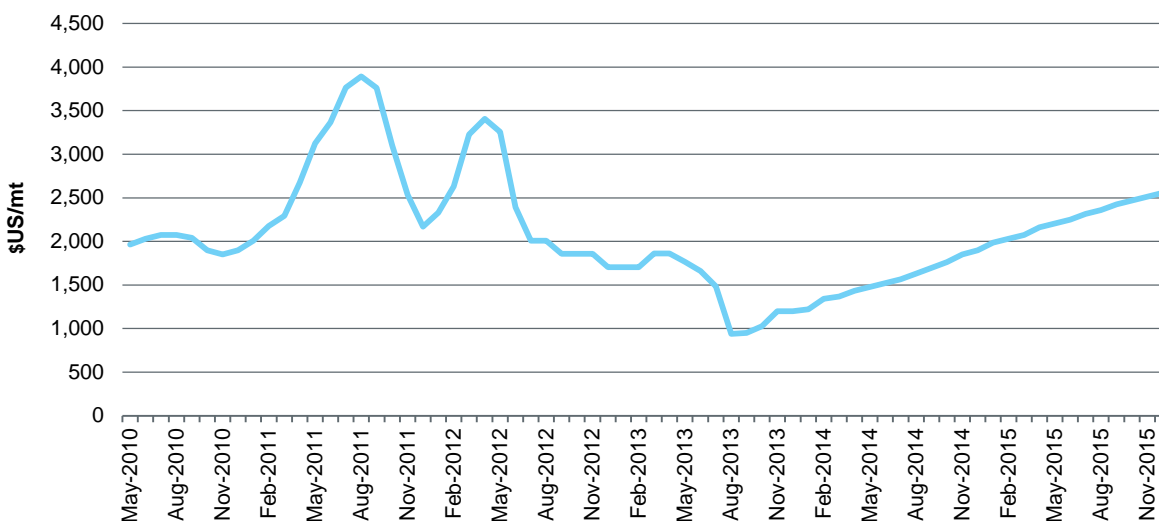
Economic comparison

The Invista and Ascend HMDA processes are well commercialized, and their production economics are presented together in the table below, along with the non-commercial cost data we estimated for Rennovia. The Invista and Ascend processes have capital cost estimates that are similar. What makes the production cost for the Invista process much lower than the Ascend process is the use of lower unit price butadiene feedstock, which in 2013 had a much lower market price than the acrylonitrile used by Ascend for its electro-dimerization technology.

Table 2.10: Production cost comparison

Capital costs (\$US-million)	Invista	Ascend	Rennovia
Inside battery limits	387.5	325.5	532.5
Outside battery limits	168.1	151.5	253.9
Total fixed capital	556.6	477.1	786.4
Production cost (\$US/MT)			
Raw materials	1148.5	2064.6	1117.6
Utilities	145.5	249.2	319.3
Operations & maintenance	74.7	54.0	72.3
Plant overhead	24.4	17.6	23.1
Taxes + insurance	44.4	38.2	62.9
Depreciation	222.2	190.8	314.5
Corporate SG&A	29.0	29.0	29.0
Total production cost	1688.7	2643.4	1938.7

Most commercial butadiene is produced as a by-product of steam cracking to produce ethylene. As the economically optimum ethylene steam cracking feedstock has gravitated from steam cracking naphtha (which produces large amounts of butadiene) to steam cracking ethane (which produces almost no butadiene), the market price for butadiene has become extremely volatile. The graph below plots historic butadiene market prices between May 2010 and August 2013, showing a monthly price range between \$4000/mt to below \$1000/mt. Extension of the price line represents the IHS forecast for future butadiene pricing. For the economic analysis presented in this report for the Invista process, we used a butadiene feedstock price of \$1466/metric ton, which was the average annual contract price in the US during 2013. Future butadiene prices will be driven largely by a combination of the price for crude oil, plus the supply/demand balance for butadiene. Any major change in butadiene unit pricing will have a profound effect on the competitiveness of the butadiene-based Invista/DuPont HMDA process.

Figure 2.10: IHS historic and forecast butadiene prices

Source: IHS Chemical

Whether butadiene pricing will continue to be volatile, or stabilized around a price that allows Invista production economics to remain the lowest of the three processes evaluated, is not knowable.

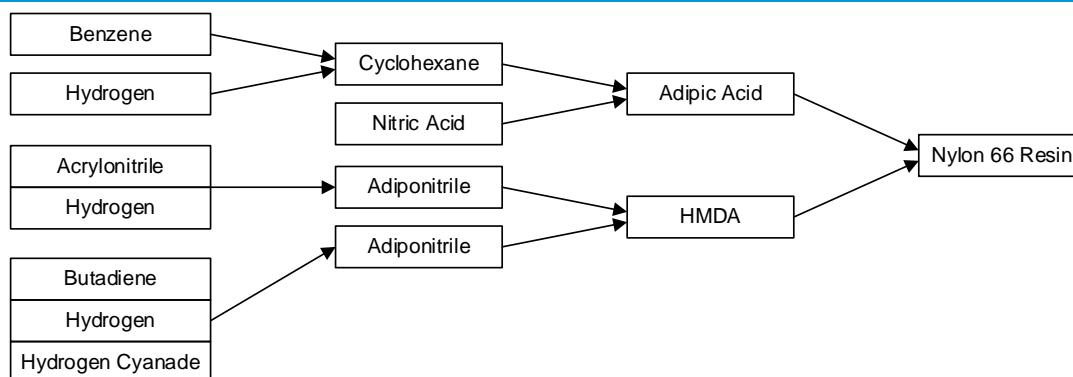
The Rennovia process has attractive raw material costs, based upon its use of relatively low cost high fructose corn syrup. However, the utility and fixed production costs are burdened by the high capital cost estimate. As explained above, we believe that continued development of process technology by Rennovia can substantially reduce the capital cost required to build and operate a 250 kty HMDA plant, which would make its production economics competitive with that of Invista.

3. ADN and HMDA industry status

Uses of ADN and HMDA

Adiponitrile (ADN) is used primarily as an intermediate organic monomer in the production of hexamethylenediamine (HMDA), which is one of two organic monomers required to produce nylon 66, a polyamide engineering resin. The integrated product chain for nylon 66 is shown in the figure below.

Figure 3.1: Nylon 66 integrated product chain



Source: IHS Chemical Global Engineering Resin Report [31C07]

ADN is commercially hydrogenated to produce HMDA. There is minor use of ADN as a powerful solvent used in pharmaceutical separations. Minor uses for ADN are presented in the table below.

Table 3.1: Commercial uses for adiponitrile

Extraction solvent for fatty acids, oils and unsaturated hydrocarbons
Solvent for spinning and casting and extractive distillation based on its selective miscibility with organic compounds
Removing agent of coloring matters and aromatic alcohols
Non-aqueous solvent for titrations and for inorganic salts
Recrystallization of steroids
Parent compound for organic synthesis
Solvent or chemical intermediate in biochemistry (DNA sequencing and pesticide synthesis)
High-pressure liquid chromatographic analysis
Catalyst and component of transition-metal complex catalysts
Stabilizer for chlorinated solvents
Chemical intermediate and solvent for perfumes and pharmaceuticals

HMDA is copolymerized with adipic acid (ADA) to produce nylon 66. Minor uses for HMDA are presented in the table below.

Table 3.2: Non-nylon commercial uses for hexamethylenediamine

Organic coatings
Epoxy curing agents
Oilfield chemicals
Solvent for adhesive and ink formulations
Water treatment chemicals
Solvent for corrosion prevention coatings

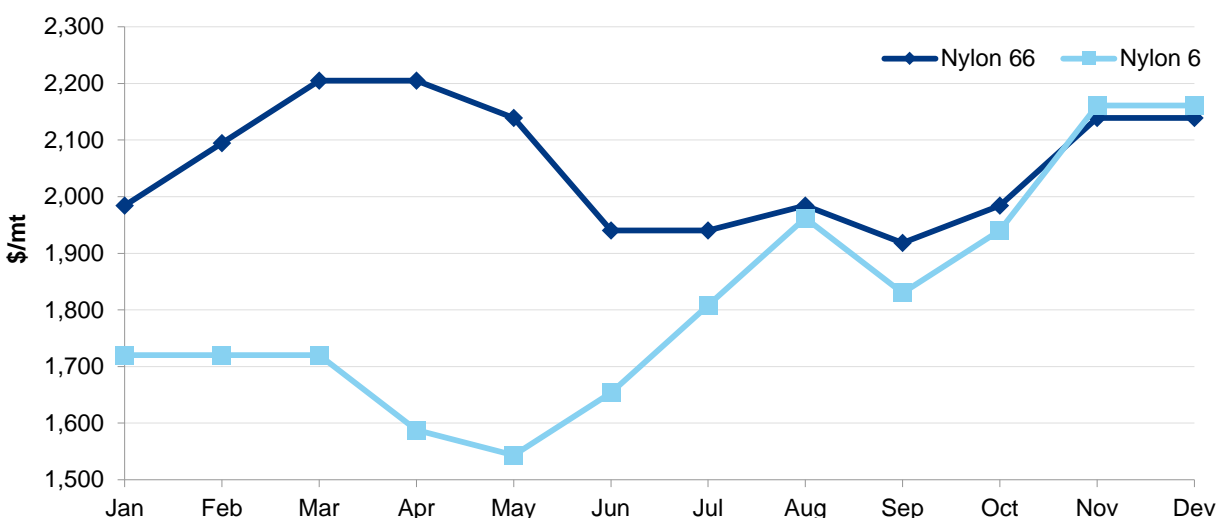
Uses of nylon 66

Nylon 66 is a polyamide historically used to produce synthetic fibers as carpet facing material in residential rugs, and as an industrial fiber used in high strength applications such as tire cord. More recently, it has found wide use as a high temperature engineering resin useful in castable parts for automotive engine (under the hood) applications, wire and cable insulation, and brake lining hoses.

Inter-material substitution between nylon 66 and nylon 6

The high volume forms of nylon sold into the commercial market place are primarily nylon 66 and nylon 6. Nylon 66 has slightly better high temperature properties, but also usually higher feedstock costs for manufacturing. A comparison of nylon 6 versus nylon 66 monthly raw material historical costs for 2012 is shown in the figure below. Most of the time, the raw material cost for nylon 6 was lower than that for nylon 66.

Figure 3.2: Nylon 66 versus nylon 6 raw material costs



Source: IHS Chemical Global Nylon Feedstocks & Fibers Report (May 2013)

Other forms of nylon (nylon 11, 12, 46, 69, 610, 612, 6T, M6, etc.) are specialty products sold at much higher prices than nylon 66, and in 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 high volume nylon producers.

Table 3.3: Production integration for nylon 66 and nylon 6

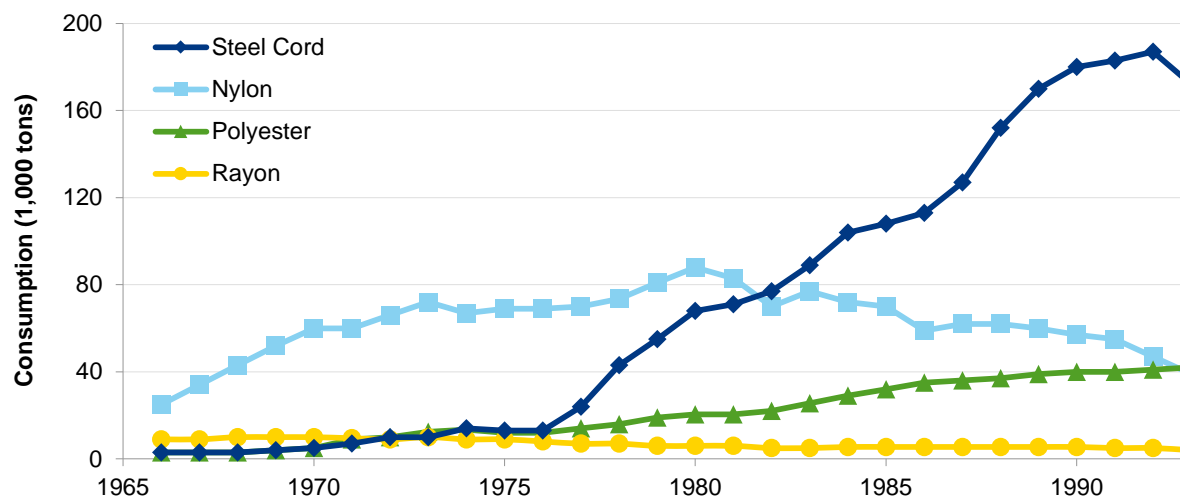
Producer	ADA	HMDA	Capro	Nylon 66	Nylon 6
Asahi Kasei	√	√		√	
Ascend	√	√		√	
BASF	√	√	√	√	√
China Petrochemical Development Corp			√		√
DSM			√		√
DuPont				√	
Honeywell			√		√
Hua Long Corporation			√		√
Hyosung			√	√	√
Invista	√	√		√	
Kolon Industries			√	√	√
Lanxess			√	√	√
Li Peng Enterprise Co.	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

Source: IHS

Polymer inter-material substitution

In many end-use applications, there are inter-material substitution opportunities between nylon and other synthetic polymers. As mentioned above, nylon fiber originally 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 3.3: Trends in materials consumption for tire cord (kty)

Source: Toyo Tires

In resin applications, the chemical industry often 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 3.4: Competing engineering plastics

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

In addition to 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. Arkema commercially produces Rilsan-T™, a nylon 11 polyamide made in part from castor oil.

Other forms of polyamide

Different monomers are used to form various types of polyamide, of which nylon 66 along with nylon 6 dominate global high volume production. In the process of copolymerizing, water is a reaction by-product, such that most nylons absorb water to the detriment of their physical and performance properties. Absorbed water acts as a nylon plasticizer, swelling and softening the polymer.

Compared with other polyamides, nylon 66 has outstanding toughness (wear and abrasion) properties, thermal stability, and chemical and oil resistance. It has high flame resistance, which is improved by adding fillers and compounding chemicals. Many nylon 66 grades are provided to the marketplace, with many differentiated by the use of fiber fillers to add mechanical tensile strength and improve high temperature performance.

A list of specialty polyamide compositions is proved in the table below.

Table 3.5: Commercially available polyamides

Type	Monomer feedstocks
Nylon 6	Caprolactam
Nylon 11	Aminoundecanoic acid
Nylon 12	Aminolauric acid
Nylon 66	HMDA + ADA
Nylon 610	HMDA + sebacic acid
Nylon 612	HMDA+ 1,12-dodecanedioic acid
Nylon 666	Nylon 6 + nylon 66 copolymer
Nylon 46	1,4-Diaminobutane + ADA
Amorphous nylon	Trimethyl hexamethylenediamine and TPA
PPA	Any diamine and IPA and/or TPA

Source: Permeability Properties of Plastics and Elastomers [31C08]

Market desire for bio-based nylon

For certain customer end markets such as automotive ‘under the hood’ fabricated parts, some customers have indicated a preference for more sustainable material inputs, with that translating to a desire for more plastics to be made from bio-based materials rather than crude oil derived materials. Another customer preference is for fabricated plastic parts that can be recycled.

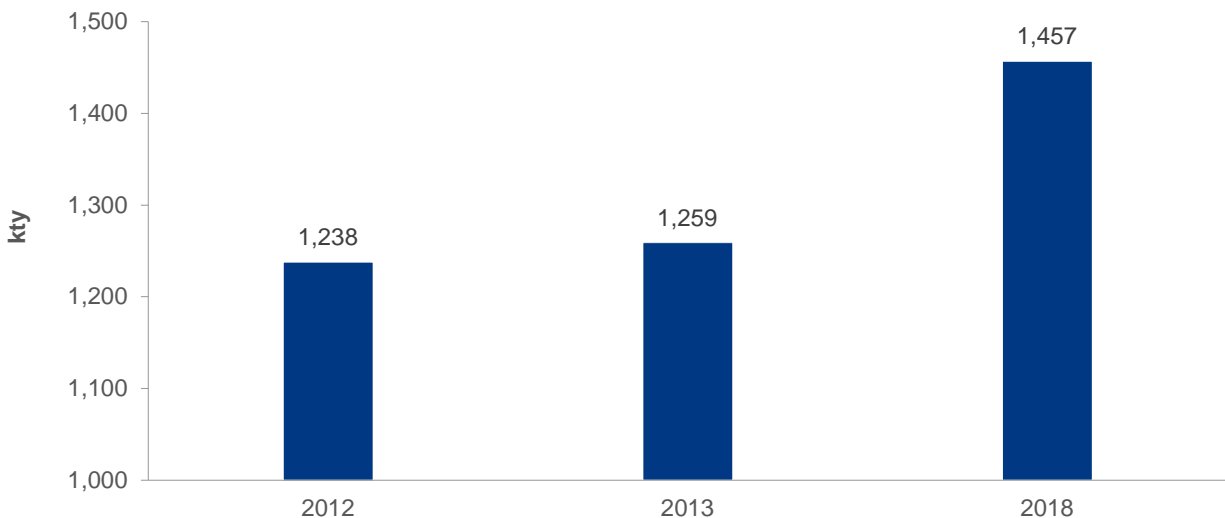
In response to this preference, Solvay announced [31C09] in 2013 a commercial plant to be built to produce nylon 610, which is produced by copolymerizing crude oil derived HMDA with bio-based sebacic acid. The plant site is Saint-Fons, France. If successfully commercialized, the product is claimed to be 62.5% derived from a renewable source.

As presented in Section 8 of this report, Rennovia (Menlo Park, California, USA) has developed both bio-based adipic acid, and bio-based HMDA, and combined them to form 100% bio-based nylon 66. Rennovia is currently (in 2013) in the pilot plant stage of its technology development effort, and believes that its product is a drop-in substitute for conventional nylon 66, potentially capable of being produced in high volumes at competitive production costs.

Adiponitrile demand

In 2013, ADN demand globally was approximately 1,259 kty. The historical and forecast IHS global demand projection for ADN is presented in the table below. IHS projects that future ADN demand growth will average 3% per year globally.

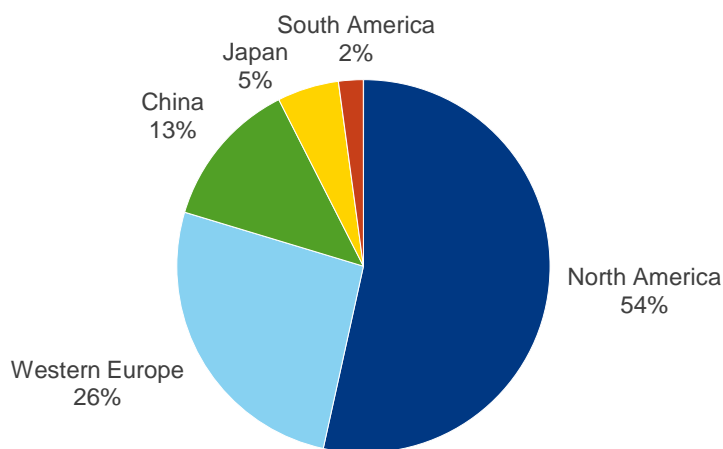
Figure 3.4: Global demand for adiponitrile



Source: IHS Chemical Economics Handbook (HMDA/ADN)

The distribution of ADN demand in 2013 by geographic region is shown in the chart below. The US portion of demand represents all of total North American demand, and represents over half of global demand, principally as feedstock for producing HMDA.

Figure 3.5: Regional distribution of 2013 adiponitrile demand

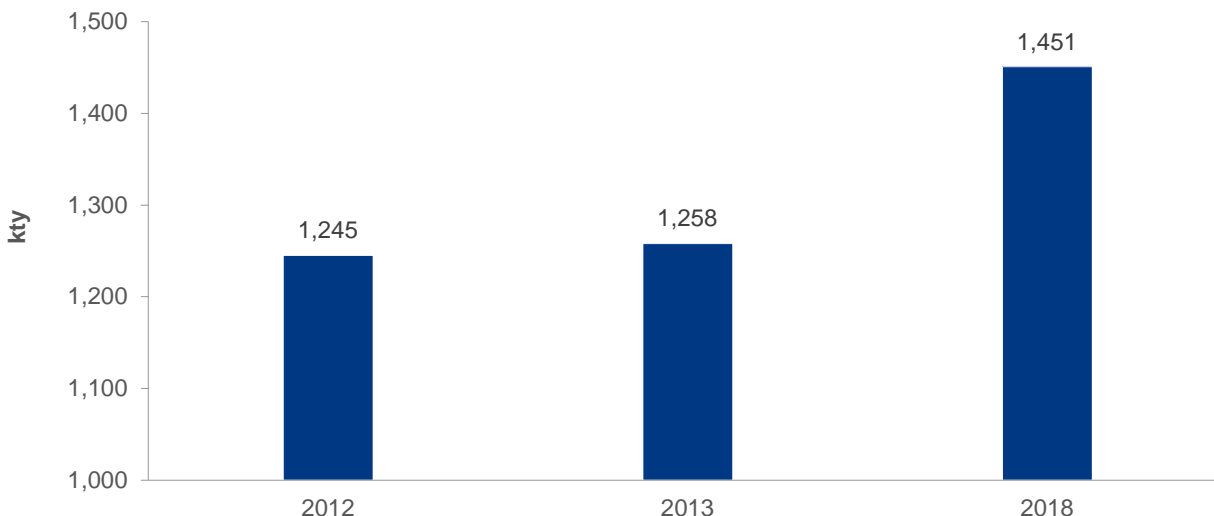


Source: IHS Chemical Economics Handbook (HMDA/ADN)

Hexamethylenediamine demand

IHS estimated global demand for HMDA in 2013 to be 1,258 kty, and projects it to increase annually by 3% annually to reach aggregate demand of 1,458 kty by 2018. The segmentation of demand by region is shown in Figure 3.7 below.

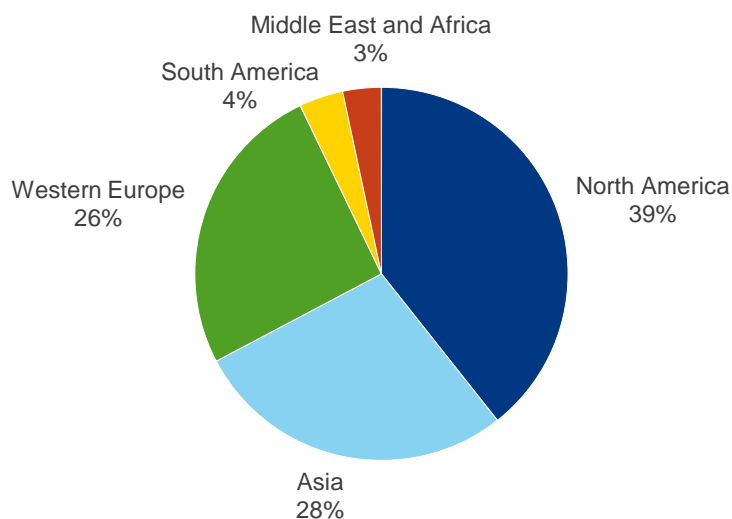
Figure 3.6: Global demand for hexamethylenediamine



Source: IHS Chemical Economics Handbook (HMDA/ADN)

HMDA demand has not in 2013 recovered fully from the global recession of 2008, in contrast to the demand for both caprolactam and nylon 6. Prior to the global recession, HMDA demand was 1.4 million mty. The reluctance of producers to adjust capacity in the face of lower demand has had the secondary effect of reducing industry capacity utilization, thus also reducing industry profit margins. IHS believes that the lower production cost of nylon 6, compared to nylon 66, has caused producers to preferentially make end-use fabricated products from nylon 6 rather than nylon 66, where viable from a performance perspective. Although nylon 66 has better high temperature performance than nylon 6, in most applications that performance improvement is not great enough to justify the higher price of nylon 66.

The distribution of HMDA demand by geographic region is shown in the graph below. Since North America (only the United States) has the largest capacity of nylon 66 production, this region has the largest market share for consuming HMDA to produce nylon 66. IHS expects only minor debottlenecking capacity for HMDA to be added between 2013 and 2018 in the industrial regions, but substantial (215 kty) of new Invista HMDA capacity in China (Shanghai) during that period.

Figure 3.7: Global demand for hexamethylenediamine

Source: IHS Chemical Economics Handbook (HMDA/ADN)

Although most HMDA production is consumed to make nylon 66, a small proportion is used as feedstock to make hexamethylene diisocyanate and hexamethylenediaminic carbamate.

ADN and HMDA producers

Major producers of adiponitrile and hexamethylenediamine are listed in the table below.

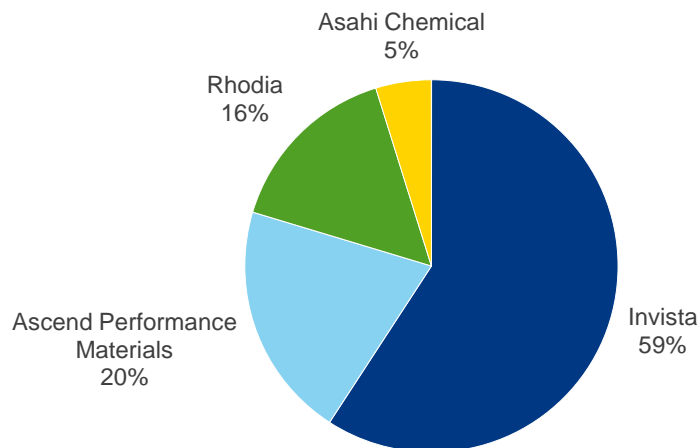
Table 3.6: Major producers of ADN and HMDA

Producer	Location	2013 HMDA capacity (kty)	2013 ADN capacity (kty)	Process
Ascend Performance Materials	Decatur, AL, USA	175	340	Acrylonitrile
	Pensacola, FL, USA	185		Adiponitrile
Invista	Orange, TX, USA	325	360	Butadiene
	Victoria, TX, USA	225	365	Butadiene
Rhodia	Paulina, Brazil	130		Adiponitrile
Butachimie	Chalampe, France	165	515	Butadiene
Rhodia	Saint-Fons, France	125		Adiponitrile
Radici Chimica SpA	Novara, Italy	40		Adiponitrile
BASF SE	Middlesbaugh, UK	120		Adiponitrile
Asahi Chemical	Nobeoka, Japan	45	80	Acrylonitrile
Guorui Chemical	Anshan, China	28		Adiponitrile
Shenma Chemical	Pingdinshan, China	150		Adiponitrile
Total		1,713	1,660	

Source: IHS Chemical Economics Handbook (HMDA)

There are few producers of both ADN and HMDA. The figure below shows the relative market share of ADN producers.

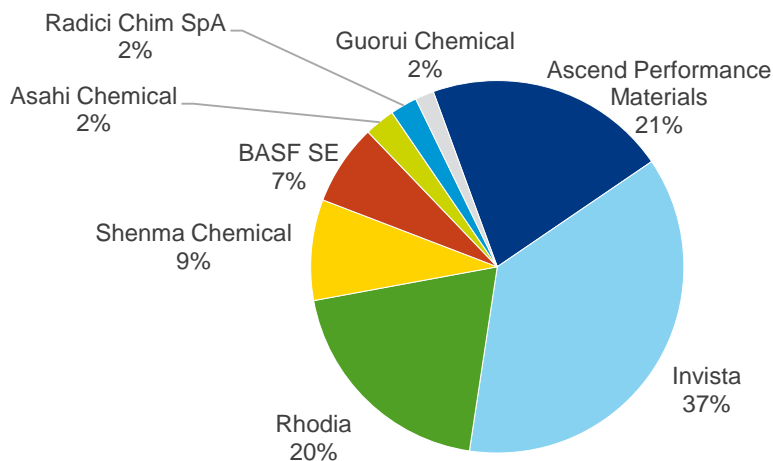
Figure 3.8: Market share of ADN producers



Source: IHS Chemical Economics Handbook (HMDA)

As shown above, over 50% of global ADN capacity is owned by Invista. The top three producers (Invista, Ascend, and Rhodia) collectively represent over 90% of global ADN capacity. The concentration of capacity is similar for HMDA. The figure below represents the global market share of major HMDA producers.

Figure 3.9: Market share of HMDA producers



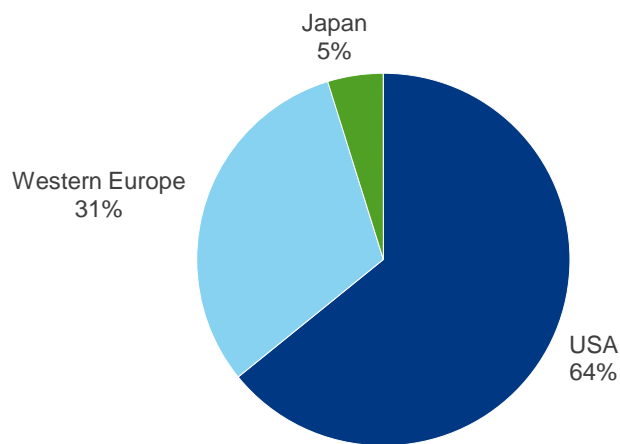
Source: IHS Chemical Economics Handbook (HMDA)

As in ADN, the same top three producers (Invista, Ascend, and Rhodia) dominate global HMDA capacity, although less so than for ADN.

Regional distribution of capacity

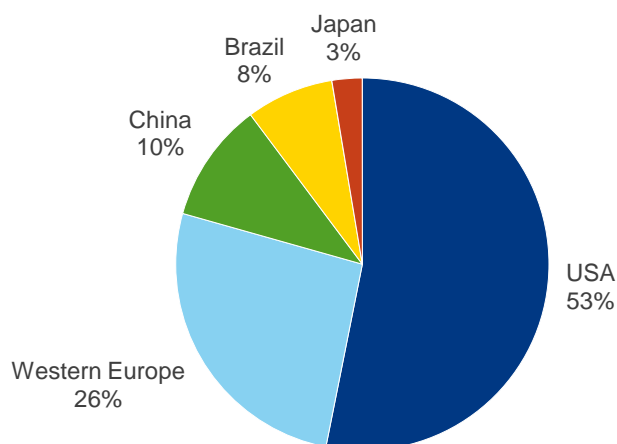
IHS estimates that ADN global nameplate production capacity in 2013 was 1,660 kty, and is not expected to grow appreciably during the next five years. When compared to 2013 estimated demand of 1,259 kty, industry capacity utilization for 2013 was only 76%. Historically, profit margins have only expanded when industry capacity utilization exceeded 85%. For this reason, the low rate of ADN capacity utilization in 2013 was unlikely to create sufficient profit margin to justify the addition of new production capacity. The geographical distribution of 2013 ADN capacity is shown in the chart below. As shown, nearly two-thirds of world ADN capacity is located in the United States.

Figure 3.10: 2013 adiponitrile capacity by region



Source: IHS Chemical Economics Handbook (HMDA)

The regional distribution of 2013 HMDA capacity is presented in the chart below. As shown, over half of world HMDA capacity is located in the United States.

Figure 3.11: 2013 hexamethylenediamine capacity by region

Source: IHS Chemical Economics Handbook (HMDA)

ADN and HMDA announced changes in capacity

The global recession of 2008–2009 caused significant reduction in the demand for durable goods such as carpeting and related household discretionary ‘big ticket’ expenditures, which significantly reduced demand for ADN and HMDA used in nylon 66-based carpet. In response to lower demand, western companies permanently shut down several significant production facilities for ADN and HMDA. The shut-down facilities are listed in the table below.

Table 3.7: Shut down ADN and HMDA production capacity (kty)

Producer	Location	HMDA	ADN
Invista	Maitland, Ontario, Canada	70	
Invista	Wilton, UK	125	
BASF	Seal Sands, UK		125
SSME Azot	Ukraine	11	

Source: IHS Chemical Economics Handbook (HMDA)

Following the slow global economic recovery after 2009, the one significant new announcement of grassroots capacity is Invista’s plan to build 215 kty of HMDA capacity in Shanghai, China, using its new ‘low benzene’ process technology. Invista already has a nylon 66 polymer plant in Shanghai, and is likely to source adipic acid domestically in China given the huge excess of adipic acid capacity in China, as of 2013. Whether the adipic acid product specifications are suitable for fiber-grade nylon 66, given the predominant use of Chinese adipic acid capacity for lower specification polyurethane end uses, is not known.

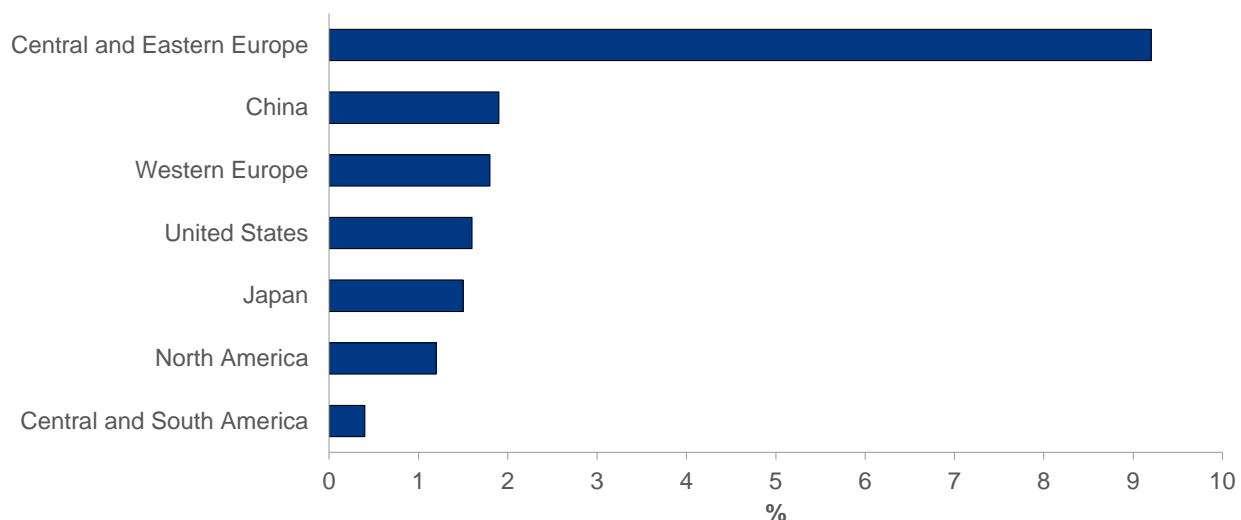
The Invista project is expected to have a total capital cost of approximately US\$1 billion, and includes, in addition to the HMDA plant, and 300 kty adiponitrile plant using third generation butadiene hydrocyanation technology, and 150 kty of nylon 66 polymer capacity.

Beside marketing its own nylon 66 and precursor production, Invista in 2013 signed a long-term exclusive agreement with Petrochemical Conversion Company (PCC) of Saudi Arabia to market the nylon 66 output from PCC's proposed 50 kty nylon 66 complex in Al-Jubail (KSA). PCC is a 50:50 joint venture between Saudi Industrial Investment Group and Chevron Phillips Chemical Company. Proposed project start-up is late 2016 or early 2017. The nylon 66 manufacturing plant is expected to feed imported HMDA and ADA, but includes a nylon compounding plant such that total plant output, including compounded products, will be 120 kty.

Demand growth for ADN and HMDA

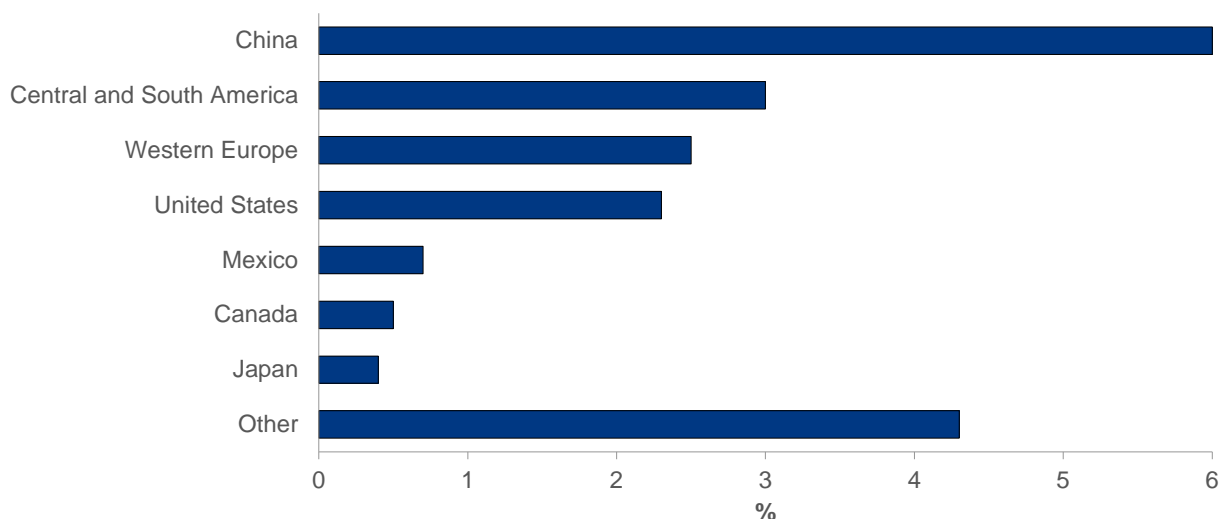
IHS anticipates that demand growth for ADN between 2013 and 2018 will average globally 2% per year. Due to the importation into China of nylon AH salt rather than either ADN or HMDA for producing nylon 66, demand growth in China for ADN is expected to be modest, although demand growth for nylon 66 is expected to average approximately 10% per year over that period of time.

Figure 3.12: 2013–2018 annual demand growth for adiponitrile



Source: IHS Chemical Economics Handbook (HMDA)

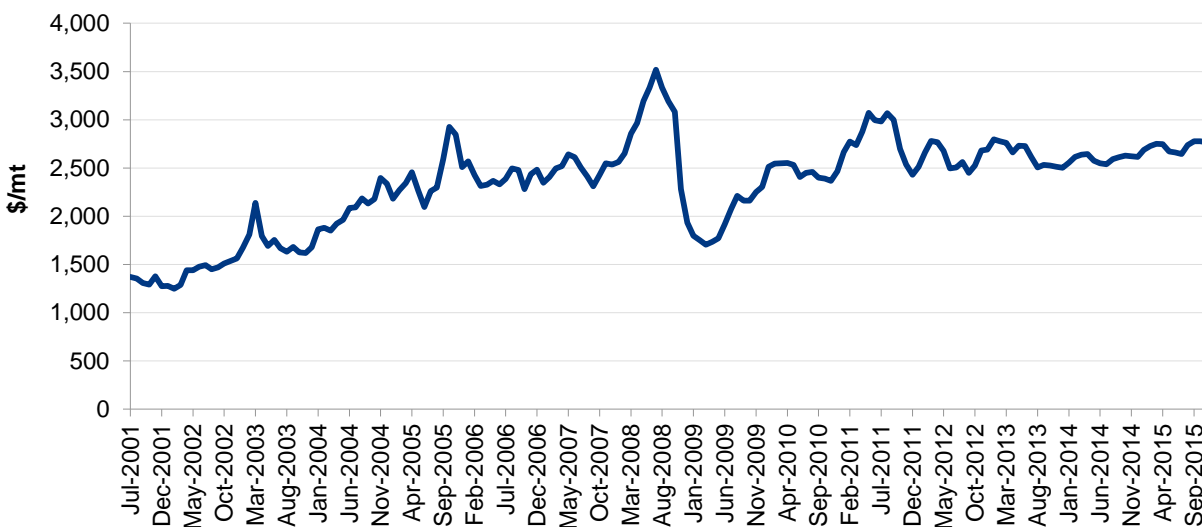
Global HMDA demand growth is expected to average 2.6%/year between 2013 and 2018. As shown in the bar chart below, the largest geographical demand growth is expected to occur in China and in Central and South America, as improving living standards create significant demand for HMDA into nylon 66 residential and commercial carpeting.

Figure 3.13: 2013–2018 annual demand growth for HMDA

Source: IHS Chemical Economics Handbook (HMDA)

Nylon 66 product pricing

US fiber-grade historical nylon 66 contract prices between 2001 and 2013, plus IHS projections to 2015 are shown in the figure below.

Figure 3.14: US nylon 66 fiber-grade resin prices

Source: IHS Chemical Market Pricing Service

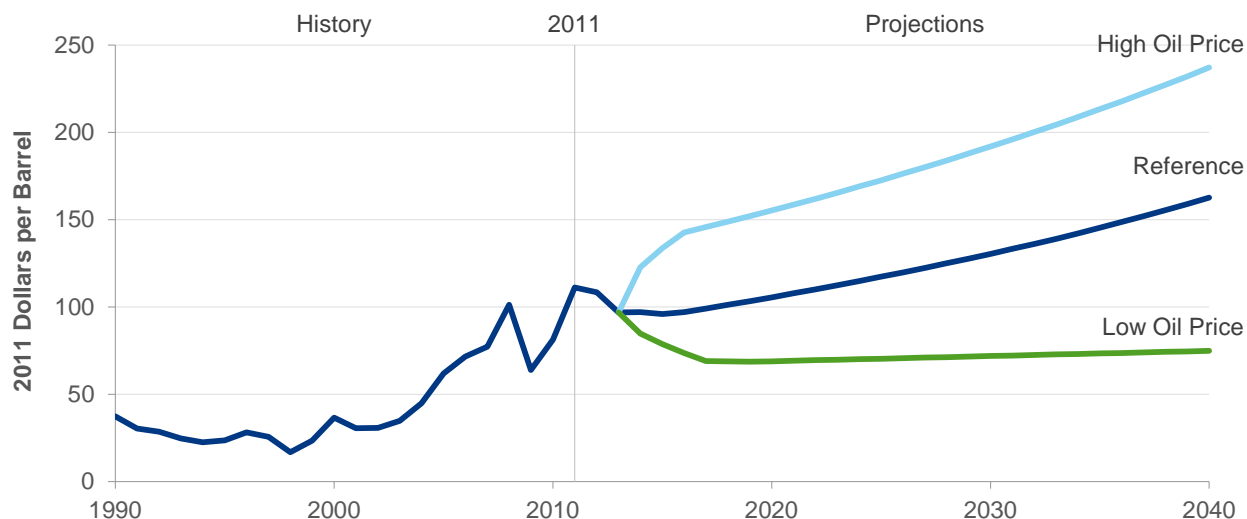
Fundamental energy and feedstock costs

The principal primary feedstocks for making nylon 66 are butadiene using the DuPont/Invista production technology, and acrylonitrile using the Monsanto/Ascend production technology. Both feedstocks are derived from steam cracking, and therefore tied in their fundamental cost structure to the feedstocks used for steam cracking. Most of the world relies on naphtha steam cracking, whose cost is directly tied to the

price of crude oil. Middle Eastern and North American countries have access to lower cost natural gas-based feedstocks (ethane, propane, butane) for steam cracking, and are expected to maintain that feedstock cost advantage.

The US Department of Energy maintains a forecast for benchmark crude oil prices. Its 2013 annual energy outlook projects that average spot prices for Brent benchmark crude oil will increase modestly from US\$100/bbl in 2010 to US\$150/bbl in 2035, as shown in the figure below.

Figure 3.15: US DOE crude oil price forecast

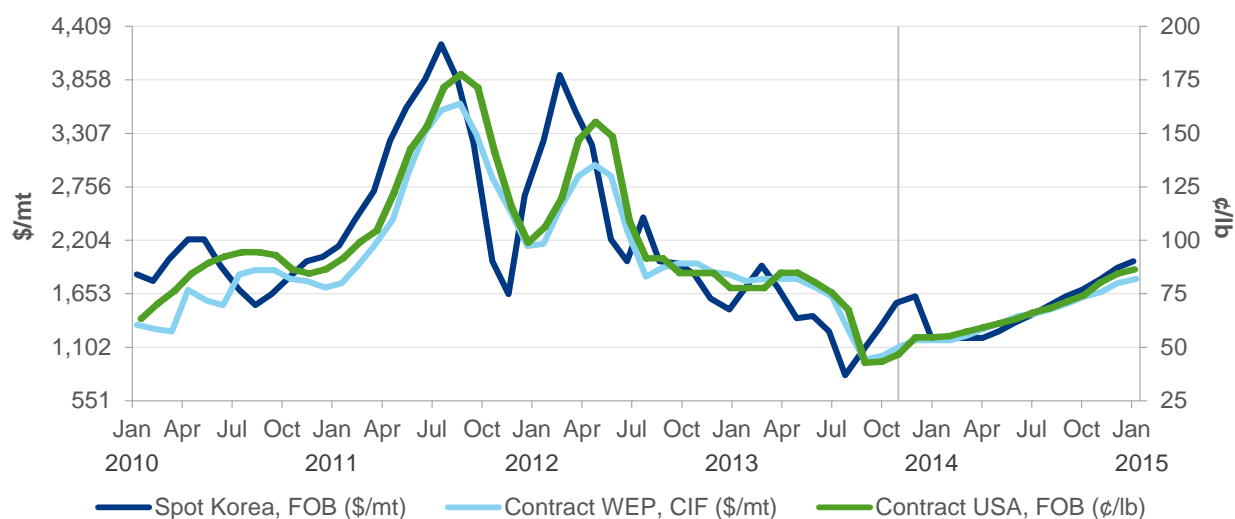


Source: Annual average spot price for Brent crude oil in three cases, 1990–2040 (2011 dollars per barrel), US EIA Annual Energy Outlook 2013

Butadiene pricing outlook

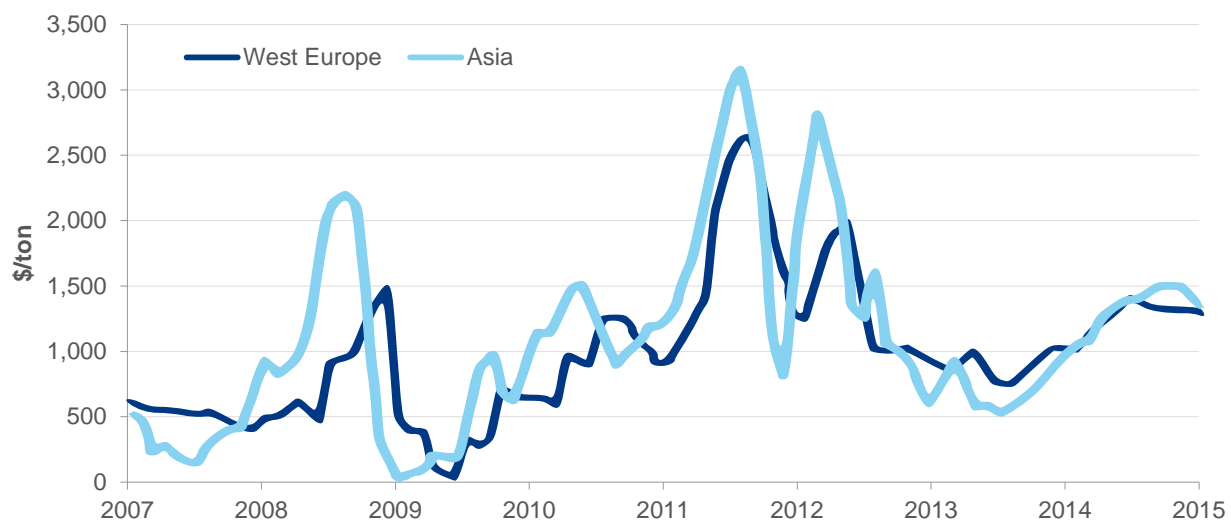
As steam crackers globally gravitate toward cracking lower cost natural gas by-product feedstocks (ethane, propane, butane) rather than higher cost liquid feedstocks (naphtha, gas oil), the steam cracker yield of by-product butadiene decreases. As a result, butadiene prices have increased substantially faster than other materials sourced from petroleum.

The figure below presents IHS Chemical's historical and forecast price for butadiene. Compared to naphtha at approximately US\$900/mt (tied to crude oil at US\$100/bbl), the butadiene price range of US\$1,600–2,000/mt is well above the naphtha steam cracking feedstock cost, and is forecast by IHS Chemical to remain that way.

Figure 3.16: Butadiene historic and forecast price

Source: IHS Chemical Global C4 Olefins & Elastomers (May 2013)

The historical and forecast price spread (differential) between naphtha and butadiene is shown in the figure below. Although there were unusual short-term butadiene price spikes in 2011, and again in 2012, the IHS Chemical forecast anticipates the spread to increase from US\$500/mt to US\$1,500/mt, as the shortage of butadiene increases with progressively more steam cracking of lighter feedstocks.

Figure 3.17: Butadiene to naphtha price spread

Source: IHS Chemical Global C4 Olefins & Elastomers (May 2013)

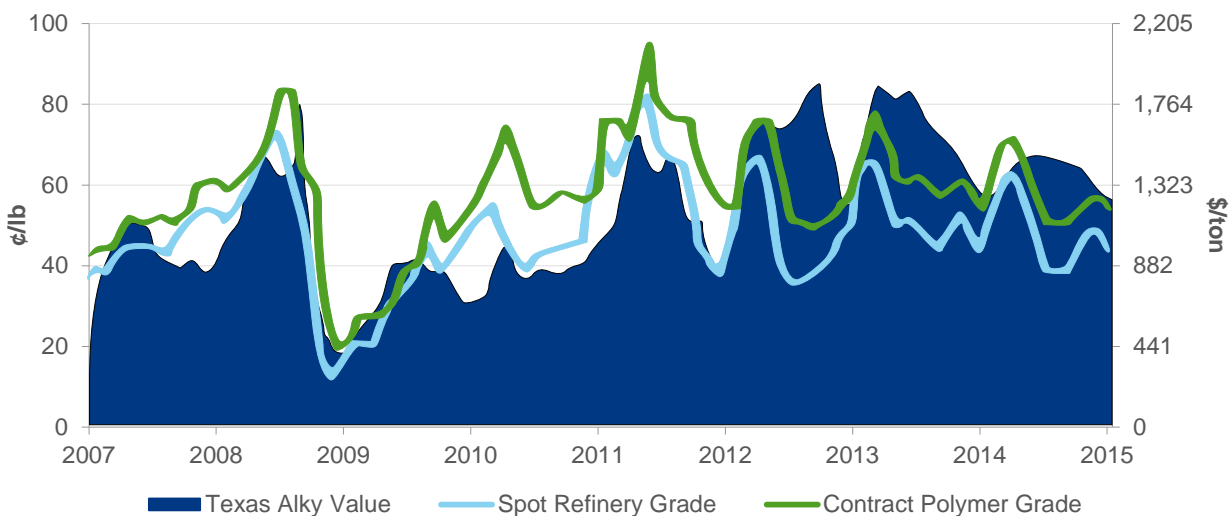
Acrylonitrile pricing outlook

Acrylonitrile is produced directly from propylene, which, in turn, is produced as a main coproduct of steam cracking. Similar to the situation with butadiene, steam cracking gas feedstocks produce less propylene than steam cracking naphtha. As a result, propylene prices are forecast by IHS Chemical to

increase faster than naphtha prices, and propylene price is also expected to maintain a price premium over comparable ethylene prices.

The figure below shows IHS Chemical's 2013 short-term historical and forecast price scenario for North American propylene. Contract propylene prices are expected to remain well above naphtha prices.

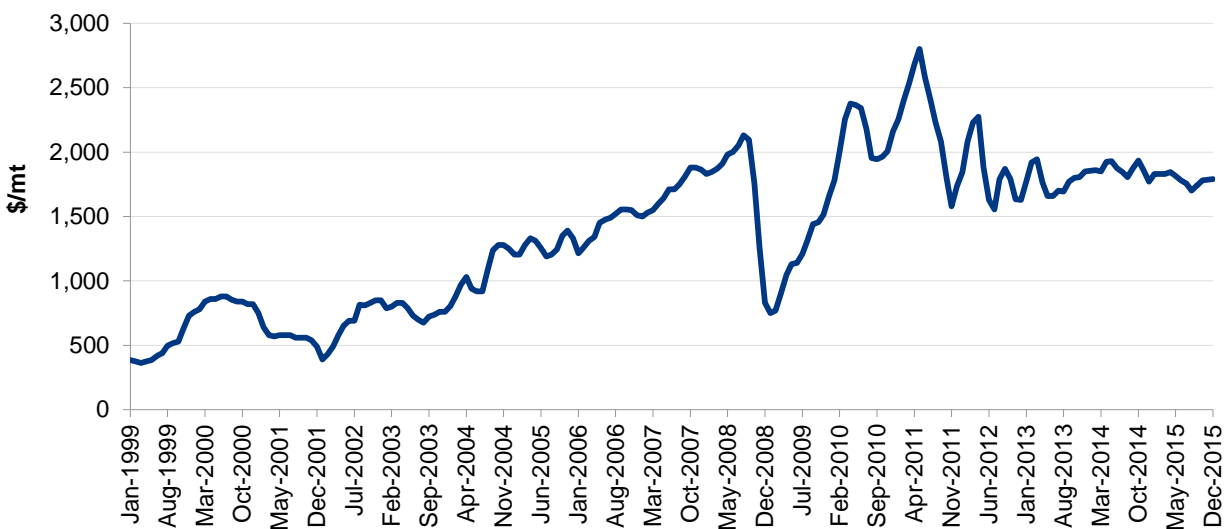
Figure 3.18: US short-term propylene prices



Source: IHS Chemical North America Light Olefins Market Report (May 2013)

The figure below shows IHS Chemical's 2013 spot export historical and forecast price scenario for North American acrylonitrile.

Figure 3.19: US historical and forecast acrylonitrile prices



Source: IHS Chemical North America Light Olefins Market Report (May 2013)

Invista legal proceedings

When DuPont sold its nylon, polyester, and spandex fiber business to Koch Industries in 2004 for approximately US\$4 billion, the acquired business was subsequently re-named Invista, and the business has been beset by highly publicized lawsuits between Invista and DuPont, and also between Invista and Rhodia (now owned by Solvay).

In the early 1960s, DuPont converted its HMDA manufacturing operations from cyclohexane chlorination process technology to butadiene hydrocyanation technology. The first step of the then new technology involved converting the primary HMDA feedstock to adiponitrile, which in the second step hydrogenates ADN to HMDA. The newer approach was called ‘Generation 1 Adiponitrile Hydrocyanation Technology.’

Besides operating its US nylon business, DuPont entered in 1975 into a joint venture with Rhone-Poulenc, the predecessor company to Rhodia (now owned by Solvay), to make ADN using first-generation butadiene technology. The DuPont/Rhone-Poulenc joint venture was named Butachimie. The joint venture subsequently built a nylons complex in Chalampe, France with an ADN capacity of approximately 500 kty. The terms of the JV [31C10] included non-disclosure of proprietary information for 15 years. When DuPont sold its nylon fibers business to Koch Industries, DuPont’s portion of the Butachimie joint venture was transferred to Koch as part of the financial transaction.

In 1998, Invista sued [31C11] both DuPont and Rhodia, claiming both companies had conspired to steal the ‘first-generation ADN technology’ it had purchased from DuPont as part of the nylon fibers business transaction.

Invista’s 2008 lawsuit against both DuPont and Rhodia was based on its claim that DuPont and Rhodia were planning to jointly build new ADN capacity in Asia or the Middle East to serve those markets, using the technology that Invista had purchased from DuPont in 2004. One of the major legal issues [31C12] was whether Rhone-Poulenc (now Rhodia-Solvay) was entitled to use the process know-how from the Butachimie plant as the basis for a new plant in Asia.

Invista also sued DuPont [31C13] in March 2008, separately claiming that the US nylon complex assets it had purchased had over 600 instances of regulatory non-compliance. Part of the 2004 sales agreement between DuPont and Invista included having DuPont indemnify Invista against ‘all environmental claims’ associated with the manufacturing facilities purchased. Upon discovering instances of regulatory non-compliance, including the uncontrolled venting of benzene vapors at its Victoria, Texas nylon complex, Invista informed the US EPA and Texas Commission on Environmental Quality (TCEQ) and entered into a voluntary US\$1.7 million consent decree to remediate the identified problems. Invista claimed to have spent over US\$140 million to correct the regulatory problems. Invista also claimed that it had promptly notified DuPont of the discovered environmental problems, but that DuPont ignored the issues. The most frequently cited problem by Invista was a benzene stripper at Victoria, Texas, used to remove dilute benzene from a wastewater stream generated by the ADN process unit. Due to its discovery of this issue at Victoria, Invista identified a similar problem at the Orange, Texas ADN manufacturing plant, where benzene containing wastewater sludge was dewatered in a filter press to form a solid cake, and subsequently sent off-site for land disposal as a hazardous waste. Invista and the regulatory authorities agreed to a consent decree in 2009 [31C14] defining actions steps Invista would take to mitigate violations of its environmental permits. The terms included eliminating benzene waste emissions by installing its next-generation ADN technology at Orange and Victoria (by year end 2016), which was claimed by Invista to eliminate the formation of benzene by-products.

The DuPont first-generation ADN technology used zinc chloride as the catalyst for butadiene hydrocyanation. After the JV agreement with Rhone-Poulenc, DuPont developed on its own second-

generation ADN technology using triphenylboron catalyst, which was commercialized at Orange, Texas, in the 1980s, and later at a new plant in Victoria, Texas.

On 3 November, 2008, Invista's US lawsuit against Rhodia was dismissed by the US Federal Court for the Southern District of New York.

On September 13, 2010, DuPont and Invista jointly announced [31C15] that they have settled the three lawsuits between them involving nylon 66 technology, adiponitrile technology and supply agreements. Terms of the settlement were not disclosed.

4. Chemistry and process technology

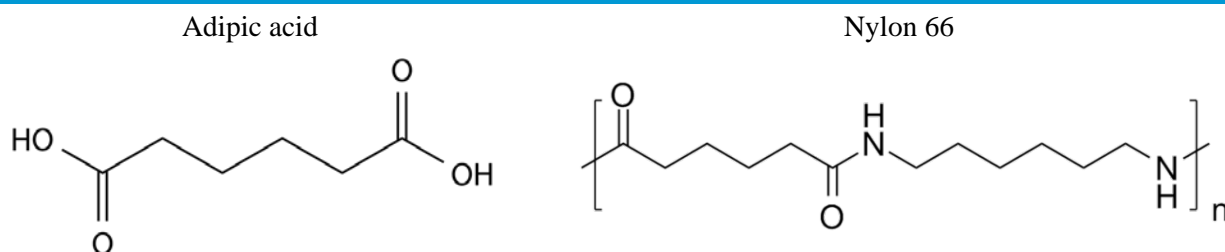
Chemical structure of adiponitrile and hexamethylenediamine

Both HMDA and ADN are linear C₆ molecules with radical groups on both terminal carbon atoms. ADN has nitrile (CN) groups on both terminal carbon atoms. HMDA has amine groups (NH₂) on both terminal carbon atoms. HMDA is a strong base, such that solutions of HMDA in water have alkaline pH. A 10% solution of HMDA in water has a pH of 12.3. When reacted with organic acids, HMDA forms stable salts. ADN at standard conditions is a clear, viscous liquid. HMDA at standard conditions is a solid.

HMDA is produced commercially by hydrogenating ADN. HMDA is then copolymerized with adipic acid (ADA) to produce nylon 66 polyamide. Adipic acid is also a C₆ linear molecular, and has organic carboxylic acid groups (COOH) on both terminal carbon atoms.

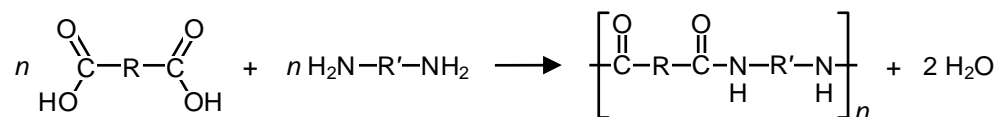
Nylon 66 is a medium molecular weight polyamide. Due to the linear carbon atom backbone of both components, nylon 66 is formed as a crystalline structure. Other specialty polyamides made with aromatic or iso-carbon structures are formed in the amorphous state. The molecular structures of adipic acid and nylon 66 are shown in the figure below.

Figure 4.1: Molecular structure of adipic acid and nylon 66



Chemical reaction for producing nylon 66

The reaction of 1 mol HMDA plus 1 mol ADA to yield 1 mol nylon 66 produces two mols of water for each mol of reacting HMDA, as shown in the stoichiometric reaction below.



Nylon 66 process summary

The copolymerization of HMDA with ADA to form nylon 66 is conducted in a water solution as a nylon salt. The water solution is subsequently removed by evaporation under pressure to produce a salt concentration of up to 80%. As the concentration increases, the reactant solution gradually converts to a melt. Final salt concentration occurs by flashing the melt under vacuum conditions to remove residual

water. Properties of the polymer are dictated by a combination of temperature, pressure, residence time, and concentration of reactants.

Nylon 66 is produced commercially using both batch processing systems and continuous processing systems. In batch environments, the reaction occurs in a single reactor, first under pressure, and then under reduced pressure (partial vacuum). In continuous systems, the reaction occurs in multiple reactors arranged in series configuration. Most large capacity nylon producers utilize the continuous process. The average nylon 66 molecular weight ranges between 11,000 and 18,000. Additional heating and melting under vacuum is used to increase the molecular weight range from 24,000 to 29,000, which is more suitable for injection molding.

Once formed, nylon 66 virgin resin is extruded in water (underwater bath or water ring) to form pellets. Fabricators melt the pellets and either extrude them or inject them into desired shapes. For fiber applications, the fiber is initially drawn from a melt into a bulk continuous filament. The filament can be chopped and bundled to form staple fibers.

Traditional compounding of virgin nylon 66 resin is conducted for the purpose of adding lubricants to improve mold release, incorporating color into the resin, adding heat stabilizers, and/or adding nucleating agents to reduce mold cycle time. Other additives are often used to reduce hydrolysis and provide oxidative stability. Silicone is often added as a wetting agent.

Nylon 66 historical background

Nylon 66 was commercialized in 1939 by DuPont, following discoveries in the 1930s by chief scientist Wallace Carothers, who was initially seeking a fiber with the strength of spider fiber. DuPont's virgin nylon 66 resin is trademarked Xytel™. DuPont initially found wide market use for nylon 66 fiber in women's hosiery and carpet facing. Later nylon 66 was used as belt material for tires, especially in radial tires.

Nylon 66 fiber is usually formed by melt spinning. It can be formed into monofilament or multi-filament yarn, or converted to staple fiber or fiber tow. Nylon 66 is generally recognized as the strongest synthetic fiber in commercial use. Properties of nylon 66 are listed in the table below.

Table 4.1: Nylon 66 properties

CAS number	32131-17-2
Formula	$(C_{12}H_{22}N_2O_2)_n$
Specific gravity	1.14
Melt temperature, °C	263
Water absorption, 24 hours %	8.5
Tensile strength, psi	12,400
Elongation % at 73°F	90
Flexural strength, psi at 73°F	17,000
Flexural modulus, psi at 73°F	4.1×10^5
Rockwell hardness, ft-lbs/in	1.2
Heat deflection, °F	455
Volume resistivity, 73°F ohm-cm	1,015
Dielectric constant, 60 Hz, 73°F, 50% RH	4
Dielectric strength V/mil	600

Technology basis for nylon 66 competing with nylon 6

Although the production cost for producing nylon 6 via the homopolymerization of caprolactam has historically been lower than the production cost for producing nylon 66 via the copolymerization of HMDA and ADA, nylon 66 has certain performance properties in market place use that compensate for its higher production cost. These superior performance properties allow nylon 66 to remain a competitive option for certain end use applications, and provide modest demand growth opportunities. The performance advantages of nylon 66 are listed in the table below.

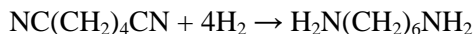
Table 4.2: Nylon 66 resin property advantages versus nylon 6

Nylon 66 molecular structure is more ordered with more, and stronger, hydrogen bonding

- Better mechanical properties
 - ✓ Higher tensile strength (nylon 66 is the strongest aliphatic nylon)
 - ✓ Higher modulus (stiffness)
 - ✓ Higher dimensional stability
 - ✓ Higher abrasion resistance
- Better low-temperature toughness
 - ✓ Higher heat tolerance, better heat aging
 - ✓ Higher temperature (265°C vs. 220°C)
 - ✓ Higher dimensional stability at elevated temperature
 - ✓ Suitable for use in engine compartment

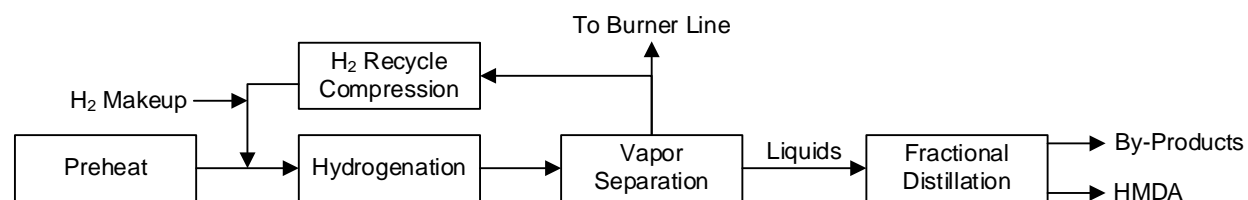
Chemical reactions for hydrogenating ADN to HMDA

All of the commercial routes (butadiene, acrylonitrile, adipic acid) to producing HMDA make ADN as an intermediate product, which is then hydrogenated to HMDA. The ADN hydrogenation reaction stoichiometry is presented below.



The hydrogenation reaction is conducted in the liquid phase in the presence of ammonia (NH_3). NH_3 is used to absorb some of the exothermic heat of reaction, and to also minimize the production of unwanted by-products by minimizing the removal of nitrogen atoms from the CN terminal carbon groups. The dominant catalyst for this hydrogenation is promoted cobalt, although iron oxide can also be used. Typical reactor conditions are a temperature range of 100–200°C, and a pressure range of 28–41 MPa. By-products from the reaction are 1,2-diaminocyclohexane, hexamethyleneimine, and bis(hexamethylenetriamine). They are typically separated from HMDA by fractional distillation, and are each purified by distillation to sales specifications and sold as commercial products. A block flow diagram for the hydrogenation process is shown in the figure below.

Figure 4.2: Hydrogenation of ADN to HMDA



Hydrogen cyanide production

The conventional DuPont/Invista process technology for producing HMDA reacts butadiene with hydrogen cyanide (HCN) to produce adiponitrile. Since HCN is extremely toxic, there are regulatory restrictions on transporting HCN on public roadways. As a result, large consumers of HCN must produce it onsite. For this project, we include an onsite HCN production plant. Other names for HCN are formonitrile, hydridonitridocarbon, hydrocyanic acid, and prussic acid.

Hydrogen cyanide properties

At standard conditions, HCN (CAS: 74-90-8) is a pale blue liquid, or a volatile gas that boils at 26°C. Therefore, under moderate warming it will evaporate to form a gas. In either state, HCN is an extremely toxic compound. Its molecular structure is shown in the figure below.

Figure 4.3: Hydrogen cyanide molecular structure



HCN is used widely in the chemical industry as a pharmaceutical precursor, and agent for polymerization. Its high reactivity is due to the triple bond between the carbon and nitrogen atoms. HCN dissolves readily in water, and partially ionizes in aqueous solutions. Most users of HCN try to avoid storing it in large quantities, and where it must be stored, the storage container is usually small in size and buried underground. Physical properties of HCN are listed in the table below.

Table 4.3: Hydrogen cyanide physical properties

CAS number	74-90-8
Chemical formula	HCN
Molecular weight	27.03
Boiling temperature, °C	26
Liquid density, g/ml	0.687
Vapor specific gravity vs. air	0.93
Melting temperature, °C	-12 to -14
K_H in $\mu\text{mol}/\text{Pa}\cdot\text{Kg}$	75
Refractive index (n_D)	1.2675
Liquid viscosity, $\mu\text{Pa}\cdot\text{s}$	201
Vapor pressure at 20°C, mmHg	620
Flash point, °C	-17.8
Autoignition temperature, °C	538
Standard entropy of formation, kJ/mol	109.9
Standard enthalpy of combustion, kJ/mol	-426.5
Standard molar entropy, J/K-mol	113.01
Specific heat capacity, kJ/K-mol	71
Upper flammability limit, %	40
Lower flammability limit, %	5.6

HCN safety considerations

Hydrogen cyanide is extremely toxic to humans. Exposure to vapor concentrations of HCN at 300 ppm can be fatal. Breathing HCN vapors at 300+ ppm can be fatal almost instantly. HCN's effect on the body is thought to affect the cell oxidation process. HCN can poison people via inhalation, physical contact with eyes or skin, or if swallowed. HCN readily enters the body through skin.

The US limit for occupational exposure to HCN [31C16] is 10 ppm in air averaged over an 8 hour period. This is equivalent to 11 milligrams HCN per cubic meter of air (mg/m^3). The US Occupational Safety and Health Administration (OSHA) is evaluating the reduction of the exposure standard down to 5 ppm. The US National Institute for Occupational Safety and Health (NIOSH) recommends the use of personnel protective equipment for exposure to HCN at the concentrations listed in the table below.

Table 4.4: US NIOSH personal protective equipment for HCN exposure

Respirator recommendations	
Up to 47 ppm	(APF = 10) Any supplied-air respirator
Up to 50 ppm	(APF = 25) Any supplied-air respirator operated in a continuous-flow mode
	(APF = 50) Any self-contained breathing apparatus with a full facepiece
	(APF = 50) Any supplied-air respirator with a full facepiece

Source: US NIOSH

If an HCN fire occurs, it should be extinguished with dry chemical, carbon dioxide, or alcohol foam. Direct dousing with water is not recommended.

Commercial HCN uses

HCN is both produced as an on-purpose chemical, and also as a by-product from acrylonitrile manufacture. Due to its extreme toxicity, acrylonitrile producers are usually located adjacent to producers of methyl methacrylate (MMA), which consumes HCN as a primary feedstock to produce MMA via the acetone cyanohydrin process. In the absence of an MMA plant, most commercial acrylonitrile producers consume HCN in an on-purpose process unit to manufacture sodium cyanide (NaCN), which is used as a mining chemical especially in extracting gold and silver from ore.

Due to its highly polar nature, HCN is an excellent solvent for many reactions, but its use is limited by high toxicity and high volatility. In the presence of alkaline chemicals (ammonia or sodium cyanide), HCN readily polymerizes. HCN readily reacts with aldehydes and ketones (especially acetone) to form cyanohydrins.

Commercial HCN production technologies

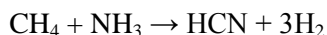
The classical Andrussov technology is practiced at the two DuPont/Invista HMDA plants in Texas. This process forms HCN by the direct ammoxidation (using ammonia) of natural gas in air over platinum catalysts. The DuPont technology has been licensed to Kvaerner [31C17] for worldwide application, based on a former DuPont HCN plant serving an MMA production site (originally owned by ICI) in Memphis, Tennessee, USA. The DuPont technology incorporates technology improvements in the areas of high temperature catalyst reaction performance, high efficiency excess ammonia recovery, and high yield of HCN. As of 2013, DuPont continues to out-license [31C18] the process technology as 'DuPont Andrussov HCN process.' The basic reaction is shown below.



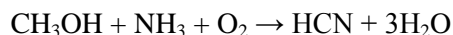
The ammoxidation reaction is exothermic (-114.9 kcal/g-mol). The reaction can be operated adiabatically, with a large increase in temperature from inlet to outlet. Operating temperatures approach 1,200°C. The platinum catalyst is provided in gauze form (90% Pt/10% Rh). A key characteristic of the process is pretreatment of both natural gas and ammonia. The original process operated a low pressure (atm to 65 psia). Excess ammonia is used to drive the forward vapor-phase reaction to completion, increase kinetics, and minimize side reactions. Excess ammonia is recovered via absorption into a liquid solvent (ammonium dihydrogen phosphate), which can be subsequently steam stripped to recover the ammonia in pure form. Due to the corrosivity of HCN and high temperature operations, metallurgy at modest

temperature is stainless steel, at elevated temperature is nickel alloy (Incoloy 800), while the reactor internals are refractory lined.

Also well commercialized and out-licensed is the Evonik (formerly Degussa) BMA process for HCN production. The Evonik process reacts natural gas with ammonia in the absence of air to produce HCN and hydrogen. The key reaction stoichiometry is presented below.



Other approaches to HCN production include the vapor-phase ammoxidation of methanol [31C19] over supported catalysts (iron/bismuth oxide). The chemical reaction is presented below:

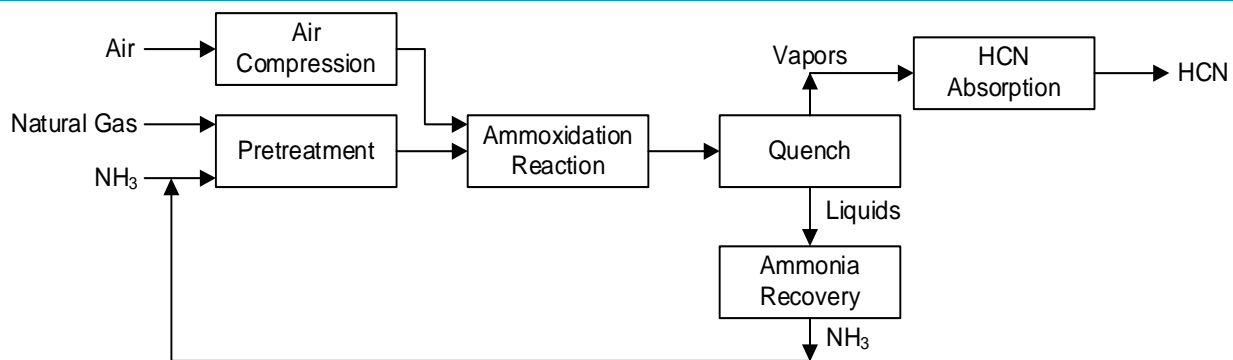


All of the ammoxidation reaction approaches are highly exothermic, requiring either external pump around cooling, internal cooling coils, or a jacketed reactor with cooling coils.

Process description

A block flow diagram for our understanding of the DuPont Andrussow process is shown below.

Figure 4.4: DuPont Andrussow process for HCN production



Liquid ammonia from storage is vaporized and combined with recycle ammonia after both are passed through fine filters. The combined ammonia stream is mixed with filtered and compressed air, heated, and enters the ammoxidation reactor along with preheated natural gas. The reaction occurs at 30 psia and 1,200°C. Conversion is almost instantaneous over the platinum wire gauze catalyst bed. A close coupled boiler quenches the reactor product gases while producing high pressure (1,200 psia) superheated steam, which is used to drive a steam turbine which spins the compressor for the feed air. The quench must be rapid to minimize the formation of azulmic acids.

Quenched reactor products are passed through a second heat exchanger used to preheat the feed components. The combined cooled vapor stream from the reactor is scrubbed with a solution of 30% ammonium dihydrogen phosphite in water to absorb excess ammonia while condensing water that is produced by the reaction. The vapor stream from the scrubber contains HCN in nitrogen from the air feed.

The ammonium dihydrogen phosphite aqueous solution, containing the excess absorbed ammonia, is processed through a stripping column to remove residual HCN. The liquid solution is then heated in a

second stripping column to release the excess ammonia as a vapor, which is recompressed and recycled to the front of the process. The ammonia free solution is then reconcentrated by partial evaporation to remove the water produced by the reaction, and recycled. The water-rich stream is sent to the plant's wastewater treatment plant.

The HCN-rich vapor stream from the scrubber is chilled to 21°C (70°F), and directed to an HCN absorption column. The HCN is absorbed in acidic water to an HCN solution strength of 5 weight %. The HCN free vapor stream is sent to a vapor incineration system for complete destruction of residual HCN. The HCN aqueous solution is then sent to a distillation column to produce pure HCN as the overhead distillate product, and water as the bottoms product.

Adiponitrile from butadiene via DuPont/Invista hydrocyanation

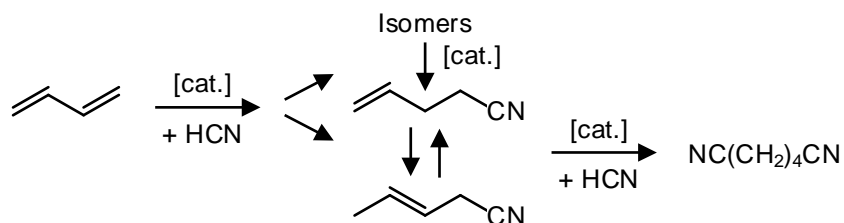
Background

The historical DuPont/Invista process for making adiponitrile, and subsequently HMDA, was initially commercialized via the 4-step chlorination of butadiene. This process was later replaced with the 3-stage hydrocyanation of butadiene with HCN at DuPont's Orange (Texas, USA) plant in 1971. The 3-step technology was also used when DuPont built its Victoria (Texas, USA) nylon 66 complex in 1983. The 3-step process includes hydrocyanation of butadiene first to linear pentenenitrile, and subsequently adiponitrile, followed by isomerization of by-product methyl butenenitrile to linear pentenenitrile, followed by hydrogenation of adiponitrile to HMDA. Both Texas plants used what DuPont called first-generation technology. An improved second-generation DuPont ADN process was licensed by DuPont to a joint venture of DuPont with Rhone Poulenc (now Rhodia/Solvay) called Butachimie in France. We believe that the two Texas plants currently (2013) utilize second-generation technology. In 2001, DuPont commercialized its third-generation ADN technology at the Butachimie plant.

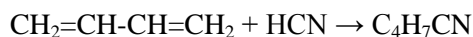
Chemistry

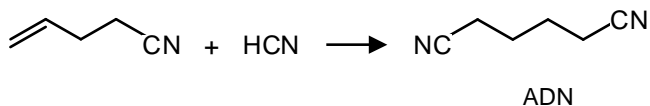
Since the ownership transfer of DuPont's nylon 66 business to Invista, a fourth-generation technology has been developed by Invista. Invista is believed to be planning to use the fourth-generation technology at its announced (in 2013) Shanghai, China, HMDA plant, which is designed with a capacity of 215 kty.

Butadiene in a liquid solvent reacts with HCN to form isomers of pentene nitriles and methyl butene nitriles, as shown by the equation below.



In general, when butadiene first reacts with HCN, a mononitrile is formed, as shown in the equation below.





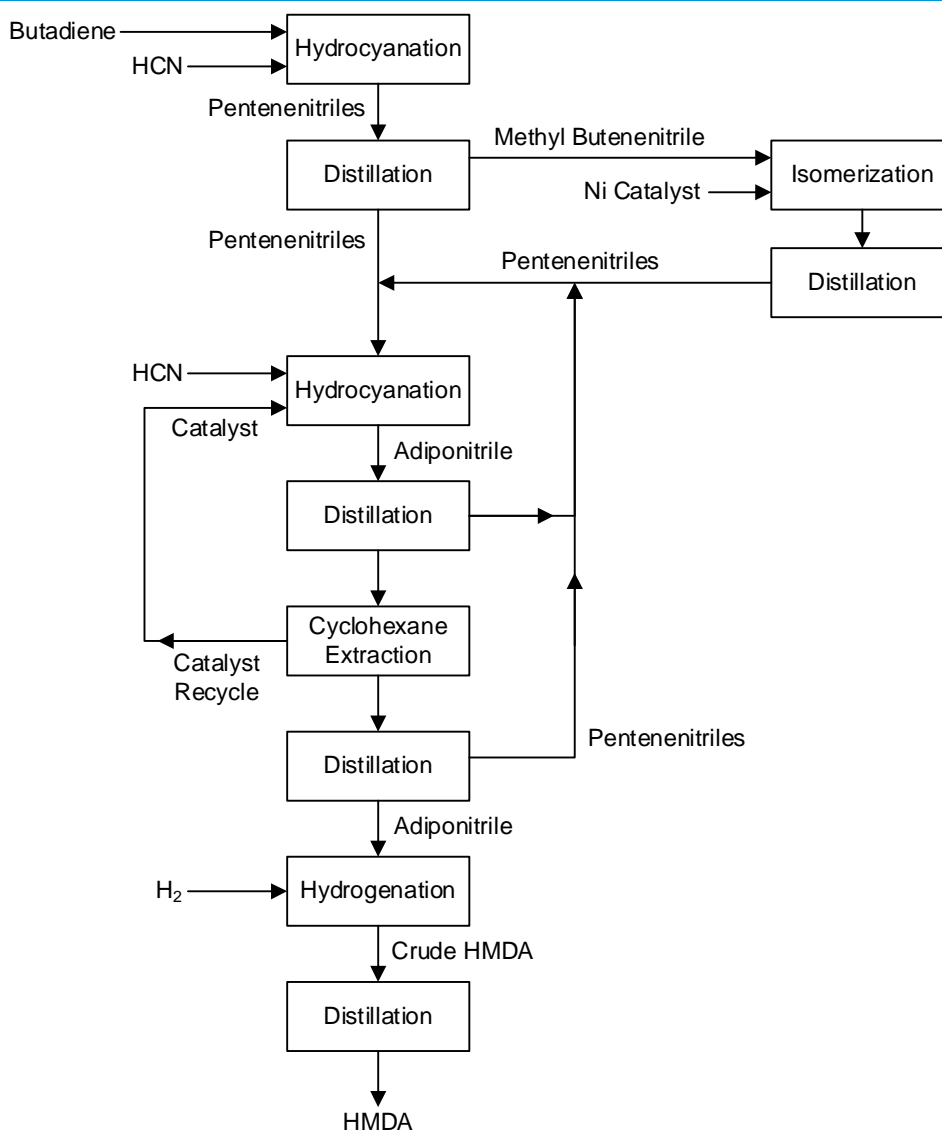
By-product pentenenitriles are separated from ADN by distillation, and recycled to the front of the reaction sequence after 2-pentenitrile is removed via sulfite addition. The final hydrocyanation to form ADN also makes by-products 2-methylglutaronitrile (MGN), ethylsuccinonitrile (ESN), and 2-pentenitrile (2PN). The by-products can be separated from ADN via fractional distillation.

At the completion of the hydrocyanation reactions, the nickel catalyst is recovered using an extraction solvent, usually cyclohexane. Tetrahydrofuran has also been used as catalyst recovery solvent. The nickel catalyst is soluble diphosphite-nickel, which replaced the earlier monodentate phosphite catalyst. Following extraction, the catalyst is recovered by a combination of ammoniation, evaporation, calcination, and reaction with tri-*o*-tolyl phosphite.

Block flow diagram

A block flow diagram for this processing sequence is presented below.

Figure 4.5: HMDA from butadiene via direct hydrocyanation



Butadiene vapor and hydrogen cyanide are reacted in the gas phase at 80°C and 115 psi to produce crude pentenenitriles. The reactor product is distilled to recover and recycle excess butadiene. The catalyst package is a combination of nickel tri-*o*-tolyl and phosphite. The distillation separates by-product methyl butenenitrile and isomerizes it using nickel catalyst also to pentenenitrile, which is directed to a hydro cyanation reactor. The reactor operates within a range of 41–85°C and ambient pressure to produce crude adiponitrile. The catalyst package for this hydro cyanation is of nickel tri-*o*-tolyl, phosphite, and triphenyl borane promoter.

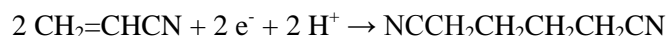
The crude adiponitrile is distilled to separate and recycle pentenenitriles. The bottoms product from distillation contains both adiponitrile and catalyst residue. The catalyst residue is extracted with cyclohexane and recycled to the hydro-cyanation reactor. Another separation is performed to recover the extraction solvent, with the product being purified adiponitrile.

Purified adiponitrile is hydrogenated to produce crude HMDA, which is purified via distillation.

Adiponitrile from acrylonitrile by electrodimerization

Chemistry

Ascend, Asahi, and most of the European HMDA producers (BASF, Rhodia/Solvay) make ADN via the electrodimerization of acrylonitrile. Monsanto first commercialized this technology in 1965, where the dimerization occurs on the cathode side of the cell. The chemical reaction is shown below.



The reactions in the cell occur at 50–60°C. By-products from the reaction include propionitrile and bis(cyanoethyl) ether. The cathode solution contains a combination of water, acrylonitrile, and tetraalkylammonium salt. A representative composition is 15% ADN, 15% acrylonitrile, 39% quaternary ammonium salt, 29% water, and 2% water. On the anode side of the electrolytic cell, the solution is sulfuric acid in water. As ADN is formed on the cathode side of the cell, the solution is continuously circulated so that ADN can be removed outside the cell and recovered, with the now ADN free solution returned to the cathode side of the cell. As the reaction proceeds, oxygen is stripped from water on the anode side of the cell, and is vented to atmosphere. The cathode solution is distilled to purify ADN, such that overall yield from acrylonitrile is 92–95%.

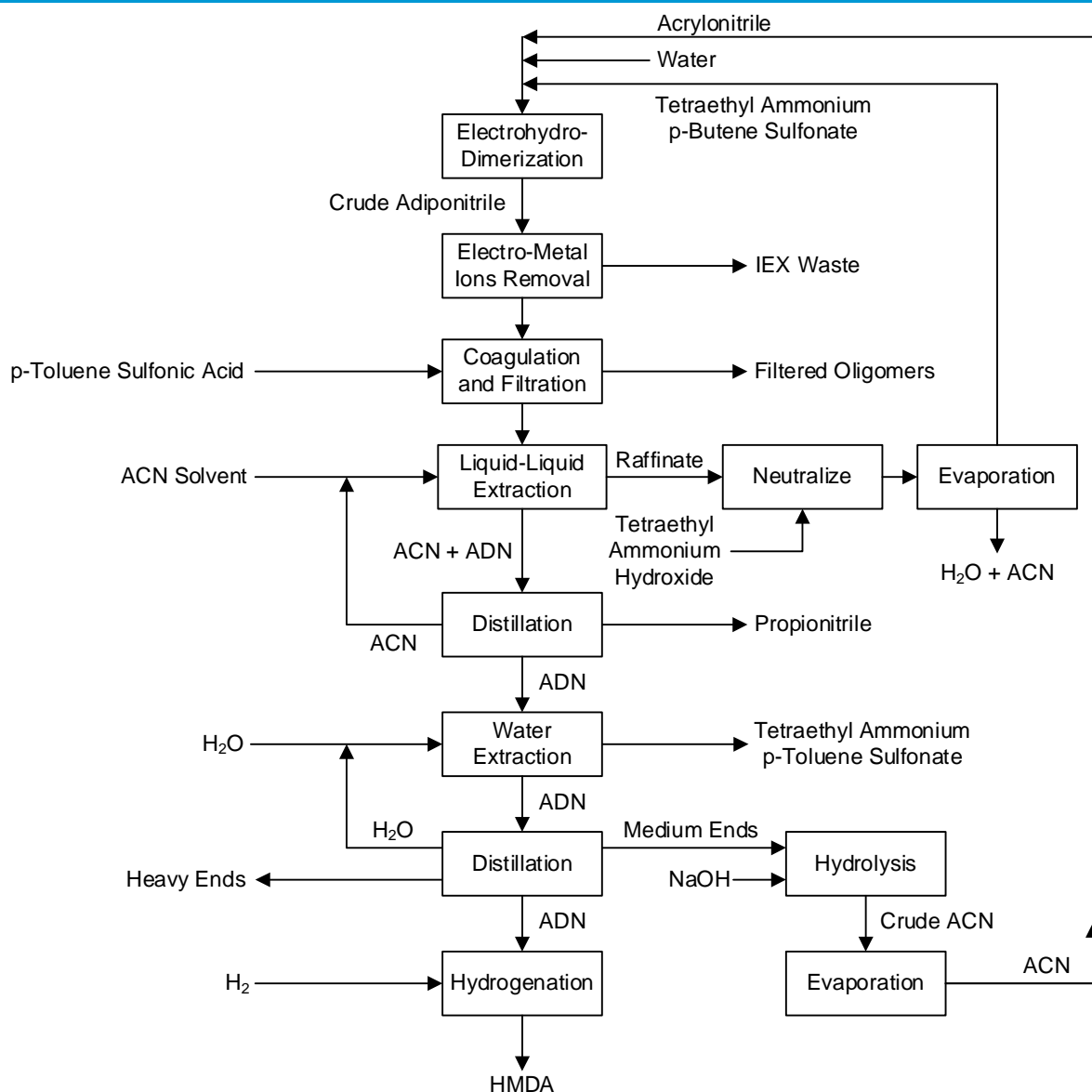
Process technology

There are three primary commercial routes to ADN using acrylonitrile as feedstock via electrodimerization. The three routes are:

1. Electrohydrodimerization in solution using a membrane cell
2. Electrohydrodimerization in emulsion in a divided cell
3. Electrohydrodimerization in an undivided cell

HMDA from acrylonitrile via electrohydrodimerization in solution

An aqueous solution of acrylonitrile in water is formed, and circulated through the cathode side of the electrolytic cell, where crude adiponitrile is formed. To increase the electrical conductivity of the solution, tetraethylammonium p-toluene sulfonate is added. As adiponitrile is formed in the solution, the solution is removed and distilled to remove the ADN while reconcentrating and recycling the aqueous solution containing unconverted acrylonitrile. A block flow diagram of the process is presented below.

Figure 4.6: Solution electrodimmerization of acrylonitrile to adiponitrile

The aqueous solution continually circulates through the electrolytic cell. As the crude adiponitrile solution is removed from the electrolytic cell for purification, it is first passed through beds of alkaline ion exchange resin to capture the small concentration of metal ions formed during the process, and remove them from the system. The metal loaded ion exchange resin can be re-generated offline by processing with strong alkaline solution. The stream also contains small concentrations of oligomers (dimers, trimmers, tetramers) that would otherwise foul downstream processing equipment. The oligomers are precipitated out of solution using p-toluenesulfonic acid, with the solution then filtered to physically remove the oligomers.

The crude adiponitrile solution passes through a liquid-liquid extraction unit fed with fresh acrylonitrile, which is used to remove the adiponitrile from water. The water-rich liquid raffinate stream (now nearly free of adiponitrile) is neutralized with tetraethyl ammonium hydroxide, and partially evaporated to reconcentrate the solution. Water is a by-product of the primary chemical reaction, and must be removed from the system. Most of the excess acrylonitrile in the aqueous stream, along with the triethyl

ammonium p-toluene sulfonate, is combined with fresh acrylonitrile feedstock and recycled to the electrolytic cell. The water-rich stream from the evaporator contains small amounts of acrylonitrile (not enough to justify recovery), and is sent to the plant's wastewater treatment plant.

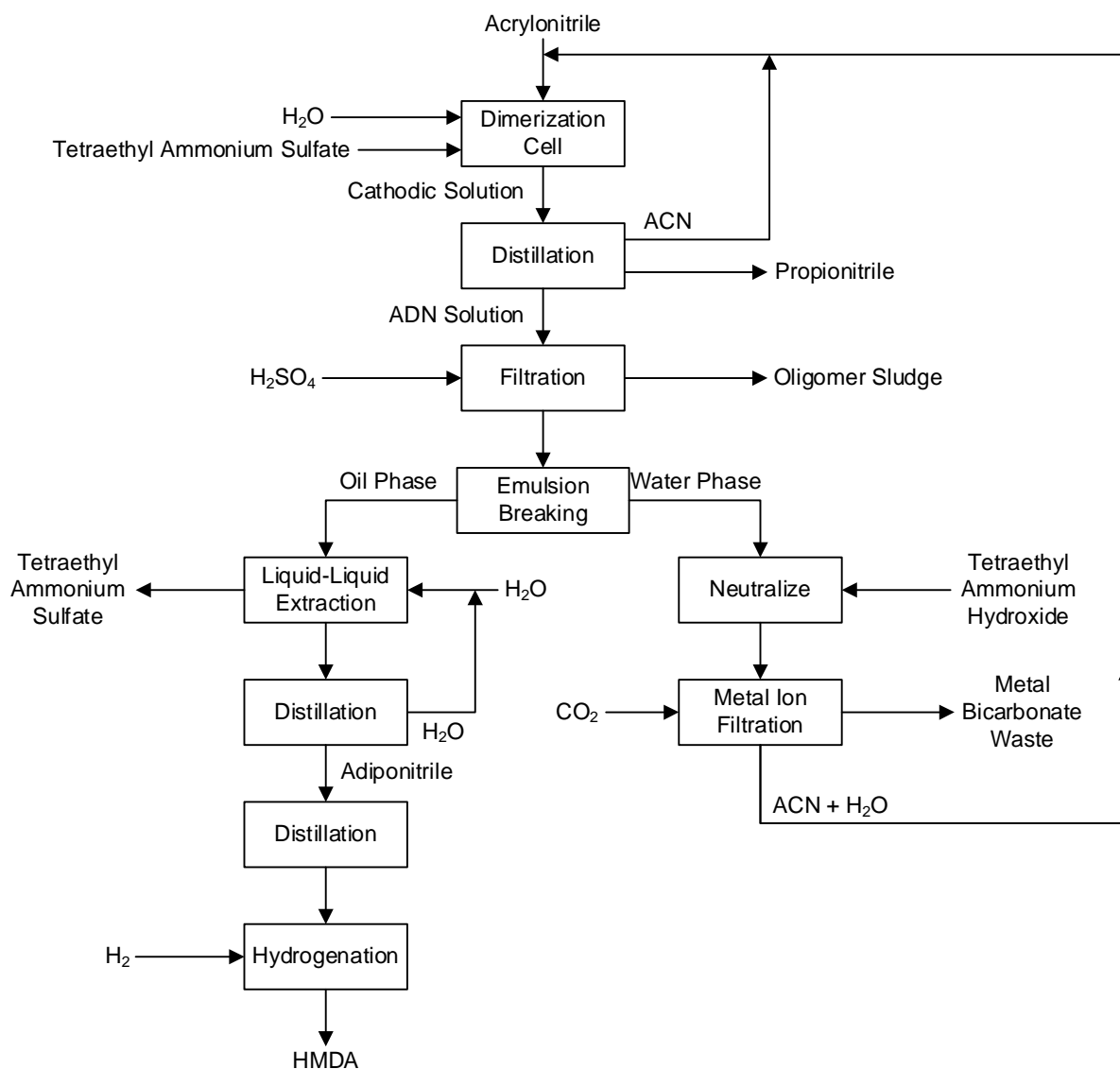
The acrylonitrile-rich extract from the liquid-liquid extraction contains most of the adiponitrile formed in the electrolytic cell, and is sent to a distillation train to separate ADN from ACN. The concentrated ACN is recycled to the liquid-liquid extraction unit. Propionitrile is purified in the same distillation train, and sold as a commercial by-product.

The ADN-rich stream from the distillation train contains water and excess tetraethylammonium p-toluene sulfonate, which was added to improve electrolytic solution conductivity. Extraction solvent water is added to capture most of the tetraethylammonium p-toluene sulfonate, and separate it from the adiponitrile. The water extraction process produces a water-rich stream containing the conductivity promoter, and an ADN stream also containing water but free of conductivity promoter. The water-rich stream is evaporated to remove and recycle water, such that the now concentrated promoter can be recycled to the cathode side of the electrolytic cell. The ADN stream containing water but free of conductivity promoter is distilled to produce pure ADN and pure water. The purified water stream is recycled to the aqueous extraction unit, while the purified ADN is sent to the hydrogenation unit to produce HMDA via ammoniation. The distillation train also removes as a separate stream the oligomers (medium ends and heavy ends) formed by the reaction. The medium ends stream is rich in hydroxyl-propionitrile, which is hydrolyzed in a caustic soda solution for conversion to acrylonitrile, which is recycled as feedstock to the electrolytic cells. The heavy ends stream is burned as plant liquid fuel, or incinerated.

Over time, the aqueous sulfuric acid solution on the anode side of the electrolytic cell becomes contaminated with nitrate ions formed by the leakage of acrylonitrile across the cell boundary. As this solution circulates outside the cell, it is treated with a heavy amine diluted in xylene solvent to absorb the nitrate contaminants.

HMDA from acrylonitrile via electrohydrodimerization in emulsion

The cathode side of the electrolytic cell is where adiponitrile is formed, and in this technology the cathode side contains an emulsion (rather than a solution). The emulsion is water-based, contains acrylonitrile feedstock, adiponitrile product, tetraethylammonium sulfate as conductivity promoter, and impurity by-products formed during the reaction of acrylonitrile to ADN. The conductivity promoter reduces the electrical resistance of the solution, but does not readily dissolve in the cathodic solution. A block flow diagram for this process is presented below.

Figure 4.7: Emulsion electrodimmerization of acrylonitrile to adiponitrile

As the emulsion from the cathodic side of the cell is removed from the cell, it is processed in a distillation train for the purpose of separating and purifying unconverted acrylonitrile, which is recycled to the feed side of the cell. Also separating in the same stream from the distillation is propionitrile, which is purified to commercial specifications and sold as a by-product. The distillation train also removes oligomers as a waste product. They are precipitated from solution by adding sulfuric acid to reduce pH, and then filtered out.

The ADN-rich emulsion from distillation is broken by the addition of heat into two liquid phases in a decanting drum: an upper oil phase of organics, and a lower aqueous phase. The water phase is neutralized using tetraethylammonium hydroxide. Carbon dioxide (CO₂) is added to the water phase on the cathode side of the electrolytic cell to precipitate the previously dissolved metal ions as metal bicarbonates, which can then be filtered out of the aqueous solution. The metal free aqueous solution of unconverted ACN and water is recycled to the feed side of the emulsion cell, where it is mixed with fresh ACN feed and emulsified.

The upper organic phase from the emulsion breaking drum is rich in crude ADN, but also contains conductivity promoter tetraethyl ammonium sulfate. Water is added as a liquid-liquid extractant to separate a mixture of ADN and water from the conductivity promoter. The separated promoter can either be discarded or recovered and recycled, depending on concentration and economics.

The ADN-rich aqueous solution is separated and purified from water in a distillation train. The concentrated water is recycled as extracting solution. The now pure ADN from distillation is hydrogenated to HMDA using the process technology described above. The sulfuric acid aqueous solution from the anode side of the electrolytic cell is also purified by the same means presented above for the solution electrodimmerization of acrylonitrile.

HMDA from acrylonitrile via electrohydrodimerization in an undivided cell

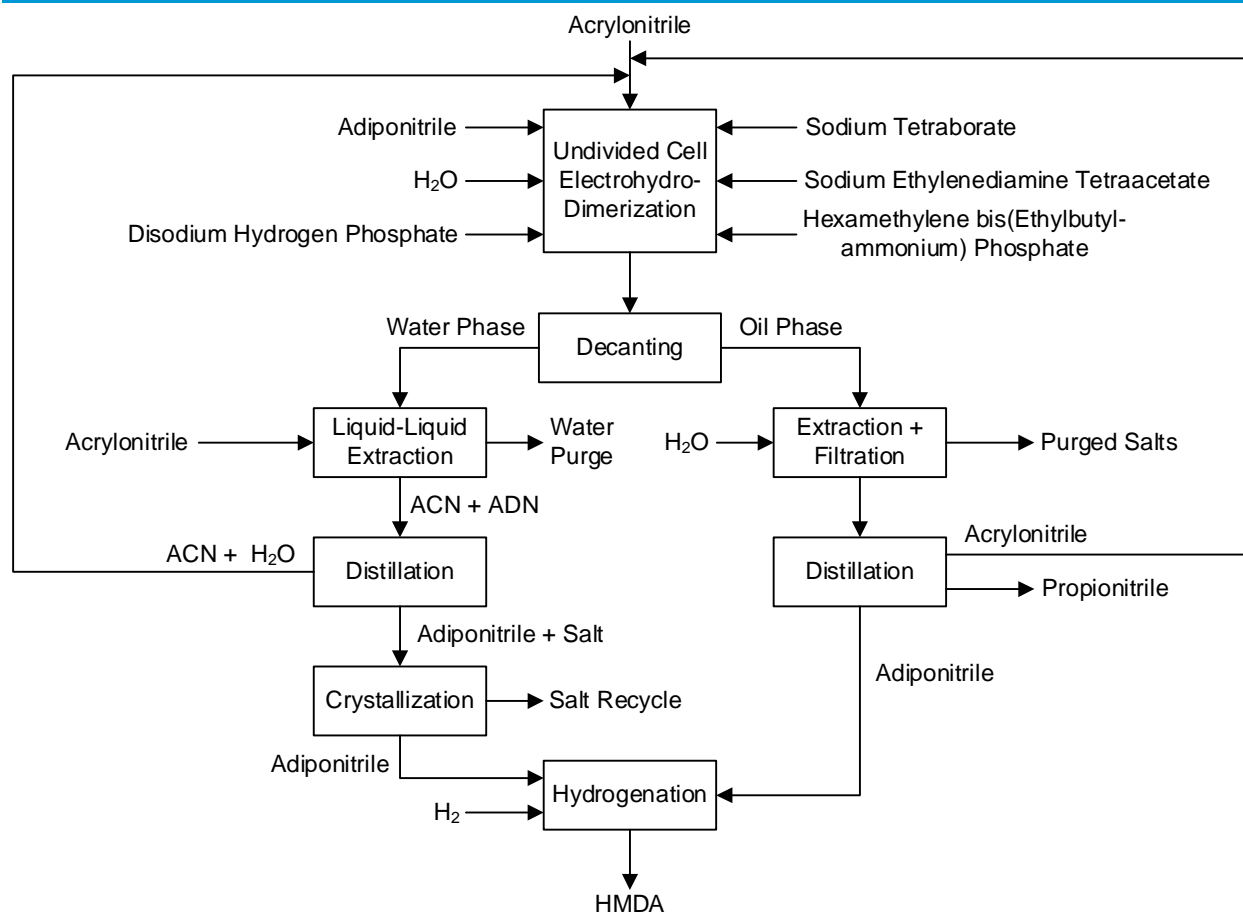
An undivided electrolytic cell is used, in which there is no membrane boundary between the cathode side and the anode side. A single solution is used in the cell, in which both the cathode electrode (cadmium) and anode electrode (carbon steel plates) operate.

The electrolyte solution in the undivided cell consists of water, feedstock acrylonitrile, product adiponitrile, four principal chemical additives, and contaminants created by the reaction. The chemical additives are listed below:

- Disodium hydrogen phosphate
- Sodium tetraborate
- Sodium ethylenediamine tetracetate
- Hexamethylene bis(ethylbutylammonium) phosphate

The chemical additives are used to increase the electrical conductivity of the cell solution, minimize corrosion of electrodes, and minimize the formation of hydrogen at the anode electrode.

The solution discharged from the undivided cell is sent to a large horizontal settling drum, where a 2-phase liquid mixture forms as an upper organic layer, and a lower aqueous layer. Both layers contain appreciable amounts of ADN, requiring recovery of ADN from both liquid streams. Water is added to the settling drum to capture most of the dissolved salts into the aqueous lower layer. A block flow diagram for the undivided cell appears in the figure below.

Figure 4.8: Electrodimerization of acrylonitrile to adiponitrile in an undivided cell

The upper organic oil phase from the settler is directed to a liquid-liquid extraction unit where water is used as the solvent. The addition of water causes salts to precipitate, where they can be removed via filtration. The salt free organic phase is then sent to a distillation train where acrylonitrile is separated and concentrated for recycle to the front of the process as feedstock. Propionitrile is separated and purified in the distillation train, and sold as commercial by-product. Purified adiponitrile, as the highest boiling material in the organic phase, leaves the distillation train as a concentrated bottoms product at high purity. It is ammoniated to HMDA product.

The bottom water-rich phase from the settling drum also undergoes liquid-liquid extraction, using acrylonitrile as the solvent. The introduction of acrylonitrile captures nearly all of the ADN in the aqueous solution, leaving a water stream virtually free of organics. The water stream is purged to wastewater treatment.

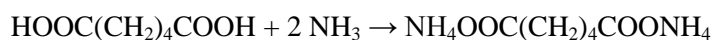
The organic stream containing acrylonitrile and adiponitrile, with a small amount of water, is directed to a distillation train. The relatively low boiling water and acrylonitrile are both separated as a column distillate, and recycled back to the front of the process. The higher boiling crude adiponitrile is the bottoms product from distillation, but also contains the chemical additives used for conductivity and corrosion control. Adiponitrile is purified from the additive via crystallization, and treated with sodium sulfide to remove residual cadmium from the cathode. The purified ADN is sent to the hydrogenation unit to produce HMDA. The salt stream from crystallization is recycled to the electrolytic cell.

Adiponitrile from adipic acid

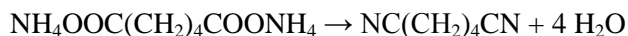
The original DuPont commercialization of nylon 66 produced HMDA via reacting adipic acid with ammonia to produce adiponitrile over a dehydrating catalyst. This process was abandoned by DuPont and others for more economically competitive processes (butadiene, acrylonitrile), but it is believed that several small companies in China still make adiponitrile (and HMDA) from adipic acid in small quantities.

Chemistry

Molten adipic acid is reacted with vapor-phase ammonia at 200–250°C and atmospheric pressure to form adiponitrile. The reaction chemistry is shown below. The first reaction step is to combine adipic acid with ammonia to produce ammonium adipate.



In this reaction, the ammonia simply adds to the carboxylic acid groups at both ends of the molecule. In the second reaction, ammonium adipate is dehydrated to adiponitrile plus water. The reaction chemistry is shown below.



Process technology

The reaction of adipic acid with ammonia to form ammonium adipate is conducted in an up-flow reactor where ammonia is in the vapor phase at 200–250°C. Reactor pressure is slightly above atmospheric (20 psia). A large excess of ammonia is used to drive the forward reaction and maximize adipic acid conversion. The feed adipic acid is in the melt phase, and flows downward through the up flowing stream of ammonia. This type of reaction is usually conducted in a vertical column reactor with a large ratio of length to diameter, in order to maximize contact time between gas and melt, while trying to prevent short-circuiting of the ammonia either along the interior walls of the reactor, or through the center line of the reactor. The reactor is filled with high surface area to volume random packing.

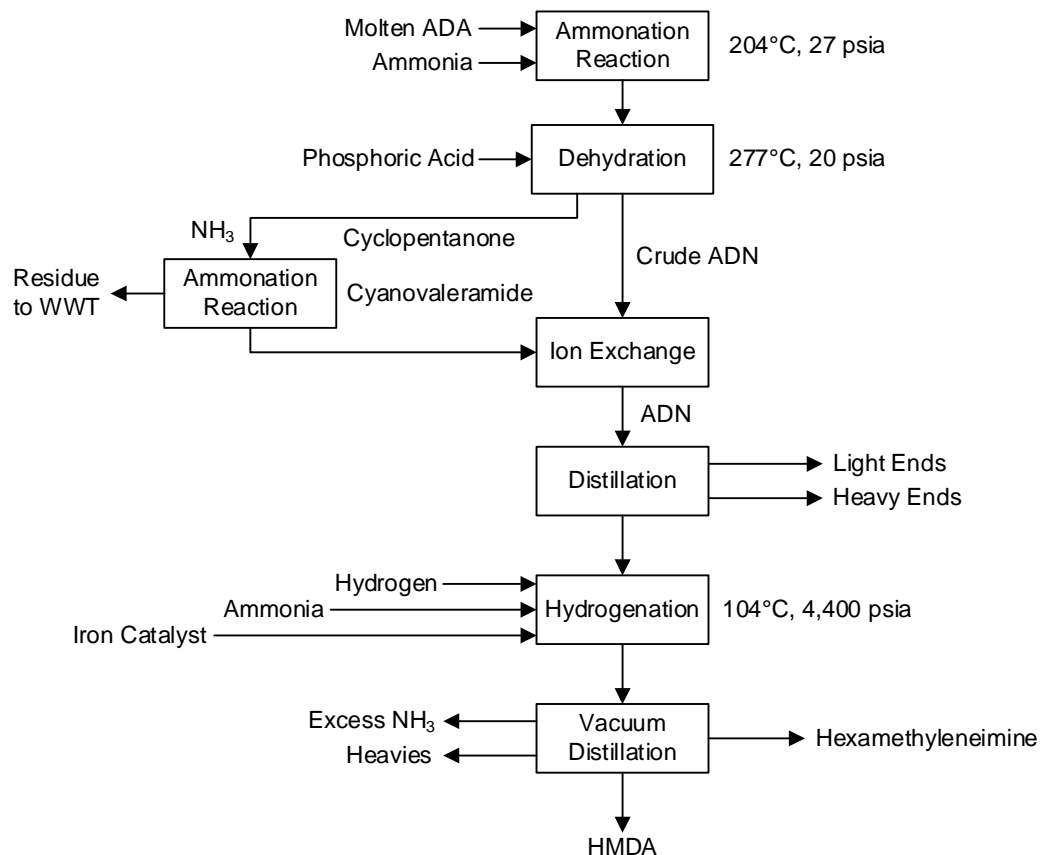
Molar selectivity to adiponitrile is approximately 90%, and boron phosphate catalyst is used for the ammoniation reaction. Although initially conducted in fixed bed reactors, over time most producers converted the reactor to fluidized bed operation. By-products cyanovaleramide and cyclopentanone are recycled for conversion to ammonium adipate. The reaction also produces a heavy polymer waste product that is either incinerated or discharged to a hazardous waste disposal facility. The excess unconverted ammonia is captured, purified, and recycled to the reactor. The dehydration of ammonium adipate to adiponitrile occurs at a higher temperature (270°C) in a column reactor using phosphoric acid as the catalyst.

While the adiponitrile formed in the dehydration reactor is in the melt phase, the water removed from the molecule is vaporized and leaves the reactor as the overhead vapor stream.

Crude adiponitrile from the dehydration reactor is further reacted with ammonia to drive the reaction to completion, and is purified by passing the mixture through an ion exchange resin column. The adiponitrile stream is then distilled as a heart cut to remove both lights and heavies. Other reaction by-products removed by the heart cut distillation are hexamethyleneimine and diaminocyclohexane. Due to the high boiling temperature of ADN, the distillation is effected under vacuum conditions to reduce

bottoms temperature. The heavy amine bottoms stream can be sold as a commercial product. A block flow diagram for this process is presented below.

Figure 4.9: HMDA from ADA block flow diagram



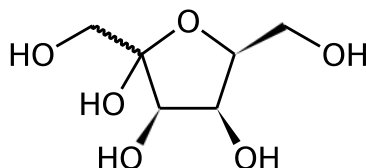
HMDA from biomass via Rennovia processing

Rennovia (Menlo Park, California, USA) has previously developed a bio-based route to adipic acid using glucose as the feedstock, and industrial catalysts that convert the terminal carbon atoms to carboxylic acids, while removing the internal hydroxyl groups (OH-) via hydrodeoxygenation. PEP covered this process in 2012 in PEP Report 284. Rennovia has since developed [31C20] process technology to convert biomass to HMDA using industrial catalysis. The combination of bio-ADA and bio-HMDA allows Rennovia to produce 100% bio-nylon 66. Rennovia operates (in 2013) kilogram scale lab facilities for making bio-based ADA and HMDA, with the intent of producing demonstration scale quantities (metric tons) in 2015.

Rennovia's bio-based HMDA process uses a by-product of corn wet milling as the primary feedstock. Given the reduction in demand for corn sugars in industrial countries, Rennovia believes that its acquisition cost of non-food bio-feedstock will provide significant production cost advantage over the conventional hydrocarbon-based processes (butadiene, acrylonitrile), and potentially also provide lower capital costs than conventional processes.

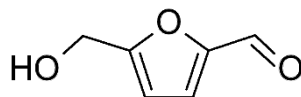
IHS believes that the fructose (CAS: 57-48-7) basic feedstock for the Rennovia process can be bought in commercial quantities from global producers (Cargill, ADM, etc.) under long-term contracts at prices [31C21] of approximately US\$ 450/mt. The molecular formula for fructose is $C_6H_{12}O_6$, and the molecular structure of fructose is shown in the figure below.

Figure 4.10: Molecular structure of fructose



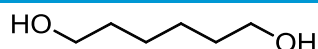
The feedstock acquired by Rennovia eventually in commercial quantities will be a derivative of glucose processing that produces high fructose corn syrup. Rennovia first dehydrates a solution of fructose in water to produce 5-hydroxymethylfurfural (HMF, CAS: 67-47-0), a furanic compound with the chemical formula $C_6H_6O_3$. The molecular structure of HMF is shown in the figure below.

Figure 4.11: Molecular structure of 5-hydroxymethyl furfural



In the second step of the process, HMF is hydrogenated to open up the furanic ring, saturate the double bonds, and drive off both oxygen ($O=$) and hydroxyl ($OH-$) groups to produce 1,6-hexanediol (HDO). The molecular structure of 1,6-hexanediol (CAS: 629-11-8) is shown below, with a chemical formula of $C_6H_{14}O_2$.

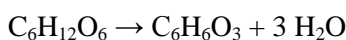
Figure 4.12: Molecular structure of 1,6-hexanediol



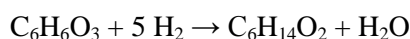
In the third and final step, Rennovia ammoniates the 1,6-HDO to produce HMDA. By-products include mono-amines and heavy oligomers (dimers, trimers, and tetramers).

Chemistry

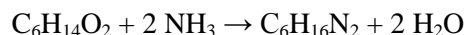
The chemical reaction stoichiometry for the first stage dehydration of fructose to 5-hydroxymethylfurfural is shown below.



The chemical reaction stoichiometry for the second stage hydrogenation of HMF to 1,6-HDO is shown below.



The chemical reaction stoichiometry for the third-stage ammoniation of 1,6-HDO to HMDA is shown below.

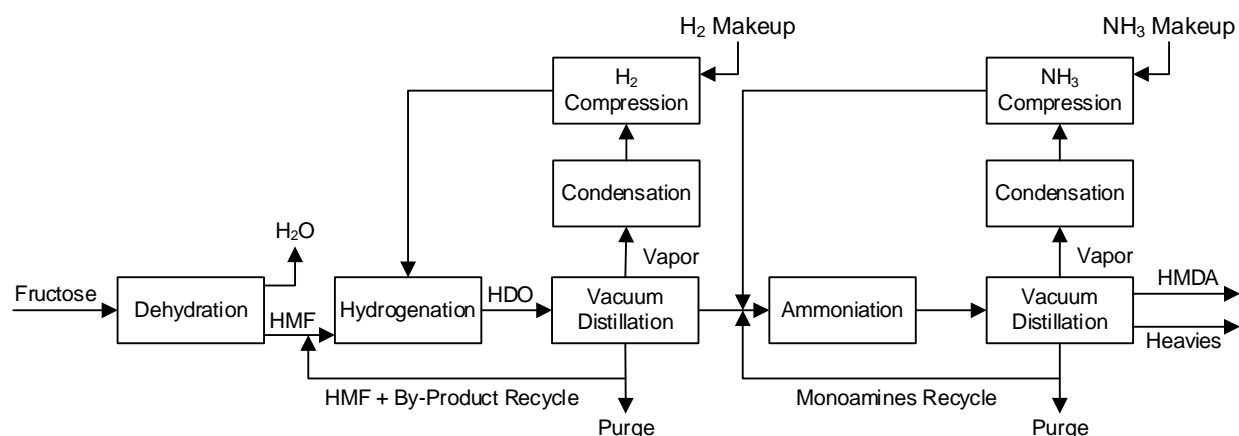


Process technology

The Rennovia technology has operated in a continuous bench scale plant for over one year, with pilot plant operations commencing during 3Q 2013. US patents have been granted, and supplemental patent applications have been filed.

A block flow diagram of the IHS understanding of Rennovia technology is provided in the figure below.

Figure 4.13: Rennovia HMDA from fructose process

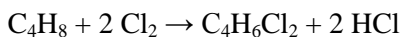


Other HMDA production processes

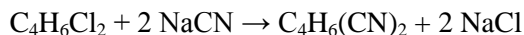
There are a variety of other process technologies for producing HMDA. Several once used methods have since been replaced by lower cost technologies, while other approaches are yet to be commercialized.

HMDA from butadiene via direct chlorination

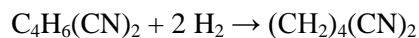
DuPont's original commercial technology for HMDA production used adipic acid as the feedstock. In the 1960s, this approach was replaced by using butadiene direct chlorination to dichloro butene, following by reaction with HCN to form dicyano butene. This route was replaced with the current DuPont/Invista butadiene direct hydrocyanation process to adiponitrile. The chemical stoichiometry for the first butadiene chlorination reaction is shown below.



The chemical stoichiometry for the second reaction, in which dichloro butene plus sodium cyanide produces 1,4-dicyanobutene plus sodium chloride, is shown below.



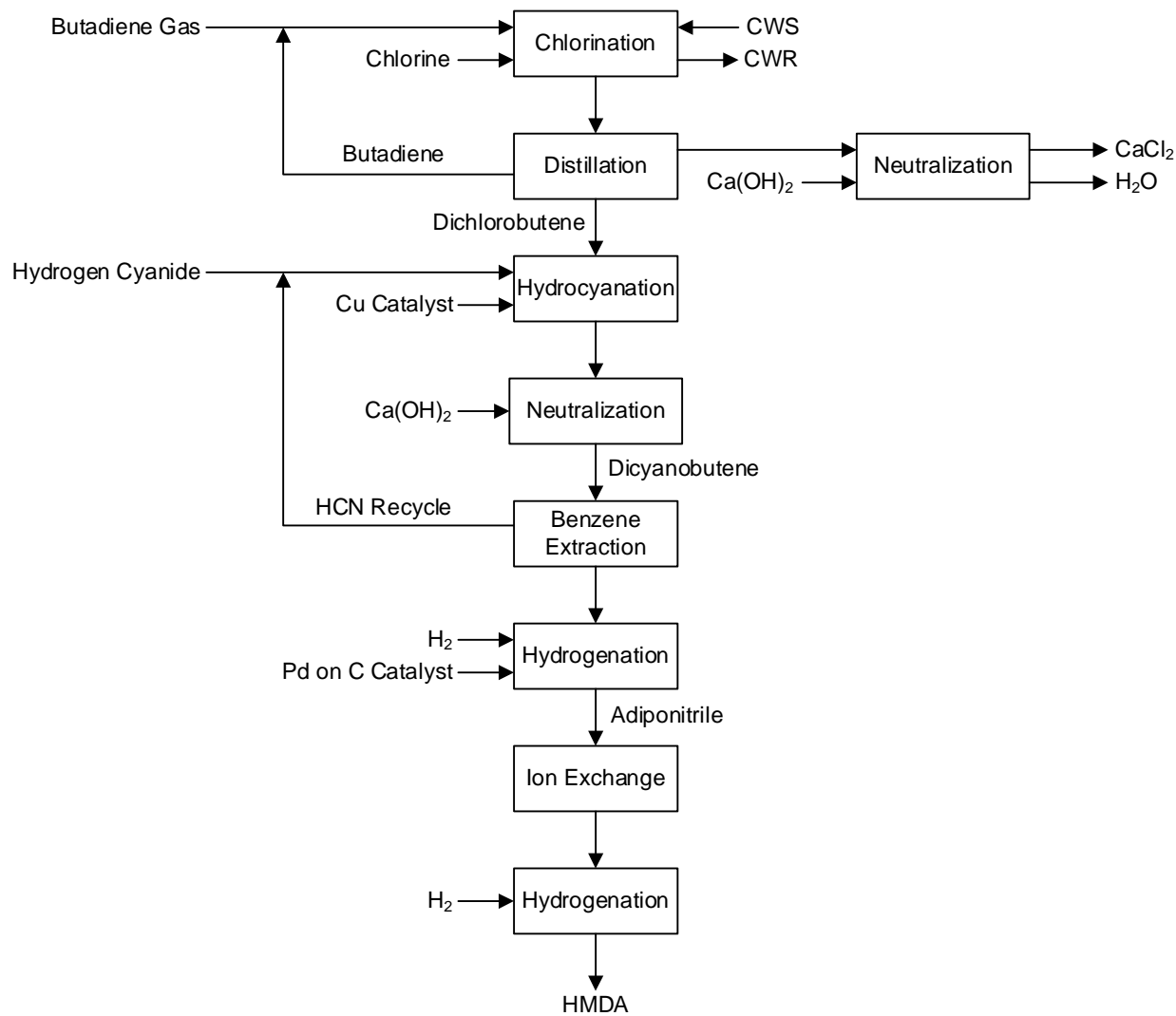
The chemical stoichiometry for the final reaction in which dichloro butene plus sodium cyanide produces 1,4-dicyanobutene plus sodium chloride is shown below.



The chlorination route involves vaporizing butadiene and reacting it in the vapor phase with chlorine gas at 154–190°C to produce dichlorobutene with 96% selectivity while completely consuming the chlorine. The reaction is highly exothermic, and requires cooling jackets on the walls of the reactor vessel. Reactor product does not completely consume the butadiene. As a result, a distillation train downstream of the chlorination reactor recovers and recycles excess butadiene, while neutralizing the HCl formed in the reaction using caustic soda. The distillation train also removes light and heavy by-products.

The dichlorobutene in an aqueous solution reacts with sodium cyanide at 93°C and 75 psia using a copper catalyst to form dicyanobutene at 95% selectivity. Lime is used to neutralize residual acidity formed by the reaction. A solvent, either benzene or cyclohexane, is used to extract the dicyanobutene from the reactor product stream. The extract solution is distilled to recycle the solvent, recover the dicyanobutene, and also recover residual HCl.

The hydrogenation of dicyanobutene to adiponitrile occurs in a liquid solvent solution of benzene or cyclohexane. Reactor conditions are 150°C and 400 psia, using a palladium catalyst on carbon substrate. Reactor products are distilled, and adiponitrile is passed through a polishing step using an ion exchange resin to remove residual acidity. A block flow diagram for this commercial process is presented below.

Figure 4.14: HMDA from butadiene via chlorination

HMDA from adipic acid and hydroxycaproic acid

Celanese, which no longer produces HMDA, commercialized a process in the 1960s using cyclohexane as the basic feedstock. Their plant in Bay City, Texas USA was shut down in 1981. Cyclohexane was oxidized to a mixture of hydroxycaproic acid and adipic acid at 150°C and 500 psia. Adipic acid was then hydrogenated to 1,6-hexanediol, which was reacted with ammonia to produce HMDA.

Hexamethylenediamine and caprolactam from adiponitrile by partial hydrogenation and cyclization of aminocapronitrile

In the mid-1990s, DuPont and BASF initiated consideration of building a joint venture HMDA plant in China. The starting material would be adiponitrile that would be supplied by DuPont using its established commercial butadiene process hydrocyanating to ADN. BASF would then hydrogenate ADN to a mixture of HMDA and 6-aminocapronitrile (ACPN). The ACPN would then be cyclized by BASF to caprolactam,

for consumption in a BASF plant to make nylon 6. DuPont would copolymerize the HMDA with ADA to produce nylon 66. The venture was subsequently terminated without a commercial project being built. This process is covered in PEP Review 96-4, published in June, 1998.

5. Process Design Basis

Process safety

The key chemicals of process safety concern in this project, which are either produced or consumed in high volumes, are listed below:

Table 5.1: Project chemicals of significant concern

Hexamethylenediamine
Adiponitrile
Acrylonitrile
Hydrogen
Butadiene
Hydrogen cyanide
Ammonia

Several of the chemicals used to make HMDA and ADN are highly hazardous. Most of the feedstocks and intermediate chemicals are highly volatile and flammable. Hydrogen cyanide is highly toxic. Acrylonitrile is carcinogenic. When either acrylonitrile or adiponitrile combusts, a combustion by-product is hydrogen cyanide, which is extremely toxic. Butadiene is an extremely reactive low boiling point hydrocarbon, and, on occasion, has exploded when in storage or within processing areas.

Processing conditions for making HMDA and ADN also provide the potential for creating significant process safety issues. Catalysts become deactivated over time via carbon lay-down. During catalyst removal and reactor cleaning, residual amounts of combustibles on catalyst can create pyrophoric conditions. High pressure and medium pressure steam is used throughout the process area for heating purposes within heat exchangers, and presents a high pressure hazard. Hydrogenation and ammoniation reactions are designed to operate at high pressure.

Hexamethylenediamine (HMDA)

HMDA is processed in liquid form at elevated temperature, although it is a solid at room temperature. HMDA is sold commercially as a heated liquid, or in an aqueous solution at various concentrations. HMDA is corrosive, and requires upgraded alloys for storage and processing. HMDA is harmful if swallowed, and causes severe burns if it comes in contact with skin [31C24]. HMDA may cause an irritation to the upper respiratory track if inhaled as a vapor. HMDA is not believed to be carcinogenic, mutagenic, nor have a genetic effect. If released into the environment, HMDA is harmful to invertebrates, but not harmful to fish or algae. HMDA is readily biodegradable, and not believed to be bio-accumulative.

One person was seriously injured with burns, and 16 others hospitalized [31C22] when a leak of HMDA at the BASF Teesside (UK) nylon intermediates plant ignited on 4 January, 2007. An additional 20 workers were given medical treatment at the plant. HMDA is not only flammable, but highly corrosive, which may have contributed to the leaking condition. Injuries included burns, skin irritation, and breathing difficulties.

Figure 5.1: Teesside (UK) site of BASF HMDA fire in 2007

Source: Google Earth

As a result of the fire, the plant was closed down [31C23], pending an investigation of the cause of the leak.

Adiponitrile (ADN)

ADN in this process design is an intermediate organic monomer formed by the hydrocyanation of butadiene, or a dimerization of acrylonitrile. ADN is then hydrogenated directly to HMDA. ADN at room temperature is a clear and colorless liquid. Its flash point is 93°C. Dinitriles such as ADN are toxic to humans by inhalation and ingestion [31C25], and also to animals. Adversely affected human organs include eyes, skin, central nervous system, and cardiovascular system. ADN is classified as being acutely toxic to humans. Absorption of ADN in the body causes cyanosis [31C26], creating an oxygen deficiency in blood.

Persons handling nitriles should take precautions to prevent inhalation of fumes or skin contact [31C27]. Butyl rubber gloves are frequently used because they resist permeation by many nitriles more efficiently than most gloves. Inhalation may cause headache, nausea, vomiting, irritation of mucosal membranes, and dizziness. Skin contact may result in similar symptoms, but may develop more slowly. Other symptoms of cyanide poisoning include rapid pulse, flushing of the skin, and initial rapid respiration followed by labored breathing.

ADN firefighters should wear fully respiratory equipment, and can extinguish ADN fires using water spray, alcohol foam, dry chemical, or CO₂.

Acrylonitrile

Acrylonitrile is the primary feedstock used to make ADN via dimerization in an electrolytic cell. Acrylonitrile (ACN) at room conditions is a clear, colorless, and poisonous liquid with a mild peach odor. ACN is very hazardous in case of ingestion, skin contact, or inhalation [31C27]. ACN is a possible

carcinogen, with possible mutagenic effects. It is a possible reproductive toxin for females. ACN may be toxic to blood, kidneys, liver, cardiovascular system, and central nervous system.

ACN is highly flammable, with a flash point of -1.1°C , and a boiling temperature of 77°C . It may explode in the presence of oxidizing agents, and of acids and alkalis. ACN may become explosive if allowed to polymerize. ACN is corrosive to aluminum and copper. If ignited, ACN fires should be fought with dry chemical powder, alcohol foam, water spray or water fog.

On 4 May, 2013, one person was killed and 116 other persons hospitalized in Belgium [31C28] when a freight train carrying tank cars of DSM's acrylonitrile derailed, and caught fire. Burning acrylonitrile formed hydrogen cyanide, which caused the fatality via exposure to HCN toxic gas.

Hydrogen

Hydrogen (H_2) is used primarily in the Rennovia process to convert 5-HMF to 1,6-HDO. H_2 is also used to assist in the ammoniation of ADN to HMDA. Hydrogen is a very light and very flammable gas [31C29]. It is almost always supplied in high pressure containers or high pressure pipelines, and therefore creates additional hazards for high pressure (risk of pressure rupture or explosion). Since hydrogen will rapidly expand when released from pressure, it can cause personnel suffocation (asphyxiation) if personnel are located in a contained space when the release occurs. Since hydrogen is under high pressure, upon release of pressure it will rapidly cool to temperatures that can cause freeze burn to personnel (frostbite).

Hydrogen may cause damage upon exposure to lungs. It is not known to be carcinogenic, mutagenic, or be a reproductive toxin.

If a hydrogen fire occurs, it should be extinguished by first applying water to the hydrogen container to prevent pressure failure. Fire water should be discharged directly to the fire from a safe distance. Firefighters should wear complete respirators and full face shields.

Butadiene

Butadiene is the primary feedstock in the Invista/DuPont process to make ADN via hydrocyanation. Butadiene is a highly flammable [31C30] and highly reactive gas at standard conditions, and is usually stored under pressure as a liquid. Its boiling temperature is -4°C . As a gas stored under pressure, butadiene will quickly depressure creating the potential for personnel suffocation in confined spaces. Rapid depressurization will also reduce its temperature, creating the potential for personnel freeze burn (frostbite). Ventilation equipment should be explosion proof, given the high reactivity and combustibility of butadiene. Butadiene may cause cancer. It will adversely affect the central nervous system. Butadiene may be a mild toxin.

Butadiene fires should be fought with a water fog, dry chemical, or carbon dioxide. Direct water is not appropriate.

Hydrogen cyanide

Hydrogen cyanide (HCN) is a highly toxic liquid [31C31] at standard conditions that boils from liquid to vapor at slightly elevated temperature (26°C). US OSHA exposure limit is 10 ppm. HCN is potentially fatal if inhaled or swallowed. HCN also is an irritant to the respiratory system and eyes. Short-term

exposure can cause suffocation. Long-term exposure, if not fatal, can cause vomiting, digestive disorders, and dizziness. HCN is a weak acid, but can safely be stored in carbon steel containers.

HCN presents a severe fire hazard. When stored as a liquid, upon heating HCN will quickly vaporize increasing the pressure within the container, and potentially causing a physical rupture or a thermal explosion. HCN fires should be fought with foam, or flooded with water spray.

Ammonia (NH₃)

Ammonia is used in this process to promote the conversion of mononitriles in the hydrocyanation of butadiene to adiponitrile, and to convert ADN to HMDA. Ammonia (NH₃) is a colorless gas at standard conditions, with a strong odor [31C32]. NH₃ is often stored as a liquid at elevated pressure, and presents a high pressure hazard if the storage container gets heated in a fire. When depressured from liquid to vapor state, NH₃ will quickly reduce its temperature, presenting the personnel danger of both asphyxiation in a contained setting, and a danger of frostbite.

NH₃ is a personnel irritant. It may cause damage to the lungs, upper respiratory tract, skin, and eyes. NH₃ is not known to be carcinogenic, mutagenic, or cause reproductive toxicity.

NH₃ is nonflammable, but can present a significant fire hazard if it reacts with other chemicals that cause oxidation. If a fire occurs, it can be safely extinguished with direct water spray from a distance.

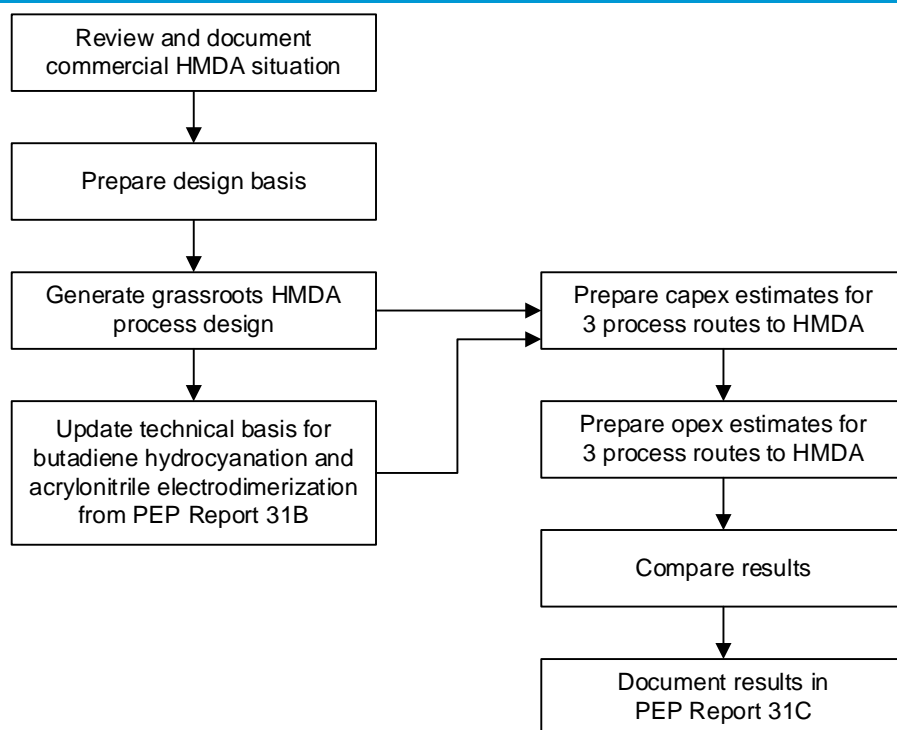
Business objectives

The principal business purpose of this assessment is to provide technical and economic insights into the potential installation of industrial scale HMDA plants utilizing three process technologies: 1) hydrocyanation of butadiene to HMDA (DuPont/Invista process), 2) electrodimmerization of acrylonitrile to HDMA (Monsanto/Ascend process), and 3) industrial catalytic conversion of biomass to HMDA (Rennovia process). It is also a purpose to compare the economics (capex, opex) of such proposed processes to determine market competitiveness.

We have chosen the DuPont/Invista hydrocyanation process as our ‘base case,’ incorporating our understanding of Invista’s enhanced technologies that reduce historic problems dealing with benzene emissions in the process. We compare the DuPont/Invista process to incremental improvements by Ascend Performance Materials in the conventional electrodimmerization of acrylonitrile. We then present a new process not yet commercialized but well documented in the trade literature by Rennovia, which provides the potential eventually to produce both bio-HMDA, and bio-adipic acid, which can be copolymerized to produce 100% bio content nylon 66.

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 and Monsanto/Ascend that dominate the nylon 66 feedstock business with the largest installed production capacity.

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 each of the three process routes after reviewing the commercial HMDA business, as we understand it. Since PEP has never evaluated a bio-based route to HMDA, we developed a grassroots Class-3 process design package around patents and applications assigned to Rennovia.

Figure 5.2: Project scope of work

When the process engineering design was completed, we developed current (for 2013) 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. We then compared results to draw conclusions about the viability of all three process routes to HMDA.

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 (250 kty) of HMDA in a single process train at a grassroots facility.

Project deliverables included the design basis, process descriptions accompanied by process flow diagrams, stream-by-stream heat and material balances, equipment lists that included duty specifications, itemized capital cost estimates segmented by the ISBL (inside battery limits) 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 HMDA 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 were provided in terms of both cash cost and fully loaded totally production cost (including depreciation).

Discussions with industry participants and review of the publicly available literature suggest that construction schedules for grassroots HMDA plants usually take about 2-3 years from site preparation to commercial plant 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 HMDA manufacturing facility is world-class operating 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 debottlenecking 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 2-step process in which a process license is first acquired from a firm like Invista, Ascend, or Rennovia, and then the construction of the plant is executed via normal lump sum turnkey manufacturing based on the basic engineering package provided by the licensor. More capital cost is expected to be incorporated into this project if a bio-based technology is selected, since such a plant would be ‘first of a kind.’ The extra capital cost would be justified in providing at least 15% DCF (discounted cash flow) return on the incremental economic benefits it would provide over the kind of design that is likely to be offered on an LSTK (lump sum turnkey) basis. The nature of these benefits are likely to be:

- Better overall yield (conversion x selectivity) of feedstock to product
- Higher energy conversion efficiency
- Lower lifetime cost to operate
- Longer run time between scheduled turnarounds
- Fewer unscheduled plant outages
- 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 than 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
- Environmental conformance to emissions requirements
- Operating reliability and control stability
- Ease of producing on-spec product consistently
- 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

HMDA production using the conventional hydrocyanation or electrodimmerization processes involves using flammable liquids (butadiene, acrylonitrile) at elevated temperatures and pressures. Most of the safety problems documented by this industry have been in the form of explosions and fires caused fundamentally by leaks of flammable materials. Beside project specific safety mitigations, the project incorporates conventional fire protection facilities (fire monitors, inert gas deluge system, snuffing steam, portable fire extinguishers). Two independent process flare systems interconnected by looped flare blow-down piping manifolds are provided in the design.

Operating reliability

In today's highly competitive business environment, the major difference between economically competitive and economically noncompetitive 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/surge 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 product 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, waste water treatment system) will have their critical rotating machinery provided with dual drivers (1 electric motor, 1 steam turbine) to operate through a power interruption. The steam-generation system will be designed to operate in the absence of purchased bulk power.

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
- Tertiary biox wastewater treatment plant
- Floating roof storage tanks for high vapor pressure liquids

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 pre-existing cultural resources. This design does not incorporate facilities to address environmental justice concerns.

The key recurring environmental emissions from HMDA manufacturing facilities are discharge gases from the high temperature reactors, fugitive hydrocarbon leaks from seals, vapor discharges from pressure safety valves. Provided in the design is a flare gas looped header and process flare discharge system with blow-down 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.
- Sitewide 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 NO_x burners and exhaust gas recirculation. The expected pollutant emissions of combustion gas from the boilers when burning natural gas are:

- Carbon monoxide (CO) <100 mg/m³
- Nitrous oxides (NO_x) <100 mg/m³
- Sulfur oxides (SO_x) <40 mg/m³
- Particulates <5 mg/m³

Fugitive emissions from pumps 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.

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. Hazardous vapor streams will be incinerated in a separate vapor incinerator.

Flexibility for economic optimization

Since the process design for the Rennovia catalytic HMDA plant would be a 'first of a kind plant,' the facilities have been designed very conservatively in order to deal with the unanticipated conditions that often 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 wetted materials of construction.

Ease of operations and maintenance

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

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 off-sites 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 HMDA 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 (nickel alloy, titanium) for high temperature environments in the presence of strong oxidizing agents. 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. Emergency rotating machinery 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.

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 the September 11 attack 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), entitled “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 nonhazardous 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 for large flammable material 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 HMDA 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 HMDA 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 (KPI’s) 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. In-line filters are provided downstream of packed bed reactors.

Plant location factor

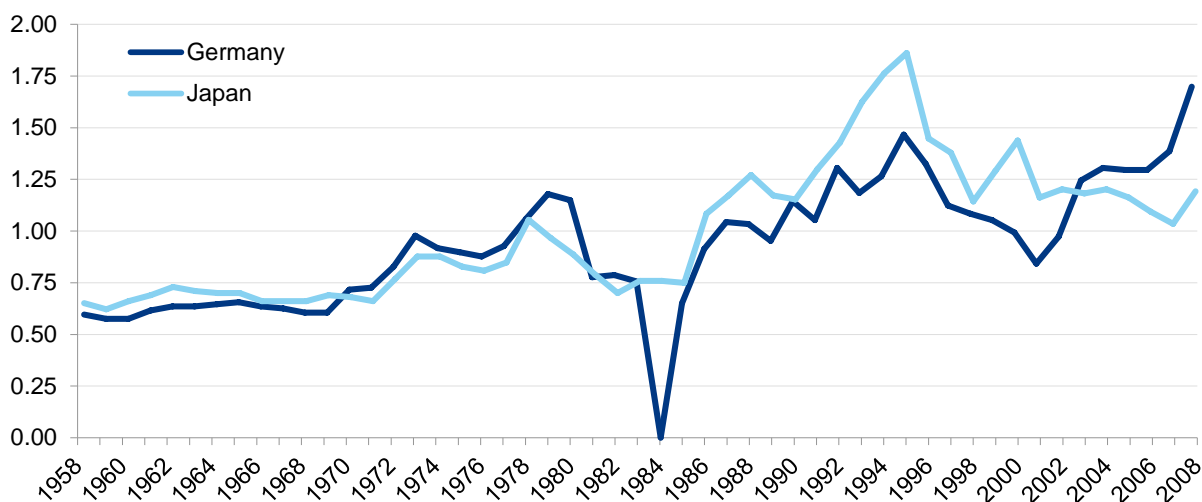
The HMDA manufacturing plants provided by this design are assumed to be sited at grassroots facilities, rather than brownfield industrial sites that have been previously used. Our capital cost estimates incorporate factored estimates for off-site battery limits facilities required for operable plants, 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-2013 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-2013 location factors are presented below. The economic factor that dominates the difference in location factor between geographical regions is currency translation rates.

Table 5.2: Construction cost location factors

Location	Location factor
USGC	1.00
Canada, Western (Alberta)	1.35
Canada, Eastern	1.10
Germany	1.05
Japan	1.10
Saudi Arabia	1.03
Mexico	1.06
Thailand	0.92
Colombia (coastal)	1.03
India	0.85
China	0.75

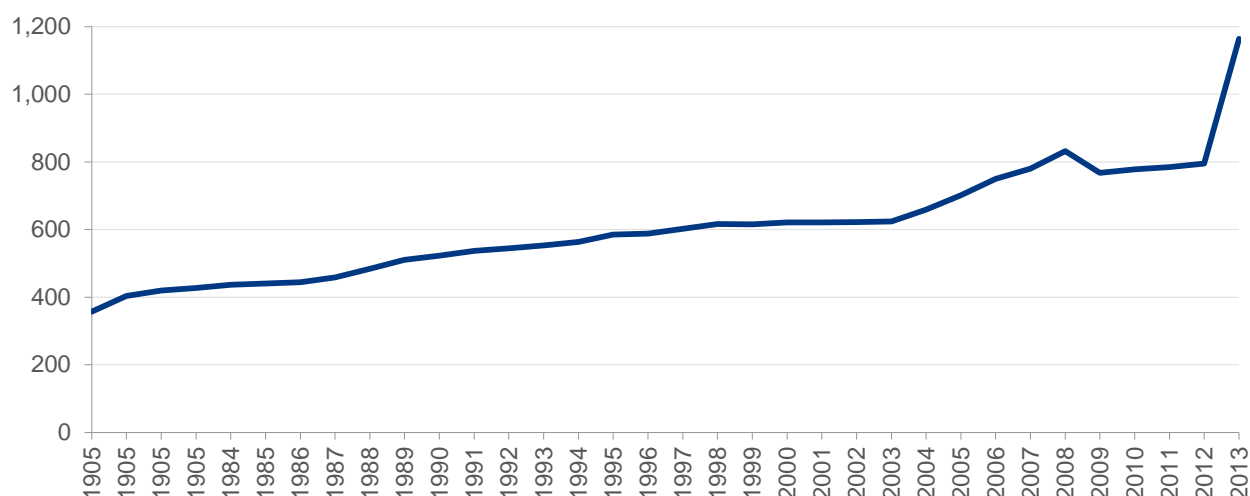
The following graph shows how the location factors for Germany and Japan have changed over an extended period of time. The high values post-2000 are mostly driven by currency exchange values between the euro, yen, and US dollar.

Figure 5.3: Historical location factors for Germany and Japan

PEP capital cost 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 program 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 1,164. In 2012, PEP conducted an evaluation of the PEP Cost Index, and made a significant upward revision (over 40%) to reflect actual market place conditions.

Historical index values for the United States are presented in the graph below.

Figure 5.4: Historical values of US PEP Cost Index

Regulatory environment and EH&S 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 18,000 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 best current practice in EU countries or the United States. Wastewater will either be treated onsite using tertiary biox treatment technology to achieve 95% removal of BOD/COD, the elimination of suspended solids to 20 ppmw, and 100% removal of hazardous materials. Nonhazardous solid waste will be removed and disposed of by a government approved landfill operator. Hazardous materials will either be incinerated onsite, or removed by a government 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).

Off-site 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 off-site and infrastructure facilities. The kind of off-site and infrastructure facilities normally factored into IHS off-site costs are listed below, along with the specific off-site facilities that are incorporated in the capital and operating cost estimate for this project.

Table 5.3: IHS off-site capital cost components

	HMDA		HMDA
Cooling water supply	√	Wastewater treatment plant	√
Process water supply	√	Process waste incinerator	√
Boiler feed water preparation	√	Safety flare and flare header	√
Steam generation	√	Fuel gas header	√
Inert gas generation	√	Religious/cultural facilities	
Instrument air plant	√	Safety/health care facility	√
Feedstock and product storage	√	Cafeteria	√
Fencing and plant security	√	Training facility	√
Laboratory	√	Electricity generation	
Administrative building	√	Power distribution and letdown transformers	√
Storehouse	√	Sanitary facilities	√
Maintenance warehouse and shop	√	Air separation plant	
Firefighting facilities		Desalinated water facility	
Rail and truck loading	√	Crude oil storage	
Extra catalyst charges	√	Pier/jetty for crude receipts	
Maintenance vehicles	√	Refined products pier	
Car/truck fleet	√	Liquids loading dock	√
Polymer warehouse and 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 HMDA plants are not designed to operate with black start capability.

Process control philosophy

The overall approach to process control for the HMDA manufacturing plants is to maximize automation for the twin purposes of minimizing labor and maximizing conformance with specifications. A comprehensive computerized process control system such as Honeywell Experion, Invensys/Foxboro Avantis, or Yokogawa Centum VP systems is provided.

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 down-time associated with equipment failure is spent waiting for needed parts to arrive, rather than for tear-down, diagnosis, repair, or re-installation. 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 on compressors
- Ultra sound sensors for equipment integrity
- Speed measurement and automatic shutdown of turbine drivers
- 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 [31C33] 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 [31C34] 16–30% chromium and 3–22% nickel. At elevated temperatures (>100°C), stainless steels and

tantalum are no longer suitable for service [31C35]. In this environment, the recommended material is titanium. For elastomers used in seals and gaskets, Viton and Teflon have been found to provide acceptable service and long-term reliability. Nickel alloy (monel, inconel, incoloy) is used in hydrochloric acid service for the Rennovia process.

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 HMDA manufacturing are:

Table 5.4: 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 Assn
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 process vessels and process piping. Electric power and process control systems conform to IEEE and NEMA 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 2013. For utility calculations specific temperature assumptions are:

Table 5.5: 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 1,164.

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 Chemical'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 (ISBL) investment and off-sites (OSBL 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. “Off-sites” 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 prior to capital appropriation
- Cost of permitting or engineering required for permits (environmental impact statements, dispersion modeling, etc.)
- Acquisition of 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 2013. In estimating plant capital costs, we assume “overnight construction.”

Available utilities

Our design assumes that the HMDA 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 (N₂)
- Instrument air
- Fuel gas header (without 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 U.S. 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 US\$46.23 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. Construction labor cost for 2013 is expected to be US\$49.72.

The total maintenance costs are estimated to be 4% 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 HMDA 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 yr. for fixed capital.

Feedstock, product, and energy pricing

Our technoeconomic analysis is based upon feedstock and product pricing as of mid-2013. In this environment, desired US crude oil prices have been targeted as between a range of US\$90–100/barrel (bbl), with a desired average of US\$95/bbl. As recently as mid-2003, actual crude oil prices were approximately US\$30/bbl, and spiked up later in the decade to as high as US\$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 US\$4.12/MM-Btu (million British thermal units) 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 5.6: Project utility unit costs in US cents

Material	Unit	USGC midyear 2013 (US cents)
Cooling water	Mgal	15.49
Electricity	kWh	5.93
Fuel oil	MMBtu	1,423.8
Inert gas, HP	MSCF	235.1
Inert gas, LP	MSCF	192.6
Natural gas	MMBtu	412.0
Process water	Mgal	132.3
Steam, LP	Mlb	570
Steam, MP	Mlb	760
Steam, HP	Mlb	810

Unit feedstock costs for project economics are listed below, and are based on mid-2013 US bulk costs on a contract FOB basis.

Table 5.7: Project feedstock unit costs

Feedstock	Unit cost	Pricing
Nylon 66	158.73¢/lb	\$3,500/mt
HMDA	131.52¢/lb	\$2,900/mt
Adiponitrile	108.84¢/lb	\$2,400/mt
Butadiene	65.6¢/lb	\$1,446/mt
Acrylonitrile	81.67¢/lb	1,801¢/lb
Fructose	20.408¢/lb	\$450/mt
Adipic acid	73¢/lb	\$1,610/mt
Ammonia	27.21¢/lb	\$600/mt
Benzene	55.93¢/lb	\$1,233/mt
Caustic soda	29.48¢/lb	\$650/mt

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 (freight on board) 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 HMDA technologies presented is 250 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

Hexamethylenediamine

The production specification in this project conforms to Invista's product specification [31C05] is shown in the table below

Table 5.8: Invista commercial DYTEK™ HMDA specification

HMDA wt%	60–100
Water wt%	0.1–40
Color, APHA	2
1,2-Diaminocyclohexane, mols per million mols	4
2-Aminomethylcyclopentylamine, mols per million mols	19
2-Methylpentamethylenediamine, mols per million mols	3
Polarographically reducible impurities, mols per million mols	8

Source: Invista

Adiponitrile

Our product specification for adiponitrile conforms to Invista's sales specifications [31C03] for its DYTEK™ adiponitrile, as shown below.

Table 5.9: Invista adiponitrile product specifications

Purity	Water content	Other organics
99.9%	0.05%	0.2%

Source: Invista

Butadiene

The feedstock specification for butadiene is consistent with the sales specification by Equistar [31C36], as shown in the table below.

Table 5.10: Equistar butadiene sales specification

Parameter	Value
1,3-Butadiene purity %	99.5% min
1,2-Butadiene purity	20 ppm max
Acetylenes ppm	20 max
Dimer %	0.1 max
Carbonyl ppm	10 max
Nonvolatile residue 5	0.05 max
O ₂ content vol%	0.1 max
Peroxides ppm	5 max
Sulfur as H ₂ S ppm	5 max
TBC inhibitor ppm	150 max

Acrylonitrile

The feedstock specification for acrylonitrile is consistent with the sales specification by Ineos [31C37], as shown in the table below.

Table 5.11: Ineos acrylonitrile sales specification

Parameter	Value
Acetone ppm	75 max
Acetonitrile ppm	150 max
Acidity ppm	15 max
Acrolein ppm	10 max
Aldehydes ppm	20 max
Appearance	Clear, free of suspended matter
Color APHA	10 max
Copper ppm	0.1 max
Hydrogen cyanide ppm	5 max
Inhibitor (MEHQ) ppm	35–45
Iron ppm	0.1 max
Methacrylonitrile ppm	250 max
Methyl vinyl ketone ppm	10 max
Non-volatile matter ppm	100 max
Oxazole ppm	80 max
Peroxide ppm	0.2 max
pH	6.0–7.5
Titration value (0.1 N H ₂ SO ₄) ml.	2 max
Water wt%	0.2–0.5

6. HMDA and ADN via Invista butadiene processing

Butadiene hydrocyanation technology background

Adiponitrile came to prominence when DuPont began commercially manufacturing nylon 66 in the 1930s. The initial route to ADN was the vapor-phase catalytic dehydration of adipic acid (ADA), which was difficult to manufacture due to the instability of ADA under these conditions. The ADA process was also adopted by Monsanto, ICI, Rhone-Poulenc (now Rhodia/Solvay), Montedison (now Radici), and Badische (now BASF). This process continued until 1948, when DuPont converted one plant in Niagara Falls, New York, USA to making ADN from furfural, and another plant in Victoria, Texas, USA to making ADN from butadiene via direct chlorination. Based on technology initially developed in Russia, Monsanto and Asahi later converted to the acrylonitrile electrodimmerization process.

DuPont shut down its furfural-based ADN commercial units in 1961, and adopted direct hydrocyanation of butadiene at Orange, Texas, USA in 1971 using a homogeneous catalyst (Generation 1). That process involves first mononitrile formation by producing C₅ pentenenitrile isomers from C₄ butadiene by the addition of a CN group to a terminal carbon atom on a butadiene molecule. 3-pentenenitrile (3PN) and 4-pentenenitrile (4PN), representing two-thirds of reaction product, can be converted easily to ADN, but isomer 2-methyl-3-butenitrile (2MBN), representing one-third of reaction product, must be separated from the reactor product stream (by distillation) and then isomerized to either 3PN or 4PN, and then undergo a second hydrocyanation at the opposite terminal carbon atom.

The second hydrocyanation adds a second CN group to the opposite terminal carbon atom on C₅ pentenenitrile to form C₆ adiponitrile. Both hydrocyanation reactions are conducted in the liquid phase with homogeneous nickel ligand catalyst, at a slight pressure sufficient to maintain the butadiene feedstock in the liquid phase. This catalyst formulation is used for both hydrocyanation steps, and also for the 2MBN isomerization step.

The reactor product from the second hydrocyanation step contains adiponitrile, unconverted pentenenitriles, and undesirable by-products methylglutaronitrile and ethylsuccinonitrile, which are removed from ADN by distillation.

Invista the company

In 2004, Koch Industries, Inc. (Wichita, Kansas, USA) purchased the DuPont textiles and interiors business, which included its integrated nylon salt and fiber derivatives business. This DuPont subsidiary at the time was named Invista. Once acquired, Koch merged into Invista its previously acquired (1998 from DuPont) polyester fibers, polymers, and intermediates business. Koch Industries is privately owned [31C38], and worldwide employs approximately 60,000 people in 60 countries.

Invista BV is headquartered in Goes, the Netherlands. Beside the integrated nylon 66 (polyamides) business produces nylon 66 resin and fiber, Invista also purifies, markets and sells the many by-products produced in the ADN and HMDA production units. The list of nylon 66-based Invista products is presented in the table below.

Table 6.1: Nitrile products made and sold by Invista

Invista product	CAS number	Formula
Methyleneglutaronitrile	1582-52-72	C ₆ H ₆ N ₂
Pentenitrile	13284-42-92	C ₅ H ₇ N
Methyl-2-butenitrile	4403-62-62	C ₅ H ₇ N
1,6-Hexanediamine (HMDA)	124-09-41	C ₆ H ₁₆ N ₂
cis-2-Pentenitrile	25899-50-7	C ₅ H ₇ N
Aminopentanitrile	75405-06-03	C ₅ H ₁₀ N ₂
Methyl-3-butenitrile	16529-56-92	C ₅ H ₇ N
Hexamethylenimine	105-60-2	C ₆ H ₁₃ N
Adiponitrile	111-69-3	C ₆ H ₈ N ₂
Pentenitrile	4635-87-43	C ₅ H ₇ N

Invista next-generation adiponitrile technology

In May 2012, Invista announced [31C39] plans to commercialize its next-generation adiponitrile manufacturing technology, in plants to be built in China and the United States. The novelty comes primarily from the use of a new catalyst which claims to provide the following advancements, compared to Invista's current catalyst:

- Increased product yield
- Reduced energy consumption
- Higher catalyst activity
- Reduced CO₂ greenhouse gas emissions
- Improved operating stability
- Lower capital cost

The new Invista catalyst is also claimed to eliminate benzene emissions in the adiponitrile manufacturing process. Benzene is carcinogenic, and therefore requires extraordinary process safety considerations for worker safety and exposure prevention.

Invista's next-generation technology was developed over several years with an expenditure of US\$40 million, including a two-year pilot plant program at its adiponitrile manufacturing site in Orange, Texas. Invista claims 60% global market share in adiponitrile manufacturing capacity, including the Butachemie joint venture with Rhodia/Solvay.

Intended commercialization of Invista ADN technology

Invista intends (as of late 2013) to commercialize its new technology initially at its 70 acre (28 hectares) Orange, Texas, USA integrated nylon 66 production site, at an estimated capital investment of US\$100 million [31C40]. Beside the economic benefits, the new technology is expected to eliminate benzene emissions at its production unit, while also lowering CO₂ emissions.

In 2013, Invista announced [31C45] contracting engineering and construction firm KBR to provide construction services for its next-generation adiponitrile plant, to be built at its existing nylon 66 complex in Orange, Texas, USA.

Beside commercializing the technology at Orange, Invista intends to follow-up by converting to this technology at its other Texas manufacturing site in Victoria, and its grassroots HMDA plant at the Shanghai Industrial Chemical Park, China, which is expected to start up in 2015 (31C43, 31C44). The total capital investment for the entire China complex is expected to exceed US\$1 billion.

In early 2012, Invista announced [31C42] that it would build a grassroots nylon manufacturing complex in Shanghai, China. The 215 kty HMDA plant component of the project is scheduled to start commercial operations in 2015, and consist primarily of an HMDA plant and a nylon 66 polymer, with purchases of adipic acid from local Chinese sources. The HMDA plant will use in-house Invista technology to initially produce HMDA from imported ADN, and later convert feedstock butadiene first to adiponitrile, and then hydrogenate the ADN to HMDA. The other comonomer adipic acid (ADA) will be sourced from local producers inside China. Invista indicated that the complex is intended to serve markets both in China and the greater Southeast Asia region.

There are several reasons that China now provides an attractive business environment to Invista for considering a grassroots nylon 66 manufacturing complex. Unlike many basic petrochemicals whose average selling price in China is well below world levels, nylon 66 pricing in China closely approximates western values. The spot price of nylon 66 in China is generally only slightly below the global contract price. The recovery of the world economy after the 2008 global recession resulted in a large increase in automobile manufacturing in China, approximating 20% growth per year. In this environment, nylon 66 required for 'under the hood' auto components has generally been tight. To exacerbate the situation, the 2008 recession caused several nylon 66 producers to reduce output short term, and reduce capacity long term.

Invista's butadiene-based technology has often been short of feedstock, due to the preference of steam crackers to crack light gases rather than higher cost naphtha, resulting in small coproduction rates of butadiene. Competitor Rhodia has suffered intermittent labor-management problems in France. An investigation for the high nylon 66 prices in China, conducted in 2010 by the China Engineering Plastics Association [31C46], attributed the causes to market forces, rather than price manipulation.

Hydrogen cyanide production

Section 100 of the process flow diagrams presents the hydrogen cyanide generation unit for the process. DuPont currently (2013) offers a process license for its version of the Andrussow HCN process. Physical properties of HCN are presented in the table below.

Table 6.2: Physical properties of hydrogen cyanide

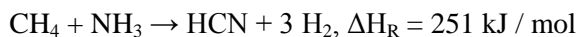
Property	Value
CAS number	74-90-8
Chemical formula	HCN
Molecular weight	27.03
Boiling temperature °C	26
Liquid density g/ml	0.687
Vapor specific gravity vs. air	0.93
Melting temperature °C	-12 to -14
K _H in µmol/Pa-Kg	75
Refractive index (n _D)	1.2675
Liquid viscosity µPa-s	201
Vapor pressure at 20°C mmHg	620
Flash point °C	-17.8
Autoignition temperature °C	538
Standard entropy of formation kJ/mol	109.9
Standard enthalpy of combustion kJ/mol	-426.5
Standard molar entropy J/K-mol	113.01
Specific heat capacity kJ/K-mol	71
Upper flammability limit %	40
Lower flammability limit %	5.6

Andrussow HCN process chemistry

In this process unit, natural gas is reacted with ammonia and air to produce dilute hydrogen cyanide (HCN) using Leonid Andrussow's IG Farben process patented in the 1930s (USP 2105831, 2006981). In the Andrussow process, excess natural gas is combusted with air to generate the exothermic heat of reaction that is necessary to reduce ammonia and natural gas to HCN. The reaction chemistry is shown below.



HCN can be produced without air using the BMA process, but this chemistry is highly endothermic, requiring expensive high temperature furnaces and corrosion resistant alloys. Evonik/Degussa practices the BMA process commercially in Germany. The BMA reaction chemistry is shown below.

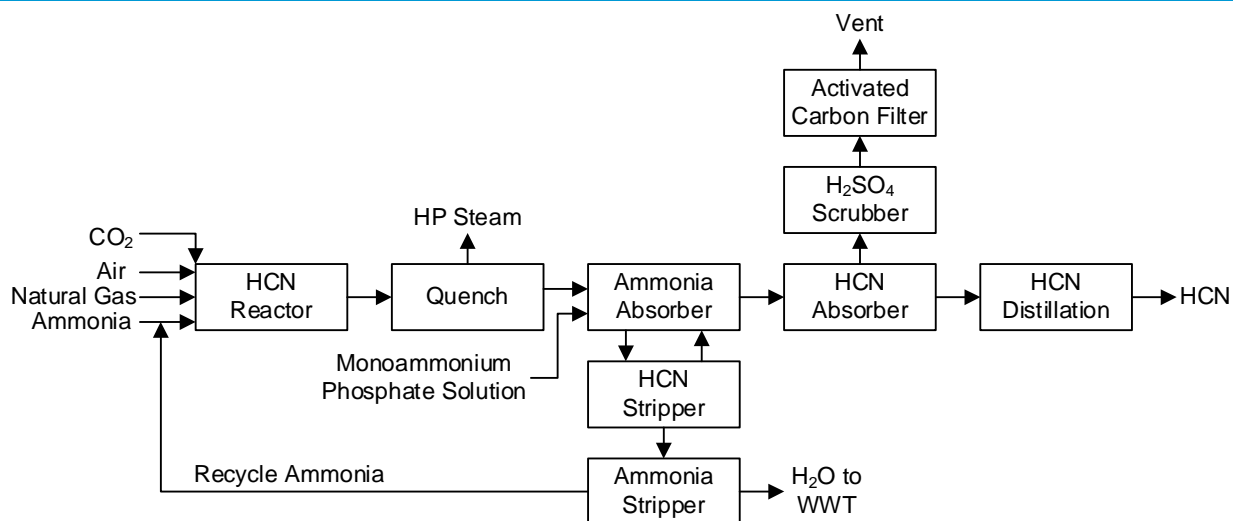


The Andrussow reaction occurs at very high temperatures (1,100–1,200°C) over a platinum (90%) and rhodium (10%) wire gauze catalyst. Catalyst suppliers are noble metal companies like Johnson Matthey, BASF/Englehard, and Umicore. The reaction is generally practiced commercially at slightly above atmospheric pressure (30 psia).

Andrussow process design

For our design, we have increased the reactor pressure to 40 psia, in order to treat waste gases through a dilute sulfuric acid scrubber followed by an activated carbon filter, in order to meet current environmental discharge requirements in industrial countries. A block flow diagram for the Andrussow process is presented below.

Figure 6.1: DuPont Andrussow HCN process



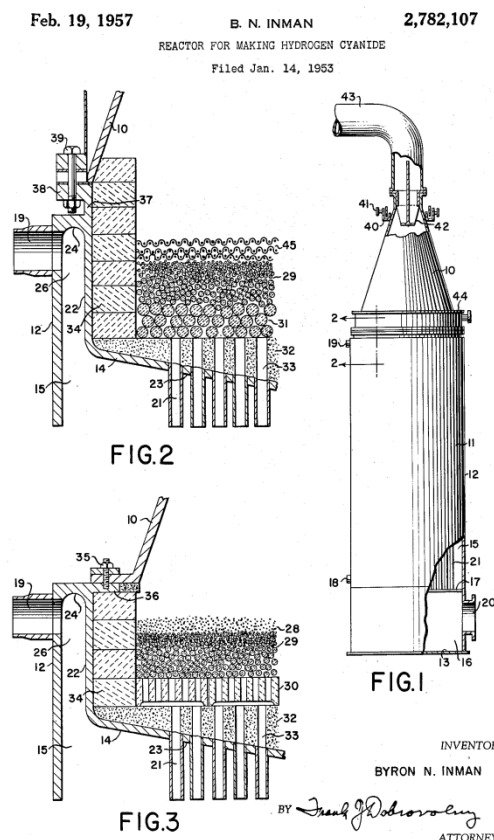
Filtered air is compressed and used as the oxygen source for the Andrussow process. In order to minimize deactivation of the noble metal catalysts, both the ammonia feed and natural gas feed are pretreated to remove contaminants. Vaporized ammonia from tankage is passed through a desiccant drying bed to remove residual water that may have been picked up during storage and transportation. The desiccant bed can be regenerated using hot nitrogen offline. Natural gas is first passed through a bed of zinc oxide to remove residual H_2S that could deactivate the catalyst. The zinc oxide desulfurization bed is regenerated by passing hydrogen gas through it offline.

The IHS design represents our understanding of the DuPont Andrussow process, with a minor enhancement patented by DuPont (USP 4107278) incorporating the intermittent injection of CO_2 into the reaction feed. Since the deactivation of the platinum/rhodium wire gauze catalyst most often is caused by carbon build-up, adding CO_2 intermittently at the very high reaction temperature will cause the CO_2 to reduce to CO , which will inhibit the formation of carbon, and remove some of the carbon already deposited on the catalyst.

Andrussow HCN reactor design

Our design utilizes the basic Andrussow reactor design, which is a conical downflow reactor in which the feed gases pass through the wire gauze catalyst, and then continue downward through a close coupled shell and tube heat exchanger designed to quench the reaction quickly. The heat transferred from the reactor product gases through the tube metallurgy is used to boil BFW to produce high pressure steam. Below is a diagram of a DuPont designed and patented HCN reactor.

Figure 6.2: DuPont HCN reactor (USP 2782107)

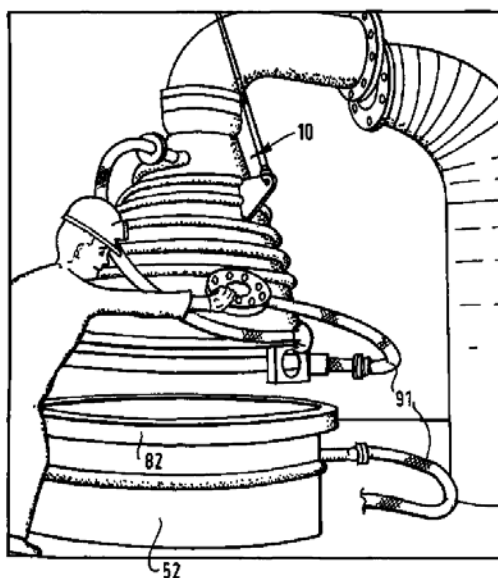


In our design, high pressure superheated steam is produced in a steam drum outside the heat exchanger, allowing high thermal flux across the tubes, and providing a second heat exchanger so that the saturated high pressure steam (1,200 bar) formed in the steam drum can be super-heated for use as a power source for driving steam turbines. The air compressor is driven by such a condensing steam turbine. Our design is based on 65% NH_3 conversion, 70% natural gas conversion, and an overall 90% HCN yield.

Due to the very high temperatures in the Andrussow reactor, the reactor must be lined with high temperature refractory, and provided with a cooling water jacket to maintain metallurgy temperatures within acceptable ranges that do not compromise the tensile strength of the metal. The quench cooler cannot be made of pure iron or steel, as iron is a hydrogen cyanide decomposition catalyst. For our process, we have used high nickel content Inconel heat exchanger tubes.

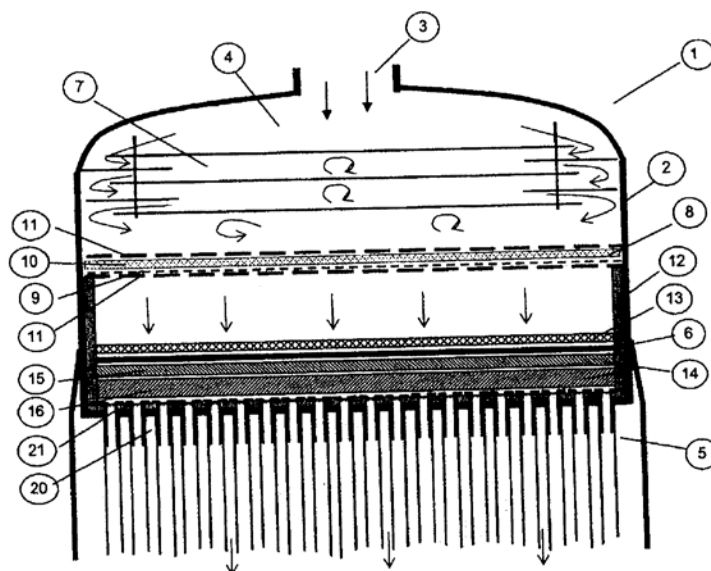
An alternative configuration for the head design of an HCN reactor was patented by Rohm & Haas in 2006 (USP 7063827), as shown in the figure below. This design provides for the easy removal of the reactor head for catalyst change-out during schedule turnarounds, and provides for a water cooled external jacket to maintain acceptable pressure vessel metallurgical temperature.

Figure 6.3: Rohm & Haas HCN reactor design (USP 7063827)



Evonik/Degussa has applied for a US patent (USPA 2011 0171101) for a more modern concept of the Andrussow HCN reactor. The Evonik reactor is also configured for vapor-phase downflow, where the entering gas mixes well through a baffling arrangement near the inlet nozzle of the reactor. A diagram of the Evonik reactor is presented below

Figure 6.4: Evonik HCN reactor design (USPA 2011 0171101)



Directly below the mixing chamber is a permeable membrane, which directs the feed gas uniformly down through the catalyst bed, which is also a platinum-based wire gauze through which feed gases can permeate and react to form HCN. After the gases react across the catalyst wire gauze, they flow immediately through the quench chamber, which is designed as a vertical shell-and-tube heat exchanger. Boiler feed water flows on the shell side of the heat exchanger, where it is heated and leaves the pressure

vessel to vaporize in a steam drum outside the reactor. The HCN product yield from the Evonik reactor design is presented in the table below.

Table 6.3: HCN product yield from Evonik HCN reactor

	HCN yield [kg/h]	HCN yield based on NH ₃ [%]	HCN yield based on methane [%]	HCN conc. in reaction gas [% by vol.]
Example 1	2.76	67.8	69.9	7.81
Example 2	2.67	65.8	67.6	7.63
Example 3	2.58	64.67	65.46	7.40
Example 4	2.61	64.25	65.42	7.15
Example 5	2.37	58.69	59.95	6.43
Example 6	2.11	52.41	53.86	5.77

Reaction gas purification

After the reactor product gases are quenched, they are further cooled through two feed/product exchangers against air feed and natural gas/ammonia feed, for the purpose of heat recovery. The cooled gases are then brought down to nearly ambient temperature by passing them through a heat exchanger using cooling tower water.

The cooled reactor gases are injected into the bottom of an ammonia absorber. The liquid absorbent is a solution of mono-ammonium phosphate (MAP). When MAP contacts the ammonia in the vapor stream, it absorbs the ammonia to produce di-ammonium phosphate (DAP). The DAP is steam stripped downstream to release ammonia as a vapor, which is recompressed and recycled to the Andrussov reactor.

The DAP solution is first passed through an HCN stripper. The MAP solution, though designed to absorb ammonia, also absorbs some HCN. The solution is passed through a stripper to release the dissolved HCN vapor at a lower temperature than the ammonia stripper. The HCN vapor along with low pressure steam evaporated from the solution is sent back to the ammonia absorber, leaving a DAP solution that is virtually free of HCN.

The DAP solution is then stripped by heating to release the dissolved ammonia as a vapor, which is compressed and recycled. The now ammonia free DAP solution from the bottoms of the ammonia stripper is distilled to remove a water-rich overhead product, and a MAP-rich bottoms product. The bottoms product stream is recycled to the ammonia absorber.

The vapor stream leaving the ammonia absorber, free of most of the ammonia in the feed to the absorber, is sent to an HCN absorber. Cold water is used to dissolve HCN from the vapor stream into the water stream, producing a 20% solution of HCN in water. The 20% solution is fed to a distillation column producing pure (99.5%) HCN as overhead distillate stream, and nearly pure water as the bottoms product stream. The bottoms product stream is cooled in a heat exchanger to below ambient temperature using cold glycol solution, and recycled to the HCN absorber.

The overhead vapor stream from the HCN absorber is mostly nitrogen gas from the air feed to the Andrussov reactor, plus combustion products CO₂ and CO, with residual amounts of HCN. The vapor

stream is sent to a weak caustic soda scrubber to remove by neutralization residual HCN, with the overhead from the scrubber being sent through an activated carbon bed to remove residual hydrocarbons prior to being vented to atmosphere.

The design basis table for the HCN generation unit is presented below.

Table 6.4: Andrussow HCN generation design basis table

Parameter	Value
Reactor operating temperature °C	1,100–1,200
Reactor operating pressure psia	40
Reactor residence time sec	3
Reactor catalyst	90% Pt/10% Rh
Type reactor	Plug flow, downward, refractory lined, jacket cooled
HCN yield %	90
NH ₃ conversion per pass %	70
CH ₄ conversion per pass %	100

Development status of Invista ADN process technology

The new Invista catalyst technology was developed at its pilot plant facilities at the Orange, Texas manufacturing site, and was operated for more than two years. Invista claims to have spent more than US\$40 million to develop the new technology [31C41].

One business driver for conversion to the new ‘benzene free’ technology is avoidance of governmental regulatory claims of excessive benzene environmental emissions at both of Invista’s Texas petrochemical manufacturing sites.

Due to excessive benzene emissions at its Orange and Victoria Texas nylon complexes, Invista negotiated a consent decree in 2009 with the states of Delaware and South Carolina, plus the Chattanooga (Tennessee) regional environmental authority, to mitigate these emissions by installing its next-generation ADN technology, which is claimed by Invista to inherently avoid benzene generation, and therefore avoid benzene emissions. The relevant paragraph of the consent decree is shown below. This agreement further encouraged the commercialization of its next-generation technology.

Option A—Invista shall install and fully implement a new ADN production technology that is expected to eliminate benzene from the ADN production process as follows: (i) for the first (or only, as applicable) Facility for which this option is elected, by no later than December 31, 2013, and (ii) for the second, if applicable, Facility for which this option is elected, by no later than December 31, 2016. If Invista elects to implement this new technology pursuant to this Option A at the Victoria and/or Orange facility(ies), the other requirements of this Section VI and their corresponding stipulated penalties provisions of this Consent Decree (Subparagraphs 89.i–89.t) shall not apply to the relevant facility(ies). Until the new technology referenced above is fully implemented under this Option, Invista will continue to comply with the 2 Mg Compliance Option.

Invista's HMDA and ADN patent position

Invista has continued the long-time DuPont strategy of patenting their know-how extensively, often, and across the globe. Our analysis includes reviews of granted patents via the US, EP, and WIPO patent offices. Most international patents cover the same intellectual property patented in the United States. As a result, for convenience purposes, we present mostly US granted patents, and US patent applications. Invista's US patent position in HMDA and ADN, excluding the know-how acquired from DuPont, is listed in the table below.

Table 6.5: Invista US patents involving HMDA and ADN

Number	Title
6812352	Multidentate phosphite ligands, catalytic compositions containing such ligands, and catalytic processes utilizing such catalytic compositions
6855799	Polymeric phosphite composition and hydrocyanation of unsaturated organic compounds and the isomerization of unsaturated nitriles
6924345	Phosphorus-containing compositions and their use in hydrocyanation, isomerization and hydroformylation reactions
6936171	Process for catalyst recovery from hydrocyanation product mixtures
6984604	Supported bis(phosphorus) ligands and their use in the catalysis
7612223	Process for the hydrocyanation of unsaturated compounds
7629484	Method for the purification of triorganophosphites by treatment with a basic additive
7659422	Hydrocyanation process with reduced yield losses
7709673	Process for making 3-pentenitrile by hydrocyanation of butadiene
7709674	Hydrocyanation process with reduced yield losses
7880028	Process for making 3-pentenitrile by hydrocyanation of butadiene
7897801	Process for the preparation of dinitriles
7919646	Hydrocyanation of 2-pentenitrile
7973174	Process of making 3-aminopentanitrile
7977502	Process for making and refining 3-pentenitrile, and for refining 2-methyl-3-butenitrile
8088943	Hydrocyanation of pentenenitriles
8101790	Process for improving adiponitrile quality
8178711	Method for the purification of triorganophosphites by treatment with a basic additive
8247621	Process for making 2-secondary-alkyl-4,5-di-(normal-alkyl)phenols
8338636	Hydrogenation and esterification to form diesters
8373001	Method of producing dinitrile compounds
8394981	Hydrocyanation of 2-pentenitrile

Invista's more recent (as of 2013) US patent applications are listed in the subsequent table.

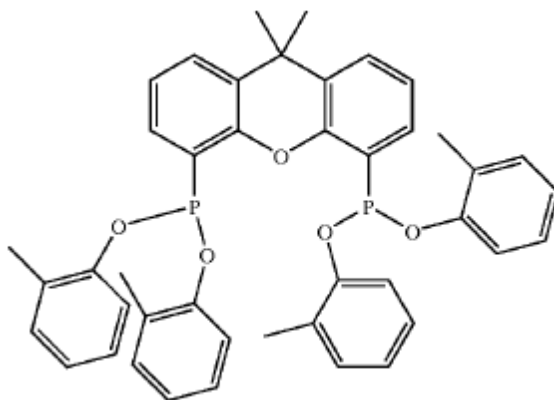
Table 6.6: Invista US patent applications involving HMDA and ADN

Number	Title
20060058545	Separation of 6-aminocapronitrile and hexamethylenediamine from a mixture comprising hexamethylenediamine, 6-aminocapronitrile and tetrahydroazepine
20060058555	Separation of 6-aminocapronitrile and hexamethylenediamine from a mixture comprising hexamethylenediamine, 6-aminocapronitrile and tetrahydroazepine
20080015381	Hydrocyanation process with reduce yield losses
20080015382	Hydrocyanation process with reduce yield losses
20080319219	Process for improving adiponitrile quality
20090182164	Hydrocyanation of pentenenitriles
20130150610	Process for making nitriles
20130211121	Process for making nitriles
20130211122	Process for making nitriles
20130211123	Process for making nitriles
20130211124	Process for making nitriles
20130211125	Process for making nitriles
20130211126	Process for making nitriles
20130211127	Process for making nitriles
20130267728	Process for making nitriles

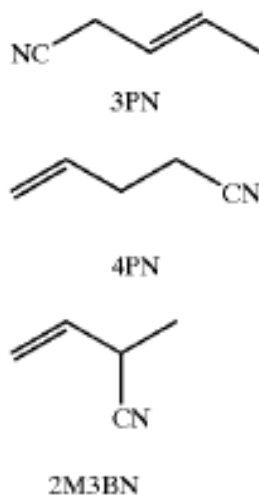
Major characteristics of Invista butadiene-based patents and applications

An IHS review of the **Invista** patents and applications listed **above** provide, in our opinion, the following fundamental advancements beyond the process technology inherited from DuPont:

- Consideration of using direct HMDA crystallization as an alternative approach to purification, when compared to conventional fractional distillation.
- Using a hydrocyanation catalyst that is a multidentate phosphonite ligand of a Group VIII metal, preferably nickel, along with a Lewis acid promoter. The metal is zero-valent nickel. The preferred catalyst pre-cursor is nickel di-(1,5-cyclooctadiene) (COD), which is reacted with a phosphonite ligand to produce a nickel phosphonite complex. Other Group VIII metals considered in the patent literature are iron and cobalt. The catalyst structure is shown in the figure below.

Figure 6.5: Structure of nickel phosphonite ligand catalyst

- Catalyst preparation methods are disclosed in USPA 2013 0144079, and in USP 6729484, USP 7470805, USP 6844289, and USP 6069267.
- Hydrocyanation of butadiene and HCN in the liquid phase to a mononitrile.
- Operating both of the hydrocyanation reactions and the isomerization reaction in the liquid phase with no need for external solvent. The feed to the reactors is butadiene or nitriles, plus HCN, plus catalyst.
- Hydrocyanation of 3 or 4-pentenitrile and HCN in the liquid phase to a dinitrile (adiponitrile).
- Although the hydrocyanation reaction has historically been conducted in a liquid solvent such as benzene or acetonitrile, recent patents indicate that no solvent is necessary, and that the reacting hydrocarbon (butadiene or C₅ mono-amines) can be used as the reacting liquid medium for the homogeneous nickel ligand catalyst, HCN and promoter. If a solvent is used, toluene is preferred to benzene because it is non-carcinogenic.
- The hydrocyanation reactor is well mixed with an agitator.
- Reaction temperature is approximately 80–100°C.
- Reactor products are purified via fractional distillation.
- Atmospheric pressure is suitable for conducting the reaction.
- Metal halides are the preferred Lewis acid promoters. Examples are ZnBr₂, ZnCl₂, ZnSO₄, CuCl₂, and FeCl₃. Zinc chloride is preferred. The promoter to catalyst ratio is 1:1.
- Primary reactor products when butadiene is fed to the hydrocyanation reactor are 3-pentenitrile (3PN), 4-pentenitrile (4PN), and 2-methyl-3-butenitrile (2M3BN). The chemical structures of these intermediate products are shown in the figure below.
- Where multiple reactors are used in hydrocyanation, nickel ligand catalyst is fed separately to each reactor such that the overall catalyst concentration increases as the feedstocks flow through the reactor sequences.

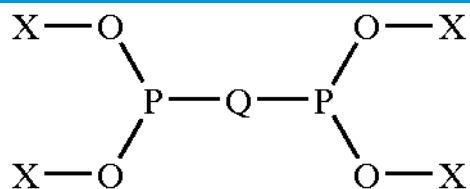
Figure 6.6: Structure of hydrocyanation intermediate products (USP 6737539)

- For the reaction hydrocyanating mononitrile to dinitrile, selectivity to ADN averages 90%, while conversion of pentenenitrile averages 70%.
- The zero valent nickel phosphorus ligand catalyst used for hydrocyanating butadiene to pentenenitriles is also used as the catalyst for isomerizing methyl butenenitriles to pentenenitriles.
- Although both hydrocyanation steps and the isomerization reaction use the same catalyst, the second hydrocyanation reaction also uses a Lewis acid promoter to increase the rate of the reaction. The Lewis acid promoter must be prevented from entering the first hydrocyanation reaction. The accidental presence of Lewis acid in the first hydrocyanation reaction potentially increases the reaction rate beyond safe kinetics, and the Lewis promoter also tends to form undesirable MGN by reacting 2M3BN with HCN.
- Although a single nickel catalyst formulation can be used for all three reactions, this is not the optimum process. For our design, we use a monodentate formulation for the hydrocyanation of butadiene to 3PN and for the isomerization of 2M3BN to 3PN, and we use a bidentate formulation plus triphenyl borane promoter for the hydrocyanation of 3PN to ADN.

Hydrocyanation catalyst composed of Group VIII metal and phosphonite ligand

DuPont patented the current generation of butadiene hydrocyanation catalysts with US Patent 6737539 (18 May 2004), where the catalyst is a Group VIII metal containing a phosphonite ligand. The structure of the ligand is shown in the figure below. In the figure below, the X groups are unbridged aromatic compounds. Q is a divalent aromatic or non-aromatic hydrocarbon (C_1 – C_{12} range). The metal components are nickel, cobalt, or palladium, where nickel (especially Raney nickel) is preferred. Specific nickel catalyst precursor compositions are nickel 1,5-cyclooctadiene, and the reaction occurs in the liquid phase.

The reaction operates successfully to produce mono-amine when the feedstock is butadiene, or to produce di-amine (in particular hexamethylenediamine) when the feedstock is a mono-amine such as 3- and/or 4-pentenitrile, alkyl 3-, and 4-pentenoates. 3-Pentenitrile and 4-pentenitrile are the most preferred.

Figure 6.7: DuPont hydrocyanation phosphonite ligand

The primary patent application providing know-how about the current Invista catalyst technology is USPA 2013 0150610. The butadiene hydrocyanation reaction and the 2M3BN isomerization reaction proceed at adequate commercial rates without the need for a catalyst initiator or promoter. The 3PN hydrocyanation reaction proceeds at much slower rates, requiring the use of a Lewis acid promoter (triphenylboron or zinc chloride) to accelerate kinetics.

Invista's primary claim for USPA 2013 0150610 is contained in the following excerpt:

A process for making adiponitrile, said process comprising the steps of: (a) reacting in a first reaction zone a mixture comprising 1,3-butadiene (BD) and hydrogen cyanide (HCN) in the presence of a first catalyst comprising zero-valent Ni and a first phosphorus-containing ligand to produce a reaction product comprising 3-pentenitrile (3PN) and 2-methyl-3-butenitrile (2M3BN); (b) isomerizing at least a portion of the 2M3BN of step (a) in a second reaction zone in the presence of a second catalyst comprising zero-valent Ni and a second phosphorus-containing ligand to produce reaction product comprising 3PN; and (c) reacting in a third reaction zone a mixture comprising 3PN from step (b) and hydrogen cyanide (HCN) in the presence of a third catalyst comprising zero-valent Ni and a third phosphorus-containing ligand and in the presence of Lewis acid promoter to produce a reaction product comprising adiponitrile. wherein catalyst flows through the first, second and third reaction zones along with reactants and products, wherein the reaction product of step (a) further comprises dinitriles comprising adiponitrile (ADN) and methylglutaronitrile (MGN), wherein at least a portion of catalyst flowing from the first reaction zone is concentrated in one or more distillation steps and recycled in at least one catalyst recycle stream to the first reaction zone, wherein a portion of the catalyst recycle stream is contacted with a first extraction solvent in a first liquid/liquid extraction step to produce a solvent phase and a raffinate phase, wherein said third catalyst is not contacted with said extraction solvent in said first liquid/liquid extraction step, wherein the first liquid/liquid extraction step comprises introducing a portion of the catalyst recycle stream, a first extraction solvent stream and a dinitrile recycle stream comprising adiponitrile (ADN) into a first liquid/liquid extraction zone, wherein the first liquid/liquid extraction step further comprises separating the liquids in the first liquid/liquid extraction zone into a first solvent phase comprising first extraction solvent and catalyst and a first raffinate phase comprising adiponitrile (ADN), methylglutaronitrile (MGN), compounds with a higher boiling point than adiponitrile (ADN) and compounds with a lower boiling point than methylglutaronitrile (MGN); wherein catalyst from said solvent phase obtained in said liquid/liquid extraction step is recycled to the first reaction zone or the second reaction zone or both the first and second reaction zone, wherein said first raffinate phase is distilled in one or more distillation steps to separate adiponitrile (ADN) and methylglutaronitrile (MGN) from compounds with a higher boiling point than adiponitrile (ADN) and compounds with a lower boiling point than methylglutaronitrile (MGN) to obtain a first refined dinitrile stream, wherein said first refined dinitrile stream is further distilled to remove methylglutaronitrile (MGN) from the first refined dinitrile stream to obtain a second refined dinitrile stream enriched in adiponitrile, and wherein at least a portion of said second refined dinitrile stream is recycled to the liquid/liquid extraction step.

Source: USPA 2013 0267728

Butadiene feed pretreatment

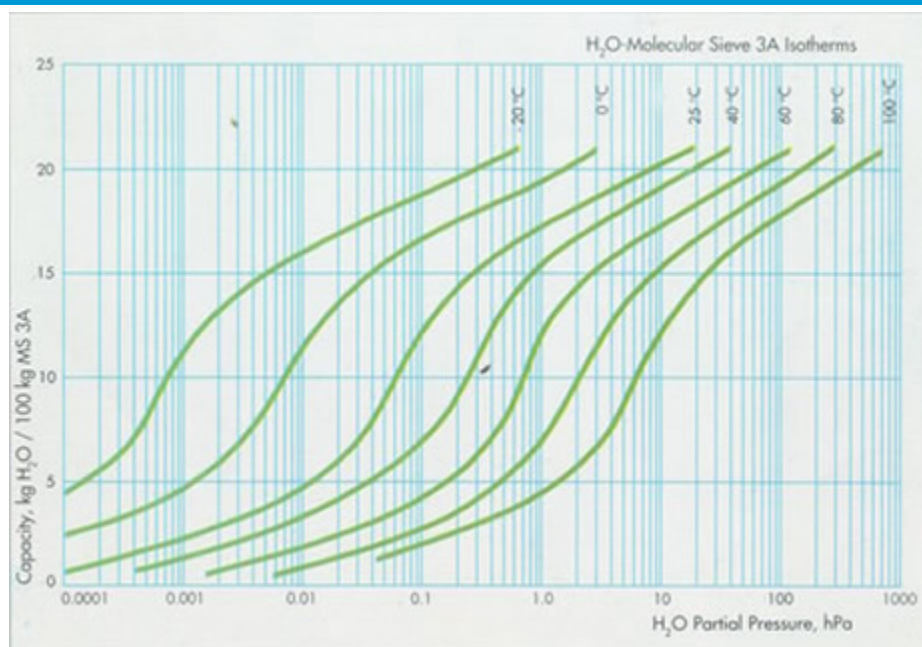
Due to the sensitivity of the hydrocyanation catalyst to the presence of water, the butadiene feedstock must be absolutely dry to maximize reaction performance. Installed just downstream of the butadiene feed pumps are two beds of 3 angstrom [31C47] synthetic zeolites (metal aluminosilicates) that will remove small quantities of water present in the butadiene, while also removing other small molecule contaminants that may be present in the feed. The drying beds are regenerated in-place, requiring that periodically they be taken off-line and exposed to a stream of hot, dry nitrogen gas. Regeneration temperature ranges between 175 and 260°C. Molecular sieve characteristics are presented in the table below.

Table 6.7: Butadiene dehydration 3A molecular sieve zeolite properties

	PG-3A48MS	PG-3A812MS
Generic name	4x8 beaded	8x12 beaded
Minimum pore diameter	3A	3A
Shape	Sphere	Sphere
Size	4x8	8x12
Packaging density (bulk)	40–47 lb/feet	42–48 lb/feet
Resistance to break	14–20 lb	7–12 lb
Absorption capacity	20.5 lbs water/100 lbs at 25°C and 17.5 MM HG min.	20.5 lbs water/100 lbs at 25°C and 17.5 MM HG min.
Heat absorption	1,800 Btu/lb H ₂ O	1,800 Btu/lb H ₂ O
Specific heat	0.23 Btu/lb °F	0.23 Btu/lb °F
Moisture content	1.5% in maximum weight	1.5% in maximum weight
Size qualification	≥95.0%	≥95.0%
Ethylene absorption	≤3.0 MG/G	≤3.0 MG/G
Wear rate	≤0.10% weight	≤0.10% weight
Package: residual moisture	≤1.5% weight	≤1.5% weight
Country of origin	China	China
Packaging	150 KG steel drum (supersacks available)	150 KG steel drum (supersacks available)

Source: Hengye USA

The water holding capacity of the molecular sieves is a function of the partial pressure of water entering the absorber with the butadiene. Below are representative field data for Hengye USA 3 angstrom sieve material.

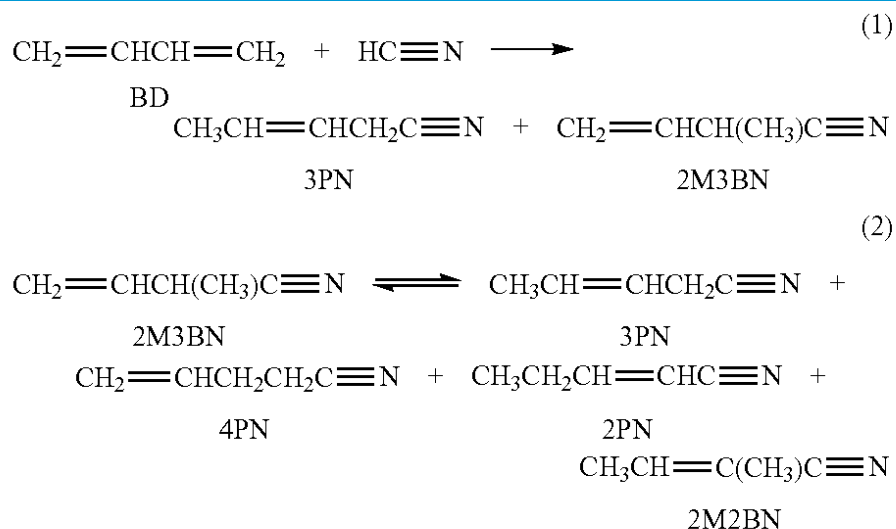
Figure 6.8: Water retaining capacity of 3A molecular sieves

Source: Hengye USA

Process configuration of Invista hydrocyanation of butadiene

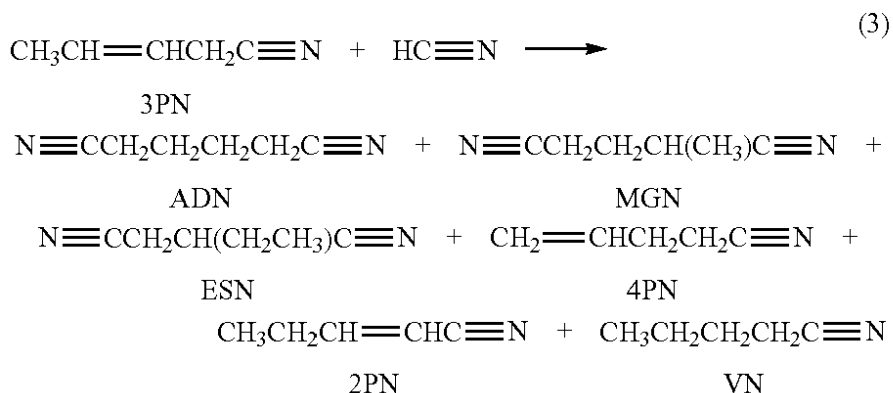
The process sequence we have adopted is derived from Invista USPA 2013 0150610 (13 Jun 2013). Due to the sensitivity of the catalyst to the presence of water, butadiene feed is first directed through a desiccant bed of alumina dehydrating absorbent, and then through a second absorption bed containing molecular sieves to remove residual contaminants. The absorbent is periodically dried out and regenerated offline with a counter current flow of hot and dry nitrogen.

In this sequence, butadiene is reacted with HCN in a solution of zero valence nickel phosphorus ligand homogeneous catalyst, as described earlier. The reaction is carried out at 80°C and 120 psia in two CSTR reactors configured in series and equipped with overhead agitators and cooling jackets. The reactors are nitrogen blanketed. The primary products from the first hydrocyanation reaction are 3-pentenitrile (3PN) and 2-methyl-3-butenitrile (2M3BN). Other reaction products include 4-pentenitrile (4PN), 2-pentenitrile (2PN), and 2-methyl-2-butenitrile (2M2BN). The reaction chemistry for these products is shown in the figure below.

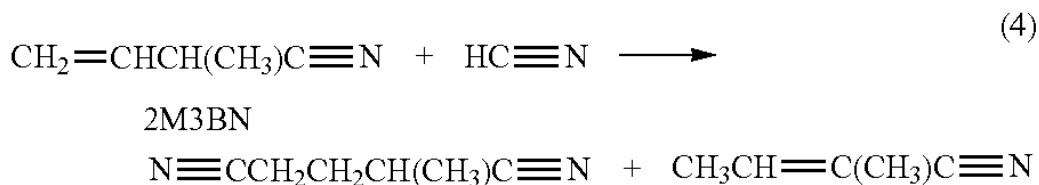
Figure 6.9: Butadiene hydrocyanation stoichiometry (USPA 2013 0150610)

The most desired reaction product is 3PN, which is easiest to convert upon further hydrocyanation to ADN, and in the process produces the least amount of by-products. This is the reason that 2M3BN is separated by distillation from the butadiene hydrocyanation reactor products, and separately isomerized to 3PN. 4PN is also produced, but its reaction rate and selectivity to ADN are lower than when using 3PN.

During the second hydrocyanation that converts 3PN to ADN, and the isomerization that converts 2M3BN to 3PN, an undesirable by product made is ethylsuccinonitrile (ESN), as shown in the chemical stoichiometry below, as well as 2-methylglutaronitrile (MGN) and valeronitrile (VN). The hydrocyanation of di-olefins (such a butadiene to nitriles) can proceed at acceptable kinetic rates with only the primary catalyst. However, the hydrocyanation of mono-olefins such as 3PN requires a promoter to increase kinetic rates to acceptable levels. Lewis acids provide good promoter capability. Particularly desirable Lewis acids are zinc chloride and triphenyl borane.

Figure 6.10: Hydrocyanation of 3PN to form ESN (USPA 2013 0150610)

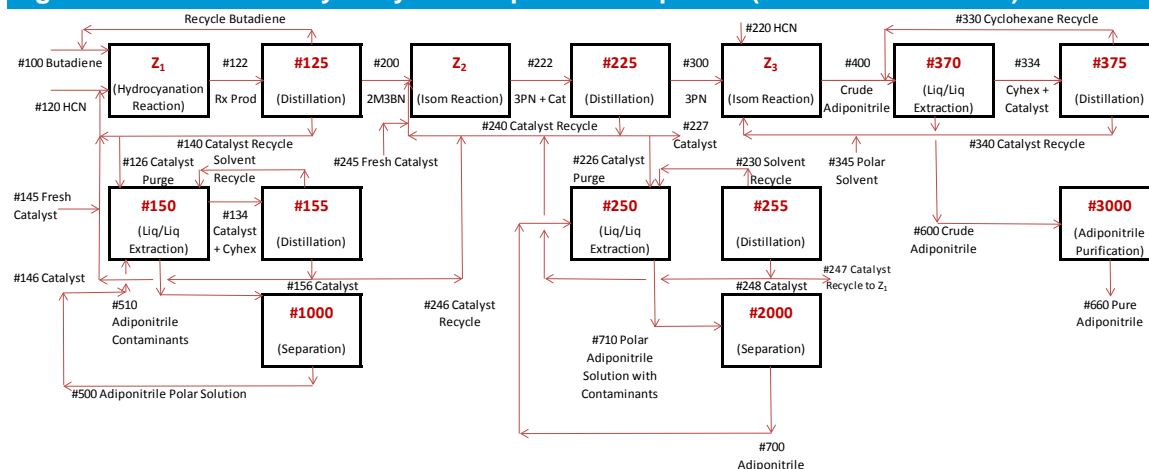
When 2M3BN is hydrocyanated, another reaction by-product is 2-methyl-2-butenenitrile (2M2BN), as shown in the figure below, plus methylglutaronitrile.

Figure 6.11: By-products of hydrocyanation of 2M3BN (USPA 2013 0150610)

2M3BN is separated from the first hydrocyanation reactor product stream by distillation, and isomerized to 3PN in a separate reactor using the same zero valence nickel phosphorus ligand homogeneous catalyst.

A combined 3PN-rich stream from the first hydrocyanation reaction and the isomerization reaction product stream are directed to a second hydrocyanation reaction to form adiponitrile (ADN). The second hydrocyanation reaction is assisted by the addition of a Lewis acid promoter, in order to increase kinetic rate of reaction. The primary by-product from the second cyanohydration reaction is methylglutaronitrile (MGN).

The overall process configuration for the hydrocyanation of butadiene to ADN is shown in the figure below, where we have added labels to represent the function of the unit operations, and the major constituents of the process streams. A larger version Figure 6.12 is available in Appendix C.

Figure 6.12: Butadiene hydrocyanation process sequence (USPA 2013 0150610)

Hydrocyanation of butadiene to form mononitriles (first hydrocyanation reaction)

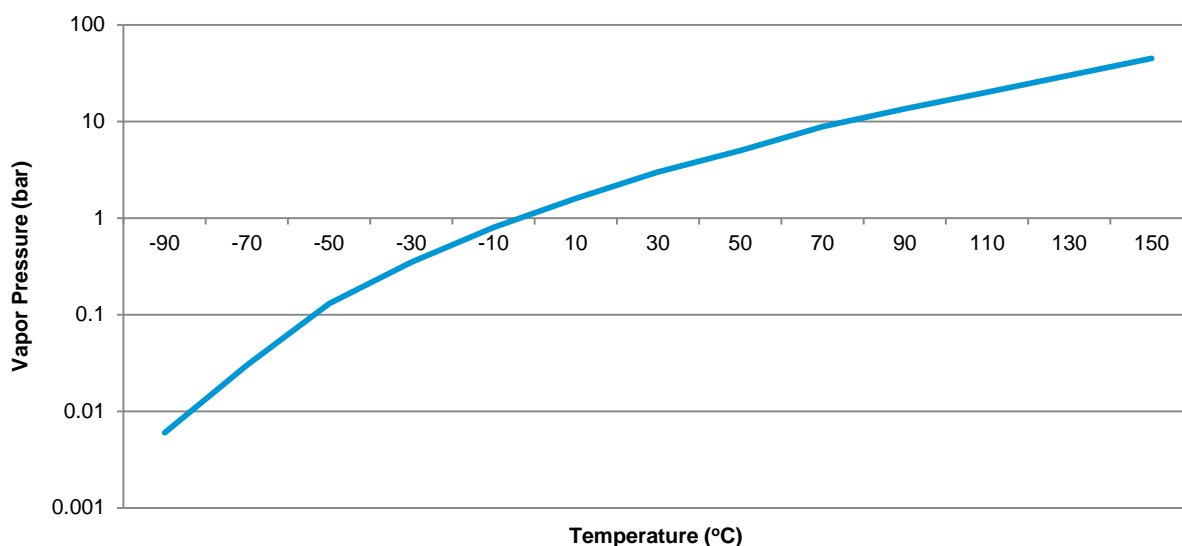
Feedstock dry butadiene is mixed with HCN, pumped together through a feed preheater to 100°C reaction design temperature, and pumped into the first of two CSTR butadiene hydrocyanation reactors. The first reaction is designed to convert butadiene to linear pentenenitriles (3PN, 4PN, 2PN). By-products formed include branched methyl butenenitriles (2M3BN, 2M2BN), some dimer-based nitriles ($\text{C}_8\text{H}_{13}\text{CN}$), a small proportion of dinitriles (ADN, MGN, ESN), catalyst degradation products (phenol, cresol), plus heavies.

Each reactor is equipped with a top entering mixer, and both reactors are blanketed with inert nitrogen. Since the reactions are exothermic, each reactor is provided with a cooling water jacket. Each reactor is designed for a 2.5 hour residence time, and the reactors are configured in series.

Although the flow of feedstock and reaction products from the first reactor to the second reactor includes liquid catalyst, additional catalyst is added to the second reactor to double its concentration from 0.2% to 0.4%.

Invista's patent literature suggests that operating pressure for the reactors is not critical, although the pressure should be high enough to maintain the feedstocks in the liquid phase. The following chart shows the boiling point curve for the more volatile feed butadiene as a function of pressure. The curve indicates that for a reactor temperature of 100°C, the vapor pressure is 15 atmospheres (225 psia), which is the operating pressure that will maintain the solution in the liquid state.

Figure 6.13: Butadiene vapor pressure curve



Source: Air Liquide Gas Encyclopedia

The design basis for butadiene hydrocyanation is presented in the table below.

Table 6.8: Design basis for butadiene hydrocyanation

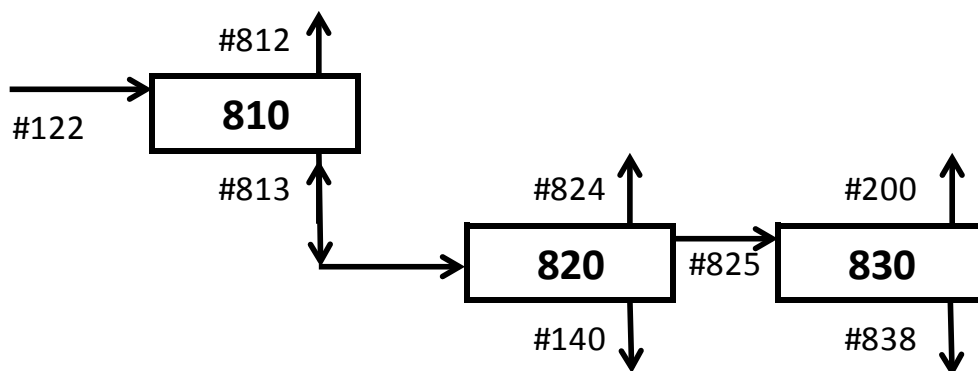
Temperature °C	100
Pressure psia	225
Catalyst	Nickel phosphorus ligand
Catalyst concentration ppmw	2,000
Residence time hrs	2.5 each reactor
Reactor type	Agitated CSTR with cooling coils
Number of reactors	2 in series
Blanketing	N ₂ inert
Jacketing	Cooling water
1-pass conversion of BD %	90
Selectivity to PN %	63
Selectivity to 2M3PN/2M2PN	32

Distillation of reactor products from butadiene hydrocyanation reaction

The reaction of butadiene with HCN in the liquid phase (unit Z₁ in Figure 6.12) using a homogeneous nickel phosphorus ligand catalyst, produces a reactor product stream containing unconverted butadiene, linear pentene mononitriles (3PN, 4PN, and 2PN), and methyl-butene nitriles (2M3BN, 2M2BN), a small amount of adiponitrile, as well as the catalyst.

The reactor product is directed to a distillation train, shown in Figure 6.12 as unit #125. USPA 2013 0150610 expands on the details of the distillation train with Figure 4 from the patent application, shown in the figure below.

Figure 6.14: Butadiene hydrocyanation reactor product distillation scheme (USPA 2013 0150610)



The first distillate column #810 is operated under pressure (100 psia), in order to condense overhead butadiene stream #812 using cooling water. The butadiene stream #812 is recycled back to the first hydrocyanation reactor feed. If operated at atmospheric or sub-atmospheric pressure, a refrigerant would have to be used to condense the overhead butadiene stream. The remaining distillation columns are

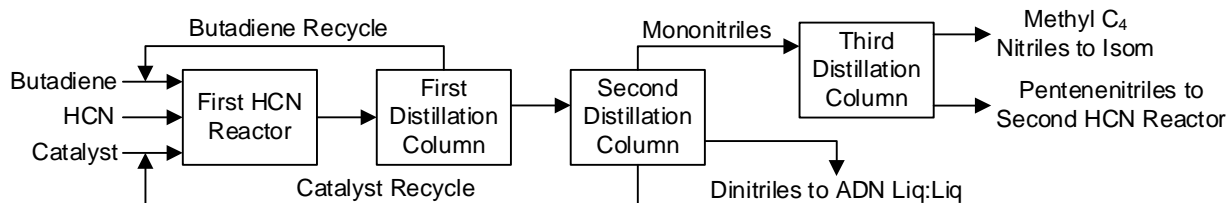
operated under vacuum to maintain bottoms temperatures below 140°C, in order to avoid degradation of the catalyst.

The bottoms product #813 from the first distillation column #810 is fed to a second distillation column #820 that takes residual butadiene as overhead product #824, and catalyst plus contaminants as the bottoms product #140. The catalyst stream is also recycled back to the first hydrocyanation reactor. Column #820 takes a side-stream #825 containing mononitriles, both linear pentenenitriles (3PN + 4PN), and also branched mononitriles (2M3BN, 2M2BN). The side-stream is directed to the third column #830, which takes purified branched nitriles (2M3BN, 2M2BN) as a purified overhead distillate #200 that is directed to the isomerization reactor feed, and a bottoms stream #838 that is a linear pentenenitriles stream #838 that is directed as feed to the second hydrocyanation reactor.

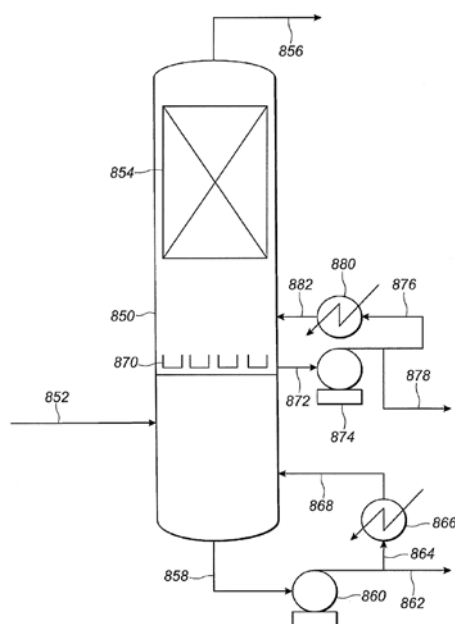
In our design, we operate the butadiene removal column at higher pressure to remove substantially all of the unconverted butadiene in the first column, allowing the second column to operate taking mononitriles as the overhead distillate and catalyst as the bottoms. Our design also takes a side-stream draw-off from the second column that is rich in dinitriles such as ADN and MGN. The dinitriles-rich side-stream is directed to the liquid:liquid extraction section of the second hydrocyanation reactor product recovery section, where ADN and MGN can be separated from other components by preferentially dissolving them in a polar solution of ADN. The solvent stream now containing ADN and MGN is directed to a distillation column that takes MGN as the overhead distillate, and ADN as the bottoms product.

The mononitriles distillate from the second column is fed to the third column, where branched mononitriles (2M3BN, 2M2BN) are taken as overhead distillate and fed to the isomerization unit, while the bottoms linear pentenenitriles stream (3PN, 4PN, 2PN) is fed to the second hydrocyanation reactor. The sequence of reactors for the distillation train is shown in the figure below.

Figure 6.15: Distillation train for first hydrocyanation reactor product (USPA 2013 0150610)



The Invista patent application presents a design for a distillation column that can take a side-stream draw-off, as presented above. The schematic for the Invista design of the distillation column with the side draw is presented in the figure below.

Figure 6.16: Invista design for distillation column side side-stream draw (USPA 2013 0150610)

In the Invista distillation column design, liquid product is taken off an intermediate tray using a chimney tray, which is a conventional tray (sieve, valve, etc.) that allows rising vapor to pass upward through the tray, but prevents downflowing liquid from passing through this tray. This tray design blocks what is usually a liquid downcomer. The location of the chimney tray is set just above the feed tray, providing ample liquid flow to the section of the column below the chimney tray.

In our design, where we use a side-stream draw-off tray, our columns have internal configurations using structured packing in a vertically divided wall configuration (as practiced by BASF), rather than using a chimney tray as proposed above by Invista. We believe divided wall distillation provides a greater concentration of dinitriles and intermediate products in the side-stream draw-off tray, with a lower concentration of catalyst in the side-stream draw-off tray. The reason for this is that the distribution of hydrocarbon concentrations along the vertical axis of the right side of the column (the side with the side-stream draw-off tray) is unaffected by the presence of the feed tray, which otherwise forces catalyst in the feed to pass by the side-stream draw-off tray on its way down the column.

Isomer properties

The hydrocyanation of butadiene to mononitriles, and the subsequent hydrocyanation of mononitriles to dinitriles (especially adiponitrile), produces a variety of by-product molecules with similar structures that have to be removed during subsequent product purification. The table below provides data on the primary products and by-products of hydrocyanation.

Table 6.9 Property table

Molecule	Molecular weight	Formula	CAS number	Boiling point °C
Hexamethylenediamine	116.2	C ₆ H ₁₆ N ₂	124-09-04	205
Adiponitrile	108.14	C ₆ H ₈ N ₂	111-69-3	295
Butadiene	54.09	C ₄ H ₆	106-99-0	-4.4
Acrylonitrile	53.06	C ₃ H ₃ N	107-13-1	77
Hydrogen cyanide	27.03	HCN	74-90-8	26
Fructose	180.16	C ₆ H ₁₂ O ₆	57-48-7	degrades
Hydrogen	2	H ₂	1333-74-0	-253
Methane	16.04	CH ₄	74-82-8	-164
Water	18	H ₂ O	7732-18-5	100
3-Pentenitrile	81.12	C ₅ H ₇ N	4635-87-4	144
4-Pentenitrile	81.12	C ₅ H ₇ N	592-51-8	140
2-Pentenitrile	81.12	C ₅ H ₇ N	25899-50-7	128
2-Methyl-3-butenitrile	81.12	C ₅ H ₇ N	16529-56-9	124
2-Methyl-2-butenitrile	81.12	C ₅ H ₇ N	4403-61-6	120
2-Methylglutaronitrile	108.14	C ₆ H ₈ N ₂	4553-62-2	270
Ethyl succinonitrile	108.14	C ₆ H ₈ N ₂	17611-82-4	264
Valeronitrile	82.13	C ₅ H ₉ N	110-59-8	140
Vinyl cyclohexene	108.13	C ₈ H ₁₂	100-40-3	129
Triphenylboron (promoter)	242.12	B(C ₆ H ₅) ₃	960-71-4	203
Cyclohexane	84.16	C ₆ H ₁₂	110-82-7	80.7
Hexamethyleneimine	99.17	C ₆ H ₁₃ N	111-49-9	138
Diamino cyclohexane	114.19	C ₆ H ₁₀ (NH ₂) ₂	1121-22-8	80 at 15 mm Hg
Tetrahydroazepine	197.27	C ₁₁ H ₁₉ NO ₂	178172-25-3	degrades
Nonylamine	143.27	C ₉ H ₂₁ N	112-20-9	201
Phenol	94.11	C ₆ H ₆ O	108-95-2	182
Cresol (alpha)	108.3	C ₇ H ₈ O	95-48-7	191

Isomerization of 2M3BN to 3PN

Branched mononitriles (2M3BN, 2M2BN) are directed as the feed to an isomerization reactor that uses the same nickel phosphorus ligand catalyst as used in the butadiene hydrocyanation reaction. The reactor is designed to convert methyl butenenitriles to pentenenitriles. The design basis for the isomerization reaction is shown in the table below.

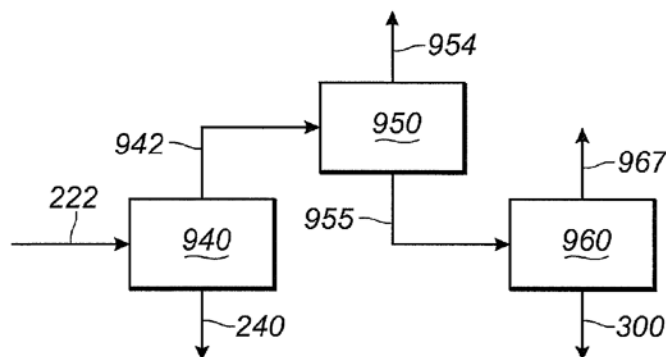
Table 6.10: Design basis for isomerization reaction

Temperature °C	100
Pressure psia	150
Catalyst	Nickel phosphorus ligand
Catalyst concentration ppmw	5,000
Residence time hrs	5
Reactor type	Agitated CSTR with cooling coils
Number of reactors	1
Blanketing	N ₂ inert
Jacketing	Cooling water
1-Pass conversion 2M3BN %	60
Selectivity to PN %	95

Besides carrying over the nickel phosphorus ligand catalyst from the butadiene hydrocyanation reactor, additional catalyst is added to the isomerization reactor to bring it to 5,000 ppm. Since the isomerization reaction has much slower kinetics than butadiene hydrocyanation, additional catalyst is required to obtain acceptable commercial kinetic rates of reaction.

Distillation of reactor products from isomerization reactor

The reactor product from the isomerization reactor will contain catalyst, unconverted methyl butenenitriles (2M3BN, 2M2BN), product linear pentenenitriles (3PN, 4PN, 2PN) and a small quantity of butadiene dimers (vinyl cyclohexene, ethylidene cyclohexene). The product stream will also contain dinitriles (ADN, MGN, ESN), catalyst degradation products (C₈H₁₃CN, phenol, cresol), and heavies. This stream #222 is directed in the Invista patent application to a distillation train shown below from USPA 2013 0150610.

Figure 6.17: Distillation train for isomerization reactor product (USPA 2013 0150610)

As shown in the figure above, the isomerization reactor product stream is #222. After a distillation column (not shown) that is designed to remove the lightest components (butadiene, cyclohexane), stream #222 is fed to distillation column #940 that is designed to remove nitriles as the overhead distillate stream #942, and catalyst as the bottoms product stream #240. The catalyst stream #240 is recycled to the isomerization reactor inlet. The distillate stream #942 is directed to column #950 where the overhead stream #954 is primarily branched mononitriles (2M3BN, 2M2BN and butadiene dimers), while the bottoms stream #955 is primarily linear mononitriles (3PN, 4PN, 2PN), plus residual dinitriles (ADN, MGN). The branched mononitriles stream #954 is recycled as feed to the isomerization reactor. The bottoms stream #955 is directed to distillation column #960 where the linear mononitriles stream #967 is taken as the overhead distillate, while the bottoms product stream #300 is dinitriles ADN and MGN. The linear mononitriles are sent to the second hydrocyanation reactor feed, while the ADN and MGN stream is sent to the ADN product liquid:liquid extraction unit.

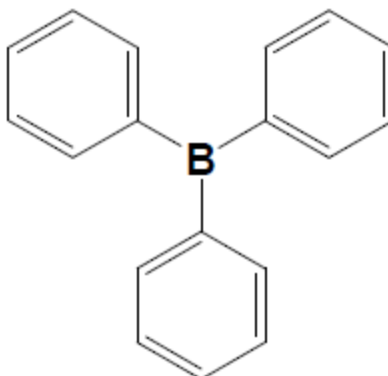
The sequence of separations presented above is almost identical to the distillation train required to purify the butadiene hydrocyanation reactor product. As a result, our design feeds the isomerization reactor product stream to the same distillation train as is used for the butadiene hydrocyanation reaction product purification.

Hydrocyanation of 3PN to produce crude ADN

The 3PN (3-pentenitrile) rich stream from the butadiene hydrocyanation reaction distillation train is further hydrocyanated with HCN, converting the stream from a mononitrile to a dinitrile. This reaction unit operation is shown in Figure 6.12 as unit Z3. 3PN and 4PN react readily with HCN to form adiponitrile (ADN), plus dinitrile by-products MGN and ESN. The kinetic rate reacting butadiene with HCN is rapid, while that for reacting 3PN with HCN is slow. To increase the kinetic rate of the 3PN reaction to commercially viable levels, a reaction promoter is used. The Invista patent literature identifies triphenylboron (TPB) and zinc chloride (ZnCl₂) as good candidates. In our design, we use TPB.

TPB (CAS: 960-71-4) in pure form is a crystalline powder, but is sold commercially as an 6.5–10% weight aqueous solution containing caustic soda to maintain strong alkalinity. TPB's pure boiling point is 203°C, but as a commercial alkaline aqueous solution, has a solution boiling point of 104°C. TPB is supplied commercially by Invista. TPB in solution form should be handled as a corrosive liquid. It is a mild acid. The molecular structure of TPB is shown below.

Figure 6.18: Molecular structure of triphenylboron (TPB)



The Invista patent application identifies the process safety hazard of accidentally allowing TPB from the 3PN catalyst mixture to enter the butadiene hydrocyanation reaction, where it would accelerate the rate of reaction and could potentially cause a thermal runaway. For this reason, our design utilizes two entirely separate and independent catalyst systems: one catalyst system for butadiene hydrocyanation plus 2M3BN isomerization, and an independent catalyst system containing TMB used in 3PN hydrocyanation to ADN.

To maximize the conversion of HCN to ADN, a molar excess of 3PN is used. The molar feed ratio of 3PN to HCN is 2.5:1, whereas the reaction stoichiometry under ideal conditions would be a molar ratio of 1:1. The 3PN feed stream is typically 95% 3PN, with other components being 4PN, 2PN, and C₉ mononitriles. The conversion of HCN is virtually 100% in a single pass. The residence time in a single CSTR reactor equipped with top entering agitator, cooling water jacket, and nitrogen inert gas blanket is 10 hours. Reactor design conditions are presented in the table below.

Table 6.11: 3PN hydrocyanation reaction design basis table

Temperature °C	55
Pressure psia	150
Catalyst	Nickel phosphorus ligand
Feed catalyst concentration ppm	5,000
Residence time hrs	10
Reactor type	Agitated CSTR with cooling coils
Number of reactors	2 in series
Conversion of HCN %	99+
Selectivity to ADN %	95
Feed molar ratio 3PN:HCN	2.5
1-Pass conversion of 3PN %	80

Due to the excess feed ratio of 3PN to HCN, the reactor product stream is first directed to a distillation column that takes unconverted 3PN (and other mononitriles) as the overhead distillate for recycle, with the bottoms product stream directed to a liquid:liquid extraction unit designed to recover catalyst for recycle, and to purify the ADN product for subsequent hydrogenation to HMDA.

Liquid:liquid extraction of hydrocyanation reactor product

The bottoms stream product from the 3PN recovery column, containing the crude ADN stream exiting the second hydrocyanation reactor, is directed to a liquid:liquid extraction unit designed to recover and recycle the catalyst using non-polar cyclohexane as the solvent, and to recover nitriles using a polar solvent of pure ADN. The extraction unit consists of a vertical mixing column with a top entering agitator, and a settling/decanting drum in which the cyclohexane solvent and the ADN solvent are immiscible. The cyclohexane solvent, which has dissolved the catalyst, forms an upper layer in the settling drum, while the ADN polar solvent also containing nitriles and contaminants forms the bottom layer.

The upper cyclohexane-rich layer is pumped to a simple distillation column that takes cyclohexane as the overhead distillate, and recycles it to the mixing column. The bottom stream from the distillation column is cleaned catalyst that is recycled to the PN3 hydrocyanation reactor.

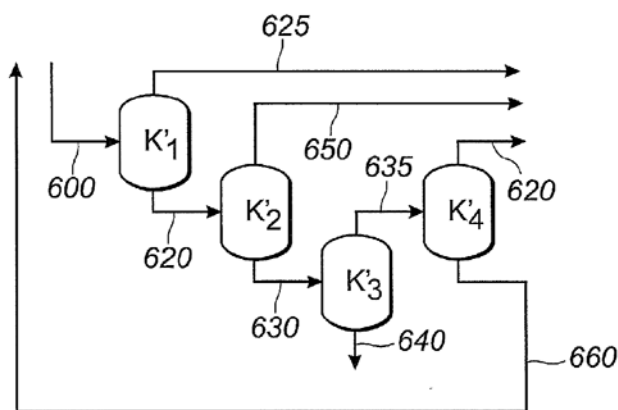
Crude adiponitrile product purification by distillation

The reactor product from the hydrocyanation of 3PN is primarily crude ADN product. A schematic of the distillation train used to purify product ADN, after it has been recovered in the liquid:liquid extraction unit, is shown in the figure below. The distillation train is nearly identical to the process configuration for purifying extraction solvent ADN used in the catalyst recovery section, except that the feed composition is considerably different. The crude adiponitrile feed stream #600 enters the first distillation column K'_1 as shown in the figure below, where the lightest components exit as the distillate #625. The lightest component is primarily residual cyclohexane non-polar solvent. The bottoms product #620 from K'_1 is the feed to K'_2 , where the next lightest component is taken as the overhead distillate product #650. This stream is primarily unconverted mononitriles such as 3PN and 4PN, which are recycled as feed to the 3PN hydrocyanation reactor. The bottoms stream from K'_2 #630 is the feed to column K'_3 .

The overhead distillate stream from K'_3 is primarily dinitriles #635, which is used as the feed to column K'_4 . The bottoms product #640 from K'_3 is a residual heavies stream containing oligomer, polymer, sludge, and tar. This stream is incinerated. The dinitriles stream #635 is primarily a mixture of product ADN and unwanted product MGN and ESN. The MGN/ESN mixture boils at a lower temperature than ADN, and therefore exits K'_4 as a purified by-product stream that is sold as commercial product. Since the market demand for by-product dinitriles such as MGN and ESN is not known, the stream is sent to product tankage. In a commercial setting, market demand would cause the owner to contract with a toll processor to purify these small quantities of specialty monomers, as required.

The bottoms product #660 from K'_4 is purified ADN that is directed to ADN product tankage. This distillation sequence is shown in the figure below.

Figure 6.19: Crude product adiponitrile purification sequence (USPA 2013 0150610)



Adiponitrile hydrogenation to HMDA

Historical development

Adiponitrile, which is purified from the hydrocyanation reactor product stream by distillation, is currently hydrogenated to produce HMDA in fixed bed, adiabatic reactors using Raney nickel catalyst [31C48]. Ammonia is added to enhance selectivity to amines, rather than imines. Cobalt catalyst is also used industrially. Fixed-bed reactions generally require modest temperature (90–150°C) and high pressure (20–60 MPa). The hydrogenation process is exothermic, requiring some method for heat removal. In most industrial practices, the reactors are operated isothermally with reactor cooling jackets.

In the 1970s, DuPont was granted US patents (USP 3696153, 3152184) for using iron oxide catalysts for the hydrogenation process at temperatures of 105–165°C, and pressures of approximately 340 atmosphere. The purpose for operating at these conditions was to extend catalyst life, and reduce the production of by-product hexamethyleneimine, which adversely affects polymer color in downstream (nylon 66) processing.

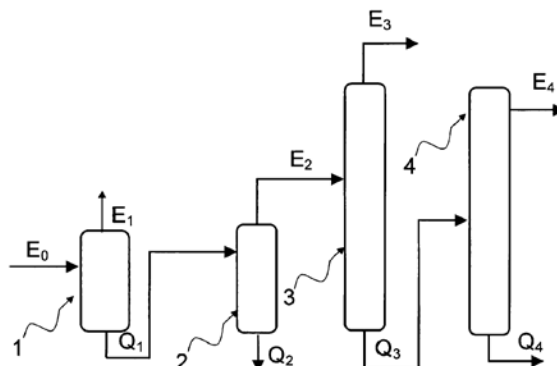
Radici has also considered replacing Raney nickel catalyst [31C48] with a more active precious metal catalyst (rhodium on alumina). The Radici concept uses a slurry, 3-phase reactor at a temperature of 80°C and 3 MPa pressure. The rhodium catalyst exhibited equal or higher conversion to HMDA, but lower selectivity to HMDA. The economics of using (and losing through attrition) precious metal catalyst are not known, nor is the extent of deactivation with commercial feedstocks (versus reagent feedstocks) known. Given the mature nature of the nylon 66 business, there may be limited opportunities to economically justify the capital investment for a new reaction system, unless built into a grassroots manufacturing plant.

To maintain catalyst activity, a strong alkaline presence is created by adding caustic soda (NaOH) or potassium hydroxide (KOH) to the reactor solution. Ammonia is also added to the solution to enhance

selectivity to HMDA, and reduce by-product imine production. By-products from the reaction are 1,2-diaminocyclohexane, hexamethyleneimine, and bis(hexamethylenetriamine).

Rhodia's USP 7939691 provides guidance on a reasonable distillation train sequence to purify the crude HMDA reactor product stream from hydrogenation, as shown in the figure below.

Figure 6.20: Rhodia purification sequence for HMDA (USP 7939691)



In the figure above, the reactor product stream is #E₀, which is fed to distillation column #1 for the purpose of taking water and light imines as the overhead distillate (E₁), and feeding the bottoms product Q₁ to the second distillation column #2. Column 2 takes crude HMDA as the overhead distillate E₂, and rejects heavies as the bottoms product Q₂. The crude HMDA stream is fed to column #3 where light by-products are taken as the overhead distillate E₃. The bottoms stream Q₃ is fed to the final column #4, where purified HMDA (boiling point 205°C) is taken as the overhead distillate E₄, and sent to product tankage, while unreacted ADN (boiling point 295°C) is taken as the bottoms product Q₄. The Q₄ stream is recycled to the hydrogenation reactor. To minimize product degradation, the last two columns (#3 and #4) are operated under vacuum conditions to reduce reboiler temperature.

IHS Design basis for ADN hydrogenation to HMDA

Our design for the ADN hydrogenation reaction to HMDA is based on DuPont USP 5900511 using Raney cobalt catalyst promoted with nickel, as described in WR Grace USP 5105015. The primary benefit of using nickel promoted Raney cobalt catalyst is that the reaction can be commercially conducted at relatively low pressure (600 psia) and modest temperature (85°C) in a fixed bed reactor. The reaction is conducted in an HMDA solution in which small amounts of ammonium hydroxide (NH₄OH) and water are added to minimize catalyst deactivation, while also minimizing by-product make. Our design uses a liquid downflow reactor through the fixed catalyst bed, in which hydrogen is sparged into the bottom of the reactor, flowing upward.

A reactor liquid product stream is continuously withdrawn from the bottom of the reactor, depressured to recover and recycle dissolved hydrogen. To enhance mixing of the liquid components, a continuous external pump-around loop is employed through an external cooler to remove the exothermic heat of reaction. For safety reasons, the reactor is also jacketed with cooling water coils, providing reaction at isothermal conditions. The design basis for our ADN hydrogenation reaction to HMDA is presented in the table below.

Table 6.12: Adiponitrile hydrogenation design basis table

Temperature °C	85
Pressure psia	600
Catalyst	Nickel promoted Raney cobalt
Residence time min	15
Reactor type	Fixed bed with jacketed cooling
Reactor configuration	External pumparound with cooler
Number of reactors	2
Conversion of ADN %	100
Selectivity to HMDA %	98
1-Pass conversion to HMDA %	90

Hydrocyanation catalyst purification and recycle system

Two separate and independent hydrocyanation catalyst purification and recycle sections are provided in this design, which are nearly identical in configuration. The first catalyst recovery system, as described below, takes purge streams from the butadiene hydrocyanation reaction product and the isomerization reaction product streams. These catalyst streams do not contain triphenylboron promoter.

The second catalyst recovery system is part of the 3PN hydrocyanation system producing ADN, as described above, and contains triphenylboron promoter.

Contaminant removal from homogeneous catalyst by liquid-liquid extraction

The liquid catalyst system that is separated by distillation as the heaviest component from the reaction products from the two hydrocyanation reactions (first stage butadiene hydrocyanation to 3PN, isomerization of 3MBN to 3PN) is recycled back to the butadiene hydrocyanation and isomerization reactors. However, the catalyst stream over time becomes contaminated with both heavy and light hydrocarbon by-products, and heavier components representing oligomers, polymers, tars and sludge. To remove catalyst contaminants, a purge stream from the catalyst recycle is continuously taken and directed to a liquid:liquid extraction system consisting of a vertical high intensity mixing drum, followed by a settling drum that allows decanting of the immiscible liquid phases (upper non-polar cyclohexane solvent solution, lower polar adiponitrile solvent solution). The liquid:liquid extraction unit is designed to operate at atmospheric pressure and ambient temperature (25–45°C). The liquid:liquid extraction mixing drum and settling drum are blanketed with inert nitrogen.

The zero valent nickel monodentate phosphonite catalyst liquid can be almost entirely recovered and recycled to the front of the process, using intellectual property from USPA 2007 0260086. Two organic phases will form: a heavy and viscous lower liquid phase that contains most of the catalyst, and an upper and lighter liquid phase that only contains a low (less than 100 ppm) catalyst concentration, compared to a feed catalyst concentration of approximately 2,000 ppm. The catalyst-rich lower liquid phase can be recycled directly to the first hydrocyanation reactor and isomerization reactors after clean-up. Cyclohexane is used as a light non-polar solvent that will remove virtually all of the catalyst from the contaminated catalyst purge streams sent to the liquid:liquid extraction unit.

The feed streams to the high intensity mixing drum include the catalyst purge stream, a stream of clean cyclohexane (non-polar solvent), and a clean stream of adiponitrile (polar solvent). During intense

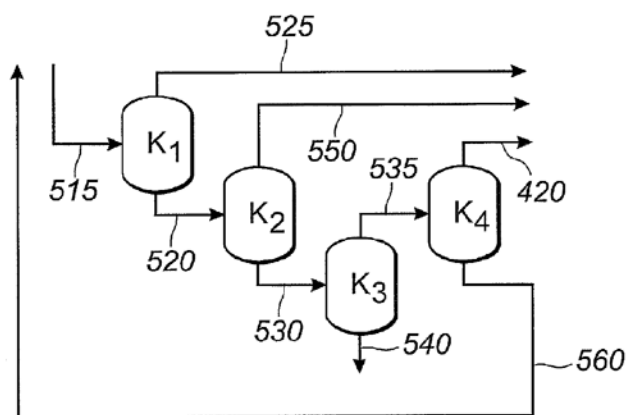
mixing, the contaminants which are mostly polar migrate to and dissolve in the adiponitrile bottom layer liquid. The catalyst solution, now cleaned of most contaminants, dissolves primarily into the non-polar cyclohexane stream. The cyclohexane stream containing catalyst is directed to a single distillation column, where cyclohexane is taken as the overhead distillate, and is recycled to the intense mixing drum. The bottoms stream from the distillation column is cleaned catalyst, which is recycled to the catalyst holding tank for use in either the butadiene hydrocyanation reactor, or the isomerization reactor.

Contaminated ADN polar solvent recovery scheme

Purified ADN is used as the polar extraction solvent that is directed to the liquid:liquid extraction unit that is designed to purify and recycle purged catalyst after the catalyst leaves the butadiene hydrocyanation or isomerization reactors. By mixing purged and contaminated catalyst with ADN, most of the catalyst contaminants (which are polar compounds), will dissolve in the ADN solution. The liquid:liquid extraction unit also feeds a pure solution of non-polar cyclohexane, which preferentially dissolves the catalyst in a relatively pure form.

The ADN solution leaving the liquid:liquid extraction unit contains ADN from both the pure ADN fed to the unit, and the ADN produced in the reaction, polar contaminants, mononitriles (3PN, 4PN, 2PN, 2M3BN, 2M2BN) formed in the reaction, and dinitriles such as 2-methyl glutaronitrile (MGN), and ethylsuccinonitrile (ESN). The contaminated ADN stream also contains both light and heavy miscellaneous compounds that have dissolved in the ADN solvent during the liquid:liquid extraction. A schematic of the purification scheme as described in USPA 2013 0150610 is presented in the figure below.

Figure 6.21: Extraction adiponitrile purification sequence (USPA 2013 0150610)



As shown the figure above, the contaminated adiponitrile rich solvent stream is #515. It is directed to distillation column K_1 , where the lightest low boiling components, such as cyclohexane, exit K_1 as the distillate product #525, and are recycled for use as non-polar solvent for the catalyst liquid:liquid extraction unit. The remaining components from the feed stream exit the column bottoms as stream #520,

and are fed to column K_2 , where the next lightest components (mono nitriles) exit as the distillate product #550. The distillate is primarily 3PN and 2M3PN. This stream is recycled as feed to the isomerization reaction unit. The remaining components leave K_2 as the bottom stream #530, and are fed to column K_3 . The overhead distillate #535 from K_3 is dinitriles, while the remaining products are contained in stream #540, composed mainly of heavy degradation products such as tars, oligomers, sludge, and solids. The heavy by-product stream #540 is incinerated. The overhead distillate product #535 from K_3 contains product ADN and by-product MGN and ESN. The overhead distillate #420 from K_4 is a stream rich in MGN + ESN, which is collected in tankage for sale as a commercial product. High purity ADN exits K_4 as the bottoms product #560, and can either be stored as intermediate product for the hydrogenation unit to produce HMDA, or can be recycled as polar solvent for the liquid:liquid extraction unit.

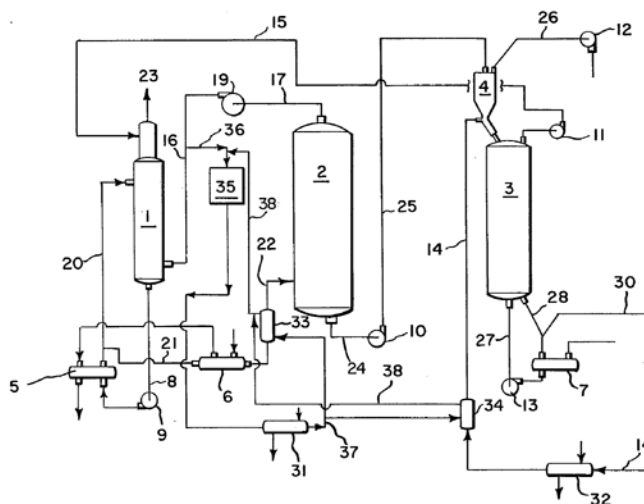
Crude HMDA purification by distillation versus crystallization

Although the conventional method for purifying product HMDA from the hydrogenation of ADN is by fractional distillation, DuPont patented (USP 4282381) in 1981 an alternate crystallization purification method. The procedure involves the direct cooling of hydrogenation reactor effluent crude HMDA melt by adding ammonia to the HMDA melt at high pressure, and then depressuring the container in order to vaporize the ammonia. The cooling that occurs upon depressuring ammonia will cause the HMDA melt to partially crystallize. The crystal slurry can then be washed with HMDA liquid to separate the crystals in conventional process equipment (crystallizer plus centrifuge), producing purer HMDA than can be effected by distillation alone. If even purer HMDA is required, the separated crystals can be re-melted and recrystallized in a second step.

In the figure below, vessel #1 is the absorber column where ammonia is injected into the hydrogenation reactor product melt, for the purpose of subsequently being depressurized, causing HMDA to crystallize in the melt. Vessel #2 is the crystallizer, and vessel #3 is the crystal washing column. The bottoms liquid of the absorber column is pumped through an external cooling heat exchanger (#5) to remove heat and promote the crystallization of HMDA. The absorber is operated at 80–140 psia and 35–50°C.

Crude HMDA is introduced to the system via line #14, and enters clarifier (#4) and washing column #3. It is pumped (#11) through line #15 to the absorber column (#1). Ammonia for cooling enters the absorber column through line #16. The HMDA/ammonia solution from the bottoms of the absorber column is pumped to the crystallizer (#2). Precipitated HMDA crystals concentrate at the bottom of the crystallizer, and are pumped to the wash column (#3) where pure HMDA is added to wash clean the crystals of surface contaminants.

Figure 6.22: DuPont process for HMDA purification by crystallization (USP 4282381)



Process description

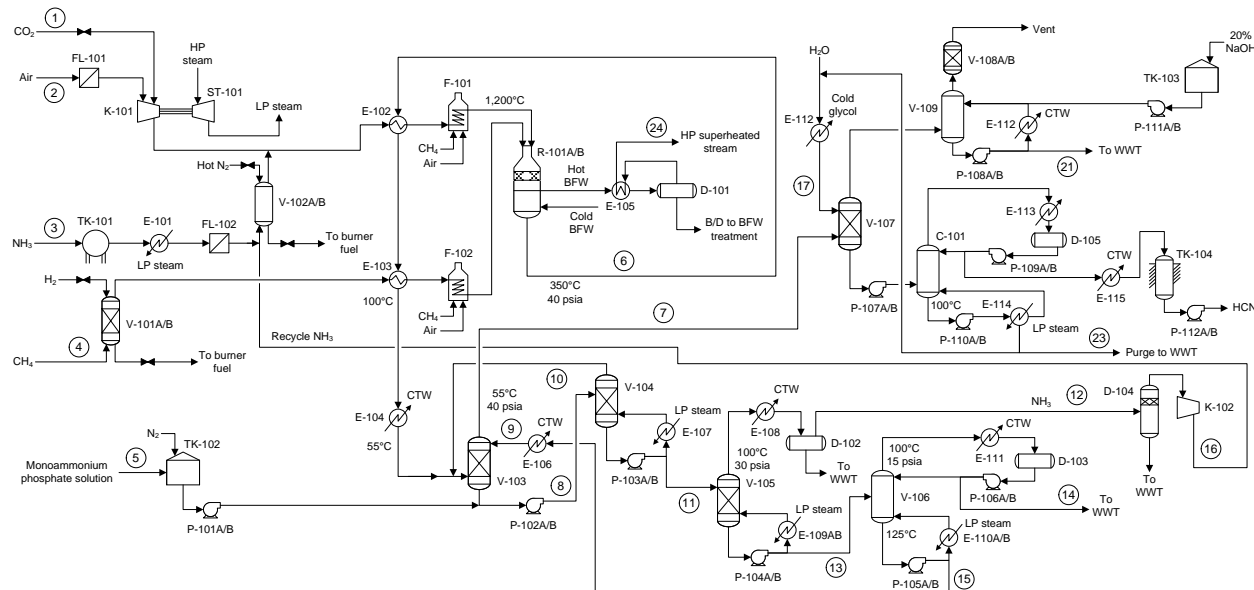
Plant sections

For our process design, we have segmented the process plant into the following sections:

- Section 100—hydrogen cyanide (HCN) production
- Section 200—butadiene hydrocyanation
- Section 300—3PN hydrocyanation
- Section 400—adiponitrile hydrogenation to HMDA
- Section 500—hydrocyanation catalyst purification and recycle

Section 100—hydrogen cyanide (HCN) production

Hydrogen cyanide (HCN) is produced in an on-purpose Andrussow process unit that feeds natural gas, ammonia and air to a high temperature and mild pressure exothermic reactor. A process flow diagram (PFD) for this process appears in the figure below.

Figure 6.23: Hydrogen cyanide (HCN) production PFD

Fresh air is pulled through a pulse air baghouse (FL-101), and compressed in a low pressure air blower (K-101) that is driven by a back pressure steam turbine (ST-101). The compressed air is brought to near reaction temperature (1,100°C) in furnace F-101 after being mixed with ammonia feed. Liquid ammonia stored in a day sphere (TK-101) is vaporized in E-101, filtered for particulates in FL-102, and dried of residual moisture in dehydrator V-102A/B. The dehydrators are periodically regenerated using hot nitrogen off-line. Natural gas is desulfurized of residual H₂S in V-101A/B, preheated in E-103, and brought to near reactor temperature in F-102, before also being directed to the HCN reactor where it mixes with the air steam containing ammonia. The desulfurizer is regenerated off-line with hydrogen.

The HCN reactor R-101 is a custom designed unit containing a mixing inlet section, a bed of platinum and rhodium catalyst configured as wire gauze, and an outlet section that drops immediately into a quench cooler designed to prevent appreciable reverse reaction. The quench cooler is a shell-and-tube heat exchanger with boiler feed water on the shell side that produces high pressure hot water, which is vaporized in an external steam drum (D-101) and superheated in E-105.

The quenched raw HCN gas stream from R-101 passes through two feed-product exchangers (E-102, E-103), and is further cooled with cooling tower water in E-104. The stream is then fed to ammonia absorber V-103 where an aqueous solution of mono-ammonium phosphate is converted to di-ammonium phosphate by absorbing the ammonia. The di-ammonium phosphate solution passes through an HCN stripper V-104 before being directed to an ammonia stripper (V-105) where heat will convert the di-ammonium phosphate back to mono-ammonium phosphate while releasing the ammonia as an overhead vapor. The bottoms stream from V-105 is directed to a distillation column V-106 where water absorbed in the process is removed as the overhead distillate, concentrating the MAP in the column bottoms so that it can be recycled to the ammonia stripper after being cooled in E-106.

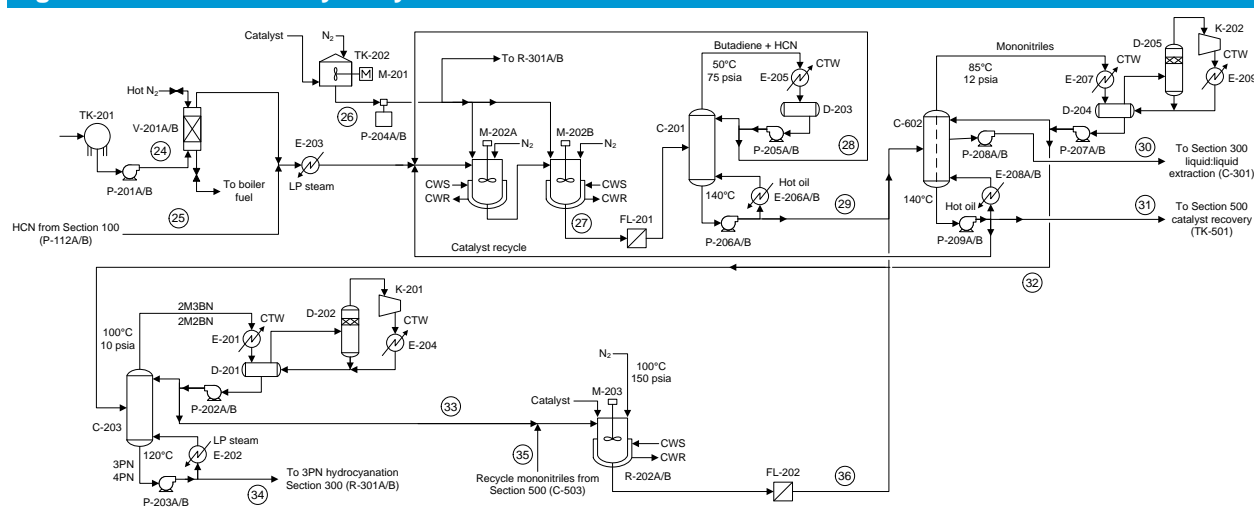
The overhead vapor stream from V-103 is now free of ammonia, and concentrated in HCN. The vapor stream is directed to HCN absorber V-107 where the HCN will be almost entirely absorbed in cold water. The overhead stream from V-107 is primarily combustion gas (nitrogen + carbon dioxide). It is passed through a caustic scrubber V-109 to remove residual HCN, and passed through activated carbon beds (V-108A/B) to remove residual hydrocarbons, before being vented to the atmosphere.

The cold water stream containing HCN from V-107 is directed to distillation column C-101 where purified HCN is taken as the overhead distillate, and stored as a liquid in a small capacity underground storage tank Tk-104. The bottoms product stream from C-101 is primarily water, and is recycled to the HCN absorber V-107.

Section 200—*butadiene hydrocyanation to 3PN*

Butadiene feedstock is reacted with HCN (produced in section 100) to produce mononitriles, primarily 3-pentenitrile, but also 4PN, 2PN, and branched methyl nitriles 2-methyl-3-butenitrile and 2-methyl-2-butenitrile. A PFD for this process appears in the figure below.

Figure 6.24: Butadiene hydrocyanation to 3PN



Butadiene from sphere TK-201 is dried of residual water in V-201A/B, combined with HCN from tank TK-104, and together they are heated in E-203. The heated stream is directed to the two butadiene hydrocyanation reactors R-201A/B that are operated in series as CSTR reactors with cooling jackets, nitrogen blankets, and mechanical agitators. Also pumped into the reactors is catalyst solution from Tk-202. The reactor product stream is filtered in FL-201, and fed to distillation column C-201 that is designed to recover unconverted butadiene and HCN as the overhead distillate, which is recycled back to the R-201A/B reactors.

The bottoms product stream from C-201 is fed to distillation column C-202, which is designed to take mononitriles produced by the butadiene hydrocyanation reaction as the overhead distillate product stream, and feed it to distillation column C-203. C-202 is also designed to take a side-stream product rich in dinitriles (ADN, but also containing MGN and ESN), for purification in column C-301. Due to concerns about thermal degradation of the hot catalyst, C-202 is operated under vacuum using a vacuum pump (compressor K-202). Tower internals are structured packing configured to operate as a divided wall distillation column, in order to minimize flow disruptions from the column feed tray affecting the side-stream draw-off tray. The bottoms product from C-202 is primarily catalyst, which is pumped to section 500 (Tk-501) for purification and recycle.

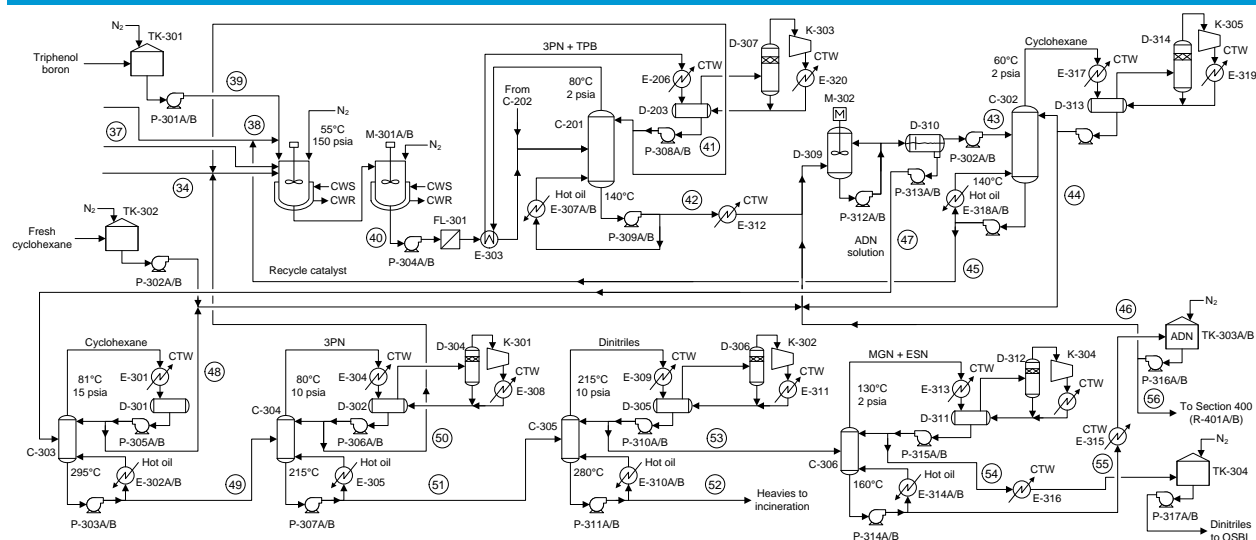
The mononitrile-rich overhead distillate from C-202 is pumped as the feed to distillation column C-203, which is designed to separate lighter branched mononitriles 2M3BN and 2M2BN from heavier linear mononitriles 3PN, 4PN, and 2PN. The lighter fraction is taken as the overhead distillate stream, and is

pumped as feed to the isomerization reactor R-202. R-202 is designed to isomerize the branched mononitriles to linear mononitriles. The bottoms product stream (linear mononitriles) from C-203 is pumped to the 3PN hydrocyanation reactor section, which is designed to hydrocyanate 3PN and isomers to adiponitrile (ADN) in reactors R-301A/B.

The product stream from isomerization reactor R-202 is pumped to the feed of distillation column C-202 for the separation of mononitriles from dinitriles and catalyst.

Section 300—3PN hydrocyanation to ADN

Figure 6.25: 3PN hydrocyanation to ADN



Purified 3PN and 4PN from section 200 (P-203A/B) are combined with HCN from section 100 (P-112A/B) and are fed to reactor R-301A/B for hydrocyanation to ADN. Directly fed into the reactor are catalyst solutions from P-204A/B and TPB promoter from P-301A/B. The reactor liquid product stream is discharged from the bottom of R-301 A/B, filtered (FL-301) and fed to distillation column C-301 for the purpose of recovering unconverted feedstock 3PN and 4PN, which are recovered as the overhead distillate stream and recycled to the R-301A/B reactors.

The bottom product stream from C-301, containing catalyst, produced dinitriles, by-products and contaminants, is fed to mixing drum D-309, where two separate purified streams of cyclohexane (non-polar solvent) and adiponitrile (polar solvent) are also added. The cyclohexane will preferentially dissolve catalyst. The adiponitrile will preferentially dissolve dinitriles, polar by-products, and contaminants. The highly mixed product from D-309 is pumped (P-312A/B) to settling drum D-310 for the purpose of forming two immiscible liquid phases: an upper phase containing the cyclohexane solution containing recovered catalyst, and a lower phase containing the adiponitrile solution that also contains polar contaminants.

The upper cyclohexane phase is fed to distillation column C-302 for the purpose of taking an overhead distillate product stream of pure cyclohexane, which is recycled to the mixing drum D-309. The bottoms product stream is cleaned catalyst, which is recycled to R-301 A/B reactors.

The lower phase adiponitrile rich solution from D-310 is pumped to distillation column C-303 for the purpose of taking an overhead distillate that is purified cyclohexane. The purified cyclohexane stream is recycled back to the mixing drum D-309.

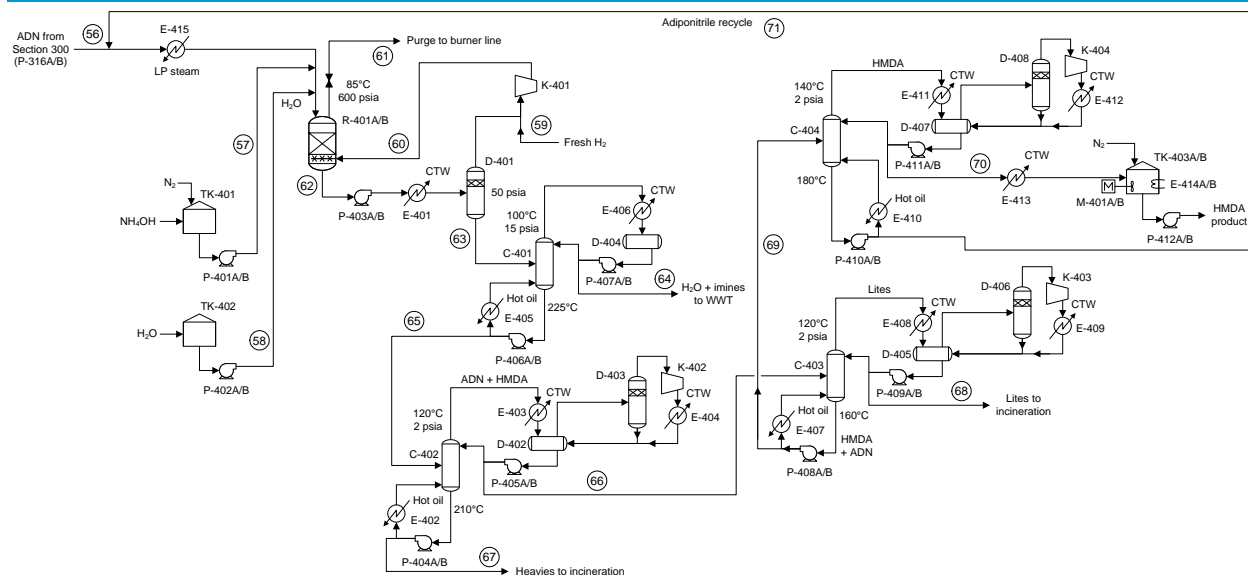
The bottoms product stream from C-303 is pumped to distillation column C-304 for the purpose of taking an overhead distillate product that is unconverted 3PN and 4PN feedstock. This stream is recycled back to the ADN reactor R-301A/B.

The bottoms product stream from C-304 is pumped to distillation column C-305 for the purpose of taking an overhead distillate product that is produced dinitriles (rich in ADN), leaving a bottoms product stream of heavy by-products that is incinerated.

The C-305 distillate product is pumped to distillation column C-306 for the purpose of separating dinitrile by-products MGN and ESN from desired product ADN. The MGN + ESN rich stream is taken as the overhead distillate from C-306, cooled in E-316, and pumped to tank TK-304 for either commercial sales, or to an outside toll processor for separating MGN from ESN. ADN product is the bottoms product stream from C-306, which is pumped through cooler E-315 to product tanks Tk-303A/B.

Section 400—ADN hydrogenation to HMDA

Figure 6.26: ADN hydrogenation to HMDA



Our process assumes that high purity hydrogen is produced adjacent to the plant by an outside 3rd party vendor (usually an industrial gas company like Air Products, Air Liquide, Linde, or Praxair), and sold to the plant on a 'take or pay' basis as feedstock.

Purified ADN from section 300 (P-316A/B) is combined with purchased (take or pay) hydrogen gas provided by the external supplier, compressed to 650 psia in K-401, combined with recycle hydrogen, and fed to hydrogenation reactors R-401A/B. Two reactors are operated in parallel as fixed bed reactors designed for counter-current, plug flow operation. H₂ is fed to a bottom distribution manifold in the reactors, while liquid ADN is fed to the top of the reactors. A small amount of water and ammonium

hydroxide (TK-401) are added intermittently to mitigate catalyst deactivation and enhance product selectivity.

Hydrogenation reactor product is passed through a cooler (E-401) to condense most of the stream, which is depressured and then directed to a knock-out drum (D-401) designed to separate vapor hydrogen from liquids. The overhead H_2 vapor from D-401 is passed through a recycle compressor (K-401), and recycled to the reactors.

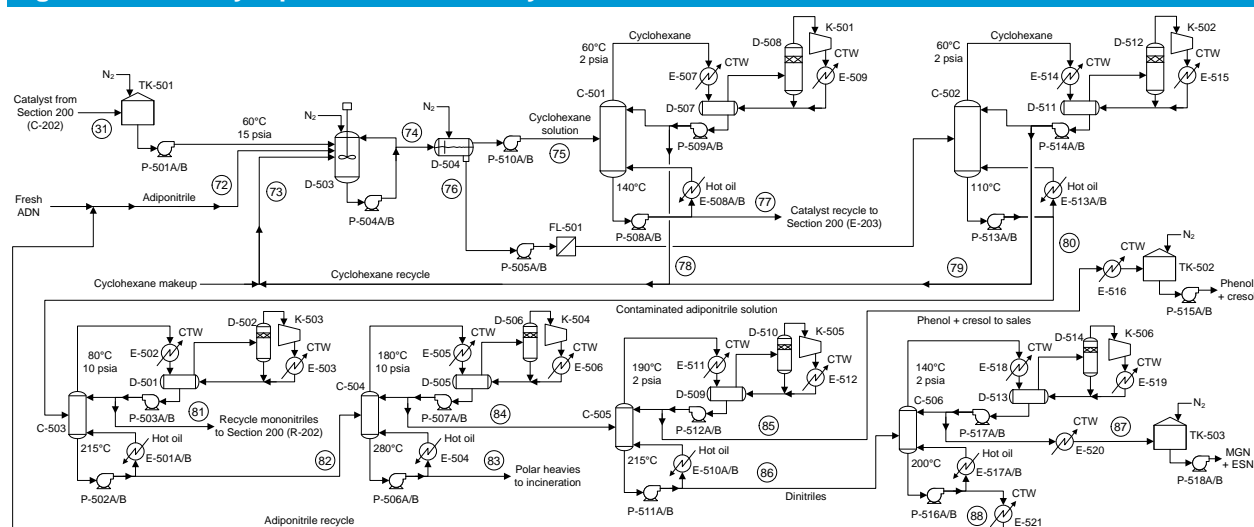
The de-pressured reactor liquid stream is directed to a distillation column (C-401) designed to remove water and the lightest organic by products such as imines as the overhead distillate. The distillate stream is sent to the plant's wastewater treatment plant. The bottoms product stream from the column is fed to distillation tower C-402, which is designed to take the remaining organic liquids (mostly crude HMDA product and un-converted ADN) as the overhead distillate product. The bottoms product is heavy tars and polymer, which is incinerated.

The HMDA plus dinitriles distillate stream from C-402 is fed to distillation tower C-403, which is designed to take lite nitriles such as MGN and ESN as the overhead distillate product to incineration, and heavier dinitriles (ADN) + HMDA as the bottoms product stream.

The bottoms product is directed to distillation tower C-404, which takes pure HMDA as the overhead distillate product stream, and ADN as the bottoms product. HMDA is cooled and sent to product tankage (Tk-403A/B), while the bottoms purified ADN stream is recycled to the hydrogenation reactors R-401A/B.

Section 500—catalyst purification and recycle

Figure 6.27: Catalyst purification and recycle



Contaminated catalyst from the C-202 bottoms product stream is held in temporary storage in Tk-501, and then pumped to extraction mixing tank D-503 where it combines with non-polar solvent cyclohexane and polar solvent adiponitrile. The mixing tank contents are transferred via pumps P-504A/B to settling tank D-504. The upper phase layer containing cyclohexane and catalyst is pumped via P-510A/B to distillation column C-501, which is designed to recover pure cyclohexane as the upper distillate product.

The upper distillate product stream is recycled to the extraction mixing tank, while the clean catalyst product in the bottoms product stream is recycled to the butadiene hydrocyanation and isomerization reactors in section 200.

The lower phase layer from Tk-504 is pumped to distillation column C-502, which is designed to recover residual cyclohexane as the distillate, and recycle it to the extraction mixing tank D-503. The bottoms product stream from C-502 is pumped to distillation column C-503, which is designed to remove mononitriles as the distillate product stream, which are recycled as feed to the isomerization reactor in section 200.

The bottoms product from C-503 is pumped to distillation column C-504, which is designed to remove heavies as the bottoms product, and discharge it to the plant's liquid incinerator. The upper distillate product stream from C-503 is pumped to distillation column C-505, which is designed to remove by-product phenols and cresols as the upper distillate product. The phenols and cresols are pumped to tankage Tk-502 for commercial sales as a mixed product.

The bottoms product from C-505 is an ADN rich dinitriles stream which is pumped to distillation column C-506, which is designed to recover MGN and ESN as the upper distillate product for sales, and purified ADN as the bottoms product. The purified ADN stream is recycled to extraction mixing drum D-503.

Stream-by-stream material balance

We have prepared a steam-by-stream material balance for the five PFDs using a combination of published literature, Invista and DuPont patents and patent applications, chemistry, and our own engineering calculations. Due to the size of the database, we first summarize below the major component production levels, and major feedstock consumption levels, but in terms of kty rather than the mt/hr used in the stream-by-stream material balance. Since Section 500 is a catalyst clean-up unit, there are not major feeds or products used in Section 500.

Table 6.13: Major feedstock and production levels for Invista HMDA process

Resource	Stream number	Consumption (kty)	Production (kty)
Section 100—HCN production			
HCN production	22		125
Ammonia feed	3	87	
Natural gas feed	4	72	
Section 200—butadiene hydrocyanation to 3PN			
3PN Production	54		187
Butadiene feed	24	144	
HCN feed	25	62	
Section 300—adiponitrile from 3PN via hydrocyanation			
Adiponitrile production	56		237
3PN feed	34	187	
HCN feed	37	62	
Section 400—HMDA from adiponitrile via hydrogenation			
HMDA production	70		250
Adiponitrile feed	56	237	
Hydrogen feed	59	19	

Table 6.14: Stream-by-stream material balance for Invista HMDA process

	Stream number							
	1	2	3	4	5	6	7	8
Label	CO ₂ feed	Compressed air	Ammonia feed	Natural gas feed	MAP solution	Reactor product	Crude HCN	Rich MAP solution
From	BL	K-101	TK-101	V-101	TK-102	R-101	V-103	V-103
To	K-101	R-101	R-101	R-101	P-102	V-103	V-107	V-104
Temperature (°C)	25	75	75	45	45	1,200	50	40
Pressure (psia)	15	55	55	55	75	40	37	75
Phase	gas	gas	gas	gas	soln	gas	gas	liq
Total flow (mt/hr)	0.0066	496.28	11.08	9.12	0.9	521.226	482.486	138.15
Components	MW	Boiling pt °C						
Hydrogen	2.00	-253						
Methane	16.00	-164		9.12				
Ammonia	17.00	-28	11.08			4.74		
Water	18.00	100			0.74	35.6	1.6	119.64
Hydrogen cyanide	27.03	26				15.86	15.86	0.16
Nitrogen	28	-196	392.06			392.06	392.06	
Oxygen	32	-183	104.22			72.96	72.96	
Carbon dioxide	44	-57	0.0066			0.006	0.006	
Sodium hydroxide	40	1,388						
Butadiene	54	-4						
Cyclohexane	84.16	81						
2-methyl-3-butenitrile	81	124						
3-pentenitrile	81	144						
2-methylglutaronitrile	108.14	270						
Ethyl succinonitrile	108.14	264						
Hexamethylenediamine	116.2	205						
Adiponitrile	108.14	295						
Phenol	94.11	182						
Cresol (alpha)	108.3	191						
R-401 lite HC products	na	na						
R-401 Heavy HC products	na	na						
Ammonium hydroxide	35	38						
Triphenylboron	242	203						
Nickel phosphorus ligand catalyst	na	na						
Mono ammonium phosphate	115	na			0.16			
Diammonium phosphate	132	na						18.35
Heavies								

Table 6.14 (continued): Stream-by-stream material balance for Invista HMDA process

	Stream number							
	9	10	11	12	13	14	15	16
Label	MAP recycle	HCN	Rich MAP solution	Stripped NH ₃	V-105 B/S	V-106 distillate	MAP recycle	NH ₃ recycle
From	V-106	V-104	V-104	V-105	V-105	V-106	V-106	K-102
To	V-103	V-103	V-105	K-102	V-106	WWT	V-103	R-101
Temperature (°C)	125	60	60	45	45	100	125	105
Pressure (psia)	15	75	75	50	50	15	15	100
Phase	liq	gas	liq	gas	liq	liq	liq	gas
Total flow (mt/hr)	101.62	0.16	137.99	4.74	135.62	34	101.62	4.74
Components	MW	Boiling pt °C						
Hydrogen	2.00	-253						
Methane	16.00	-164						
Ammonia	17.00	-28		4.74				4.74
Water	18.00	100	85.64	119.64	119.64	34	85.64	
Hydrogen cyanide	27.03	26	0.16					
Nitrogen	28	-196						
Oxygen	32	-183						
Carbon dioxide	44	-57						
Sodium hydroxide	40	1,388						
Butadiene	54	-4						
Cyclohexane	84.16	81						
2-methyl-3-butenenitrile	81	124						
3-pentenitrile	81	144						
2-methylglutaronitrile	108.14	270						
Ethyl succinonitrile	108.14	264						
Hexamethylenediamine	116.2	205						
Adiponitrile	108.14	295						
Phenol	94.11	182						
Cresol (alpha)	108.3	191						
R-401 lite HC products	na	na						
R-401 Heavy HC products	na	na						
Ammonium hydroxide	35	38						
Triphenylboron	242	203						
Nickel phosphorus ligand catalyst	na	na						
Mono ammonium phosphate	115	na	15.98		15.98		15.98	
Diammonium phosphate	132	na		18.35				
Heavies								

Table 6.14 (continued): Stream-by-stream material balance for Invista HMDA process

	Stream number							
	17	18	19	20	21	22	23	24
Label	Chilled H ₂ O	Purge gas	Vent gas	Scrubber solution	Scrubber purge	HCN product	C-101 B/S product	BD feed to 3PN Rx
From	C-101	V-107	V-108	P-108	C-101	C-101 O/H	C-101	C-101
To	V-107	V-109	Atm	V-109	WWT	TK-104	WWT	R-201
Temperature (°C)	10	10	40	40	40	40	110	100
Pressure (psia)	40	40	15	15	15	50	15	225
Phase	liq	gas	gas	liq	liq	Liq	liq	liq
Total flow (mt/hr)	142.74	480.886	465.026	96.26	0.26	15.86	1.6	18.21
Components	MW	Boiling pt °C						
Hydrogen	2.00	-253						
Methane	16.00	-164						
Ammonia	17.00	-28						
Water	18.00	100	142.74	77	0.08		1.6	
Hydrogen cyanide	27.03	26	15.86			15.86		
Nitrogen	28	-196	392.06	392.06				
Oxygen	32	-183	72.96	72.96				
Carbon dioxide	44	-57	0.006	0.006				
Sodium hydroxide	40	1,388		19.26	0.18			
Butadiene	54	-4						18.21
Cyclohexane	84.16	81						
2-methyl-3-butenenitrile	81	124						
3-pentenitrile	81	144						
2-methylglutaronitrile	108.14	270						
Ethyl succinonitrile	108.14	264						
Hexamethylenediamine	116.2	205						
Adiponitrile	108.14	295						
Phenol	94.11	182						
Cresol (alpha)	108.3	191						
R-401 lite HC products	na	na						
R-401 Heavy HC products	na	na						
Ammonium hydroxide	35	38						
Triphenylboron	242	203						
Nickel phosphorus ligand catalyst	na	na						
Mono ammonium phosphate	115	na						
Diammonium phosphate	132	na						
Heavies								

Table 6.14 (continued): Stream-by-stream material balance for Invista HMDA process

	Stream number							
	25	26	27	28	29	30	31	32
Label	HCN feed to 3PN Rx	Catalyst	R-201 Rx product	BD recycle	C-201 B/S product	D-nitriles	Contam catalyst	C-202 O/H product
From	P-112	TK-202	R-201	C-201	C-201	C-202 S/S	C-202	C-202
To	R-201	R-201	C-201	R-201	C-202	C-301	TK-501	C-203
Temperature (°C)	100	100	100	50	140	105	140	85
Pressure (psia)	225	225	225	250	35	30	30	50
Phase	liq	liq		liq	liq	liq	liq	liq
Total flow (mt/hr)	7.91	0.03	34.974	7.8	27.174	3.1	0.482	36.91
Components	MW	Boiling pt °C						
Hydrogen	2.00	-253						
Methane	16.00	-164						
Ammonia	17.00	-28						
Water	18.00	100						
Hydrogen cyanide	27.03	26	7.91					
Nitrogen	28	-196						
Oxygen	32	-183						
Carbon dioxide	44	-57						
Sodium hydroxide	40	1,388						
Butadiene	54	-4		7.8	7.8			
Cyclohexane	84.16	81						
2-methyl-3-butenenitrile	81	124		7.91	7.91			13.19
3-pentenitrile	81	144		15.81	15.81		0.02	23.72
2-methylglutaronitrile	108.14	270		0.69	0.69	0.69	0.007	
Ethyl succinonitrile	108.14	264		0.35	0.35	0.35	0.004	
Hexamethylenediamine	116.2	205						
Adiponitrile	108.14	295		2.06	2.06	2.06		
Phenol	94.11	182		0.05	0.05		0.005	
Cresol (alpha)	108.3	191		0.02	0.02		0.002	
R-401 lite HC products	na	na						
R-401 Heavy HC products	na	na						
Ammonium hydroxide	35	38						
Triphenylboron	242	203						
Nickel phosphorus ligand catalyst	na	na	0.03	0.174	0.174		0.254	
Mono ammonium phosphate	115	na						
Diammonium phosphate	132	na						
Heavies			0.11		0.11		0.19	

Table 6.14 (continued): Stream-by-stream material balance for Invista HMDA process

		Stream number							
		33	34	35	36	37	38	39	40
Label		C-203 O/H product	C-203 B/S product	Mononitriles from catalyst recovery	Isom Rx product	HCN to Rx	Catalyst to Rx	TPB promoter	Rx product stream
From		C-203	C-203	Section 500	R-202	P-112A/B	P-204A/B	TK-301	R-301
To		R-202	R-301	R-202	C-202	R-301	R-301	R-301	C-301
Temperature (°C)		100	120	120	100	75	25	25	105
Pressure (psia)		175	175	175	150	175	175	175	175
Phase		liq	liq	liq	liq	liq	liq	liq	liq
Total flow (mt/hr)		13.19	23.72	0.002	13.33	7.91	0.025	0.03	37.516
Components	MW	Boiling pt °C							
Hydrogen	2.00	-253							
Methane	16.00	-164							
Ammonia	17.00	-28							
Water	18.00	100							
Hydrogen cyanide	27.03	26							
Nitrogen	28	-196							
Oxygen	32	-183							
Carbon dioxide	44	-57							
Sodium hydroxide	40	1,388							
Butadiene	54	-4							
Cyclohexane	84.16	81							
2-methyl-3-butenenitrile	81	124	13.19		5.28				
3-pentenitrile	81	144	23.72	0.002	7.91			0.027	
2-methylglutaronitrile	108.14	270							1.09
Ethyl succinonitrile	108.14	264							0.4
Hexamethylenediamine	116.2	205							
Adiponitrile	108.14	295							30.07
Phenol	94.11	182							0.001
Cresol (alpha)	108.3	191							0.005
R-401 lite HC products	na	na							
R-401 Heavy HC products	na	na							
Ammonium hydroxide	35	38							
Triphenylboron	242	203						0.003	
Nickel phosphorus ligand catalyst	na	na			0.08		0.025		0.015
Mono ammonium phosphate	115	na							
Diammonium phosphate	132	na							
Heavies					0.06				0.005

Table 6.14 (continued): Stream-by-stream material balance for Invista HMDA process

	Stream number							
	41	42	43	44	45	46	47	48
Label	C-301 O/H product	C-301 B/S product	Non-polar solvent	Cyclohexane recycle	Clean catalyst	Clean ADN solvent	ADN solution	C-303 O/H
From	C-301	C-301	D-310	C-302 O/H	C-302 B/S	TK-303	D-310	C-303
To	R-301	D-309	C-302	D-309	R-301	D-309	C-303	D-309
Temperature (°C)	105	105	60	60	140	25	60	81
Pressure (psia)	175	175	50	50	50	75	50	50
Phase	liq	liq	liq	liq	liq	liq	liq	liq
Total flow (mt/hr)	5.93	31.7015	0.165	0.15	0.015	3.5	35.2165	0.03
Components	MW	Boiling pt °C						
Hydrogen	2.00	-253						
Methane	16.00	-164						
Ammonia	17.00	-28						
Water	18.00	100						
Hydrogen cyanide	27.03	26						
Nitrogen	28	-196						
Oxygen	32	-183						
Carbon dioxide	44	-57						
Sodium hydroxide	40	1,388						
Butadiene	54	-4						
Cyclohexane	84.16	81	0.15	0.15			0.03	0.03
2-methyl-3-butenenitrile	81	124						
3-pentenitrile	81	144	5.93	0.12			0.12	
2-methylglutaronitrile	108.14	270		1.09			1.09	
Ethyl succinonitrile	108.14	264		0.4			0.4	
Hexamethylenediamine	116.2	205						
Adiponitrile	108.14	295		30.07		3.5	33.57	
Phenol	94.11	182		0.001			0.001	
Cresol (alpha)	108.3	191		0.0005			0.0005	
R-401 lite HC products	na	na						
R-401 Heavy HC products	na	na						
Ammonium hydroxide	35	38						
Triphenylboron	242	203						
Nickel phosphorus ligand catalyst	na	na	0.015	0.015	0.015			
Mono ammonium phosphate	115	na						
Diammonium phosphate	132	na						
Heavies			0.005				0.005	

Table 6.14 (continued): Stream-by-stream material balance for Invista HMDA process

			Stream number							
			49	50	51	52	53	54	55	56
Label			C-303 B/S	C-304 O/H	C-304 B/S	C-305 B/S	C-305 O/H	Dinitrile product	ADN product	AND feed to hydrogenation
From			C-303	C-304	C-304	C-305	C-305 O/H	C-306 O/H	C-306 B/S	TK-303
To			C-304	R-301	C-305	Incinerator	C-306	TK-304	TK-303	R-401
Temperature (°C)			295	80	215	280	215	50	50	85
Pressure (psia)			50	50	50	50	50	50	50	50
Phase			liq	liq	liq	liq	liq	liq	liq	liq
Total flow (mt/hr)			35.1865	0.12	35.0665	0.005	35.0615	1.5315	33.53	30.03
Components	MW	Boiling pt °C								
Hydrogen	2.00	-253								
Methane	16.00	-164								
Ammonia	17.00	-28								
Water	18.00	100								
Hydrogen cyanide	27.03	26								
Nitrogen	28	-196								
Oxygen	32	-183								
Carbon dioxide	44	-57								
Sodium hydroxide	40	1,388								
Butadiene	54	-4								
Cyclohexane	84.16	81								
2-methyl-3-butenenitrile	81	124								
3-pentenitrile	81	144	0.12	0.12						
2-methylglutaronitrile	108.14	270	1.09		1.09		1.09	1.09		
Ethyl succinonitrile	108.14	264	0.4		0.4		0.4	0.4		
Hexamethylenediamine	116.2	205								
Adiponitrile	108.14	295	33.57		33.57		33.57	0.04	33.53	30.03
Phenol	94.11	182	0.001		0.001		0.001	0.001		
Cresol (alpha)	108.3	191	0.0005		0.0005		0.0005	0.0005		
R-401 lite HC products	na	na								
R-401 Heavy HC products	na	na								
Ammonium hydroxide	35	38								
Triphenylboron	242	203								
Nickel phosphorus ligand catalyst	na	na								
Mono ammonium phosphate	115	na								
Diammonium phosphate	132	na								
Heavies			0.005		0.005	0.005				

Table 6.14 (continued): Stream-by-stream material balance for Invista HMDA process

	Stream number							
	57	58	59	60	61	62	63	64
Label	NH ₄ OH feed	Water addition	H ₂ make-up	H ₂ recycle	Rx gas purge	Rx product	Degassed Rx product	Water
From	TK-401	TK-402	OSBL	K-401	R-401	R-401	D-401	C-401 O/H
To	R-401	R-401	K-401	R-401	Burner line	D-401	C-401	WWT
Temperature (°C)	25	25	225	225	85	85	80	100
Pressure (psia)	650	650	650	650	600	600	30	50
Phase	liq	liq	gas	gas	gas	liq	liq	liq
Total flow (mt/hr)	0.025	0.015	2.41	8.75	0.22	44.35	35.6	0.05
Components	MW	Boiling pt °C						
Hydrogen	2.00	-253		2.41	8.75	0.22	8.75	
Methane	16.00	-164						
Ammonia	17.00	-28						
Water	18.00	100	0.0175	0.015		0.05	0.05	0.05
Hydrogen cyanide	27.03	26						
Nitrogen	28	-196						
Oxygen	32	-183						
Carbon dioxide	44	-57						
Sodium hydroxide	40	1,388						
Butadiene	54	-4						
Cyclohexane	84.16	81						
2-methyl-3-butenenitrile	81	124						
3-pentenitrile	81	144						
2-methylglutaronitrile	108.14	270						
Ethyl succinonitrile	108.14	264						
Hexamethylenediamine	116.2	205				31.71	31.71	
Adiponitrile	108.14	295				3.34	3.34	
Phenol	94.11	182						
Cresol (alpha)	108.3	191						
R-401 lite HC products	na	na				0.3	0.3	
R-401 Heavy HC products	na	na				0.2	0.2	
Ammonium hydroxide	35	38	0.0075					
Triphenylboron	242	203						
Nickel phosphorus ligand catalyst	na	na						
Mono ammonium phosphate	115	na						
Diammonium phosphate	132	na						
Heavies								

Table 6.14 (continued): Stream-by-stream material balance for Invista HMDA process

			Stream number							
			65	66	67	68	69	70	71	72
Label			C-401 B/S	C-402 O/H product	Heavy by-products	Lite by-products	C-403 B/S	HMDA product	ADN recycle	ADN polar solvent
From			C-401	C-492 O/H	C-402 B/S	C-403 O/H	C-403	C-404 O/H	C-404 B/S	C-506 B/S
To			C-402	C-403	Incineration	Incineration	C-404	TK-403	R-401	D-503
Temperature (°C)			225	160	210	120	160	40	180	60
Pressure (psia)			50	50	50	50	50	50	50	50
Phase			liq	liq	liq	liq	liq	liq	liq	liq
Total flow (mt/hr)			35.55	35.35	0.2	0.3	35.05	31.71	3.34	2.15
Components	MW	Boiling pt °C								
Hydrogen	2.00	-253								
Methane	16.00	-164								
Ammonia	17.00	-28								
Water	18.00	100								
Hydrogen cyanide	27.03	26								
Nitrogen	28	-196								
Oxygen	32	-183								
Carbon dioxide	44	-57								
Sodium hydroxide	40	1,388								
Butadiene	54	-4								
Cyclohexane	84.16	81								
2-methyl-3-butenenitrile	81	124								
3-pentenitrile	81	144								
2-methylglutaronitrile	108.14	270								
Ethyl succinonitrile	108.14	264								
Hexamethylenediamine	116.2	205	31.71	31.71			31.71	31.71		
Adiponitrile	108.14	295	3.34	3.34			3.34		3.34	2.15
Phenol	94.11	182								
Cresol (alpha)	108.3	191								
R-401 lite HC products	na	na	0.3	0.3		0.3				
R-401 Heavy HC products	na	na	0.2		0.2					
Ammonium hydroxide	35	38								
Triphenylboron	242	203								
Nickel phosphorus ligand catalyst	na	na								
Mono ammonium phosphate	115	na								
Diammonium phosphate	132	na								
Heavies										

Table 6.14 (continued): Stream-by-stream material balance for Invista HMDA process

	Stream number							
	73	74	75	76	77	78	79	80
Label	Cyclohexane solvent	Extraction solution	Cyclohexane solution	ADN solution	Purified catalyst	Purified cyclohexane	Purified cyclohexane	C-502 B/S
From	C-501 O/H	D-503	D-504	D-504	C-501 B/S	C-501 O/H	C-502 O/H	C-502
To	D-503	D-504	C-501	C-502	E-203	D-503	D-503	C-503
Temperature (°C)	60	60	60	60	140	65	65	110
Pressure (psia)	50	50	50	50	50	50	50	50
Phase	liq	liq	liq	liq	liq	liq	liq	liq
Total flow (mt/hr)	2.54	5.172	2.544	2.628	0.254	2.29	0.25	2.378
Components	MW	Boiling pt °C						
Hydrogen	2.00	-253						
Methane	16.00	-164						
Ammonia	17.00	-28						
Water	18.00	100						
Hydrogen cyanide	27.03	26						
Nitrogen	28	-196						
Oxygen	32	-183						
Carbon dioxide	44	-57						
Sodium hydroxide	40	1,388						
Butadiene	54	-4						
Cyclohexane	84.16	81	2.54	2.54	2.29	0.25	2.29	0.25
2-methyl-3-butenenitrile	81	124						
3-pentenenitrile	81	144		0.02	0.02			0.02
2-methylglutaronitrile	108.14	270		0.007	0.007			0.007
Ethyl succinonitrile	108.14	264		0.004	0.004			0.004
Hexamethylenediamine	116.2	205						
Adiponitrile	108.14	295		2.15	2.15			2.15
Phenol	94.11	182		0.005	0.005			0.005
Cresol (alpha)	108.3	191		0.002	0.002			0.002
R-401 lite HC products	na	na						
R-401 Heavy HC products	na	na						
Ammonium hydroxide	35	38						
Triphenylboron	242	203						
Nickel phosphorus ligand catalyst	na	na	0.254	0.254	0.254			
Mono ammonium phosphate	115	na						
Diammonium phosphate	132	na						
Heavies			0.19		0.19			0.19

Table 6.14 (concluded): Stream-by-stream material balance for Invista HMDA process

		Stream number							
		81	82	83	84	85	86	87	88
Label		Recovered 3PN	C-503 B/S	Polar heavies	C-504 O/H	Phenol by-products	Dinitriles	MGN + ESN	ADN solvent recycle
From		C-503 O/H	C-503	C-504 B/S	C-504	C-505 O/H	C-505 B/S	C-506 O/H	C-506 B/S
To		R-202	C-504	Incineration	C-505	Sales	C-506	TK-503	D-503
Temperature (°C)		80	215	280	180	190	215	140	200
Pressure (psia)		50	50	50	50	50	50	50	50
Phase		liq	liq	liq	liq	liq	liq	liq	liq
Total flow (mt/hr)		0.02	2.358	0.19	2.168	0.007	2.161	0.011	2.15
Components	MW	Boiling pt °C							
Hydrogen	2.00	-253							
Methane	16.00	-164							
Ammonia	17.00	-28							
Water	18.00	100							
Hydrogen cyanide	27.03	26							
Nitrogen	28	-196							
Oxygen	32	-183							
Carbon dioxide	44	-57							
Sodium hydroxide	40	1,388							
Butadiene	54	-4							
Cyclohexane	84.16	81							
2-methyl-3-butenenitrile	81	124							
3-pentenitrile	81	144		0.02					
2-methylglutaronitrile	108.14	270		0.007	0.007	0.007		0.007	
Ethyl succinonitrile	108.14	264		0.004	0.004	0.004		0.004	
Hexamethylenediamine	116.2	205							
Adiponitrile	108.14	295		2.15	2.15	2.15		2.15	
Phenol	94.11	182		0.005	0.005	0.005			
Cresol (alpha)	108.3	191		0.002	0.002	0.002			
R-401 lite HC products	na	na							
R-401 Heavy HC products	na	na							
Ammonium hydroxide	35	38							
Triphenylboron	242	203							
Nickel phosphorus ligand catalyst	na	na							
Mono ammonium phosphate	115	na							
Diammonium phosphate	132	na							
Heavies		0.19		0.19					

Equipment list with duty specifications

Combining the material balance information with the requirements of the PFDs, we have prepared the following equipment list with duty specifications.

Table 6.15: Equipment list with duty specifications

	Buildings	Floor area (ft ²)	# Above ground stories	Sidewall materials / insulated?	Roof type / insulated?	Fit for occupancy?	HVAC (scfm)	Heating duty (MM-Btu/hr)	Refrig duty (tons/hr)	Sanitary facilities?	Crane capacity (mt)
B-101	Process Control House	5,000	1	Reinf concrete	Reinf concrete + membrane	Yes	400	0.75	35	Yes	No
B-102	Air compressor building	600	2	no	removable	No	No	No	No	No	25 ton gantry

	Distillation columns	# installed	Materials of construction	L x D (ft)	DesP (psia)	DesT (°C)	# of trays	Internals details
C-101	HCN concentrator	1	304SS	68 x 12	50	125	24	Sieve trays
C-201	BD column	1	304SS	60 x 14	100	175	20	Sieve trays
C-202	3PN column	1	304SS	92 x 14	full vac	175	36	Divided wall structured packing
C-203	2M3BN Column	1	304SS	162 x 14	full vac	150	72	structured packing
C-301	3PN column	1	304SS	60 x 14	full vac	165	24	structured packing
C-302	Cyclohexane column	1	CS	52 x 2	full vac	165	16	structured packing
C-303	Cyclohexane recovery column	1	CS	52 x 14	50	315	16	sieve trays
C-304	3PN column	1	CS	68 x 14	full vac	240	24	structured packing
C-305	Dinitrile column	1	CS	80 x 14	full vac	310	30	structured packing
C-306	ADN column	1	CS	124 x 14	full vac	165	52	structured packing
C-401	Dewatering column	1	304SS	68 x 14	50	250	24	sieve trays
C-402	ADN column	1	CS	68 x 14	full vac	235	24	structured packing
C-403	Lites column	1	CS	52 x 14	full vac	195	16	structured packing
C-404	HMDA column	1	CS	68 x 14	full vac	205	24	structured packing
C-501	Cyclohexane column	1	CS	80 x 3	full vac	165	30	structured packing
C-502	Cyhex column	1	CS	52 x 2	full vac	135	16	structured packing
C-503	Mononitriles column	1	CS	52 x 2	full vac	240	16	structured packing
C-504	Dinitriles column	1	CS	68 x 2	full vac	310	24	structured packing
C-505	Phenol column	1	CS	60 x 2	full vac	240	20	structured packing
C-506	MGN column	1	CS	92 x 2	full vac	225	36	structured packing

Table 6.15 (continued): Equipment list with duty specifications

	Drums	# installed	Materials of construction	Vol (ft3)	L x D (ft)	DesP (psia)	DesT (°C)	Orientation (ASME code vessels)
D-101	R-101 steam generator	1	304SS	1,206	24 x 8	2,500	600	horiz
D-102	NH3 condensate drum	1	304SS	678	24 x 6	50	125	horiz
D-103	E-111 receiver	1	304SS	678	24 x 6	50	125	horiz
D-104	K-102 K/O drum	1	CS	170	24 x 3	50	125	vert
D-105	E-113 receiver	1	304SS	1,608	32 x 8	50	125	horiz
D-201	E-201 receiver	1	304SS	1,608	32 x 8	50	125	horiz
D-202	K-201 K/O drum	1	CS	170	24 x 3	50	150	vert
D-203	E-205 receiver	1	304SS	1,608	32 x 8	50	125	horiz
D-204	E-207 receiver	1	304SS	1,608	32 x 8	50	125	horiz
D-205	K-202 K/O drum	1	CS	170	24 x 3	50	150	vert
D-301	E-301 receiver	1	CS	1,608	32 x 8	50	125	horiz
D-302	E-304 receiver	1	CS	1,608	32 x 8	50	125	horiz
D-303	E-306 receiver	1	CS	1,608	32 x 8	50	125	horiz
D-304	K-301 K/O drum	1	CS	170	24 x 3	50	150	vert
D-305	E-309 receiver	1	CS	1,608	32 x 8	50	125	horiz
D-306	K-302 K/O drum	1	CS	170	24 x 3	50	150	vert
D-307	K-303 K/O drum	1	CS	170	24 x 3	50	150	vert
D-309	Extraction mixing drum	1	CS	5,426	48 x 12	50	100	vet
D-310	Extraction settling drum	1	CS	5,426	48 x 12	50	100	horiz
D-311	E-313 receiver	1	CS	1,536	32 x 8	50	100	horiz
D-312	K-304 K/O drum	1	CS	170	24 x 3	50	150	vert
D-313	E-317 receiver	1	CS	1,536	32 x 8	50	100	horiz
D-314	K-305 K/O drum	1	CS	170	24 x 3	50	150	vert
D-401	K-401 K/O drum	1	304SS	1,608	32 x 8	600	125	vert
D-402	E-403 receiver	1	CS	1,536	32 x 8	50	100	horiz
D-403	K-402 K/O drum	1	CS	170	24 x 3	50	150	vert
D-404	E-406 receiver	1	CS	1,536	32 x 8	50	100	horiz
D-405	E-408 receiver	1	CS	1,536	32 x 8	50	100	horiz
D-406	K-403 K/O drum	1	CS	170	24 x 3	50	150	vert
D-407	E-411 receiver	1	CS	1,536	32 x 8	50	100	horiz
D-408	K-404 K/O drum	1	CS	170	24 x 3	50	150	vert
D-501	E-502 receiver	1	CS	25	8 x 2	50	250	horiz
D-502	K-503 K/O drum	1	CS	25	8 x 2	50	250	vert
D-503	Extraction mixing drum	1	CS	85	12 x 3	50	100	vert
D-504	Extraction settling drum	1	CS	85	12 x 3	50	100	horiz
D-505	E-505 receiver	1	CS	25	8 x 2	50	250	horiz
D-506	K-504 K/O drum	1	CS	25	8 x 2	50	250	vert
D-507	E-507 receiver	1	CS	25	8 x 2	50	250	horiz
D-508	K-501 K/O drum	1	CS	25	8 x 2	50	250	vert
D-509	E-511 receiver	1	CS	25	8 x 2	50	250	horiz
D-510	K-505 K/O drum	1	CS	25	8 x 2	50	250	vert
D-511	E-514 receiver	1	CS	25	8 x 2	50	250	horiz
D-512	K-502 K/O drum	1	CS	25	8 x 2	50	250	vert
D-513	E-518 receiver	1	CS	25	8 x 2	50	250	horiz
D-514	K-506 K/O drum	1	CS	25	8 x 2	50	250	vert

Table 6.15 (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 (°C) tube/shell	HX configuration
E-101	Ammonia vaporizer	1	CS/304SS	15.42	1,623	100/100	150/150	S&T-API660
E-102	Air feed preheater	1	304SS/CrMo	55.14	11,029	100/100	700/700	Finned tube
E-103	Natural gas feed preheater		304SS/CrMo	13.8	2,757	100/100	700/700	Finned tube
E-104	Raw HCN cooler	1	304SS/304SS	13.8	690	100/100	350/350	Finned tube
E-105	R-101 steam superheater	1	304SS/304SS	430	17,230	100/100	1,200/500	Finned tube
E-106	MAP cooler	1	304SS/304SS	22.4	2,359	100/100	150/150	S&T-API660
E-107	V-104 reboiler	1	304SS/CS	0.71	74	100/100	150/150	S&T-API660
E-108	Ammonia condenser	1	304SS/304SS	6.6	694	100/100	100/100	S&T-API660
E-109A/B	V-105 reboiler	2	304SS/CS	3.6	383	100/100	100/100	S&T-API660
E-110A/B	V-106 reboiler	2	304SS/CS	82.5	8,682	100/100	150/150	S&T-API660
E-111	V-106 condenser	1	304SS/304SS	150	15,783	100/100	150/150	S&T-API660
E-112	Caustic cooler	1	304SS/304SS	21.2	2,234	100/100	150/150	S&T-API660
E-113	C-101 condenser	1	304SS/304SS	41.97	4,417	100/100	150/150	S&T-API660
E-114	C-101 reboiler	1	304SS/CS	46.2	4,859	100/100	150/150	S&T-API660
E-115	HCN cooler	1	304SS/304SS	3.5	368	100/100	100/100	S&T-API660
E-201	C-203 condenser	1	304SS/304SS	43.6	4,592	50/100	150/100	S&T-API660
E-202	C-203 reboiler	1	304SS/CS	45.8	4,822	50/100	150/100	S&T-API660
E-203	BD feed heater	1	304SS/304SS	4.6	485	250/75	150/150	S&T-API660
E-204	K-201 condenser	1	304SS/304SS	0.5	49	250/75	150/150	S&T-API660
E-205	C-201 condenser	1	304SS/304SS	20.6	2,173	250/75	150/150	S&T-API660
E-206A/B	C-201 reboilers	2	304SS/CS	10.8	1,134	250/75	150/200	S&T-API660
E-207	C-202 condenser	1	304SS/304SS	8.2	863	75/75	100/100	S&T-API660
E-208A/B	C-202 reboilers	2	304SS/CS	4.31	453	75/75	160/260	S&T-API660
E-209	K-202 condenser	1	304SS/304SS	0.8	84	75/75	100/100	S&T-API660
E-301	C-303 condenser	1	304SS/304SS	0.1	10.5	75/75	100/75	S&T-API660
E-302A/B	C-303 reboilers	2	304SS/CS	0.05	6.2	75/75	300/75	S&T-API660
E-303	C-301 preheater	1	304SS/304SS	4.13	827	50/175	100/100	S&T-API660
E-304	C-304 condenser	1	304SS/304SS	0.1	20	50/50	100/100	S&T-API660
E-305	C-304 reboiler	1	304SS/CS	0.11	22	50/50	100/250	S&T-API660
E-306	C-301 condenser	1	304SS/304SS	13.1	1,376	50/50	100/100	S&T-API660
E-307A/B	C-301 reboiler	2	304SS/CS	6.6	702	50/50	100/165	S&T-API660
E-308	K-301 condenser	1	304SS/304SS	0.01	2	50/50	100/100	Double pipe
E-309	C-305 Condenser	1	304SS/304SS	77.3	8,138	50/50	100/250	S&T-API660
E-310A/B	C-305 reboilers	2	304SS/CS	38.7	4,425	50/50	350/300	S&T-API660
E-311	K-302 condenser	1	304SS/CS	3.9	442	50/50	350/300	S&T-API660
E-312	C-301 B/S cooler	1	304SS/304SS	6.99	736	50/50	160/100	S&T-API660
E-313	C-306 condenser	1	304SS/304SS	3.4	357	50/50	100/150	S&T-API660
E-314	C-306 reboiler	1	304SS/CS	3.6	375	50/50	250/200	S&T-API660
E-315	ADN cooler	1	304SS/304SS	7.39	778	100/100	180/100	S&T-API660
E-316	Dinitrile cooler	1	304SS/304SS	0.34	36	50/50	180/100	S&T-API660
E-317	C-302 condenser	1	304SS/304SS	0.33	34	50/50	100/100	S&T-API660
E-318	C-302 reboiler	1	304SS/CS	0.35	36	50/50	250/200	S&T-API660
E-319	K-305 condenser	1	304SS/304SS	0.04	4	50/50	100/100	double pipe
E-320	K-303 condenser	1	304SS/304SS	1.3	138	50/50	100/100	S&T-API660
E-401	R-401 cooler	1	304SS/304SS	9.8	1,029	50/75	100/100	S&T-API660
E-402	C-402 reboiler	1	304SS/CS	81.8	8,616	50/75	100/175	S&T-API660
E-403	C-402 condenser	1	304SS/304SS	77.9	8,205	50/75	100/175	S&T-API660
E-404	K-402 condenser	1	304SS/304SS	7.8	821	50/75	100/175	S&T-API660

Table 6.15 (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 (°C) tube/shell	HX configuration
E-405	C-401 reboiler	1	304SS/CS	0.46	48	50/50	150/75	S&T-API660
E-406	C-401 condenser	1	304SS/304SS	0.44	46	50/50	150/75	S&T-API660
E-407	C-403 reboiler	1	304SS/CS	0.69	74	50/75	150/100	S&T-API660
E-408	C-403 condenser	1	304SS/304SS	0.66	70	50/75	150/100	S&T-API660
E-409	K-403 condenser	1	304SS/304SS	0.07	8	50/75	150/100	double pipe
E-410	C-404 reboiler	1	304SS/CS	73.42	7,728	50/75	100/165	S&T-API660
E-411	C-404 condenser	1	304SS/304SS	69.92	7,360	50/75	100/165	S&T-API660
E-412	K-404 condenser	1	304SS/304SS	7	736	50/75	100/165	S&T-API660
E-413	HMDA cooler	1	304SS/304SS	2.8	294	50/75	100/165	S&T-API660
E-414A/B	TK-403 tank heaters	2	304SS	2.5	250	100/na	175/na	S&T-API660
E-415	ADN heater	1	304SS/CS	6.6	697	100/100	150/150	S&T-API660
E-501A/B	C-503 reboilers	2	304SS/CS	0.0071	0.8	50/75	100/105	double pipe
E-502	C-503 condenser	1	304SS/304SS	0.0135	1.42	50/75	100/105	double pipe
E-503	K-503 K/O condenser	1	304SS/304SS	0.00135	0.142	50/75	100/105	double pipe
E-504A/B	C-504 reboilers	2	304SS/CS	0.75	79	75/50	100/205	S&T-API660
E-505	C-504 condenser	1	304SS/304SS	1.43	151	75/50	100/205	S&T-API660
E-506	K-504 condenser	1	304SS/304SS	0.143	15	75/50	100/205	S&T-API660
E-507	C-501 condenser	1	304SS/304SS	1.51	159	75/50	100/85	S&T-API660
E-508	C-501 reboiler	1	304SS/CS	1.59	167	75/50	100/85	S&T-API660
E-509	K-501 condenser	1	304SS/304SS	0.15	16	75/50	100/85	S&T-API660
E-510	C-505 reboiler	1	304SS/CS	0.008	0.9	75/50	100/215	double pipe
E-511	C-505 condenser	1	304SS/304SS	0.008	0.8	75/50	100/215	double pipe
E-512	K-505 condenser	1	304SS/304SS	0.001	0.1	75/50	100/215	double pipe
E-513A/B	C-502 reboilers	2	304SS/CS	0.17	18	75/50	100/85	double pipe
E-514	C-502 condenser	1	304SS/304SS	0.17	18	75/50	100/85	double pipe
E-515	K-502 condenser	1	304SS/304SS	0.2	2	75/50	100/85	double pipe
E-516	Phenol cooler	1	304SS/304SS	0.015	0.2	75/50	100/85	double pipe
E-517	C-506 reboiler	1	304SS/CS	0.03	3	75/50	100/165	double pipe
E-518	C-506 condenser	1	304SS/304SS	0.03	3	75/50	100/165	double pipe
E-519	K-506 condenser	1	304SS/304SS	0.003	0.3	75/50	100/165	double pipe
E-520	MGN cooler	1	304SS/304SS	0.024	0.3	75/50	100/165	double pipe
E-521	ADN cooler	1	304SS/304SS	0.47	50	75/50	100/165	S&T-API660

	Fired heaters	# installed	Materials of construction	Duty (MM-btu/hr)	DesP (psia) tubes	DesT (°F) tubes	Fuel	
F-101	Air furnace	1	CrMo tubes	630	100	2,500	nat gas	API941 alloys
F-102	Natural gas furnace	1	CrMo tubes	28.5	100	2,500	nat gas	API941 alloys

	Filters	# installed	Materials of construction	Flow rate (lbs/hr)	DesP (psia) tubes	DesT (°C) tubes	Opening size (microns)	Fluid
FL-101	Air compressor pulse air filter	1	CS	1.3 MM	AMB	AMB	0.05	gas
FL-102	Ammonia feed filter	1	304SS	25 K	AMB	AMB	0.05	gas
FL-201	R-201 inline filter	1	304SS	775	100	200	0.5	liq
FL-202	R-202 inline filter	1	304SS	775	100	200	0.5	liq
FL-301	R-301 inline filter	1	304SS	83 K	275	100	0.5	liq
FL-501	ADN solution filter	1	304SS	6 K	50	100	0.5	liq

Table 6.15 (continued): Equipment list with duty specifications

	Compressors	# installed	Fluid	BHP	SCFM	Pin (psia)	Pout (psia)	Material of construction/ design details	Machine type	K-lbs/hr	mt/hr	Avg MW
K-101	Air compressor	1	Air	1.68E+02	1.32E+03	15	60	CS	Centrifugal	1.09E+03	496.28	28
K-102	NH3 rcycle compr	1	Ammonia	9.88E-01	2.08E+01	40	60	304SS	Centrifugal	1.05E+01	4.74	17
K-201	C-203 vacuum pump	1	2M3BN	5.03E-02	7.94E-01	10	20	304SS	Sliding Vane	2.91E+00	1.32	124
K-202	C-202 vacuum pump	1	Mononitriles	5.47E-02	1.73E-01	2	20	304SS	Sliding Vane	6.84E-01	0.31	134
K-301	C-304 vacuum pums	1	3PN	3.94E-04	6.22E-03	10	20	304SS	Sliding Vane	2.65E-02	0.012	144
K-302	C-305 vacuum pump	1	Di-nitriles	5.62E-02	8.88E-01	10	20	304SS	Sliding Vane	7.74E+00	3.51	295
K-303	C-301 vacuum pump	1	3PN	9.68E-02	3.06E-01	2	20	304SS	Sliding Vane	1.30E+00	0.59	144
K-304	C-306 vacuum pump	1	MGN	1.31E-02	4.14E-02	2	20	304SS	Sliding Vane	3.31E-01	0.15	270
K-305	C-302 vacuum pump	1	Cyclohexane	4.22E-03	1.33E-02	2	20	304SS	Sliding Vane	3.31E-02	0.015	84
K-401	H2 compressor	1	H2	1.34E+02	3.26E+02	50	650	CrMo	Centrifugal	1.93E+01	8.75	2
K-402	C-402 vacuum pump	1	Adiponitrile	2.84E-01	8.95E-01	2	20	304SS	Sliding Vane	7.81E+00	3.54	295
K-403	C-403 vacuum pump	1	ADN-lites	2.89E-03	9.13E-03	2	20	304SS	Sliding Vane	6.62E-02	0.03	245
K-404	C-404 vacuum pump	1	HMDA	3.65E-01	1.15E+00	2	20	304SS	Sliding Vane	6.99E+00	3.17	205
K-501	C-501 vacuum pump	1	Cyclohexane	6.47E-02	2.04E-01	2	20	304SS	Sliding Vane	5.07E-01	0.23	84
K-502	C-502 vacuum pump	1	Cyclohexane	7.03E-03	2.22E-02	2	20	304SS	Sliding Vane	5.51E-02	0.025	84
K-503	C-503 vacuum pump	1	Mononitriles	7.05E-05	1.11E-03	10	20	304SS	Sliding Vane	4.41E-03	0.002	134
K-504	C-504 vacuum pump	1	Dinitriles	3.52E-03	5.56E-02	10	20	304SS	Sliding Vane	4.85E-01	0.22	295
K-505	C-505 vacuum pump	1	Phenol	1.30E-04	4.10E-04	2	20	304SS	Sliding Vane	2.21E-03	0.001	182
K-506	C-506 vacuum pump	1	MGN	8.75E-05	2.76E-04	2	20	304SS	Sliding Vane	2.21E-03	0.001	270

	Mixers and agitators	# installed	Materials of construction	BHP	DesT (°C)	Liquid	Viscosity (cs)	Mixer type
M-201	TK-202 tank mixer	1	304SS	2	100	Cat soln	50	Tank side entering
M-202A/B	R-201 agitators	2	304SS	150	125	Butadiene	0.6	Tank top entering
M-203	R-202 agitator	1	304SS	45	125	2M3PN	5	Tank top entering
M-301A/B	R-301 agitators	2	304SS	150	125	3PN	0.6	Tank top entering
M-302	D-309 agitator	1	304SS	50	100	Adiponitrile	2.5	Tank top entering
M-401A/B	TK-403 agitators	2	304SS	50	125	HMDA	5	Tank side entering

Table 6.15 (continued): Equipment list with duty specifications

Pumps	# installed	Materials of construction	gpm x hd (ft)	Liquid	DesP (psia)	DesT (°C)	Type pump	Pump HP
P-101A/B MAP feed pumps	2	304SS	4 x 115	MAP soln	50	100	API610-Horiz Centrif	0.104
P-102A/B NH ₃ absorber B/S pumps	2	304SS	609 x 115	MAP soln	50	100	API610-Horiz Centrif	15.9
P-103A/B V-104 B/S pumps	2	304SS	2,434 x 115	MAP soln	50	100	API610-Horiz Centrif	63.4
P-104A/B V-105 B/S pumps	2	304SS	2,393 x 115	MAP soln	50	125	API610-Horiz Centrif	62.4
P-105A/B V-106 B/S pumps	2	304SS	1,785 x 115	MAP soln	50	150	API610-Horiz Centrif	46.5
P-106A/B V-106 reflux pumps	2	304SS	600 x 115	MAP soln	50	125	API610-Horiz Centrif	15.6
P-107A/B V-107 B/S pumps	2	304SS	72 x 115	HCN soln	75	50	API610-Horiz Centrif	1.9
P-108A/B V-109 B/S pumps	2	304SS	1.15 x 115	water	75	100	API675-Meter Pumps	0.03
P-109A/B C-101 reflux pumps	2	304SS	280 x 115	HCN	50	100	API610-Horiz Centrif	7.3
P-110A/B C-101 B/S pumps	2	304SS	630 x 115	water	50	125	API610-Horiz Centrif	16.4
P-111A/B Caustic pumps	2	304SS	22 x 115	caustic	50	50	API610-Horiz Centrif	0.57
P-112A/B HCN feed pumps	2	304SS	70 x 115	HCN	50	50	API610-Horiz Centrif	1.8
P-201A/B BD feed pumps	2	304SS	80 x 600	BD	250	100	API610-Horiz Centrif	10.9
P-202A/B C-203 reflux pumps	2	304SS	233 x 115	2M3BN	50	125	API610-Horiz Centrif	6.1
P-203A/B C-203 B/S pumps	2	304SS	418 x 115	3PN	50	150	API610-Horiz Centrif	10.9
P-204A/B Catalyst feed pumps	2	304SS	0.3 x 600	Cat Soln	250	100	API675-Meter Pumps	0.04
P-205A/B C-201 reflux pumps	2	304SS	14 x 115	BD	100	100	API610-Horiz Centrif	0.36
P-206A/B C-201 B/S pumps	2	304SS	48 x 115	3PN	100	165	API610-Horiz Centrif	1.25
P-207A/B C-202 reflux pumps	2	304SS	65 x 115	3PN	100	165	API610-Horiz Centrif	1.7
P-208A/B C-202 sidestream pumps	2	304SS	14 x 115	ADN	100	165	API610-Horiz Centrif	0.36
P-209A/B C-202 B/S pumps	2	304SS	9 x 115	Cat Soln	100	165	API610-Horiz Centrif	0.23
P-301A/B TPB feed pumps	2	304SS	0.13 x 400	TPB	175	100	API675-Meter Pumps	0.012
P-302A/B Cyclohexane feed pumps	2	304SS	0.7 x 115	Cyclohexane	50	100	API610-Horiz Centrif	0.018
P-303A/B C-303 B/S pumps	2	304SS	621 x 115	ADN soln	50	315	API610-Horiz Centrif	16.2
P-304A/B R-301 pumps	2	304SS	165 x 115	ADN soln	225	100	API610-Horiz Centrif	4.3
P-305A/B C-303 reflux pumps	2	304SS	0.6 x 115	Cyclohexane	50	100	API675-Meter Pumps	0.016
P-306A/B C-304 reflux pumps	2	304SS	2 x 600	3PN	175	100	API675-Meter Pumps	0.27
P-307A/B C-304 B/S pumps	2	304SS	618 x 115	ADN soln	50	225	API610-Horiz Centrif	16.1
P-308A/B C-301 reflux pumps	2	304SS	105 x 450	3PN	175	100	API610-Horiz Centrif	10.7
P-309A/B C-301 B/S pumps	2	304SS	560 x 115	ADN soln	50	160	API610-Horiz Centrif	14.6
P-310A/B C-305 reflux pumps	2	304SS	617 x 115	Dinitriles	100	240	API610-Horiz Centrif	16.1
P-311A/B C-305 B/S pumps	2	304SS	0.1 x 115	Heavies	50	310	API675-Meter Pumps	0.0026
P-312A/B D-309 pumps	2	304SS	547 x 115	ADN soln	50	85	API610-Horiz Centrif	14.3
P-313A/B D-310 B/S pumps	2	304SS	154 x 115	ADN soln	50	85	API610-Horiz Centrif	4.01
P-314A/B C-306 B/S pumps	2	304SS	591 x 115	ADN	50	185	API610-Horiz Centrif	15.4
P-315A/B C-306 reflux pumps	2	304SS	27 x 115	MGN	50	155	API610-Horiz Centrif	0.7
P-316A/B ADN pumps	2	304SS	148 x 115	ADN	50	100	API610-Horiz Centrif	3.86
P-317A/B DiNitrile pumps	2	304SS	7 x 115	Dinitriles	50	100	API610-Horiz Centrif	0.18
P-401A/B NH ₄ OH pumps	2	304SS	0.1 x 115	NHOH	50	100	API675-Meter Pumps	0.0026
P-402A/B Demin water pumps	2	304SS	.07 x 115	Water	50	100	API675-Meter Pumps	0.0018
P-403A/B R-401 pumps	2	304SS	196 x 115	HMDA soln	650	105	API610-Horiz Centrif	5.16
P-404A/B C-402 B/S pumps	2	304SS	3.5 x 115	Heavies	50	330	API610-Horiz Centrif	0.09
P-405A/B C-402 reflux pumps	2	304SS	624 x 115	HMDA soln	50	200	API610-Horiz Centrif	16.3
P-406A/B C-401 B/S pumps	2	304SS	627 x 115	HMDA soln	50	250	API610-Horiz Centrif	16.3
P-407A/B C-401 reflux pumps	2	304SS	0.9 x 115	Water	50	125	API675-Meter Pumps	0.023
P-408A/B C-403 B/S pumps	2	304SS	618 x 115	HMDA soln	50	185	API610-Horiz Centrif	16.1
P-409A/B C-403 reflux pumps	2	304SS	5.3 x 115	Lites	50	145	API610-Horiz Centrif	0.138
P-410A/B C-404 B/S pumps	2	304SS	59 x 1,500	ADN soln	625	210	API610-Horiz Centrif	20.06
P-411A/B C-404 reflux pumps	2	304SS	559 x 115	HMDA	50	165	API610-Horiz Centrif	14.6
P-412A/B HMDA product pumps	2	304SS	140 x 115	HMDA	50	100	API610-Horiz Centrif	3.65

Table 6.15 (continued): Equipment list with duty specifications

Pumps	# installed	Materials of construction	gpm x hd (ft)	Liquid	DesP (psia)	DesT (°C)	Type pump	Pump HP
P-501A/B Contaminated catalyst pumps	2	304SS	2 x 115	Cat soln	50	100	API610-Horiz Centrif	0.052
P-502A/B C-503 B/S pumps	2	304SS	42 x 115	Dinitriles	50	240	API610-Horiz Centrif	1.09
P-503A/B C-503 reflux pumps	2	304SS	0.4 x 400	3PN	200	105	API675-Meter Pumps	0.036
P-504A/B Extraction transfer pumps	2	304SS	91 x 115	ADN soln	50	105	API610-Horiz Centrif	2.37
P-505A/B ADN solution pumps	2	304SS	12 x 115	ADN soln	50	105	API610-Horiz Centrif	0.313
P-506A/B C-504 B/S pumps	2	304SS	4 x 115	Heavies	50	305	API610-Horiz Centrif	0.104
P-507A/B C-504 reflux pumps	2	304SS	38 x 115	Dinitriles	50	205	API610-Horiz Centrif	0.99
P-508A/B C-501 B/S pumps	2	304SS	5 x 115	Cyclohexane	50	85	API610-Horiz Centrif	0.13
P-509A/B C-501 reflux pumps	2	304SS	40 x 115	Cyclohexane	50	85	API610-Horiz Centrif	1.04
P-510A/B Cyclohexane transfer pumps	2	304SS	11 x 115	Cyhex soln	50	85	API610-Horiz Centrif	0.29
P-511A/B C-505 B/S pumps	2	304SS	38 x 115	Dinitriles	50	240	API610-Horiz Centrif	0.99
P-512A/B C-505 reflux pumps	2	304SS	0.11 x 115	Phenol	50	215	API675-Meter Pumps	0.0029
P-513A/B C-502 B/S pumps	2	304SS	42 x 115	ADN soln	50	135	API610-Horiz Centrif	1.09
P-514A/B C-502 reflux pumps	2	304SS	5 x 115	Cyclohexane	50	85	API610-Horiz Centrif	0.13
P-515A/B TK-502 pumps	2	304SS	0.03 x 115	Phenol	50	50	API675-Meter Pumps	0.0008
P-516A/B C-506 B/S pumps	2	304SS	38 x 115	ADN	50	225	API610-Horiz Centrif	0.99
P-517A/B C-506 reflux pumps	2	304SS	0.2 x 115	MGN	50	165	API675-Meter Pumps	0.0052
P-518A/B TK-503 pumps	2	304SS	0.05 x 115	MGN	50	165	API675-Meter Pumps	0.0013

Reactors	# installed	Materials of construction	Vol (ft3)	L x D (ft)	DesP (psia)	DesT (°C)	Internals
R-101A/B HCN reactor	2	CS with refractory	6,782	60 x 12	100	1,500	Cat gauze with CrMo tubes for stm gen
R-201A/B BD reactors	2	316LSS	3,140	10 x 20	250	125	Cooling jacket
R-202A/B Isom reactor	2	316LSS	1,608	8 x 16	175	125	Cooling jacket
R-301A/B 3PN reactors	2	316LSS	3,140	10 x 20	175	80	Cooling jacket
R-401A/B ADN reactors	2	316LSS	3,140	40 x 10	625	110	Cooling jacket

Specially packaged equipment		# installed	Duty
S-101	Dowtherm hot oil system	1	100 MM-Btu/hr
S-102	Glycol chiller system	1	400 tons
S-103	Vapor stream incinerator with header	1	5 MM-Btu/hr
S-104	Liquids incinerator	1	50 MM-Btu/hr
S-105	2-flare system with blowdown drums and header	1	500 MM-Btu/hr + 18 in LP header
S-106	Process computer control system	1	1,500 loops at 6 operator stations

Steam turbine drivers	# installed	Mechanical or electrical?	BHP	KW	Inlet steam (pres)	Outlet steam (pres)	Steam turbine details
ST-101 K-101 steam turbine	1	Mech	1,350	1,007	1,200	50	1-stage

Table 6.15 (concluded): Equipment list with duty specifications

	Storage tanks	# installed	Materials of construction	Vol (m3)	L x D (ft)	DesP (psia)	DesT (°C)	Type tank with details (API?)
TK-101	Ammonia sphere	1	CrMo	3,052	9 ft dia	350	100	API 2510
TK-102	MAP solution tank	1	CS epoxy lined	29,080	21 x 42	ATM	150	API 650
TK-103	Caustic tank	1	304SS	678	6 x 12	ATM	ATM	
TK-104	HCN tank	1	304SS	4,440	28 x 14	50	100	API 650
TK-201	BD storage sphere	1	CS	4,847	10.5 ft dia	100	ATM	API 650
TK-202	Catalyst tank	1	CS	200	4 x 8	ATM	350	API 650
TK-301	Triphenol boron tank	1	304SS	200	4 x 8	ATM	ATM	API 650
TK-302	Cyclohexane tank	1	CS	200	4 x 8	ATM	100	API 650 / Floating Roof
TK-303A/B	ADN product tanks	2	304SS	5,426	12 x 24	ATM	250	API 650
TK-304	Dinitrile Tank	1	304SS	678	6 x 12	ATM	250	API 650
TK-401	Ammonium hydroxide tank	1	304SS	200	4 x 8	ATM	ATM	API 650
TK-402	Demin water tank	1	FRP	200	4 x 8	ATM	ATM	
TK-403A/B	HMDA tanks	2	304SS	5,426	12 x 24	ATM	ATM	API 650
TK-501	Contaminated catalyst tank	1	CS	200	4 x 8	ATM	300	API 650
TK-502	Phenol tank	1	CS	200	4 x 8	ATM	ATM	API 650
TK-503	MGN tank	1	304SS	200	4 x 8	ATM	ATM	API 650

	Pressure vessels (API 510-ASME BPVC)	# installed	Materials of construction	Vol (m3)	L x D (ft)	Orientation	DesP (psia)	DesT (°C)
V-101 A/B	Natural gas dehydrator	2	304SS	1,206	24 x 8	Vert	50	100
V-102 A/B	Ammonia dehydrator	2	304SS	1,206	24 x 8	Vert	50	100
V-103	Ammonia absorber	1	304SS	3,618	32 x 12	Vert	50	100
V-104	MAP HCN Stripper	1	304SS	3,618	32 x 12	Vert	50	150
V-105	Ammonia stripper	1	304SS	1,206	24 x 8	Vert	50	100
V-106	MAP concentrator	1	304SS	1,608	32 x 8	Vert	50	100
V-107	HCN absorber	1	304SS	3,618	32 x 12	Vert	50	100
V-108 A/B	Activated carbon filters	2	CS	2,712	24 x 12	Vert	50	100
V-109	HCN scrubber	1	304SS	1,608	32 x 8	Vert	50	100
V-201A/B	BD dehydrator	2	304SS	2,712	24 x 12	Vert	350	100

Itemized capital cost

Using the IHS PEPCOST computer program, we prepared an itemized capital cost of the ISBL equipment presented in the equipment list. We then segmented the results by section of the plant, and by equipment type. In the table below, we present the installed cost (in US\$-k) for the ISBL itemized equipment by section of the plant

Table 6.16: Installed cost of ISBL equipment by section of plant (US\$-k)

Section	Description	Installed cost (all units)
100	HCN production	71,402.0
200	Butadiene hydrocyanation	12,457.7
300	3PN hydrocyanation	18,468.2
400	Adiponitrile hydrogenation	14,422.5
500	Catalyst purification and recycle	7,566.8
	Special purpose and packaged	86,600.0
	Total	210,917.2

The segmentation of ISBL itemized costs by equipment type is presented in the table below.

Table 6.17: Installed cost of ISBL equipment by equipment type (US\$-k)

	FOB (1 unit)	FOB (all units)	Installation (1 unit)	Installation (all units)	Installed cost (all units)
Buildings	530.0	530.0	810.0	810.0	1,340.0
Reactors	5,074.3	10,148.6	427.6	855.2	11,003.8
Distillation columns	11,106.8	11,106.8	10,926.4	10,926.4	22,033.2
Drums	3,560.6	3,560.6	2,291.7	2,291.7	5,852.3
Filters	4,518.8	4,518.8	2,321.9	2,321.9	6,840.7
Heat exchangers	11,623.8	12,304.3	4,104.3	4,526.7	16,831.0
Pumps	1,392.2	2,784.4	5,382.5	10,765.1	13,549.5
Compressors	1,150.1	1,150.1	3,271.0	3,271.0	4,421.1
ISBL storage tanks	4,591.1	5,346.5	885.8	996.7	6,343.2
Pressure vessels	1,442.2	1,928.5	669.6	926.9	2,855.4
Fired heaters	17,175.0	17,175.0	7,449.5	7,449.5	24,624.5
Mixers and agitators	1,117.5	1,992.5	335.3	391.1	2,383.6
Steam turbine drivers	3,758.0	3,758.0	2,481.0	2,481.0	6,239.0
Special packaged equipment	26,750.0	30,250.0	56,350.0	56,350.0	86,600.0
Total	93,790.3	106,554.0	97,706.6	104,363.2	210,917.2

We present in the table below the itemized capital cost of the ISBL equipment shown on the equipment list.

Table 6.18: Itemized ISBL equipment capital cost (US\$-k)

		Floor area (ft ²)	FOB (1 unit)	FOB (all units)	Install (1 unit)	Install (all units)	Installed cost (all units)
Buildings							
B-101	Process control house	5,000	500.0	500.0	750.0	750.0	1,250.0
B-102	Air compressor building	600	30.0	30.0	60.0	60.0	90.0

Table 6.18 (continued): Itemized ISBL equipment capital cost (US\$-k)

		# installed	FOB (1 unit)	FOB (all units)	Install (1 unit)	Install (all units)	Installed cost (all units)
Distillation columns							
C-101	HCN concentrator	1	572.7	572.7	596.4	596.4	1,169.1
C-201	BD column	1	792.6	792.6	612.2	612.2	1,404.8
C-202	3PN column	1	1,033.6	1,033.6	697.4	697.4	1,731.0
C-203	2M3BN Column	1	2,012.2	2,012.2	924.7	924.7	2,936.9
C-301	3PN column	1	724.2	724.2	608.5	608.5	1,332.7
C-302	Cyclohexane column	1	72.4	72.4	374.6	374.6	447.0
C-303	Cyclohexane recovery column	1	474.3	474.3	541.3	541.3	1,015.6
C-304	3PN column	1	585.6	585.6	585.9	585.9	1,171.5
C-305	Dinitrile column	1	698.6	698.6	617.0	617.0	1,315.6
C-306	ADN column	1	1,109.6	1,109.6	751.3	751.3	1,860.9
C-401	Dewatering column	1	759.0	759.0	634.9	634.9	1,393.9
C-402	ADN column	1	585.6	585.6	585.9	585.9	1,171.5
C-403	Lites column	1	474.3	474.3	528.3	528.3	1,002.6
C-404	HMDA column	1	585.6	585.6	571.3	571.3	1,156.9
C-501	Cyclohexane column	1	139.2	139.2	406.3	406.3	545.5
C-502	Cyhex column	1	72.4	72.4	366.1	366.1	438.5
C-503	Mono-nitriles column	1	72.4	72.4	366.7	366.7	439.1
C-504	Dinitriles column	1	98.7	98.7	380.8	380.8	479.5
C-505	Phenol column	1	83.6	83.6	373.7	373.7	457.3
C-506	MGN column	1	160.0	160.0	403.1	403.1	563.1
Drums							
D-101	R-101 steam generator	1	1,228.0	1,228.0	80.1	80.1	1,308.1
D-102	NH3 condensate drum	1	67.1	67.1	53.1	53.1	120.2
D-103	E-111 receiver	1	67.1	67.1	53.1	53.1	120.2
D-104	K-102 K/O drum	1	35.6	35.6	45.7	45.7	81.2
D-105	E-113 receiver	1	103.8	103.8	57.6	57.6	161.4
D-201	E-201 receiver	1	103.8	103.8	57.6	57.6	161.4
D-202	K-201 K/O drum	1	35.6	35.6	45.7	45.7	81.2
D-203	E-205 receiver	1	103.8	103.8	57.6	57.6	161.4
D-204	E-207 receiver	1	103.8	103.8	57.6	57.6	161.4
D-205	K-202 K/O drum	1	35.6	35.6	45.7	45.7	81.2
D-301	E-301 receiver	1	69.2	69.2	56.1	56.1	125.3
D-302	E-304 receiver	1	69.2	69.2	56.1	56.1	125.3
D-303	E-306 receiver	1	69.2	69.2	56.1	56.1	125.3
D-304	K-301 K/O drum	1	35.6	35.6	45.7	45.7	81.2
D-305	E-309 receiver	1	69.2	69.2	56.1	56.1	125.3
D-306	K-302 K/O drum	1	35.6	35.6	45.7	45.7	81.2
D-307	K-303 K/O drum	1	35.6	35.6	45.7	45.7	81.2
D-309	Extraction mixing drum	1	157.3	157.3	83.2	83.2	240.5
D-310	Extraction settling drum	1	132.9	132.9	65.5	65.5	198.4
D-311	E-313 receiver	1	67.5	67.5	55.8	55.8	123.2

Table 6.18 (continued): Itemized ISBL equipment capital cost (US\$-k)

		# installed	FOB (1 unit)	FOB (all units)	Install (1 unit)	Install (all units)	Installed cost (all units)
D-312	K-304 K/O drum	1	35.6	35.6	45.7	45.7	81.2
D-313	E-317 receiver	1	67.5	67.5	55.8	55.8	123.2
D-314	K-305 K/O drum	1	35.6	35.6	45.7	45.7	81.2
D-401	K-401 K/O drum	1	123.7	123.7	62.8	62.8	186.5
D-402	E-403 receiver	1	67.5	67.5	55.8	55.8	123.2
D-403	K-402 K/O drum	1	35.6	35.6	45.7	45.7	81.2
D-404	E-406 receiver	1	67.5	67.5	55.8	55.8	123.2
D-405	E-408 receiver	1	67.5	67.5	55.8	55.8	123.2
D-406	K-403 K/O drum	1	35.6	35.6	45.7	45.7	81.2
D-407	E-411 receiver	1	67.5	67.5	55.8	55.8	123.2
D-408	K-404 K/O drum	1	35.6	35.6	45.7	45.7	81.2
D-501	E-502 receiver	1	18.0	18.0	43.5	43.5	61.5
D-502	K-503 K/O drum	1	22.4	22.4	42.0	42.0	64.4
D-503	Extraction mixing drum	1	29.9	29.9	44.0	44.0	74.0
D-504	Extraction settling drum	1	24.4	24.4	45.5	45.5	69.9
D-505	E-505 receiver	1	18.0	18.0	43.5	43.5	61.5
D-506	K-504 K/O drum	1	22.4	22.4	42.0	42.0	64.4
D-507	E-507 receiver	1	18.0	18.0	43.5	43.5	61.5
D-508	K-501 K/O drum	1	22.4	22.4	42.0	42.0	64.4
D-509	E-511 receiver	1	18.0	18.0	43.5	43.5	61.5
D-510	K-505 K/O drum	1	22.4	22.4	42.0	42.0	64.4
D-511	E-514 receiver	1	18.0	18.0	43.5	43.5	61.5
D-512	K-502 K/O drum	1	22.4	22.4	42.0	42.0	64.4
D-513	E-518 receiver	1	18.0	18.0	43.5	43.5	61.5
D-514	K-506 K/O drum	1	22.4	22.4	42.0	42.0	64.4
Heat exchangers							
E-101	Ammonia vaporizer	1	170.6	170.6	57.3	57.3	227.9
E-102	Air feed preheater	1	844.4	844.4	82.3	82.3	926.7
E-103	Natural gas feed preheater	0	291.2	0.0	60.8	0.0	0.0
E-104	Raw HCN cooler	1	100.6	100.6	53.4	53.4	154.0
E-105	R-101 steam superheater	1	1,304.9	1,304.9	127.1	127.1	1,432.0
E-106	MAP cooler	1	258.7	258.7	59.7	59.7	318.4
E-107	V-104 reboiler	1	21.0	21.0	39.7	39.7	60.7
E-108	Ammonia condenser	1	101.1	101.1	53.4	53.4	154.5
E-109A/B	V-105 reboiler	2	63.5	127.0	51.7	103.4	230.4
E-110A/B	V-106 reboiler	2	350.9	701.8	63.8	127.5	829.3
E-111	V-106 condenser	1	1,205.3	1,205.3	117.4	117.4	1,322.7
E-112	Caustic cooler	1	248.2	248.2	59.3	59.3	307.5
E-113	C-101 condenser	1	415.9	415.9	64.9	64.9	480.8
E-114	C-101 reboiler	1	243.7	243.7	56.9	56.9	300.6
E-115	HCN cooler	1	60.6	60.6	51.6	51.6	112.2

Table 6.18 (continued): Itemized ISBL equipment capital cost (US\$-k)

		# installed	FOB (1 unit)	FOB (all units)	Install (1 unit)	Install (all units)	Installed cost (all units)
E-201	C-203 condenser	1	422.0	422.0	65.3	65.3	487.3
E-202	C-203 reboiler	1	236.0	236.0	56.8	56.8	292.8
E-203	BD feed heater	1	75.3	75.3	52.3	52.3	127.6
E-204	K-201 condenser	1	21.5	21.5	48.2	48.2	69.7
E-205	C-201 condenser	1	239.3	239.3	59.1	59.1	298.4
E-206A/B	C-201 reboilers	2	95.6	191.1	46.4	92.8	283.9
E-207	C-202 condenser	1	117.8	117.8	54.2	54.2	172.0
E-208A/B	C-202 reboilers	2	54.1	108.1	43.2	86.4	194.5
E-209	K-202 condenser	1	22.9	22.9	48.8	48.8	71.7
E-301	C-303 condenser	1	18.4	18.4	46.9	46.9	65.3
E-302A/B	C-303 reboilers	2	16.0	31.9	37.6	75.1	107.1
E-303	C-301 preheater	1	114.0	114.0	54.0	54.0	168.0
E-304	C-304 condenser	1	19.5	19.5	47.3	47.3	66.9
E-305	C-304 reboiler	1	18.0	18.0	38.4	38.4	56.4
E-306	C-301 condenser	1	168.7	168.7	56.4	56.4	225.1
E-307A/B	C-301 reboiler	2	70.9	141.9	44.5	89.0	230.9
E-308	K-301 condenser	1	16.2	16.2	46.0	46.0	62.2
E-309	C-305 condenser	1	648.9	648.9	71.9	71.9	720.8
E-310A/B	C-305 reboilers	2	223.6	447.2	55.9	111.9	559.1
E-311	K-302 condenser	1	53.2	53.2	43.1	43.1	96.4
E-312	C-301 B/S cooler	1	104.1	104.1	53.6	53.6	157.7
E-313	C-306 condenser	1	59.2	59.2	51.5	51.5	110.7
E-314	C-306 reboiler	1	48.1	48.1	42.7	42.7	90.8
E-315	ADN cooler	1	108.7	108.7	53.8	53.8	162.5
E-316	Dinitrile cooler	1	20.8	20.8	47.9	47.9	68.6
E-317	C-302 condenser	1	18.8	18.8	38.8	38.8	57.7
E-318	C-302 reboiler	1	19.0	19.0	38.9	38.9	57.9
E-319	K-305 condenser	1	17.0	17.0	46.3	46.3	63.3
E-320	K-303 condenser	1	28.4	28.4	49.6	49.6	77.9
E-401	R-401 cooler	1	134.9	134.9	54.9	54.9	189.8
E-402	C-402 reboiler	1	339.7	339.7	63.7	63.7	403.4
E-403	C-402 condenser	1	652.9	652.9	72.0	72.0	724.9
E-404	K-402 condenser	1	113.3	113.3	54.0	54.0	167.3
E-405	C-401 reboiler	1	19.6	19.6	39.2	39.2	58.8
E-406	C-401 condenser	1	21.3	21.3	48.1	48.1	69.4
E-407	C-403 reboiler	1	20.7	20.7	39.7	39.7	60.4
E-408	C-403 condenser	1	22.4	22.4	48.6	48.6	71.0
E-409	K-403 condenser	1	18.0	18.0	46.7	46.7	64.7
E-410	C-404 reboiler	1	317.3	317.3	62.2	62.2	379.5
E-411	C-404 condenser	1	601.8	601.8	70.5	70.5	672.3

Table 6.18 (continued): Itemized ISBL equipment capital cost (US\$-k)

		# installed	FOB (1 unit)	FOB (all units)	Install (1 unit)	Install (all units)	Installed cost (all units)
E-412	K-404 condenser	1	104.1	104.1	53.6	53.6	157.7
E-413	HMDA cooler	1	50.8	50.8	51.1	51.1	101.9
E-414A/B	TK-403 tank heaters	2	44.7	89.4	25.3	50.6	140.0
E-415	ADN heater	1	70.6	70.6	44.5	44.5	115.1
E-501A/B	C-503 reboilers	2	14.0	28.0	36.8	73.5	101.5
E-502	C-503 condenser	1	15.9	15.9	45.8	45.8	61.7
E-503	K-503 K/O condenser	1	3.9	3.9	37.0	37.0	40.8
E-504A/B	C-504 reboilers	2	20.9	41.8	39.8	79.5	121.3
E-505	C-504 condenser	1	30.0	30.0	49.7	49.7	79.7
E-506	K-504 condenser	1	19.0	19.0	47.1	47.1	66.1
E-507	C-501 condenser	1	31.3	31.3	49.8	49.8	81.1
E-508	C-501 reboiler	1	29.2	29.2	40.9	40.9	70.2
E-509	K-501 condenser	1	19.1	19.1	47.2	47.2	66.3
E-510	C-505 reboiler	1	15.5	15.5	45.7	45.7	61.2
E-511	C-505 condenser	1	15.5	15.5	45.7	45.7	61.2
E-512	K-505 condenser	1	3.4	3.4	36.8	36.8	40.2
E-513A/B	C-502 reboilers	2	17.6	35.2	38.3	76.6	111.8
E-514	C-502 condenser	1	19.3	19.3	47.2	47.2	66.6
E-515	K-502 condenser	1	16.2	16.2	46.0	46.0	62.2
E-516	Phenol cooler	1	3.4	3.4	36.4	36.4	39.8
E-517	C-506 reboiler	1	15.1	15.1	37.2	37.2	52.3
E-518	C-506 condenser	1	16.7	16.7	46.2	46.2	62.8
E-519	K-506 condenser	1	3.8	3.8	35.1	35.1	38.8
E-520	MGN cooler	1	3.8	3.8	35.1	35.1	38.8
E-521	ADN cooler	1	21.5	21.5	48.2	48.2	69.7
Fired heaters							
F-101	Air furnace	1	16,140.0	16,140.0	7,000.3	7,000.3	23,140.3
F-102	Natural gas furnace	1	1,035.0	1,035.0	449.2	449.2	1,484.2
Filters							
FL-101	Air compressor pulse air filter	1	4,350.0	4,350.0	2,205.0	2,205.0	6,555.0
FL-102	Ammonia feed filter	1	25.6	25.6	18.5	18.5	44.1
FL-201	R-201 inline filter	1	35.8	35.8	24.6	24.6	60.4
FL-202	R-202 inline filter	1	35.8	35.8	24.6	24.6	60.4
FL-301	R-301 inline filter	1	35.8	35.8	24.6	24.6	60.4
FL-501	ADN solution filter	1	35.8	35.8	24.6	24.6	60.4

Table 6.18 (continued): Itemized ISBL equipment capital cost (US\$-k)

		# installed	FOB (1 unit)	FOB (all units)	Install (1 unit)	Install (all units)	Installed cost (all units)
Compressors							
K-101	Air compressor	1	372.5	372.5	1,736.0	1,736.0	2,108.5
K-102	NH ₃ recycle compressor	1	137.1	137.1	392.7	392.7	529.8
K-201	C-203 vacuum pump	1	8.5	8.5	76.1	76.1	84.6
K-202	C-202 vacuum pump	1	9.2	9.2	82.7	82.7	91.9
K-301	C-304 vacuum pump	1	2.5	2.5	4.8	4.8	7.3
K-302	C-305 vacuum pump	1	9.3	9.3	78.9	78.9	88.2
K-303	C-301 vacuum pump	1	16.0	16.0	135.8	135.8	151.8
K-304	C-306 vacuum pump	1	4.2	4.2	51.7	51.7	55.9
K-305	C-302 vacuum pump	1	2.5	2.5	4.8	4.8	7.3
K-401	H ₂ compressor	1	564.7	564.7	662.2	662.2	1,226.9
K-402	C-402 vacuum pump	1	2.5	2.5	4.8	4.8	7.3
K-403	C-403 vacuum pump	1	2.5	2.5	4.8	4.8	7.3
K-404	C-404 vacuum pump	1	3.6	3.6	6.9	6.9	10.5
K-501	C-501 vacuum pump	1	2.5	2.5	4.8	4.8	7.3
K-502	C-502 vacuum pump	1	2.5	2.5	4.8	4.8	7.3
K-503	C-503 vacuum pump	1	2.5	2.5	4.8	4.8	7.3
K-504	C-504 vacuum pump	1	2.5	2.5	4.8	4.8	7.3
K-505	C-505 vacuum pump	1	2.5	2.5	4.8	4.8	7.3
K-506	C-506 vacuum pump	1	2.5	2.5	4.8	4.8	7.3
Mixers and agitators							
M-201	TK-202 tank mixer	1	5.0	5.0	1.5	1.8	6.8
M-202A/B	R-201 agitators	2	375.0	750.0	112.5	131.3	881.3
M-203	R-202 agitator	1	112.5	112.5	33.8	39.4	151.9
M-301A/B	R-301 agitators	2	375.0	750.0	112.5	131.3	881.3
M-302	D-309 agitator	1	125.0	125.0	37.5	43.8	168.8
M-401A/B	TK-403 agitators	2	125.0	250.0	37.5	43.8	293.8
Pumps							
P-101A/B	MAP feed pumps	2	4.2	8.4	8.8	17.5	25.9
P-102A/B	NH ₃ absorber B/S pumps	2	38.0	76.0	154.6	309.2	385.2
P-103A/B	V-104 B/S pumps	2	91.8	183.6	446.8	893.6	1,077.2
P-104A/B	V-105 B/S pumps	2	90.7	181.3	441.0	882.0	1,063.3
P-105A/B	V-106 B/S pumps	2	73.6	147.1	355.5	711.0	858.1
P-106A/B	V-106 reflux pumps	2	37.7	75.4	153.3	306.6	382.0
P-107A/B	V-107 B/S pumps	2	15.7	31.3	46.9	93.8	125.1
P-108A/B	V-109 B/S pumps	2	2.2	4.3	4.6	9.1	13.4
P-109A/B	C-101 reflux pumps	2	25.9	51.8	99.0	197.9	249.7
P-110A/B	C-101 B/S pumps	2	38.7	77.4	157.6	315.2	392.6
P-111A/B	Caustic pumps	2	11.7	23.3	23.2	46.3	69.6
P-112A/B	HCN feed pumps	2	15.5	31.0	46.6	93.2	124.3
P-201A/B	BD feed pumps	2	44.3	88.5	166.2	332.4	420.9
P-202A/B	C-203 reflux pumps	2	23.9	47.8	83.4	166.8	214.7

Table 6.18 (continued): Itemized ISBL equipment capital cost (US\$-k)

		# installed	FOB (1 unit)	FOB (all units)	Install (1 unit)	Install (all units)	Installed cost (all units)
P-203A/B	C-203 B/S pumps	2	31.3	62.6	118.7	237.4	300.0
P-204A/B	Catalyst feed pumps	2	2.5	5.0	4.6	9.2	14.2
P-205A/B	C-201 reflux pumps	2	10.7	21.4	21.2	42.3	63.8
P-206A/B	C-201 B/S pumps	2	14.0	27.9	43.3	86.6	114.5
P-207A/B	C-202 reflux pumps	2	15.2	30.4	45.9	91.7	122.1
P-208A/B	C-202 sidestream pumps	2	10.7	21.4	21.2	42.3	63.8
P-209A/B	C-202 B/S pumps	2	9.5	19.1	18.3	36.7	55.7
P-301A/B	TPB feed pumps	2	2.5	5.0	4.6	9.2	14.2
P-302A/B	Cyclohexane feed pumps	2	2.5	5.0	4.6	9.2	14.2
P-303A/B	C-303 B/S pumps	2	38.4	76.8	156.3	312.6	389.4
P-304A/B	R-301 pumps	2	20.8	41.6	69.2	138.4	180.0
P-305A/B	C-303 reflux pumps	2	2.5	5.0	4.6	9.2	14.2
P-306A/B	C-304 reflux pumps	2	4.8	9.6	9.2	18.4	28.0
P-307A/B	C-304 B/S pumps	2	38.3	76.6	155.9	311.8	388.4
P-308A/B	C-301 reflux pumps	2	17.7	35.3	56.2	112.3	147.6
P-309A/B	C-301 B/S pumps	2	36.3	72.7	147.6	295.2	367.9
P-310A/B	C-305 reflux pumps	2	38.3	76.5	155.7	311.4	387.9
P-311A/B	C-305 B/S pumps	2	2.5	5.0	4.6	9.2	14.2
P-312A/B	D-309 pumps	2	35.9	71.8	145.8	291.6	363.4
P-313A/B	D-310 B/S pumps	2	20.3	40.5	67.6	135.2	175.8
P-314A/B	C-306 B/S pumps	2	37.4	74.8	152.0	304.0	378.8
P-315A/B	C-306 reflux pumps	2	12.2	24.3	35.8	71.6	95.9
P-316A/B	ADN pumps	2	20.0	39.9	66.8	133.5	173.4
P-317A/B	Dinitrile pumps	2	8.2	16.4	16.6	33.1	49.5
P-401A/B	NH ₄ OH pumps	2	2.5	5.0	4.6	9.2	14.2
P-402A/B	Demin water pumps	2	2.5	5.0	4.6	9.2	14.2
P-403A/B	R-401 pumps	2	22.3	44.5	78.1	156.2	200.7
P-404A/B	C-402 B/S pumps	2	5.9	11.7	9.1	18.1	29.9
P-405A/B	C-402 reflux pumps	2	38.5	77.0	156.7	313.4	390.4
P-406A/B	C-401 B/S pumps	2	38.6	77.2	157.1	314.2	391.4
P-407A/B	C-401 reflux pumps	2	2.5	5.0	4.6	9.2	14.2
P-408A/B	C-403 B/S pumps	2	38.3	76.6	155.9	311.8	388.4
P-409A/B	C-403 reflux pumps	2	6.2	12.4	12.5	24.9	37.3
P-410A/B	C-404 B/S pumps	2	14.8	29.5	45.0	90.0	119.5
P-411A/B	C-404 reflux pumps	2	36.3	72.6	147.5	295.0	367.6
P-412A/B	HMDA product pumps	2	19.6	39.1	65.6	131.2	170.3
P-501A/B	Contaminated catalyst pumps	2	4.2	8.3	9.2	18.3	26.6
P-502A/B	C-503 B/S pumps	2	13.5	27.0	38.0	75.9	102.9
P-503A/B	C-503 reflux pumps	2	2.5	5.0	4.6	9.2	14.2
P-504A/B	Extraction transfer pumps	2	16.8	33.7	54.1	108.2	141.9
P-505A/B	ADN solution pumps	2	10.5	20.9	20.9	41.7	62.6
P-506A/B	C-504 B/S pumps	2	7.8	15.6	32.7	65.3	80.9

Table 6.18 (continued): Itemized ISBL equipment capital cost (US\$-k)

		# installed	FOB (1 unit)	FOB (all units)	Install (1 unit)	Install (all units)	Installed cost (all units)
P-507A/B	C-504 reflux pumps	2	22.3	44.6	97.2	194.4	239.0
P-508A/B	C-501 B/S pumps	2	11.3	22.6	50.2	100.4	123.0
P-509A/B	C-501 reflux pumps	2	22.7	45.3	96.0	192.0	237.3
P-510A/B	Cyclohexane transfer pumps	2	15.9	31.9	67.6	135.1	167.0
P-511A/B	C-505 B/S pumps	2	22.3	44.6	97.2	194.4	239.0
P-512A/B	C-505 reflux pumps	2	2.5	5.0	4.6	9.2	14.2
P-513A/B	C-502 B/S pumps	2	23.0	46.0	97.8	195.7	241.7
P-514A/B	C-502 reflux pumps	2	13.4	26.8	46.8	93.6	120.4
P-515A/B	TK-502 pumps	2	2.5	5.0	4.6	9.2	14.2
P-516A/B	C-506 B/S pumps	2	22.3	44.6	97.2	194.4	239.0
P-517A/B	C-506 reflux pumps	2	2.5	5.0	4.6	9.2	14.2
P-518A/B	TK-503 pumps	2	2.5	5.0	4.6	9.2	14.2
Reactors							
R-101A/B	HCN reactor	2	4,022.0	8,044.0	141.2	282.5	8,326.5
R-201A/B	BD reactors	2	289.9	579.8	74.3	148.5	728.3
R-202A/B	Isom reactor	2	182.6	365.2	63.6	127.1	492.3
R-301A/B	3PN reactors	2	289.9	579.8	74.3	148.5	728.3
R-401A/B	ADN reactors	2	289.9	579.8	74.3	148.5	728.3
Specially packaged equipment							
S-101	Dowtherm hot oil system	1	7,500.0	7,500.0	15,250.0	15,250.0	22,750.0
S-102	Glycol chiller system	1	250.0	250.0	350.0	350.0	600.0
S-103	Vapor stream incinerator w header	1	2,500.0	2,500.0	5,500.0	5,500.0	8,000.0
S-104	Liquids incinerator	1	4,500.0	4,500.0	2,500.0	2,500.0	7,000.0
S-105	2-flare system with blowdown drums & header	1	3,500.0	7,000.0	18,250.0	18,250.0	25,250.0
S-106	Process computer control system	1	8,500.0	8,500.0	14,500.0	14,500.0	23,000.0
Steam turbine drivers							
ST-101	K-101 steam turbine	1	3,758.0	3,758.0	2,481.0	2,481.0	6,239.0

Table 6.18 (concluded): Itemized ISBL equipment capital cost (US\$-k)

		# installed	FOB (1 unit)	FOB (all units)	Install (1 unit)	Install (all units)	Installed cost (all units)
Storage tanks							
TK-101	Ammonia sphere	1	1,541.0	1,541.0	147.5	147.5	1,688.5
TK-102	MAP solution tank	1	857.7	857.7	227.8	227.8	1,085.5
TK-103	Caustic tank	1	57.0	57.0	26.8	26.8	83.8
TK-104	HCN tank	1	352.1	352.1	51.7	51.7	403.8
TK-201	BD storage sphere	1	505.5	505.5	206.7	206.7	712.2
TK-202	Catalyst tank	1	23.3	23.3	10.9	10.9	34.2
TK-301	Triphenol boron tank	1	74.5	74.5	10.9	10.9	85.5
TK-302	Cyclohexane tank	1	23.3	23.3	10.9	10.9	34.2
TK-303A/B	ADN product tanks	2	377.7	755.4	55.5	111.0	866.4
TK-304	Dinitrile tank	1	182.4	182.4	26.8	26.8	209.2
TK-401	Ammonium hydroxide tank	1	74.5	74.5	10.9	10.9	85.5
TK-402	Demin water tank	1	23.3	23.3	10.9	10.9	34.2
TK-403A/B	HMDA tanks	2	377.7	755.4	55.5	111.0	866.4
TK-501	Contaminated catalyst tank	1	23.3	23.3	10.9	10.9	34.2
TK-502	Phenol tank	1	23.3	23.3	10.9	10.9	34.2
TK-503	MGN tank	1	74.5	74.5	10.9	10.9	85.5
Pressure vessels (API 510-ASME BPVC)							
V-101A/B	Natural gas dehydrator	2	107.3	214.6	59.1	118.3	332.9
V-102A/B	Ammonia dehydrator	2	107.3	214.6	59.1	118.3	332.9
V-103	Ammonia absorber	1	200.4	200.4	75.8	75.8	276.2
V-104	MAP HCN Stripper	1	200.4	200.4	75.8	75.8	276.2
V-105	Ammonia stripper	1	107.3	107.3	59.1	59.1	166.4
V-106	MAP concentrator	1	123.7	123.7	62.8	62.8	186.5
V-107	HCN absorber	1	200.4	200.4	75.8	75.8	276.2
V-108A/B	Activated carbon filters	2	106.3	212.6	68.7	137.4	350.0
V-109	HCN scrubber	1	123.7	123.7	62.8	62.8	186.5
V-201A/B	BD dehydrator	2	165.4	330.8	70.3	140.6	471.4
Total			93,790.3	106,554.0	97,706.6	104,363.2	210,917.2

Total fixed capital cost estimate

Using IHS in-house factored estimates of ‘outside battery limits’ facilities, plus a build-up of ISBL equipment costs to incorporate other related capital costs such as indirect construction costs, rental equipment, and contingency, we have prepared a total fixed capital cost equipment for the project, as shown in the table below.

Table 6.19: Total fixed capital cost estimate (US\$-k)

Capacity: 250,000 mt/yr			
AT 0.90 stream factor			
PEP Cost Index: 1164			
	Cost (\$US-MM)	Capacity exponent	
		Up	Down
Battery limits equipment, FOB			
Buildings	530	0.55	0.53
Reactors	10,149	0.70	0.60
Distillation columns	11,107	0.61	0.58
Drums	3,561	0.67	0.62
Filters	4,519		
Heat exchangers	12,304	0.65	0.63
Pumps	2,784	0.63	0.60
Compressors	1,150	0.62	0.60
ISBL storage tanks	5,346	0.69	0.60
Pressure vessels	1,929	0.67	0.62
Fired heaters	17,175	0.85	0.85
Mixers & agitators	1,993	0.65	0.65
Steam turbine drivers	3,758	0.70	0.70
Special packaged equipment	30,250	0.70	0.70
Total BLE	106,554		
Direct installation costs	104,313	0.66	0.62
Indirect costs	78,235	0.63	0.59
Unscheduled equipment, 20%	20,863	0.65	0.62
Battery limits, installed	309,964	0.65	0.62
BLI contingency, 25%	77,491	0.65	0.62
Battery limits investment	387,455	0.65	0.62
Offsites, installed			
Cooling water	21,698	0.65	0.62
Process water	1,860	0.65	0.62
Boiler feedwater	3,100	0.65	0.62
Process steam	30,996	0.55	0.53
Fuel gas system	6,199	0.55	0.53
Inert gas & instrument air	1,860	0.55	0.53
Offsite tankage	28,500		
Utilities & storage	94,212	0.65	0.62
General service facilities	15,498	0.65	0.62
Wastewater treatment	24,797	0.65	0.62
Total offsites	134,508	0.65	0.62
Offsites contingency 25%	33,627	0.65	0.62
Offsites capital investment	168,135	0.65	0.62
Total fixed capital	555,590	0.65	0.62

Production cost estimate

Combining the technical results developed above with unit pricing for raw materials, chemicals and catalyst, and utilities, we have developed the following estimate of variable production costs (raw materials + energy) for making HMDA using our understanding of Invista process technology.

Table 6.20: Variable production cost estimate (US\$-k)

			HMDA market price		2900.0
Raw material and utility costs					
	Unit cost		Consumption		\$/mt
Raw materials					
Ammonia	600	\$US/mt	0.348	mt/mt	208.8
Butadiene	1446	\$US/mt	0.576	mt/mt	832.9
Methane	218	\$US/mt	0.288	mt/mt	62.8
Hydrogen	872	\$US/mt	0.076	mt/mt	66.3
MonoAmmonium Phosphate	475	\$US/mt	0.005	mt/mt	2.4
Cyclohexane Solvent	1550	\$US/mt	0.002	mt/mt	3.1
Ammonium Hydroxide	575	\$US/mt	0.0015	mt/mt	0.9
Caustic Soda	650	\$US/mt	0.00025	mt/mt	0.2
Triphenyl Boron	6500	\$US/mt	0.0005	mt/mt	3.3
Nickel Ligand Catalst	5000	\$US/mt	0.0004	mt/mt	2.0
Pt/Rh Gauze Catalyst	100000000	\$US/mt	0.00000005	mt/mt	5.0
By-Product Credits					
Mixed DiNitriles	750	\$US/mt	-0.0517	mt/mt	-38.8
Mixed Phenol/Cresols	900	\$US/mt	-0.00022	mt/mt	-0.2
Net raw material cost					1148.5
Utilities					
Process water	0.35	\$US/m3	9.85	m3/mt	3.4
Cooling water	0.04	\$US/m3	116.05	m3/mt	4.8
Electricity	5.93	¢US/kwh	330.56	kwh/mt	19.6
Process steam	16.758	\$US/mt	3.68	mt/mt	61.7
Fuel gas	218.0304	\$US/mt	0.257	mt/mt	56.0
Net utility cost					145.5
Variable costs					1294.1

In order to estimate the fixed costs of manufacturing HMDA, PEP has developed factors for estimating cost components as a percentage of either capital costs or unit labor requirements. These factors are listed in the table below. In the particular case of HMDA, which is primarily consumed captively by Invista and others to produce nylon 66, we have used a corporate overhead factor (G&A, sales, R&D) of only 1% of HMDA product price (US\$2,900/mt).

Table 6.21: Fixed production cost factors

Maintenance materials (% of BLI)	2
Operating supplies (% of operating labor)	10
Operating labor rate (\$/manhour)	46.23
Maintenance labor (% of BLI)	2
Control laboratory (% of operating labor)	20
Plant overhead (% of total labor)	60
Taxes & insurance (% of TFC)	2
Depreciation (% of TFC)	10
Product value premium (production cost + % TFC)	25
Number of operators per shift	6
G&A, sales, R&D (% of product price)	1

By applying the fixed cost factors to the capital and labor cost efforts that we believe are required to operate a commercial scale plant with the variable costs estimated above, we have estimated the total production costs to produce 250 kty of HMDA. In the table below, we have used this information to also estimate, on a factored cost basis, the production costs for ½ the base case capacity (125 kty), and twice the base case capacity (500 kty).

Table 6.22: Fixed production cost estimate (US\$/mt)

Capacity	MT/Y	125	250	500
Production	MT/Y	125	250	500
Investment (\$US millions)				
Battery limits		233.6	(0.73)	387.5
Off-sites		<u>119.7</u>	(0.49)	<u>168.1</u>
Total fixed capital		353.3	555.6	878.8
Production cost (\$/MT)	\$/mt		\$/mt	\$/mt
Net raw materials		1148.5	1148.5	1148.5
Net utilities		<u>145.5</u>	<u>145.5</u>	<u>145.5</u>
Variable costs		1294.1	1294.1	1294.1
Direct costs				
Maintenance materials		37.4	31.0	25.7
Operating supplies		1.9	1.0	0.5
Operating labor		19.4	9.7	4.9
Maintenance labor		37.4	31.0	25.7
Control laboratory		<u>3.9</u>	<u>1.9</u>	<u>1.0</u>
Total direct costs		1394.1	1368.7	1351.8
Plant overhead		34.1	24.4	18.3
Taxes & insurance		56.5	44.4	35.2
Depreciation		<u>282.7</u>	<u>222.2</u>	<u>175.8</u>
Plant gate cost		1767.3	1659.8	1581.0
G&A, sales, R&D		29.0	29.0	29.0
Total production cost				
AT 100% capacity		1796.3	1688.8	1610.0
AT 75% capacity		1963.8	1820.4	1715.3
AT 50% capacity		2298.6	2083.5	1926.0
Product value (Cost + 25%/YR ROI before taxes)				
AT 100% capacity		2498.9	2237.7	2040.8
AT 75% capacity		2670.4	2375.9	2154.7
AT 50% capacity		3005.2	2639.1	2365.4
Cash cost		1513.69	1466.56	1434.27
Cash cost profitability		1386.32	1433.46	1465.74
Total cost profitability		1103.68	1211.23	1289.99

When the variable and fixed costs of production are combined, the result is the conventional PEPCOST total production cost estimate, as presented in the table below.

Table 6.23: Total production cost estimate (US\$/mt)

Raw material and utility costs			HMDA market price		2900.0
	Unit cost		Consumption		\$/mt
Raw materials					
Ammonia	600	\$US/mt	0.348	mt/mt	208.8
Butadiene	1446	\$US/mt	0.576	mt/mt	832.9
Methane	218	\$US/mt	0.288	mt/mt	62.8
Hydrogen	872	\$US/mt	0.076	mt/mt	66.3
MonoAmmonium Phosphate	475	\$US/mt	0.005	mt/mt	2.4
Cyclohexane Solvent	1550	\$US/mt	0.002	mt/mt	3.1
Ammonium Hydroxide	575	\$US/mt	0.0015	mt/mt	0.9
Caustic Soda	650	\$US/mt	0.00025	mt/mt	0.2
Triphenyl Boron	6500	\$US/mt	0.0005	mt/mt	3.3
Nickel Ligand Catalst	5000	\$US/mt	0.0004	mt/mt	2.0
Pt/Rh Gauze Catalyst	100000000	\$US/mt	0.00000005	mt/mt	5.0
By-Product Credits					
Mixed DiNitriles	750	\$US/mt	-0.0517	mt/mt	-38.8
Mixed Phenol/Cresols	900	\$US/mt	-0.00022	mt/mt	-0.2
Net raw material cost					1148.5
Utilities					
Process water	0.35	\$US/m3	9.85	m3/mt	3.4
Cooling water	0.04	\$US/m3	116.05	m3/mt	4.8
Electricity	5.93	\$US/kwh	330.56	kwh/mt	19.6
Process steam	16.758	\$US/mt	3.68	mt/mt	61.7
Fuel gas	218.0304	\$US/mt	0.257	mt/mt	56.0
Net utility cost					145.5
Variable costs					1148.5
Maintenance materials (% of BLI)			2		
Operating supplies (% of operating labor)			10		
Operating labor rate (\$/manhour)			46.23		
Maintenance labor (% of BLI)			2		
Control laboratory (% of operating labor)			20		
Plant overhead (% of total labor)			60		
Taxes & insurance (% of TFC)			2		
Depreciation (% of TFC)			10		
Product value premium (production cost + % TFC)			25		
Number of operators per shift			6		
G&A, sales, R&D (% of product price)			1		

Table 6.23: Total production cost estimate (US\$/mt) (continued)

Capacity	MT/Y	125	250	500
Production	MT/Y	125	250	500
Investment (\$US millions)				
Battery limits		233.6	(0.73)	387.5
Off-sites		119.7	(0.49)	168.1
Total fixed capital		353.3	555.6	878.8
Production cost (\$/MT)	\$/mt		\$/mt	\$/mt
Net raw materials		1148.5	1148.5	1148.5
Net utilities		145.5	145.5	145.5
Variable costs		1294.1	1294.1	1294.1
Direct costs				
Maintenance materials		37.4	31.0	25.7
Operating supplies		1.9	1.0	0.5
Operating labor		19.4	9.7	4.9
Maintenance labor		37.4	31.0	25.7
Control laboratory		3.9	1.9	1.0
Total direct costs		1394.1	1368.7	1351.8
Plant overhead		34.1	24.4	18.3
Taxes & insurance		56.5	44.4	35.2
Depreciation		282.7	222.2	175.8
Plant gate cost		1767.3	1659.8	1581.0
G&A, sales, R&D		29.0	29.0	29.0
Total production cost				
AT 100% capacity		1796.3	1688.8	1610.0
AT 75% capacity		1963.8	1820.4	1715.3
AT 50% capacity		2298.6	2083.5	1926.0
Product value (Cost + 25%/YR ROI before taxes)				
AT 100% capacity		2498.9	2237.7	2040.8
AT 75% capacity		2670.4	2375.9	2154.7
AT 50% capacity		3005.2	2639.1	2365.4
Cash cost		1513.69	1466.56	1434.27
Cash cost profitability		1386.32	1433.46	1465.74
Total cost profitability		1103.68	1211.23	1289.99

Economic analysis

For the base case HMDA production plant with an annual capacity of 250 kty, our analysis shows a total production cost of US\$1688.8/mt, and a cash cost of US\$1466.6/mt. The major components of cost are raw materials at US \$1148.5/mt, and utilities of US\$145.5/mt. When these costs are compared to a nominal HMDA selling price of US\$2,900/mt, such an investment would produce a very attractive ROI. However, we believe that the selling price is rather arbitrary given that nearly all of the HMDA produced is consumed captively to make nylon 66. We believe that a more important price consideration is the market price of nylon 66, which in late 2013 is approximately US\$3,500/mt. Comparing the cost of making HMDA to the nylon 66 selling price, our analysis indicates that such a capital investment will provide an adequate ROI. Given the reality that Invista has announced a grassroots HMDA plant for China with a production capacity of 215 kty, Invista also believes that such an investment will provide an adequate ROI.

7. Monsanto/Ascend process for making HMDA from acrylonitrile

Ascend Performance Materials

Ascend Performance Materials is the successor company to the historical Monsanto integrated nylon 66 business. As of 2013, Ascend owns and operates one adiponitrile plant in Decatur, Alabama (USA) with a nameplate production capacity of 340 kty, and two HMDA plants: one in Decatur with a capacity of 175 kty, and the other in Pensacola, Florida (USA) with an HMDA capacity of 185 kty. Ascend operates 500 kty of nylon 66 capacity, segmented by 380 kty in Pensacola, and 90 kty in Greenwood, South Carolina (USA).

Ascend's integrated nylon 66 assets were built in the 1950s by Monsanto's Chemical Division. This business was spun off in 1996 into Solutia. After undergoing bankruptcy issues, Solutia sold the integrated nylon 66 business to SK Capital Partners (a private equity firm) in 2009, which renamed this business Ascend Performance Materials.

Ascend makes ADN via the electrodimmerization of acrylonitrile, and then hydrogenates ADN to HMDA using technology very similar to that practiced by Invista/DuPont. Monsanto historically had been one of the world's largest producers of acrylonitrile, primarily for polymerization to polyacrylonitrile, and subsequent fabrication to synthetic fibers (acrylic fibers) used primarily in textile end use applications. Acrylonitrile is produced in Ascend's Chocolate Bayou (Texas, USA) plant, of which 70% is consumed captively. Major Ascend commercial products are listed in the table below.

Table 7.1: Ascend major commercial products

Dibasic acids/esters
Adipic acid AGS mixture (50% dibasic acid mixture)
DME mixture (dimethyl ester mixture)
Amines
Hexamethylene diamine (HMD)
Bis-hexamethylenetriamine (BHMT)
Amine heads (AH)
Triaminononane (TAN)
Nitriles
Acrylonitrile (ACN)
Adiponitrile (ADN)
Propionitrile (PN)
1,3,6-Tricyanohexane (TCH)
Ketones/alcohols
Cyclohexanol
Cyclohexanone
Chelating agents
Sodium nitrilotriacetate monohydrate (NTA)

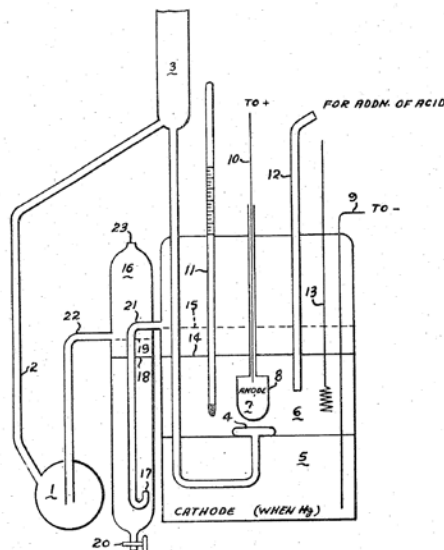
Ascend's capital plans

The global nylon 66 market is not perceived to be growing fast enough, at approximately 2–3% per year demand growth, to justify new grassroots (green field) capacity in the major process unit components: adipic acid, adiponitrile, HMDA, or nylon 66 salt. Nevertheless, Ascend is examining ways to employ new capital to substantially improve the overall cost competitiveness of the business.

Since Ascend technology uses acrylonitrile as the basic feedstock, which is dimerized to adiponitrile, and then hydrogenated to HMDA, its overall product chain economics are strongly influenced by the feedstock source to make acrylonitrile, which is propylene. In response to the 'shale gas' revolution in the US, Ascend has announced plans [31C49] to build a grassroots propane dehydrogenation plant intended to convert low cost shale gas by-product propane (a natural gas liquid) to propylene via dehydrogenation technology.

The electrohydrodimerization of acrylonitrile to adiponitrile was commercialized in the US by Monsanto in 1965. Discovered by Monsanto's Manuel Baizer, the commercial team was headed by Donald Danly. The design of the Baizer electrolytic cell from his Monsanto patent (USP 3193477) is shown in the figure below.

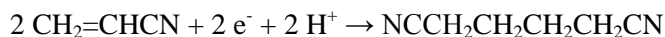
Figure 7.1: Baizer Monsanto patent for electrolytic cell (USP 3193477)



The initial technology was developed by Phillips Petroleum in the US, and by ICI in Europe. Other European developers included Rhone-Poulenc (now Rhodia/Solvay) and UCB, while Asahi developed similar technology in Japan. A key component of Baizer's discovery was the use of quaternary ammonium salts (tetraethylammonium p-toluenesulfonate) that would coat the cadmium electrode to minimize the production of hydrogen, while enhancing ADN yield from ACN, and reducing electricity consumption.

Monsanto/Ascend chemistry

The dimerization of acrylonitrile to adiponitrile, with the addition of electrons and hydrogen ions, occurs at the cathode side of an electrochemical cell, and is shown in the reaction below.



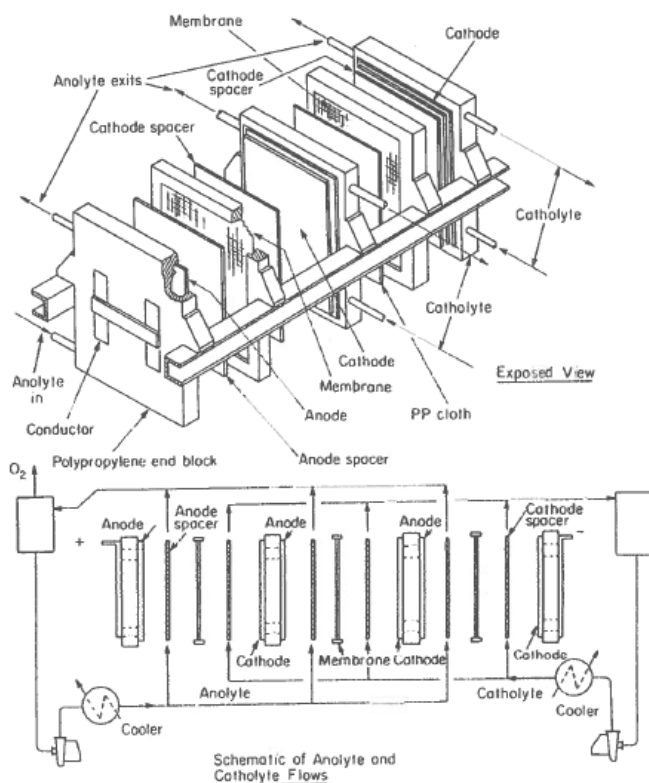
It is thought that the process initiates with two electrons being added to the double bond of an acrylonitrile molecule, allowing a second acrylonitrile molecule to bond to the beta carbon atom. The source of H^+ ions is the electrolysis of water at the anode, also forming pure oxygen which must be safely vented from the process area.

The addition of two hydrogen ions compensates for the initial addition of two electrons, again forming an electrically neutral molecule. The reaction sequence is shown below.



The initial electrochemical cells were divided into separate cathodic (negative) and anodic (positive) regions that were separated by semi-permeable ion exchange membranes. A schematic drawing of a divided (membrane barrier) electrodimmerization cell for acrylonitrile is shown in the figure below.

Figure 7.2: Divided electrodimmerization cell



Source: McKetta [31C50]

Advances by the major operating companies (Monsanto, Asahi, BASF, and UCB) eliminated the need for separate cell compartments, which is now known as ‘undivided cell’ technology.

In current practice (known as second-generation technology), a two-phase emulsion of feedstock and additives is quickly pumped through the undivided cell. The aqueous phase contains a small amount of acrylonitrile feedstock (limited by its solubility of 7% at STP) and conducting salt. The emulsion contains 15% disodium hydrogen phosphate. The oil/organic phase contains a higher concentration of acrylonitrile

and product adiponitrile. Although ADN free ACN would be preferred for the organic phase of the emulsion, the resulting high concentration of ACN results in very low selectivity to ADN. In this respect, the ADN acts as an inert diluting solvent for the ACN feedstock.

Current cathode material is cadmium coated onto carbon steel plates, while anode material is carbon steel. These materials replaced the historical use of graphite for the cathode, and iron oxide for the anode. Hydrogen is formed at the anode via the electrolysis of water.

The conducting component is made primarily of quaternary ammonium salt, which prevents the cathode from hydrolyzing water to form hydrogen gas. This minimizes the hydrogenation of acrylonitrile to propionitrile, and maximizes the dimerization of acrylonitrile to adiponitrile at the cathode.

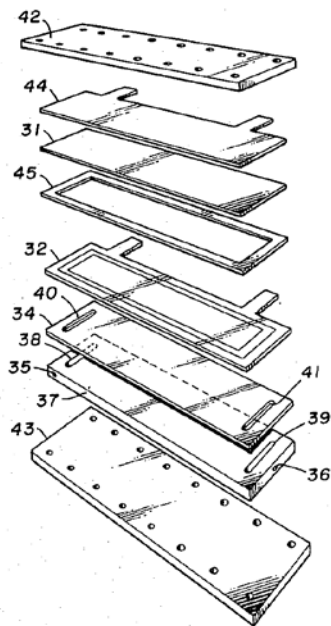
Upon discharge from the undivided cell, the emulsion separates in a decanter into an upper organic phase and a lower aqueous phase. The aqueous phase is recycled directly to the cell. The organic phase (containing adiponitrile and unconverted acrylonitrile) is washed with water to remove residual QUAT, and distilled to separate and purify the product ADN for subsequent hydrogenation to HMDA, while the unconverted acrylonitrile is recycled to the cell.

The overall selectivity of the cell to adiponitrile is above 90%, while the major by-products are propionitrile and biscyanoethyl ether.

Electrochemical cell arrangement

The Monsanto Mark-2 undivided cell [31C51] is organized as a parallel series of flat steel plates coated with cadmium serving as the cathode, where the electrodimers of acrylonitrile to adiponitrile occurs. The anode plates are made of carbon steel. The spacing between plates is approximately 2 mm. The physical organization of the plates is shown in the figure below.

Figure 7.3: Electrode plates for Monsanto electrohydrodimerization (USP 4250001)



The current technology undivided cell operates at a current density of 2 kA/m². Emulsion flows through the stack of plates at an average velocity of 1–2 m/sec. The process occurs at atmospheric pressure and a temperature of 55°C. The aqueous phase uses a bisquaternary salt (hexamethylene[bisethyltributyl]ammonium phosphate), and a phosphate buffer Na₂HPO₄ (15%). Overall electricity consumption is 2.4 kwh/kg. The quaternary ammonium salt (QUAT) most often used is hexamethylene-bis(ethyldibutylammonium). Other QUATs mentioned in the patent literature are tetraethylammonium p-toluenesulfonate and tetraethylammoniumethylsulphate.

Process design

Our design is for an undivided cell architecture using a single feed emulsion fluid with an aqueous component (water, phosphate, acrylonitrile, quaternary ammonium salt, borax, and EDTA), plus an organic phase containing feed acrylonitrile, solvent adiponitrile, and a product stream containing both produced crude adiponitrile and unconverted acrylonitrile. Once the ADN is purified to commercial specifications, the hydrogenation of ADN to HMDA is identical to the ADN hydrogenation process presented in section 6 for the Invista/DuPont butadiene hydrocyanation process.

Adiponitrile from acrylonitrile via electrohydrodimerization in an undivided cell

An undivided electrolytic cell is used, in which there is no membrane boundary between the cathode side and the anode side. A single emulsion is used in the cell, in which both the cathode electrode (cadmium) and anode electrode (carbon steel) operate.

The electrolyte emulsion in the undivided cell consists of water, feedstock acrylonitrile, product adiponitrile, four principal chemical additives, and contaminants created by the reaction. The chemical additives are listed below:

- Disodium hydrogen phosphate
- Sodium tetraborate
- Sodium ethylenediamine tetracetate
- Hexamethylene bis(ethyldibutylammonium) phosphate

The chemical additives are used to increase the electrical conductivity of the cell solution, minimize corrosion of the electrodes, and minimize the formation of hydrogen at the anode electrode.

The emulsion discharged from the undivided cell is sent to a large horizontal settling drum, where a two-phase mixture forms as an upper organic layer, and a lower aqueous layer. Both layers contain appreciable amounts of ADN, requiring recovery of ADN from both liquid streams. Water is added to the settling drum to capture most of the dissolved salts into the aqueous lower layer. The design basis for the undivided cell is provided in the table below.

Table 7.2: Design basis table

Reactor temperature °C	55
Reactor pressure psia	15
ACN once through conversion %	60
ADN selectivity %	94
Current density kA/m ²	2
Cathode material	Cd-coated CS
Anode material	Carbon steel
Emulsion flow rate through cell m/s	1–1.5
Number of cells	24

Feedstock composition

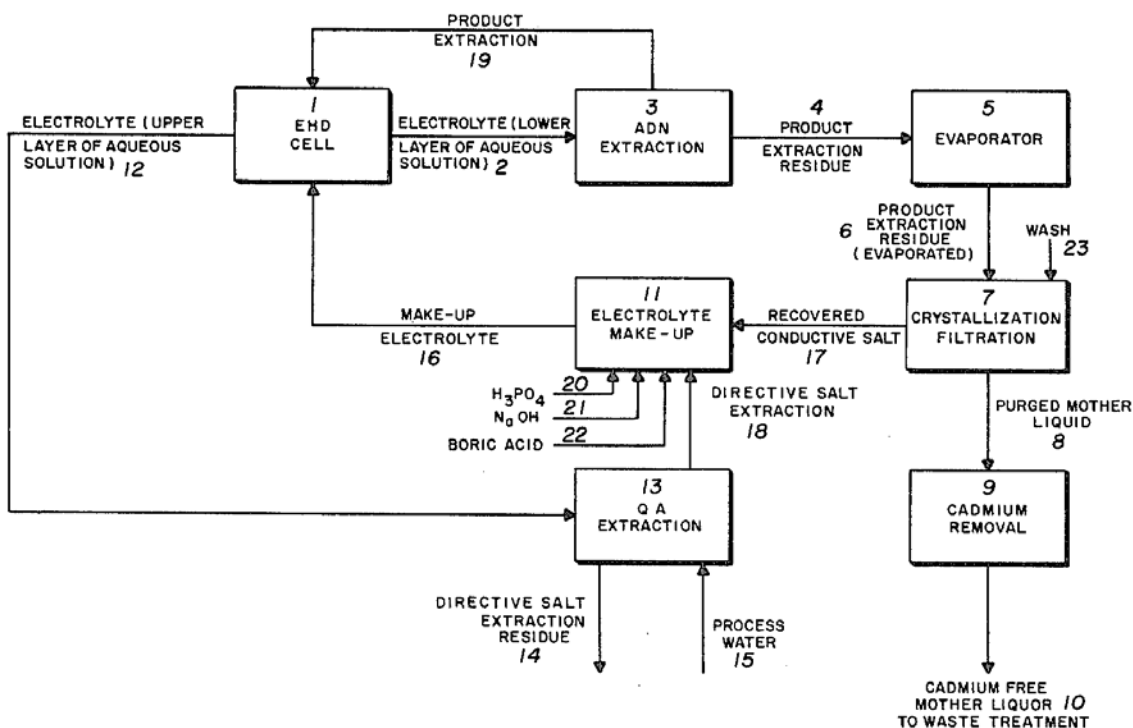
The single fluid emulsion feed composition to the undivided cells is presented in the table below.

Table 7.3: Undivided cell emulsion feed composition

Components	Weight fraction
0.3 (Organic phase)	
Acrylonitrile	0.120
Adiponitrile	0.180
0.7 (Aqueous phase)	
Acrylonitrile	0.050
Disodium hydrogen phosphate	0.150
QUAT Hexamethylene-bis-(ethyldibutylammonium)	0.004
Disodium borate (Na ₂ B ₄ O ₇)	0.010
Sodium ethylenediamine tetraacetate (NaEDTA)	0.005
Water	0.481
Total	1.000

Process configuration

Guidance on a process configuration that will provide high selectivity and acceptable kinetics is found in Monsanto USP 4207151. The Monsanto suggested configuration is shown in the figure below.

Figure 7.4: Aqueous phase product recovery (USP 4207151)

The key process characteristics for USP 4207151 and subsequent Monsanto patents for the use of an undivided cell processing a single fluid emulsion feed for electro hydrodimerization of ACN to ADN are presented below:

- The cell discharge fluid needs to have ACN added to drive product ADN from the aqueous phase to the organic phase
- Residual additives in the organic phase can be washed out with water
- The organic phase and the aqueous phase can be separated by a simple decanter, with the organic phase at the top, and the aqueous phase at the bottom
- ADN can be purified from the organic phase through fractional distillation, although vacuum distillation is required due to ADN's high boiling point (295°C)
- Enough propionitrile is produced from ACN feed (approximately 4%) to justify purification to a sales specification
- Light by products (including propionitrile) and heavies must be removed from the organic phase. Heavy by products include oligomers and polymer
- Contaminants that build up in the aqueous phase cannot simply be discharged to wastewater treatment as purge, because the additives included are too expensive to discard. They are recovered by a combination of evaporation, filtration, and crystallization

Process description/PFDs

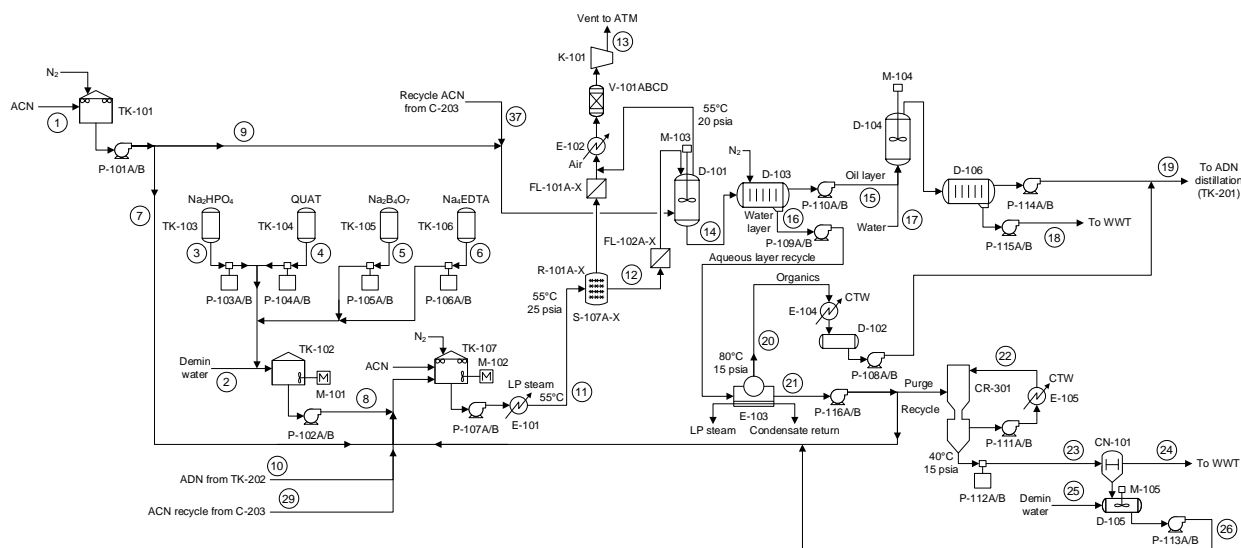
Based upon the accumulated information contained in Monsanto patents and the trade and technical literature on electro-chemistry, we have developed a process configuration scheme that we believe

reflects Monsanto (now Ascend) practice for making adiponitrile from acrylonitrile via electrohydrodimerization. We believe that our design is consistent with environmental documents [31C52, 31C53] filed with the Alabama Department of Environmental Resources (Facility 712-0010) for Morgan County, Alabama. The relevant process flow diagrams are shown in abbreviated fashion below, and in full diagrams in the appendix. The plant is segmented into three sections:

- Section 100—electrodimerization and aqueous phase treatment
- Section 200—adiponitrile purification
- Section 400—adiponitrile hydrogenation to HMDA

Section 100—electrodimerization and aqueous phase treatment

Figure 7.5: Section 100 PFD



Separate short-term day tanks are used to feed and collect separately the aqueous-phase fluid, and the organic-phase fluid, for intense mixing to form the emulsion feed to the electrolytic cells. Fresh ACN feed from Tk-101 is used both as make-up to the emulsion tank (Tk-107), and as feed for the extraction vessel (D-101). Emulsion tank Tk-107 is mixed both with ACN and with recycle ADN from Tk-202, plus the feed from the aqueous mixture tank. The aqueous mixture liquid tank Tk-102 is fed with demineralized water plus additives in liquid form Na_2HPO_4 (Tk-103), QUAT (Tk-104), $\text{Na}_2\text{B}_4\text{O}_7$ (Tk-105), and Na_4EDTA (Tk-106).

Emulsion feed is pumped to 24 parallel undivided electrolytic cells (R-101A-X), each of which has a separate DC power supply (S-107A-X). The emulsion feed is pumped through each cell, through filters FL-102A-X, and into the extraction drum D-101. While hydrogen ions are produced at the anodes within each cell, for consumption in the dimerization reaction, the ionization of water to produce these ions also produces vapor-phase oxygen, which is discharged from the top of each cell through flame arresters FL-101A-X, through cooler E-102, through activated carbon filters V-101A/B to atmosphere. To maintain sufficient vapor flow, an induction fan K-101 is used at the discharge side of the activated carbon filters.

Due to the solubility of ACN and ADN in the aqueous phase (7% at STP), additional ACN is added to the extraction drum D-101 to pull ADN from the aqueous phase into the organic phase. Liquid product from

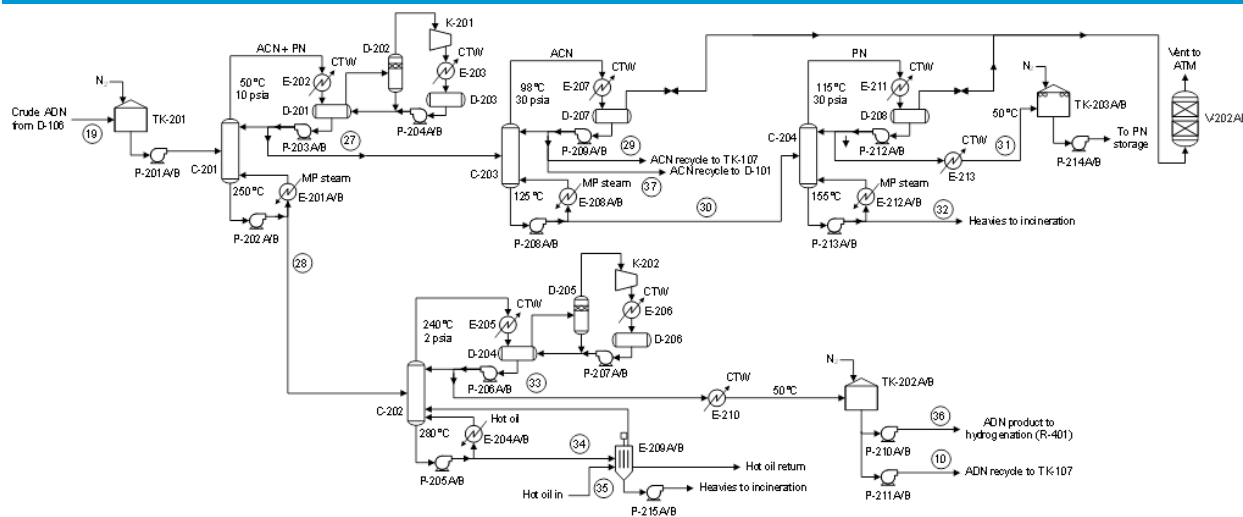
the extraction drum settles into two phases in settling drum D-103; an upper organic phase containing ADN product and unconverted ACN feedstock, plus a lower aqueous phase containing water and additives.

The organic phase is mixed with fresh water to remove residual contaminants and additives in D-104, and allowed to settle into two phases in settling drum D-106. The lower water phase is pumped to wastewater treatment. The upper organic phase is pumped to section 200 for purification of ADN, and recycle of unconverted ACN.

The lower aqueous phase from D-103 is recycled back to the emulsion tank Tk-107. Due to the creation of contaminants, a purge stream (10% of recycle flow) is further processed through an evaporator (E-103) to vaporize light hydrocarbons that are condensed in E-104, and pumped to the ADN purification section. The aqueous liquid from the evaporator is sent to a crystallizer that cools the liquid and forms crystals of additives. The crystallizer bottom product stream contains 20% solids slurry that is pumped through a centrifuge (CN-101) to form a solid crystal cake. The crystal cake is re-dissolved with water in Tk-105, and recycled to the emulsion tank Tk-107. The liquid raffinate from the centrifuge is discharged to the wastewater treatment plant.

Section 200—adiponitrile purification

Figure 7.6: Section 200 PFD



Feed for the adiponitrile distillation train is stored in day tank Tk-201. This stream is pumped to distillation column C-201, which is designed to remove lights (materials boiling at a lower temperature than adiponitrile) as the overhead distillate, and ADN plus heavies as the bottoms product stream. The lights stream is pumped to column C-203 for the purpose of taking unconverted ACN as the overhead distillate, which is recycled to emulsion tank Tk-107. The bottoms stream from C-203 is primarily propionitrile, but also contains heavier hydrocarbons. This stream is pumped to C-204, which takes pure propionitrile as the overhead distillate product, while the bottoms heavies product stream is sent to incineration.

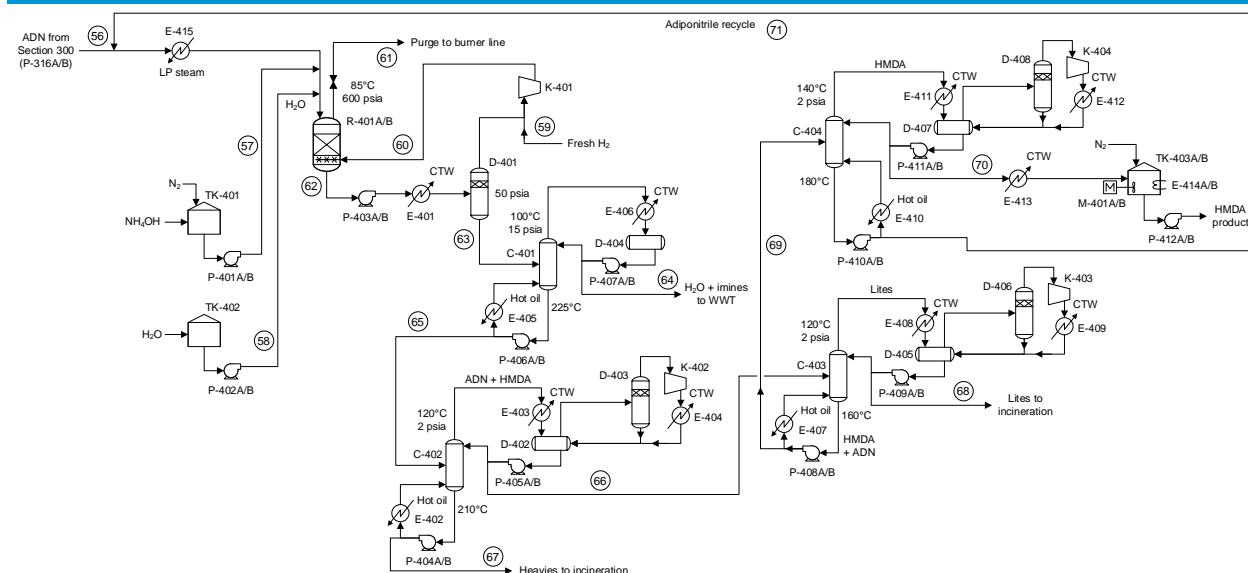
The ADN rich stream from the bottoms of C-201 is pumped to C-202 for the purpose of purifying ADN as the overhead distillate, which is cooled and pumped to product storage day tanks Tk-202A/B. The

bottoms stream, containing heavies but also residual ADN, is pumped to a scraped surface evaporator E-209, in which ADN is vaporized and recycled to C-202, while the scraped heavies (primarily oligomers, polymers, and tars) are discharged to incineration.

Section 400—ADN hydrogenation to HMDA

The hydrogenation of adiponitrile to HMDA in this section is identical to the hydrogenation unit presented in section 6 of this report. It is copied below.

Figure 7.7: Section 400 ADN hydrogenation to HMDA



Purified ADN from section 300 (P-316A/B) is combined with purchased (take or pay) hydrogen gas provided by an external supplier, which is compressed to 650 psia in K-401, plus recycle hydrogen, and fed to hydrogenation reactors R-401A/B. Two reactors are operated in parallel as fixed bed reactors designed for counter-current, plug flow operation. Hydrogen is fed to a bottom distribution manifold in the reactors, while liquid ADN is fed to the top of the reactors. A small amount of water and ammonium hydroxide (Tk-401) are added intermittently to mitigate catalyst deactivation and enhance product selectivity.

Reactor product is passed through a cooler (E-401) to condense most of the stream, which is depressured and then directed to a knock-out drum (D-401) designed to separate vapor hydrogen from liquids. The overhead H₂ vapor from D-401 is passed through a recycle compressor (K-401), and recycled to the reactors.

The liquid stream is directed to a distillation column (C-401) designed to remove water and light products such as imines as the overhead distillate. The distillate stream is sent to the plant's wastewater treatment plant. The bottoms product is fed to distillation tower C-402, which is designed to take the remaining liquids (mostly dinitriles) as the overhead distillate product. The bottoms product is heavy tars and polymer, which is incinerated.

The dinitriles distillate stream from C-402 is fed to distillation tower C-403, which is designed to take light nitriles such as MGN and ESN as the overhead distillate product to incineration, and heavier dinitriles (ADN + HMDA) as the bottoms product.

The bottoms product is directed to distillation tower C-404, which takes pure HMDA as the overhead distillate product, and ADN as the bottoms product. HMDA is sent to product day tankage (Tk-403A/B), while the bottoms purified ADN stream is recycled to the hydrogenation reactors R-401A/B.

Stream-by-stream material balance

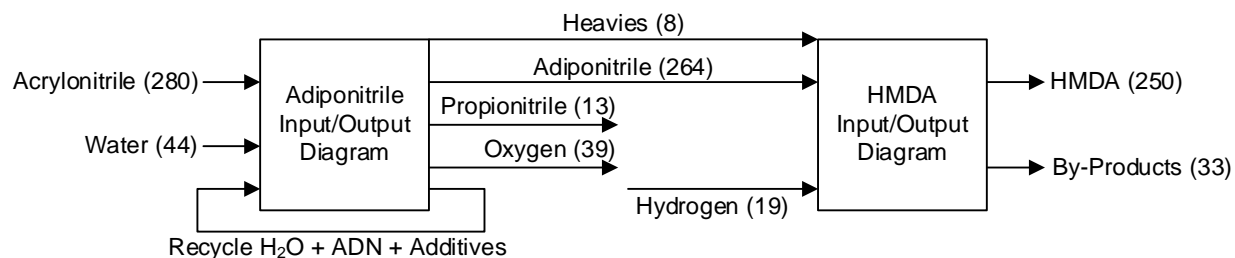
We have prepared a stream by stream material balance consistent with the process flow diagrams and process description presented above. The key reaction occurs inside the electrolytic cell, and the table below represents our understanding of the changes in mass compositions caused by the major chemical reactions taking place within the cell. The primary basis for these calculations is our assumption of 94% overall mass selectivity for producing adiponitrile from acrylonitrile (the difference being primarily the formation of propionitrile), and one pass mass conversion of 60% of the acrylonitrile feed to the cell.

Table 7.4: Electrolytic cell material balance

Components	Cell feed (mt/hr)	Cell product (mt/hr)
Acrylonitrile	59.450	23.780
Adiponitrile	62.947	96.477
Disodium hydrogen phosphate	52.456	52.456
QUAT hexamethylene-bis-(ethylidibutylammonium)	1.399	1.399
Disodium borate ($\text{Na}_2\text{B}_4\text{O}_7$)	3.497	3.497
Sodium ethylenediamine triacetate (NaEDTA)	1.749	1.749
Water	168.209	162.661
Propionitrile	0.000	1.710
Oxygen vapor	0.000	4.930
Heavies	0.000	1.048
Total	349.706	349.706

Based upon the cell balance, and assuming virtually no loss of feedstock or products through the purification train, the overall input/output diagram for the process can be represented by the figure below.

Figure 7.8: Ascend/Monsanto input/output balance (kty)



The stream-by-stream material balance is presented in the table below.

Table 7.5: Stream-by-stream material balance (mt/hr)

		Stream number								
		1	2	3	4	5	6	7	8	9
Label		Fresh ACN feed	Fresh demin water	Fresh Na ₂ HPO ₄	Fresh QUAT	Fresh Na ₂ B ₄ O ₇	Fresh Na ₄ EDTA	ACN feed	Aqueous feed	ACN solvent
From		BL	BL	TK-103	TK-104	TK-105	TK-106	TK-101	TK-102	TK-102
To		TK-101	TK-102	TK-102	TK-102	TK-102	TK-102	TK-107	TK-107	D-101
Temperature (°C)		Amb	Amb	Amb	Amb	Amb	Amb	Amb	Amb	Amb
Pressure (psia)		50	50	50	50	50	50	50	50	50
Phase		Liq	Liq	Liq	Liq	Liq	Liq	Liq	Liq	Liq
Total flow (mt/hr)		35.67	6.83	0.782	0.0249	0.0568	0.0234	14.62	7.7171	21.05
Components	MW	Boiling pt °C								
Hydrogen	2.00	-253								
Methane	16.00	-164								
Ammonia	17.00	-28								
Water	18.00	100	6.83						6.83	
Hydrogen cyanide	27.03	26								
Nitrogen	28	-196								
Oxygen	32	-183								
Carbon dioxide	44	-57								
Sodium hydroxide	40	1,388								
Butadiene	54	-4								
Acrylonitrile	53	77	35.67					14.62	21.05	
Propionitrile	55	97								
Cyclohexane	84.16	81								
2-Methyl-3-butenitrile	81	124								
3-Pentenitrile	81	144								
2-Methylglutaronitrile	108.14	270								
Ethyl succinonitrile	108.14	264								
Hexamethylenediamine	116.2	205								
Adiponitrile	108.14	295								
Phenol	94.11	182								
Cresol (alpha)	108.3	191								
R-401 lite HC products	na	na								
R-401 heavy HC products	na	na								
Ammonium hydroxide	35	38								
Triphenylboron	242	203								
Nickel phosphorus ligand catalyst	na	na								
Mono-ammonium phosphate	115	na								
Diammonium phosphate	132	na								
Heavies										
Na ₂ HPO ₄		0.782							0.782	
QUAT						0.0249			0.0249	
Na ₂ B ₄ O ₇						0.0568			0.0568	
Na ₂ EDTA						0.0234			0.0234	

Table 7.5 (continued): Stream-by-stream material balance (mt/hr)

		Stream number								
		10	11	12	13	14	15	16	17	18
Label		Recycle adipo	Emulsion feed	Cell product	Cell vent gas	Extrac drum product	Organic phase	Aqueous phase	Wash water	Waste water
From		TK-202	TK-107	C-101	R-101	D-101	D-103 S/S	D-103 B/S	BL	D-106
To		TK-107	R-101	D-101	Vent	D-103	D-104	TK-107	D-104	WWT
Temperature (°C)		Amb	55	55	40	55	35	35	25	25
Pressure (psia)		50	25	20	15	15	50	50	50	50
Phase		Liq	Emulsion	Emulsion	Vapor	Emulsion	Liq	Liq	Liq	Liq
Total flow (mt/hr)		62.95	349.72	344.79	4.93	411.85	182.9	228.95	25.2	25.5
Components	MW	Boiling pt °C								
Hydrogen	2.00	-253								
Methane	16.00	-164								
Ammonia	17.00	-28								
Water	18.00	100	168.21	162.66		162.66	1.63	161.03	25.2	25.2
Hydrogen cyanide	27.03	26								
Nitrogen	28	-196								
Oxygen	32	-183								
Carbon dioxide	44	-57								
Sodium hydroxide	40	1,388								
Butadiene	54	-4								
Acrylonitrile	53	77	59.45	23.78		90.84	82.79	8.05		
Propionitrile	55	97		1.71		1.71	1.62	0.09		
Cyclohexane	84.16	81								
2-Methyl-3-butenenitrile	81	124								
3-Pentenitrile	81	144								
2-Methylglutaronitrile	108.14	270								
Ethyl succinonitrile	108.14	264								
Hexamethylenediamine	116.2	205								
Adiponitrile	108.14	295	62.95	62.95	96.48	96.48	95.51	0.97		
Phenol	94.11	182								
Cresol (alpha)	108.3	191								
R-401 lite HC products	na	na								
R-401 heavy HC products	na	na								
Ammonium hydroxide	35	38								
Triphenylboron	242	203								
Nickel phosphorus ligand catalyst	na	na								
Mono-ammonium phosphate	115	na								
Diammonium phosphate	132	na								
Heavies				1.05		1.05	1.05			
Na ₂ HPO ₄			52.46	52.46		52.46	0.26	52.2		0.26
QUAT			1.4	1.4		1.4	0.01	1.39		0.01
Na ₂ B ₄ O ₇			3.5	3.5		3.5	0.02	3.48		0.02
Na ₂ EDTA			1.75	1.75		1.75	0.01	1.74		0.01

Table 7.5 (continued): Stream-by-stream material balance (mt/hr)

		Stream number								
		19	20	21	22	23	24	25	26	27
Label		Organic phase	Evaporator O/H	Evaporator product	Crystallizer recycle	Crystallizer slurry	Centrifuge filtrate	Makeup water	Additives recycle	C-201 distillate
From		D-106	E-103	E-103	P-111	CR-101	CN-101	BL	D-105	C-201
To		TK--201	E-104	CR-101	CR-101	CN-101	WWT	D-105	TK-107	C-203
Temperature (°C)		25	80	80	40	40	50	25	35	50
Pressure (psia)		50	15	50	50	25	25	50	50	50
Phase		Liq	Vap	Liq	Liq	Slurry	Liq	Liq	Liq	Liq
Total flow (mt/hr)		190.08	9.11	219.84	43.972	21.984	15.4411	15.2	21.7429	92.65
Components	MW	Boiling pt °C								
Hydrogen	2.00	-253								
Methane	16.00	-164								
Ammonia	17.00	-28								
Water	18.00	100								
Hydrogen cyanide	27.03	26								
Nitrogen	28	-196								
Oxygen	32	-183								
Carbon dioxide	44	-57								
Sodium hydroxide	40	1,388								
Butadiene	54	-4								
Acrylonitrile	53	77	90.84	8.05						90.84
Propionitrile	55	97	1.71	0.09						1.71
Cyclohexane	84.16	81								
2-Methyl-3-butenenitrile	81	124								
3-Pentenitrile	81	144								
2-Methylglutaronitrile	108.14	270								
Ethyl succinonitrile	108.14	264								
Hexamethylenediamine	116.2	205								
Adiponitrile	108.14	295	96.48	0.97						
Phenol	94.11	182								
Cresol (alpha)	108.3	191								
R-401 lite HC products	na	na								
R-401 heavy HC products	na	na								
Ammonium hydroxide	35	38								
Triphenylboron	242	203								
Nickel phosphorus ligand catalyst	na	na								
Mono-ammonium phosphate	115	na								
Diammonium phosphate	132	na								
Heavies		1.05								0.1
Na2HPO4				52.2	10.44	5.22	0.522		4.698	
QUAT				1.39	0.278	0.139	0.0139		0.1251	
Na2B4O7				3.48	0.696	0.348	0.0348		0.3132	
Na2EDTA				1.74	0.348	0.174	0.0174		0.1566	

Table 7.5 (continued): Stream-by-stream material balance (mt/hr)

	Stream number								
	28	29	30	31	32	33	34	35	36
Label	C-201 B/S product	C-203 distillate	C-203 B/S product	Propionitrile product	Heavies	ADN product	Heavies	Heavies	ADN to HMDA
From	C-201	C-203	C-203	C-204 O/H product	C-204 B/S product	C-202	C-202 B/S product	E-209	TK-202
To	C-202	TK-107	C-204	TK-203	Incineration	TK-202	E-209	Incineration	R-401
Temperature (°C)	250	77	97	97	130	240	280	280	40
Pressure (psia)	50	50	50	50	50	50	50	50	50
Phase	Liq	Liq	Liq	Liq	Liq	Liq	Liq	Liq	Liq
Total flow (mt/hr)	97.43	44.83	1.81	1.71	0.1	96.48	10.45	0.95	33.53
Components	MW	Boiling pt °C							
Hydrogen	2.00	-253							
Methane	16.00	-164							
Ammonia	17.00	-28							
Water	18.00	100							
Hydrogen cyanide	27.03	26							
Nitrogen	28	-196							
Oxygen	32	-183							
Carbon dioxide	44	-57							
Sodium hydroxide	40	1,388							
Butadiene	54	-4							
Acrylonitrile	53	77							
Propionitrile	55	97							
Cyclohexane	84.16	81							
2-Methyl-3-butenenitrile	81	124							
3-Pentenitrile	81	144							
2-Methylglutaronitrile	108.14	270							
Ethyl succinonitrile	108.14	264							
Hexamethylenediamine	116.2	205							
Adiponitrile	108.14	295	96.48			96.48	9.5		33.53
Phenol	94.11	182							
Cresol (alpha)	108.3	191							
R-401 lite HC products	na	na							
R-401 heavy HC products	na	na							
Ammonium hydroxide	35	38							
Triphenylboron	242	203							
Nickel phosphorus ligand catalyst	na	na							
Mono-ammonium phosphate	115	na							
Diammonium phosphate	132	na							
Heavies		0.95		0.1		0.1		0.95	0.95
Na ₂ HPO ₄									
QUAT									
Na ₂ B ₄ O ₇									
Na ₂ EDTA									

Table 7.5 (continued): Stream-by-stream material balance (mt/hr)

		Stream number								
		37	56	57	58	59	60	61	62	63
Label		ACN recycle	ADN feed to hydrogenation	NH ₄ OH feed	Water addition	H ₂ make-up	H ₂ recycle	Rx gas purge	Rx product	Degassed Rx product
From		C-203 O/H	TK-303	TK-401	TK-402	OSBL	K-401	R-401	R-401	D-401
To		D-101	R-401	R-401	R-401	K-401	R-401	Burner Line	D-401	C-401
Temperature (°C)		77	85	25	25	225	225	85	85	80
Pressure (psia)		50	50	650	650	650	650	600	600	30
Phase		Liq	Liq	Liq	Liq	Gas	Gas	Gas	Liq	Liq
Total flow (mt/hr)		46.01	30.03	0.025	0.015	2.41	8.75	0.22	44.35	35.6
Components	MW	Boiling pt °C								
Hydrogen	2.00	-253					2.41	8.75	0.22	8.75
Methane	16.00	-164								
Ammonia	17.00	-28								
Water	18.00	100		0.0175	0.015				0.05	0.05
Hydrogen cyanide	27.03	26								
Nitrogen	28	-196								
Oxygen	32	-183								
Carbon dioxide	44	-57								
Sodium hydroxide	40	1,388								
Butadiene	54	-4								
Acrylonitrile	53	77	46.01							
Propionitrile	55	97								
Cyclohexane	84.16	81								
2-Methyl-3-butenenitrile	81	124								
3-Pentenitrile	81	144								
2-Methylglutaronitrile	108.14	270								
Ethyl succinonitrile	108.14	264								
Hexamethylenediamine	116.2	205							31.71	31.71
Adiponitrile	108.14	295	30.03						3.34	3.34
Phenol	94.11	182								
Cresol (alpha)	108.3	191								
R-401 lite HC products	na	na							0.3	0.3
R-401 heavy HC products	na	na							0.2	0.2
Ammonium hydroxide	35	38	0.0075							
Triphenylboron	242	203								
Nickel phosphorus ligand catalyst	na	na								
Mono-ammonium phosphate	115	na								
Diammonium phosphate	132	na								
Heavies										
Na ₂ HPO ₄										
QUAT										
Na ₂ B ₄ O ₇										
Na ₂ EDTA										

Table 7.5 (concluded): Stream-by-stream material balance (mt/hr)

			Stream number							
			64	65	66	67	68	69	70	71
Label			Water	C-401 B/S	C-402 O/H product	Heavy by-products	Lite by-products	C-403 B/S	HMDA product	ADN recycle
From			C-401 O/H	C-401	C-492 O/H	C-402 B/S	C-403 O/H	C-403	C-404 O/H	C-404 B/S
To			WWT	C-402	C-403	Incineration	Incineration	C-404	TK-403	R-401
Temperature (°C)			100	225	160	210	120	160	40	180
Pressure (psia)			50	50	50	50	50	50	50	50
Phase			Liq	Liq	Liq	Liq	Liq	Liq	Liq	Liq
Total flow (mt/hr)			0.05	35.55	35.35	0.2	0.3	35.05	31.71	3.34
Components	MW	Boiling pt °C								
Hydrogen	2.00	-253								
Methane	16.00	-164								
Ammonia	17.00	-28								
Water	18.00	100	0.05							
Hydrogen cyanide	27.03	26								
Nitrogen	28	-196								
Oxygen	32	-183								
Carbon dioxide	44	-57								
Sodium hydroxide	40	1,388								
Butadiene	54	-4								
Acrylonitrile	53	77								
Propionitrile	55	97								
Cyclohexane	84.16	81								
2-Methyl-3-butenitrile	81	124								
3-Pentenenitrile	81	144								
2-Methylglutaronitrile	108.14	270								
Ethyl succinonitrile	108.14	264								
Hexamethylenediamine	116.2	205	31.71	31.71			31.71	31.71		
Adiponitrile	108.14	295	3.34	3.34			3.34	3.34		
Phenol	94.11	182								
Cresol (alpha)	108.3	191								
R-401 lite HC products	na	na	0.3	0.3	0.3					
R-401 heavy HC products	na	na	0.2	0.2						
Ammonium hydroxide	35	38								
Triphenylboron	242	203								
Nickel phosphorus ligand catalyst	na	na								
Mono-ammonium phosphate	115	na								
Diammonium phosphate	132	na								
Heavies										
Na ₂ HPO ₄										
QUAT										
Na ₂ B ₄ O ₇										
Na ₂ EDTA										

Equipment list with duty specifications

Based upon the process flow diagrams and stream-by-stream material balance, we have prepared an equipment list for the ISBL major tagged equipment, including duty specifications. The equipment list is presented in the table below.

Table 7.6: ISBL equipment list with duty specifications

	Buildings	Floor area (ft ²)	# above ground stories	Sidewall materials/ insulated?	Roof type/ insulated?	Fit for occupancy?	HVAC (scfm)	Heating duty (MM-Btu/hr)	Refrig duty (tons/hr)	Sanitary facilities?	Crane capacity (mt)
B-101	Process control house	3,000	1	Reinf concrete	Reinf concrete + membrane	Yes	400	0.75	35	Yes	NO
B-102	Cell building (Butler bldg)	15,000	1 (20 ft high)	14 ga galv steel + insul	removable 14 ga galv steel	No	No	No	No	Yes	25 ton gantry

	Centrifuges	# installed	Materials of construction	L x D (ft)	DesP (psia)	DesT (°C)	Duty (BHP)	Type (bowl or screen)	Screen opening (mils)
CN-101	Purge centrifuge	1	304SS	8 x 8	50	150	25	Dorr-Oliver MercoBowl	0.5

	Crystallizers	# installed	Materials of construction	L x D (m)	DesP (psia)	DesT (°C)	Duty (MM-btu/hr)	Suspension or draft tube?	Surf area (ft ²)
CR-101	Purge crystallizer	1	304SS	40 x 8	50	150	4.8	Suspension	505

	Distillation columns	# installed	Materials of construction	L x D (ft)	DesP (psia)	DesT (°C)	# of trays	Internals details
C-201	Lites column	1	CS	68 x 20	50	275	24	sieve trays
C-202	ADN column	1	CS	124 x 16	50	305	52	structured packing
C-203	ACN column	1	CS	172 x 18	50	305	76	structured packing
C-204	PN column	1	CS	124 x 3	50	305	52	sieve trays
C-401	Dewatering column	1	304SS	68 x 14	50	250	24	sieve trays
C-402	ADN column	1	CS	68 x 14	full vac	235	24	structured packing
C-403	Lites column	1	CS	52 x 14	full vac	195	16	structured packing
C-404	HMDA column	1	CS	68 x 14	full vac	205	24	structured packing

Table 7.6 (continued): ISBL equipment list with duty specifications

	Drums	# installed	Materials of construction	Vol (ft ³)	L x D (ft)	DesP (psia)	DesT (°C)	Orientation (ASME code vessels)
D-101	Extraction drum	1	304SS	6,782	60 x 12	50	100	vert
D-102	E-104 receiver	1	304SS	678	24 x 6	50	125	horiz
D-103	Extraction settler	1	304SS	6,782	60 x 12	50	100	horiz
D-104	Water wash drum	1	304SS	1,608	32 x 8	50	100	vert
D-105	Purge mixing drum	1	304SS	509	18 x 6	50	100	horiz
D-106	Water wash settler	1	304SS	5,426	48 x 12	50	100	horiz
D-201	E-202 receiver	1	CS	1,608	32 x 8	50	100	horiz
D-202	K-201 K/O Drum	1	CS	201	16 x 4	50	100	vert
D-203	E-203 receiver	1	CS	85	12 x 3	50	100	horiz
D-204	E-205 receiver	1	CS	1,608	32 x 8	50	275	horiz
D-205	K-202 K/O drum	1	CS	201	16 x 4	50	275	vert
D-206	E-206 receiver	1	CS	85	12 x 3	50	275	horiz
D-207	E-207 receiver	1	CS	678	24 x 6	50	125	horiz
D-208	E-211 receiver	1	CS	85	12 x 3	50	275	horiz
D-401	K-401 K/O drum	1	304SS	1,608	32 x 8	600	125	vert
D-402	E-403 receiver	1	CS	1,536	32 x 8	50	100	horiz
D-403	K-402 K/O drum	1	CS	170	24 x 3	50	150	vert
D-404	E-406 receiver	1	CS	1,536	32 x 8	50	100	horiz
D-405	E-408 receiver	1	CS	1,536	32 x 8	50	100	horiz
D-406	K-403 K/O drum	1	CS	170	24 x 3	50	150	vert
D-407	E-411 receiver	1	CS	1,536	32 x 8	50	100	horiz
D-408	K-404 K/O drum	1	CS	170	24 x 3	50	150	vert

Table 7.6 (continued): ISBL 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 (°C) tube/shell	HX configuration
E-101	Emulsion Heater	1	CS/304SS	77.1	8,117	50/100	100/150	S&T-API650
E-102	Cell O/H cooler	1	CS/CS	0.14	91	50/na	100/na	API661-air cooled HX
E-103	Purge evaporator	1	CS/304SS	5.27	555	75/50	75/125	S&T-API650
E-104	Purge condenser	1	CS/304SS	5.02	529	75/50	75/125	S&T-API650
E-105	Crystallizer cooler	1	CS/304SS	48.5	5,103	75/50	75/125	S&T-API650
E-201A/B	C-201 reboilers	2	CS/CS	76.5	8,064	75/50	75/125	S&T-API650
E-202	C-201 condenser	1	CS/304SS	153	16,128	50/75	75/75	S&T-API650
E-203	K-201 condenser	1	CS/304SS	15.3	1,613	50/75	75/75	S&T-API650
E-204A/B	C-202 reboilers	2	CS/CS	80	8,400	50/75	75/305	S&T-API650
E-205	C-202 condenser	1	CS/304SS	160	16,795	50/75	75/260	S&T-API650
E-206	K-202 condenser	1	CS/304SS	16	1,680	50/75	305	S&T-API650
E-207	C-203 condenser	1	CS/304SS	74.1	7,801	50/75	75/135	S&T-API650
E-208	C-203 reboiler	1	CS/CS	77.8	8,191	500/50	250/175	S&T-API650
E-209A/B	Scraped surface evaporator	2	304SS/304SS	5.8	1,213	50/75	305/325	Alfa Laval or equiv
E-210	ADN cooler	1	CS/304SS	21.3	2,239	75/50	75/265	S&T-API650
E-211	C-204 condenser	1	CS/304SS	3.8	397	75/50	75/130	S&T-API650
E-212	C-204 reboiler	1	304SS/CS	4.00	417	275/50	250/140	S&T-API650
E-213	PN cooler	1	CS/304SS	0.38	397	75/75	75/150	S&T-API650
E-401	R-401 cooler	1	304SS/304SS	9.8	1,029	50/75	100/100	S&T-API650
E-402	C-402 reboiler	1	304SS/CS	81.8	8,616	50/75	100/175	S&T-API650
E-403	C-402 condenser	1	304SS/304SS	77.9	8,205	50/75	100/175	S&T-API650
E-404	K-402 condenser	1	304SS/304SS	7.8	821	50/75	100/175	S&T-API650
E-405	C-401 reboiler	1	304SS/CS	0.46	48	50/50	150/75	S&T-API650
E-406	C-401 condenser	1	304SS/304SS	0.44	46	50/50	150/75	S&T-API650
E-407	C-403 reboiler	1	304SS/CS	0.69	74	50/75	150/100	S&T-API650
E-408	C-403 condenser	1	304SS/304SS	0.66	70	50/75	150/100	S&T-API650
E-409	K-403 condenser	1	304SS/304SS	0.07	8	50/75	150/100	double pipe
E-410	C-404 reboiler	1	304SS/CS	73.42	7,728	50/75	100/165	S&T-API650
E-411	C-404 condenser	1	304SS/304SS	69.92	7,360	50/75	100/165	S&T-API650
E-412	K-404 condenser	1	304SS/304SS	7	736	50/75	100/165	S&T-API650
E-413	HMDA cooler	1	304SS/304SS	2.8	294	50/75	100/165	S&T-API650
E-414A/B	TK-403 tank heaters	2	304SS	2.5	250	100/na	175/na	S&T-API650
E-415	ADN heater	1	304SS/CS	6.6	697	100/100	150/150	S&T-API650

	Filters	# installed	Materials of construction	Flow rate (lbs/hr)	DesP (psia) tubes	DesT (°C) tubes	Opening size (microns)	Fluid
FL-101A-X	Cell flame arresters	24	304SS	453	50	100		O ₂ vapor
FL-102A-X	Emulsion filters	24	304SS	31,678	75	100	0.5	emulsion

Table 7.6 (continued): ISBL equipment list with duty specifications

	Compressors	# installed	Fluid	BHP	SCFM	Pin (psia)	Pout (psia)	Materials of construction/ design details	Machine type	K-lbs/hr	mt/hr	Avg MW
K-101	Cell induced fan	1	O ₂ -rich vapor	1.44E+02	2.28E+03	15	30	304SS	LP induction fan	10.87065	4.93	32
K-201	C-201 vacuum pump	1	ACN + PN	3.39E+02	7.12E+03	10	15	304SS	Sliding vane	81.7173	37.06	77
K-202	C-202 vacuum pump	1	Adipo-nitrile	1.26E+03	5.29E+03	2	15	304SS	Sliding vane	85.09095	38.59	108
K-401	H ₂ compressor	1	H ₂	2.67E+04	6.48E+04	50	650	CrMo	Centrifugal	1.93E+01	8.75	2
K-402	C-402 vacuum pump	1	Adipo-nitrile	1.54E+02	4.85E+02	2	20	304SS	Sliding vane	7.81E+00	3.54	108
K-403	C-403 vacuum pump	1	ADN-lites	1.30E+00	4.11E+00	2	20	304SS	Sliding vane	6.62E-02	0.03	108
K-404	C-404 vacuum pump	1	HMDA	1.28E+02	4.05E+02	2	20	304SS	Sliding vane	6.99E+00	3.17	116

	Mixers and agitators	# installed	Materials of construction	BHP	DesT (°C)	Liquid	Viscosity (cs)	Mixer type
M-101	TK-102 mixer	1	304SS	10	125	H ₂ O+additives	1.05	side entering tank mixer
M-102	Emulsion mixer	1	304SS	150	125	emulsion	0.75	side entering tank mixer
M-103	D-101 mixer	1	304SS	50	125	emulsion	0.75	top entering mixer
M-104	D-104 mixer	1	304SS	30	125	H ₂ O+organics	0.75	top entering mixer
M-105	D-105 mixer	1	304SS	15	125	water	1.05	top entering mixer
M-401A/B	TK-403 agitators	2	304SS	50	125	HMDA	5	Tank side entering

Table 7.6 (continued): ISBL equipment list with duty specifications

Pumps	# installed	Materials of construction	gpm x hd (ft)	Liquid	DesP (psia)	DesT (°C)	Type pump	Pump BHP
P-101A/B ACN feed pumps	2	CS	157 x 115	Acrylonitrile	75	100	API610-Horiz Centrif	4.6
P-102A/B Water feed pumps	2	304SS	34 x 115	Water	75	100	API610-Horiz Centrif	0.99
P-103A/B Na ₂ HPO ₄ pumps	2	304SS	3.5 x 15	Na ₂ HPO ₄	75	100	API675-Meter Pumps	0.1
P-104A/B QUAT pumps	2	304SS	0.1 x 115	QUAT	75	100	API675-Meter Pumps	0.003
P-105A/B Na ₂ B ₄ O ₇ pumps	2	304SS	0.25 x 115	Na ₂ B ₄ O ₇	75	100	API675-Meter Pumps	0.007
P-106A/B Na ₄ EDTA pumps	2	304SS	0.15 x 115	Na ₄ EDTA	75	100	API675-Meter Pumps	0.004
P-107A/B Emulsion pumps	2	304SS	1,542 x 115	Emulsion	75	125	API610-Horiz Centrif	44.8
P-108A/B D-102 pumps	2	CS	40 x 115	Organics	75	100	API610-Horiz Centrif	1.2
P-109A/B D-103 B/S pumps	2	304SS	1,010 x 115	Aqueous soln	75	100	API610-Horiz Centrif	29.3
P-110A/B D-103 S/S pumps	2	CS	807 x 115	Organics	75	100	API610-Horiz Centrif	23.4
P-111A/B Crystallizer circulation pumps	2	304SS	194 x 115	Aqueous soln	75	100	API610-Horiz Centrif	5.6
P-112A/B Crystallizer slurry pumps	2	304SS	97 x 115	Crystal slurry	75	100	API676-Moyno	2.8
P-113A/B Purge solution pumps	2	304SS	96 x 115	Aqueous soln	75	100	API610-Horiz Centrif	2.8
P-114A/B D-106 S/S pumps	2	CS	838 x 115	Organics	75	100	API610-Horiz Centrif	24.3
P-115A/B D-106 B/S pumps	2	304SS	112 x 115	Wasteater	75	100	API610-Horiz Centrif	3.3
P-116A/B Evaporator discharge pumps	2	304SS	970 x 115	Aqueous soln	75	100	API610-Horiz Centrif	28.2
P-201A/B Distillation feed pumps	2	CS	838 x 115	ADN crude	75	100	API610-Horiz Centrif	24.3
P-202A/B C-201 B/S pumps	2	CS	1,719 x 115	ADN crude	75	275	API610-Horiz Centrif	49.9
P-203A/B C-201 reflux pumps	2	CS	1,702 x 115	PN crude	75	100	API610-Horiz Centrif	49.4
P-204A/B D-203 pumps	2	CS	163 x 115	PN crude	75	100	API610-Horiz Centrif	4.7
P-205A/B C-202 B/S pumps	2	CS	184 x 115	Heavies	75	305	API610-Horiz Centrif	5.3
P-206A/B C-202 reflux pumps	2	CS	1,702 x 115	Adiponitrile	75	275	API610-Horiz Centrif	49.4
P-207A/B D-206 pumps	2	CS	170 x 115	Adiponitrile	75	275	API610-Horiz Centrif	4.9
P-208A/B C-203 B/S pumps	2	CS	32 x 115	PN crude	75	140	API610-Horiz Centrif	0.9
P-209A/B C-203 reflux pumps	2	CS	791 x 115	ACN	75	125	API610-Horiz Centrif	23.1
P-210A/B ADN product pumps	2	CS	148 x 115	ADN	75	75	API610-Horiz Centrif	4.3
P-211A/B ADN recycle pumps	2	CS	278 x 115	ADN	75	75	API610-Horiz Centrif	8.1
P-212A/B C-204 reflux pumps	2	CS	30 x 115	PN	75	140	API610-Horiz Centrif	0.9
P-213A/B C-204 B/S pumps	2	CS	2 x 115	Heavies	75	180	API675-Meter Pumps	0.06
P-214A/B TK-203 pumps	2	CS	7.5 x 115	PN	75	75	API610-Horiz Centrif	0.2
P-215A/B E-209 pumps	2	CS	2.2 x 115	Heavies	75	305	API675-Meter Pumps	0.06
P-401A/B NH ₄ OH pumps	2	304SS	0.1 x 115	NHOH	50	100	API675-Meter Pumps	0.0026
P-402A/B Demin water pumps	2	304SS	0.07 x 115	Water	50	100	API675-Meter Pumps	0.0018
P-403A/B R-401 pumps	2	304SS	196 x 115	HMDA soln	650	105	API610-Horiz Centrif	5.16
P-404A/B C-402 B/S pumps	2	304SS	3.5 x 115	Heavies	50	330	API610-Horiz Centrif	0.09
P-405A/B C-402 reflux pumps	2	304SS	624 x 115	HMDA soln	50	200	API610-Horiz Centrif	16.3
P-406A/B C-401 B/S pumps	2	304SS	627 x 115	HMDA soln	50	250	API610-Horiz Centrif	16.3
P-407A/B C-401 reflux pumps	2	304SS	0.9 x 115	Water	50	125	API675-Meter Pumps	0.023
P-408A/B C-403 B/S pumps	2	304SS	618 x 115	HMDA soln	50	185	API610-Horiz Centrif	16.1
P-409A/B C-403 reflux pumps	2	304SS	5.3 x 115	Lites	50	145	API610-Horiz Centrif	0.138
P-410A/B C-404 B/S pumps	2	304SS	59 x 1,500	ADN soln	625	210	API610-Horiz Centrif	20.06
P-411A/B C-404 reflux pumps	2	304SS	559 x 115	HMDA	50	165	API610-Horiz Centrif	14.6
P-412A/B HMDA product pumps	2	304SS	140 x 115	HMDA	50	100	API610-Horiz Centrif	3.65

Reactors	# installed	Materials of construction	Vol (ft ³)	L x D (ft)	DesP (psia)	DesT (°C)	Internals
R-101A-X Dimerization cells	24	PP	768	12 x 8 x 8	ATM	100	CS plates w Cd layers
R-401A/B ADN reactors	2	316LSS	3,140	40 x 10	625	110	Cooling jacket

Table 7.6 (concluded): ISBL equipment list with duty specifications

	Specially packaged equipment	# installed	Duty	Details
S-101	Dowtherm hot oil system	1	150 MM-Btu/hr	
S-102	Glycol chiller system	1	400 tons	
S-103	Vapor stream incinerator w header	1	5 MM-Btu/hr	
S-104	Liquids incinerator	1	50 MM-Btu/hr	
S-105	2-flare system with blowdown drums & header	1	500 MM-Btu/hr + 18 in LP header	John Zink or equiv
S-106	Process computer control system	1	1,000 loops at 6 operator stations	Honeywell Experion or equiv
S-107A-X	Cell Power Paks	24	by vendor	

	Storage tanks	# installed	Materials of construction	Vol (m³)	L x D (ft)	DesP (psia)	DesT (°C)	Type tank with details (API?)
TK-101	ACN feed tank	1	CS	10,073	14.7 x 29.4	15	50	API 650 with floating roof
TK-102	Water tank	1	HDPE	1,916	8.5 x 17	15	50	HDPE ASTM D1998
TK-103	Na ₂ HPO ₄ soln tank	1	HDPE	221	4.1 x 8.2	15	50	HDPE ASTM D1998
TK-104	QUAT soln tank	1	HDPE	7.03	1.3 x 2.6	15	50	HDPE ASTM D1998
TK-105	Na ₂ B ₄ O ₇ soln tank	1	HDPE	16	1.7 x 3.4	15	50	HDPE ASTM D1998
TK-106	Na ₄ EDTA soln tank	1	HDPE	6.61	1.3 x 2.6	15	50	HDPE ASTM D1998
TK-107	Emulsion tank	1	CS epoxy lined	98,761	31.6 x 63.2	15	125	API 650 with floating roof
TK-201	Distillation feed tank	1	CS	53,678	25.8 x 51.6	15	125	API 650
TK-202A/B	ADN day tanks	2	CS	13,623	16.3 x 32.6	15	125	API 650
TK-203A/B	PN tanks	2	CS	241	4.25 x 8.5	15	125	API 650 with floating roof
TK-401	Ammonium hydroxide tank	1	304SS	200	4 x 8	ATM	ATM	API 650
TK-402	Demin water tank	1	FRP	200	4 x 8	ATM	ATM	FRP ASTM D 3299
TK-403A/B	HMDA tanks	2	304SS	5,426	12 x 24	ATM	ATM	API 650

	Pressure vessels (API 510-ASME BPVC)	# installed	Materials of construction	Vol (m³)	L x D (ft)	Orientation	DesP (psia)	DesT (°C)
V-101ABCD	Cell activated carbon filters	4	CS	1,206	24 x 8	vert	50	150
V-102A/B	Low boiler AC absorbers	2	CS	1,206	24 x 8	vert	100	150

Itemized capital cost estimate

Combining the ISBL duty specifications with stream by stream material balance data, we have prepared the following itemized capital cost estimate using the PEPCOST program at an index of 1,164, and a location factor of 1.00. When segmented by type of ISBL equipment, we present the results in the table below.

Table 7.7: Itemized capital cost estimate by equipment type

	FOB (1 unit)	FOB (all units)	Installation (1 unit)	Installation (all units)	Installed cost (all units)
Buildings	1,050.0	1,050.0	2,475.0	2,475.0	3,525.0
Reactors	938.9	16,155.8	559.3	11,788.5	27,944.3
Distillation columns	4,283.5	4,283.5	8,946.6	8,946.6	13,230.1
Drums	1,849.6	1,849.6	1,248.8	1,248.8	3,098.4
Filters	98.3	2,359.2	86.2	2,068.8	4,428.0
Heat exchangers	8,959.7	10,253.3	2,128.7	2,467.0	12,720.2
Pumps	956.9	1,913.9	3,044.2	6,088.3	8,002.2
Compressors	5,951.0	5,951.0	5,016.2	5,016.2	10,967.2
ISBL storage tanks	2,760.5	3,338.8	1,949.6	2,161.7	5,500.5
Pressure vessels	149.5	448.6	122.8	368.5	817.0
Fired heaters	0.0	0.0	0.0	0.0	0.0
Mixers and agitators	762.5	887.5	260.6	298.1	1,185.6
Steam turbine drivers	0.0	0.0	0.0	0.0	0.0
Special packaged equipment	20,950.0	25,550.0	45,550.0	50,150.0	75,700.0
Centrifuges	458.0	458.0	126.0	126.0	584.0
Crystallizers	3,040.0	3,040.0	595.0	595.0	3,635.0
Total	52,208.4	77,539.1	72,108.9	93,798.4	171,337.5

We have also segmented the major ISBL equipment cost by section of plant. That data is presented in the table below.

Table 7.8: Itemized capital cost estimate by section of plant

Section	Description	Installed cost (all units)
100	Acrylonitrile hydrodimerization	47,497.0
200	Adiponitrile purification	31,574.3
400	Adiponitrile hydrogenation	16,566.2
	Special purpose and packaged	75,700.0
	Total	171,337.5

The complete listing of ISBL itemized costs by equipment number is presented in the table below.

Table 7.9: Itemized capital cost estimate

		Floor area (ft ²)	FOB (1 unit)	FOB (all units)	Install (1 unit)	Install (all units)	Installed cost (all units)
Buildings							
B-101	Process control house	3,000	300.0	300.0	225.0	225.0	525.0
B-102	Cell building (Butler bldg)	15,000	750.0	750.0	2,250.0	2,250.0	3,000.0

Table 7.9 (continued): Itemized capital cost estimate

		# Installed	FOB (1 unit)	FOB (all units)	Install (1 unit)	Install (all units)	Installed cost (all units)
Centrifuges							
CN-101	Purge centrifuge	1	458.0	458.0	126.0	126.0	584.0
Crystallizers							
CR-101	Purge crystallizer	1	3,040.0	3,040.0	595.0	595.0	3,635.0
Distillation columns							
C-201	Lites column	1	484.6	484.6	1,523.0	1,523.0	2,007.6
C-202	ADN column	1	429.4	429.4	1,923.3	1,923.3	2,352.7
C-203	ACN column	1	752.2	752.2	2,627.2	2,627.2	3,379.4
C-204	PN column	1	212.8	212.8	552.7	552.7	765.5
C-401	Dewatering column	1	759.0	759.0	634.9	634.9	1,393.9
C-402	ADN column	1	585.6	585.6	585.9	585.9	1,171.5
C-403	Lites column	1	474.3	474.3	528.3	528.3	1,002.6
C-404	HMDA column	1	585.6	585.6	571.3	571.3	1,156.9
Drums							
D-101	Extraction drum	1	293.4	293.4	97.5	97.5	390.9
D-102	E-104 receiver	1	67.1	67.1	55.3	55.3	122.4
D-103	Extraction settler	1	248.0	248.0	73.2	73.2	321.2
D-104	Water wash drum	1	123.7	123.7	65.8	65.8	189.5
D-105	Purge mixing drum	1	59.1	59.1	54.0	54.0	113.1
D-106	Water wash settler	1	222.7	222.7	70.9	70.9	293.6
D-201	E-202 receiver	1	69.2	69.2	58.6	58.6	127.9
D-202	K-201 K/O drum	1	38.1	38.1	48.3	48.3	86.4
D-203	E-203 receiver	1	24.4	24.4	47.2	47.2	71.6
D-204	E-205 receiver	1	69.2	69.2	58.6	58.6	127.9
D-205	K-202 K/O drum	1	38.1	38.1	48.3	48.3	86.4
D-206	E-206 receiver	1	24.4	24.4	47.2	47.2	71.6
D-207	E-207 receiver	1	47.5	47.5	53.9	53.9	101.4
D-208	E-211 receiver	1	24.4	24.4	47.2	47.2	71.6
D-401	K-401 K/O drum	1	123.7	123.7	62.8	62.8	186.5
D-402	E-403 receiver	1	67.5	67.5	55.8	55.8	123.2
D-403	K-402 K/O drum	1	35.6	35.6	45.7	45.7	81.2
D-404	E-406 receiver	1	67.5	67.5	55.8	55.8	123.2
D-405	E-408 receiver	1	67.5	67.5	55.8	55.8	123.2
D-406	K-403 K/O drum	1	35.6	35.6	45.7	45.7	81.2
D-407	E-411 receiver	1	67.5	67.5	55.8	55.8	123.2
D-408	K-404 K/O drum	1	35.6	35.6	45.7	45.7	81.2

Table 7.9 (continued): Itemized capital cost estimate

		# Installed	FOB (1 unit)	FOB (all units)	Install (1 unit)	Install (all units)	Installed cost (all units)
Heat exchangers							
E-101	Emulsion heater	1	576.2	576.2	74.4	74.4	650.6
E-102	Cell O/H cooler	1	19.6	19.6	50.6	50.6	70.2
E-103	Purge evaporator	1	72.2	72.2	54.5	54.5	126.7
E-104	Purge condenser	1	68.6	68.6	54.3	54.3	122.9
E-105	Crystallizer cooler	1	404.6	404.6	68.7	68.7	473.3
E-201A/B	C-201 reboilers	2	573.3	1,146.6	74.3	148.5	1,295.1
E-202	C-201 condenser	1	1,080.0	1,080.0	123.9	123.9	1,203.9
E-203	K-201 condenser	1	166.6	166.6	59.2	59.2	225.8
E-204A/B	C-202 reboilers	2	275.4	550.8	65.9	131.8	682.6
E-205	C-202 condenser	1	1,134.0	1,134.0	130.1	130.1	1,264.1
E-206	K-202 condenser	1	172.0	172.0	59.5	59.5	231.5
E-207	C-203 condenser	1	559.1	559.1	73.8	73.8	632.9
E-208	C-203 reboiler	1	580.2	580.2	74.5	74.5	654.7
E-209A/B	Scraped surface evaporator	2	400.2	800.4	172.9	345.7	1,146.1
E-210	ADN cooler	1	214.8	214.8	61.4	61.4	276.2
E-211	C-204 condenser	1	55.3	55.3	53.6	53.6	108.9
E-212	C-204 reboiler	1	57.5	57.5	53.7	53.7	111.2
E-213	PN cooler	1	17.9	17.9	49.6	49.6	67.4
E-401	R-401 cooler	1	134.9	134.9	54.9	54.9	189.8
E-402	C-402 reboiler	1	339.7	339.7	63.7	63.7	403.4
E-403	C-402 condenser	1	652.9	652.9	72.0	72.0	724.9
E-404	K-402 condenser	1	113.3	113.3	54.0	54.0	167.3
E-405	C-401 reboiler	1	19.6	19.6	39.2	39.2	58.8
E-406	C-401 condenser	1	21.3	21.3	48.1	48.1	69.4
E-407	C-403 reboiler	1	20.7	20.7	39.7	39.7	60.4
E-408	C-403 condenser	1	22.4	22.4	48.6	48.6	71.0
E-409	K-403 condenser	1	18.0	18.0	46.7	46.7	64.7
E-410	C-404 reboiler	1	317.3	317.3	62.2	62.2	379.5
E-411	C-404 condenser	1	601.8	601.8	70.5	70.5	672.3
E-412	K-404 condenser	1	104.1	104.1	53.6	53.6	157.7
E-413	HMDA cooler	1	50.8	50.8	51.1	51.1	101.9
E-414A/B	TK-403 tank heaters	2	44.7	89.4	25.3	50.6	140.0
E-415	ADN heater	1	70.6	70.6	44.5	44.5	115.1
Filters							
FL-101A-X	Cell flame arresters	24	12.5	300.0	6.8	163.2	463.2
FL-102A-X	Emulsion filters	24	85.8	2,059.2	79.4	1,905.6	3,964.8

Table 7.9 (continued): Itemized capital cost estimate

		# installed	FOB (1 unit)	FOB (all units)	Install (1 unit)	Install (all units)	Installed cost (all units)
Compressors							
K-101	Cell induced fan	1	662.7	662.7	519.5	519.5	1,182.2
K-201	C-201 vacuum pump	1	1,270.0	1,270.0	1,234.0	1,234.0	2,504.0
K-202	C-202 vacuum pump	1	3,445.0	3,445.0	2,584.0	2,584.0	6,029.0
K-401	H ₂ compressor	1	564.7	564.7	662.2	662.2	1,226.9
K-402	C-402 vacuum pump	1	2.5	2.5	4.8	4.8	7.3
K-403	C-403 vacuum pump	1	2.5	2.5	4.8	4.8	7.3
K-404	C-404 vacuum pump	1	3.6	3.6	6.9	6.9	10.5
Mixers and agitators							
M-101	TK-102 mixer	1	25.0	25.0	8.8	8.8	33.8
M-102	Emulsion mixer	1	375.0	375.0	131.3	131.3	506.3
M-103	D-101 mixer	1	125.0	125.0	43.8	43.8	168.8
M-104	D-104 mixer	1	75.0	75.0	26.3	26.3	101.3
M-105	D-105 mixer	1	37.5	37.5	13.1	13.1	50.6
M-401A/B	TK-403 agitators	2	125.0	250.0	37.5	75.0	325.0
Pumps							
P-101A/B	ACN feed pumps	2	10.6	21.1	40.0	80.0	101.2
P-102A/B	Water feed pumps	2	12.8	25.6	25.1	50.1	75.7
P-103A/B	Na ₂ HPO ₄ pumps	2	26.4	52.7	56.6	113.1	165.8
P-104A/B	QUAT pumps	2	2.5	5.0	4.6	9.2	14.2
P-105A/B	Na ₂ B ₄ O ₇ pumps	2	2.5	5.0	4.6	9.2	14.2
P-106A/B	Na ₄ EDTA pumps	2	2.5	5.0	4.6	9.2	14.2
P-107A/B	Emulsion pumps	2	56.9	113.7	270.2	540.4	654.1
P-108A/B	D-102 pumps	2	11.1	22.1	28.4	56.8	78.9
P-109A/B	D-103 B/S pumps	2	80.2	160.4	188.5	377.0	537.4
P-110A/B	D-103 S/S pumps	2	47.0	93.9	160.2	320.4	414.3
P-111A/B	Crystallizer circulation pumps	2	30.2	60.3	58.5	117.0	177.3
P-112A/B	Crystallizer slurry pumps	2	22.2	44.3	40.7	81.5	125.8
P-113A/B	Purge solution pumps	2	22.1	44.2	40.6	81.2	125.3
P-114A/B	D-106 S/S pumps	2	23.6	47.1	105.8	211.6	258.7
P-115A/B	D-106 B/S pumps	2	18.1	36.1	34.7	69.4	105.5
P-116A/B	Evaporator discharge pumps	2	49.6	99.2	115.0	230.0	329.2
P-201A/B	Distillation feed pumps	2	31.1	62.2	105.8	211.6	273.8
P-202A/B	C-201 B/S pumps	2	49.0	98.0	175.1	350.2	448.2
P-203A/B	C-201 reflux pumps	2	48.7	97.4	173.9	347.8	445.2
P-204A/B	D-203 pumps	2	14.2	28.3	40.5	80.9	109.2
P-205A/B	C-202 B/S pumps	2	14.9	29.7	42.0	84.0	113.7
P-206A/B	C-202 reflux pumps	2	48.7	97.4	173.9	347.8	445.2
P-207A/B	D-206 pumps	2	14.4	28.8	41.0	81.9	110.7
P-208A/B	C-203 B/S pumps	2	8.6	17.2	24.9	49.8	67.0
P-209A/B	C-203 reflux pumps	2	30.1	60.2	102.5	205.0	265.2

Table 7.9 (continued): Itemized capital cost estimate

		# installed	FOB (1 unit)	FOB (all units)	Install (1 unit)	Install (all units)	Installed cost (all units)
P-210A/B	ADN product pumps	2	13.7	27.3	39.4	78.7	106.0
P-211A/B	ADN recycle pumps	2	17.7	35.3	54.5	109.1	144.4
P-212A/B	C-204 reflux pumps	2	8.5	17.0	24.8	49.5	66.5
P-213A/B	C-204 B/S pumps	2	2.5	5.0	4.6	9.2	14.2
P-214A/B	TK-203 pumps	2	6.7	13.4	17.6	35.1	48.5
P-215A/B	E-209 pumps	2	2.5	5.0	4.6	9.2	14.2
P-401A/B	NH ₄ OH pumps	2	2.5	5.0	4.6	9.2	14.2
P-402A/B	Demin water pumps	2	2.5	5.0	4.6	9.2	14.2
P-403A/B	R-401 pumps	2	22.3	44.5	78.1	156.2	200.7
P-404A/B	C-402 B/S pumps	2	5.9	11.7	9.1	18.1	29.9
P-405A/B	C-402 reflux pumps	2	38.5	77.0	156.7	313.4	390.4
P-406A/B	C-401 B/S pumps	2	38.6	77.2	157.1	314.2	391.4
P-407A/B	C-401 reflux pumps	2	2.5	5.0	4.6	9.2	14.2
P-408A/B	C-403 B/S pumps	2	38.3	76.6	155.9	311.8	388.4
P-409A/B	C-403 reflux pumps	2	6.2	12.4	12.5	24.9	37.3
P-410A/B	C-404 B/S pumps	2	14.8	29.5	45.0	90.0	119.5
P-411A/B	C-404 reflux pumps	2	36.3	72.6	147.5	295.0	367.6
P-412A/B	HMDA product pumps	2	19.6	39.1	65.6	131.2	170.3
Reactors							
R-101A-X	Dimerization cells	24	649.0	15,576.0	485.0	11,640.0	27,216.0
R-401A/B	ADN reactors	2	289.9	579.8	74.3	148.5	728.3
Specially packaged equipment							
S-101	Dowtherm hot oil system	1	4,500.0	4,500.0	9,250.0	9,250.0	13,750.0
S-102	Glycol chiller system	1	250.0	250.0	350.0	350.0	600.0
S-103	Vapor stream incinerator w header	1	2,500.0	2,500.0	5,500.0	5,500.0	8,000.0
S-104	Liquids incinerator	1	4,500.0	4,500.0	2,500.0	2,500.0	7,000.0
S-105	2-flare system with blowdown drums & header	1	3,500.0	3,500.0	18,250.0	18,250.0	21,750.0
S-106	Process computer control system	1	5,500.0	5,500.0	9,500.0	9,500.0	15,000.0
S-107A-X	Cell power paks	24	200.0	4,800.0	200.0	4,800.0	9,600.0

Table 7.9 (continued): Itemized capital cost estimate

		# installed	FOB (1 unit)	FOB (all units)	Install (1 unit)	Install (all units)	Installed cost (all units)
Storage tanks							
TK-101	ACN feed Tank	1	201.9	201.9	171.6	171.6	373.5
TK-102	Water tank	1	82.0	82.0	38.5	38.5	120.5
TK-103	Na ₂ HPO ₄ soln tank	1	38.5	38.5	18.1	18.1	56.6
TK-104	QUAT soln tank	1	8.5	8.5	4.0	4.0	12.5
TK-105	Na ₂ B ₄ O ₇ soln tank	1	10.9	10.9	5.1	5.1	16.0
TK-106	Na ₄ EDTA soln tank	1	8.4	8.4	3.9	3.9	12.3
TK-107	Emulsion tank	1	1,335.0	1,335.0	1,135.0	1,135.0	2,470.0
TK-201	Distillation feed tank	1	399.2	399.2	339.3	339.3	738.5
TK-202A/B	ADN day tanks	2	163.7	327.4	139.2	278.4	605.8
TK-203A/B	PN tanks	2	36.9	73.8	17.4	34.8	108.6
TK-401	Ammonium hydroxide tank	1	74.5	74.5	10.9	10.9	85.5
TK-402	Demin water tank	1	23.3	23.3	10.9	10.9	34.2
TK-403A/B	HMDA tanks	2	377.7	755.4	55.5	111.0	866.4
Pressure vessels (API 510-ASME BPVC)							
V-101ABCD	Cell activated carbon filters	4	74.8	299.0	61.4	245.6	544.7
V-102A/B	Low boiler AC absorbers	2	74.8	149.5	61.4	122.8	272.3
Total			52,208.4	77,539.1	72,108.9	93,798.4	171,337.5

Total fixed capital cost estimate

We have prepared a total fixed capital cost estimate by combining the itemized ISBL capital costs with indirect ISBL costs, and adding to these our factored cost estimates for offsite (OSBL) capital costs. This information is presented in the table below.

Table 7.10: Total fixed capital cost estimate

Capacity: 250,000 MT/YR			
AT 0.90 Stream factor			
PEP Cost Index: 1164			
		Capacity exponent	
Battery limits equipment, FOB	Cost (\$US-MM)	Up	Down
Buildings	1,050.0	0.55	0.53
Reactors	16,155.8	0.70	0.60
Distillation columns	4,283.5	0.61	0.58
Drums	1,849.6	0.67	0.62
Filters	2,359.2	0.67	0.62
Heat exchangers	10,253.3	0.65	0.63
Pumps	1,913.9	0.63	0.60
Compressors	5,951.0	0.62	0.60
ISBL storage tanks	3,338.8	0.69	0.60
Pressure vessels	448.6	0.67	0.62
Fired heaters	0.0	0.85	0.85
Mixers & agitators	887.5	0.65	0.65
Steam turbine drivers	0.0	0.70	0.70
Special packaged equipment	25,550.0	0.70	0.70
Centrifuges	458.0	0.67	0.62
Crystallizers	3,040.0	0.67	0.62
Total BLE	77,539		
Direct installation costs	93,798	0.66	0.62
Indirect costs	70,349	0.63	0.59
Unscheduled equipment, 20%	18,760	0.65	0.62
Battery limits, installed	260,446	0.65	0.62
BLI contingency, 25%	65,111	0.65	0.62
Battery limits installment	325,557	0.65	0.62
Off-sites, installed			
Cooling water	13,022	0.65	0.62
Process water	1,042	0.65	0.62
Boiler feedwater	2,474	0.65	0.62
Process steam	19,533	0.55	0.53
Fuel gas system	3,907	0.55	0.53
Inert gas & instrument air	1,042	0.55	0.53
Off-sites tankage	25,500	0.55	0.53
Utilities & storage	66,520	0.65	0.62
General service facilities	13,022	0.65	0.62
Wastewater treatment	41,671	0.65	0.62
Total off-sites	121,214	0.65	0.62
Off-sites contingency 25%	30,303	0.65	0.62
Off-sites capital investment	151,517	0.65	0.62
Total fixed capital	477,075	0.65	0.62

Production cost estimate

Combining the technical results developed above with unit pricing for raw materials, chemicals and catalyst, and utilities, we have developed the following estimate of variable production costs (raw materials + energy) for making HMDA using our understanding of Ascend/Monsanto process technology. The variable costs of production are presented in the table below.

Table 7.11: Variable production cost estimate (\$US/mt)

	Unit cost		Consumption		\$/mt
Raw materials					
Acrylonitrile	1801	\$US/mt	1.12488	mt/mt	2025.7
Disodium Hydrogen Phosphate	1768	\$US/mt	0.02466	mt/mt	43.6
Quaternary Ammonium Salt	3638	\$US/mt	0.00079	mt/mt	2.9
Disodium Borate	799	\$US/mt	0.00179	mt/mt	1.4
Sodium Ethylenediaminetriacetate	1455	\$US/mt	0.00074	mt/mt	1.1
Hydrogen	872	\$US/mt	0.076	mt/mt	66.3
Ammonium Hydroxide	575	\$US/mt	0.0015	mt/mt	0.9
Electrode replacement					30.0
By-product credits					
Propionitrile	2000	\$US/mt	-0.05361	mt/mt	-107.2
Net raw material cost					2064.6
Utilities					
Process water	0.35	\$US/m3	6.15	m3/mt	2.2
Cooling water	0.04	\$US/m3	89.6	m3/mt	3.7
Electricity	5.93	¢US/kwh	2650	kwh/mt	157.1
Process steam	16.75	\$US/mt	2.57	mt/mt	43.1
Fuel gas	218.03	\$US/mt	0.198	mt/mt	43.2
Net utility cost					249.2
Variable costs					2313.8

In order to estimate the fixed costs of manufacturing HMDA, PEP has developed factors for estimating cost components as a percentage of either capital costs or unit labor requirements. These factors are listed in the table below. In the particular case of HMDA, which is primarily consumed captively to produce nylon 66, we have used a corporate overhead factor (G&A, sales, R&D) of only 1% of HMDA product price (US\$2,900/mt).

Table 7.12: Fixed production cost factors

Maintenance materials (% of BLI)	1.75
Operating supplies (% of operating labor)	10
Operating labor rate (\$/manhour)	46.23
Maintenance labor (% of BLI)	1.75
Control laboratory (% of operating labor)	20
Plant overhead (% of total labor)	60
Taxes & insurance (% of TFC)	2
Depreciation (% of TFC)	10
Product value premium (production cost + % TFC)	25
Number of operators per shift	4
G&A, sales, R&D (% of product price)	1

By applying the fixed cost factors to the capital and labor cost efforts that we believe are required to operate a commercial scale plant with the variable costs estimated above, we have estimated the total production costs to produce 250 kty of HMDA. In the table below, we have used this information to also estimate, on a factored cost basis, the production costs for ½ the base case capacity (125 kty), and twice the base case capacity (500 kty).

Table 7.13: Fixed production cost estimate (\$US/mt)

Capacity	MT/Y	125	250	500	
Production	MT/Y	125	250	500	
Investment (\$US millions)					
Battery limits		196.3	(0.73)	325.6	540.0
Off-sites		<u>107.9</u>	(0.49)	<u>151.5</u>	<u>212.8</u>
Total fixed capital		304.2		477.1	752.8
Production cost (\$/MT)		\$/mt		\$/mt	\$/mt
Net raw materials		2064.6		2064.6	2064.6
Net utilities		<u>249.2</u>		<u>249.2</u>	<u>249.2</u>
	Variable costs	2313.8		2313.8	2313.8
Direct costs					
Maintenance materials		27.5		22.8	18.9
Operating supplies		1.3		0.6	0.3
Operating labor		13.0		6.5	3.2
Maintenance labor		27.5		22.8	18.9
Control laboratory		<u>2.6</u>		<u>1.3</u>	<u>0.6</u>
	Total direct costs	2385.6		2367.8	2355.8
Plant overhead		24.3		17.6	13.3
Taxes & insurance		48.7		38.2	30.1
Depreciation		<u>243.3</u>		<u>190.8</u>	<u>150.6</u>
Plant gate cost		2701.9		2614.4	2579.8
G&A, sales, R&D		29.0		29.0	29.0
Total production cost					
AT 100% capacity		2730.9		2643.4	2578.8
AT 75% capacity		2869.9		2753.2	2667.1
AT 50% capacity		3148.0		2972.9	2843.7
Product value (Cost + 25%/YR ROI before taxes)					
AT 100% capacity		3343.7		3122.7	2955.7
AT 75% capacity		3478.2		3230.3	3043.5
AT 50% capacity		3756.3		3450.0	3220.1
Cash cost		2487.56		2452.55	2428.23
Cash cost profitability		412.46		447.46	471.79
Total cost profitability		169.13		256.63	321.23

When the variable and fixed costs of production are combined, the result is the conventional PEPCOST total production cost estimate, as presented in the table below.

Table 7.14: Total production cost estimate (\$US/mt)

	Unit cost		Consumption		\$/mt
Raw materials					
Acrylonitrile	1801	\$US/mt	1.12488	mt/mt	2025.7
Disodium Hydrogen Phosphate	1768	\$US/mt	0.02466	mt/mt	43.6
Quaternary Ammonium Salt	3638	\$US/mt	0.00079	mt/mt	2.9
Disodium Borate	799	\$US/mt	0.00179	mt/mt	1.4
Sodium Ethylenediaminetriacetate	1455	\$US/mt	0.00074	mt/mt	1.1
Hydrogen	872	\$US/mt	0.076	mt/mt	66.3
Ammonium Hydroxide	575	\$US/mt	0.0015	mt/mt	0.9
Electrode replacement					30.0
By-product credits					
Propionitrile	2000	\$US/mt	-0.05361	mt/mt	-107.2
Net raw material cost					2064.6
Utilities					
Process water	0.35	\$US/m3	6.15	m3/mt	2.2
Cooling water	0.04	\$US/m3	89.6	m3/mt	3.7
Electricity	5.93	¢US/kwh	2650	kwh/mt	157.1
Process steam	16.75	\$US/mt	2.57	mt/mt	43.1
Fuel gas	218.03	\$US/mt	0.198	mt/mt	43.2
Net utility cost					249.2
Variable costs					2313.8
Maintenance materials (% of BLI)			1.75		
Operating supplies (% of operating labor)			10		
Operating labor rate (\$/manhour)			46.23		
Maintenance labor (% of BLI)			1.75		
Control laboratory (% of operating labor)			20		
Plant overhead (% of total labor)			60		
Taxes & insurance (% of TFC)			2		
Depreciation (% of TFC)			10		
Product value premium (production cost + % TFC)			25		
Number of operators per shift			4		
G&A, sales, R&D (% of product price)			1		

Table 7.14: Total production cost estimate (\$US/mt) (continued)

Capacity	MT/Y	125	250	500	
Production	MT/Y	125	250	500	
Investment (\$US millions)					
Battery limits		196.3	(0.73)	325.6	540.0
Off-sites		<u>107.9</u>	(0.49)	<u>151.5</u>	<u>212.8</u>
Total fixed capital		304.2		477.1	752.8
Production cost (\$/MT)		\$/mt	\$/mt	\$/mt	\$/mt
Net raw materials		2064.6		2064.6	2064.6
Net utilities		<u>249.2</u>		<u>249.2</u>	<u>249.2</u>
	Variable costs	2313.8		2313.8	2313.8
Direct costs					
Maintenance materials		27.5		22.8	18.9
Operating supplies		1.3		0.6	0.3
Operating labor		13.0		6.5	3.2
Maintenance labor		27.5		22.8	18.9
Control laboratory		<u>2.6</u>		<u>1.3</u>	<u>0.6</u>
	Total direct costs	2385.6		2367.8	2355.8
Plant overhead		24.3		17.6	13.3
Taxes & insurance		48.7		38.2	30.1
Depreciation		<u>243.3</u>		<u>190.8</u>	<u>150.6</u>
Plant gate cost		2701.9		2614.4	2579.8
G&A, sales, R&D		29.0		29.0	29.0
Total production cost					
AT 100% capacity		2730.9		2643.4	2578.8
AT 75% capacity		2869.9		2753.2	2667.1
AT 50% capacity		3148.0		2972.9	2843.7
Product value (Cost + 25%/YR ROI before taxes)					
AT 100% capacity		3343.7		3122.7	2955.7
AT 75% capacity		3478.2		3230.3	3043.5
AT 50% capacity		3756.3		3450.0	3220.1
Cash cost		2487.56		2452.55	2428.23
Cash cost profitability		412.46		447.46	471.79
Total cost profitability		169.13		256.63	321.23

Economic analysis

For the 'base case' HMDA production plant with an annual capacity of 250 kty, our analysis shows a total production cost estimate for Ascend technology of US\$2,643/mt, and a cash cost of US\$2,455/mt. When compared to an average HMDA selling price of US\$2,900/mt, these values provide an 13% total production cost ROI, and a 23% cash cost ROI, demonstrating that this is a profitable business for Ascend.

However, when compared to the production cost values generated in Section 6 for Invista, our analysis indicates that while the Ascend process has a significantly lower capital cost (30%) than Invista on a grassroots (green field) basis, its total production cost and its cash cost of production are significantly higher than for Invista. The primary reason for this difference is in the cost of feedstock (acrylonitrile for Ascend, butadiene and ammonia for Invista), and the higher unit feedstock utilization of acrylonitrile by Ascend, versus that of Invista for butadiene plus ammonia. The relevant data are shown below.

Table 7.15: Economic analysis

	Total fixed capital (\$US-MM)	Total production cost (\$US/mt)	Total cash cost (\$US/mt)
Ascend	477	2,643	2,453
Invista	682	1689	1,467

8. Bio-based HMDA via Rennovia process technology

Introduction

In October, 2013, Rennovia (Menlo Park, CA USA) announced [31C54] that it had produced 100% bio-based nylon 66 polymer, combining its separate technologies for producing bio-adipic acid and bio-hexamethylene diamine. This announcement exerts marketing pressure on existing commercial producers of nylon 66 via conventional hydrocarbon processing to respond to the market challenge from customers of conventional nylon 66 who would prefer to be buying a perceived more sustainable and eco-friendly polymer.

The Rennovia announcement also affects developers of both bio-adipic acid and bio-HMDA, as Rennovia does not have to partner with an existing commercial nylon 66 producer to go to market with a commercial product that can be sold directly into the nylon 66 engineering resins and fiber business. If a bio-developer's business plan is to only make bio-adipic acid, or bio-HMDA, it is likely that they have to partner with someone else so that the ultimate commercial product (nylon 66) can be sold.

Other bio nylon developers

Nylon producers worldwide are investigating the potential for using other bio-based components to produce bio-based polyamide. Arkema commercially produces Rilsan-T™, a nylon 11 polyamide made in part from castor oil. BASF, Kingfa and DuPont are also developing castor oil based nylon. A joint venture of Toray and Ajinomoto is developing a family of bio-based nylon products from amino acids.

Evonik (originally Chemische Werke Huels) is also developing a family of bio-based polyamides using natural oils from castor beans. DSM also produces bio-based nylon 4/10 from castor oil in its trademarked 'EcoPaXX' family of virgin and compounded polymers.

Castor oil can be hydrogenated to sebacic acid, and then aminated to decamethylene diamine. Evonik commercial products include VESTAMID™ nylon 12 (PA-12) made using amino lauric acid, and co-polymers PA-6/10, PA-10/10, and PA-10/12. Physical properties of these polyamides are presented in the table below.

Table 8.1: Evonik bio-based polyamides

Property		PA-6/10	PA-10/10	PA-10/12	PA-12
Bio-based content	%	63	100	45	0
Density	g/cm ³	1.08	1.05	1.04	1.01
Melting point	°C	222	198	181	178
Water absorption (saturation, 23 °C)	%	3.3	1.8	1.6	1.4
Yield Stress	MPa	61	54	40	46
Tensile modulus of elasticity	MPa	2100	1700	1400	1350
Notched impact strength (under -30 °C)	kJ/m ²	6C	14C	16C	9C

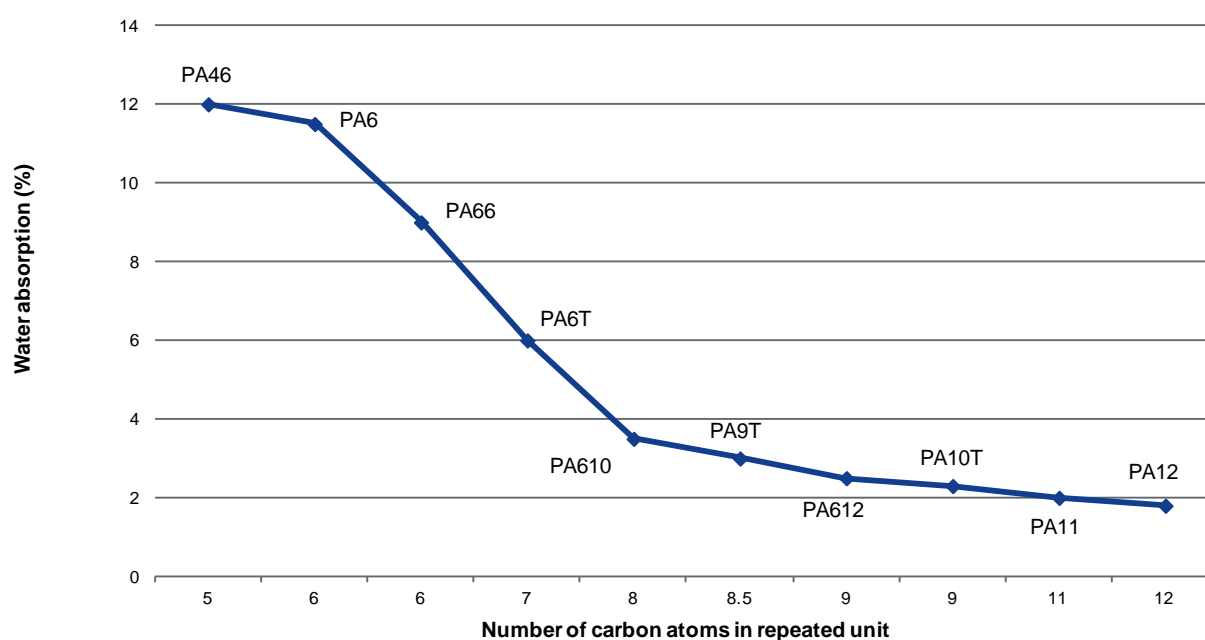
Source: IndustrySourcing.com [31C55]

Cathay Industrial BioTech (Shanghai, China) is developing a family of polyamides around bio-based 1,5-pentamethylene diamine, as a replacement for HMDA. It is thus able to produce bio-based PA-5/6, PA-5/11, PA-5/12, PA-5/13, and PA-5/14.

Shell Oil developed nylon alternatives around bio-based gamma-valerolactone, by converting it to methyl pentenoate. Bio-nylon can also be produced from poly-gamma-glutamate via fermentation [31C56].

One of the reasons for preferentially developing polyamides from long chain carbon molecules is that these grades have lower water absorbency than grades made from shorter carbon chain monomers, as shown in the figure below. The sensitivity of nylon to water absorbency was implicated as a contributing cause to Toyota Motor Company's billion dollar recall of vehicles in 2010 over claimed 'sticking' of accelerator pedals. The original pedal linkages were made of metal housed in a short carbon chain nylon sheath at tight tolerance. When the nylon became wet, it swelled and bound up the metal activator so that it would not move when the driver removed their foot from the accelerator. As an outcome, Toyota replaced the nylon sheath with one made of PPS (polyphenylene sulfide).

Figure 8.1: Water absorbency of nylon grades



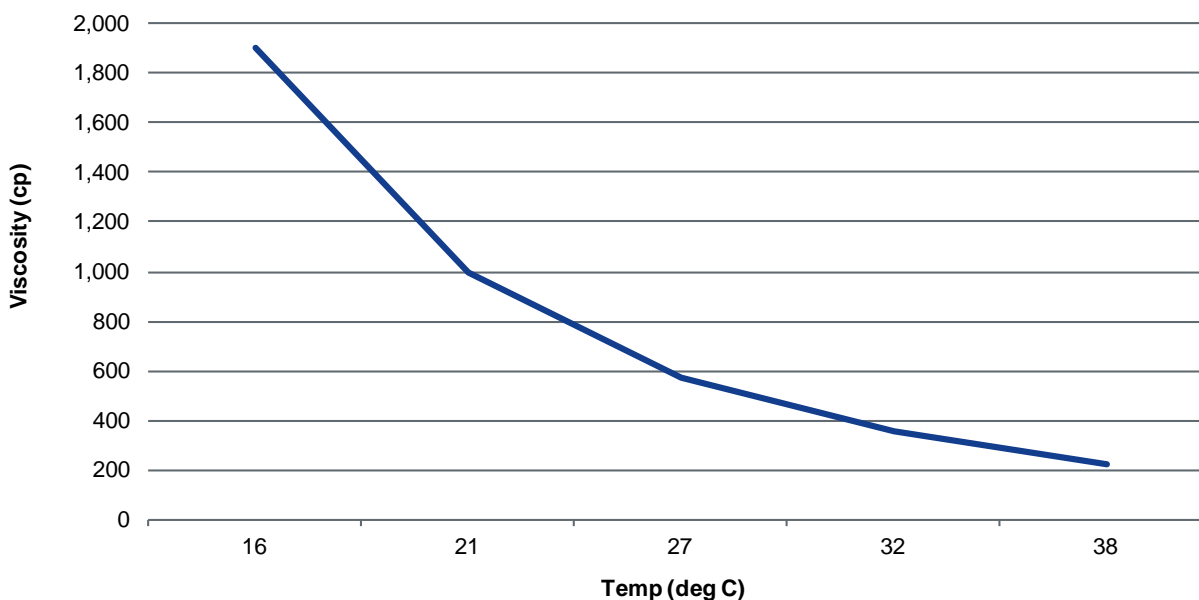
Source: Plastics Today [31C57]

Rennovia feedstock

As described in Section 5 of this report, The Rennovia bio-based HMDA process starts with fructose produced as a by-product from corn wet milling as feedstock. High fructose corn syrups (HFCS) are produced from glucose in three grades, designated by the % fructose content. HFCS-42 is generated by partial enzymatic conversion of glucose to fructose. HFCS-90 is produced by chromatographic glucose-fructose separation of HFCS-42. Finally, HFCS-55 is produced by blending HFCS-90 and HFCS-42. These products are used extensively as sweeteners in processed foods, beverages, cereals and baked products. HFCS-55 is preferred in beverages, while HFCS-42 in processed foods. HFCS-90 is used in small specialty applications. Per annum global production of HFCS products (dry weight basis) is approximately 11.5 million tons.

One such commercial supplier of HFCS-90 is Archer Daniels Midland (Decatur, IL USA), with its CORNSWEET®-90 product. The commercial product specification is 90% fructose, 8.5% dextrose, and 1.5% higher saccharides. Characteristic of other syrups, HFCS-90 is high viscosity, and needs to be maintained at room temperature (70 – 85°F) to avoid crystallization, and be heated in order to be pumped through conventional process equipment. The figure below shows the relationship between temperature and HFCS-90 viscosity.

Figure 8.2: HFCS-90 temperature versus viscosity curve



Source: Archer Daniels Midland

Physical properties of fructose are presented in the table below. Fructose is highly soluble in water, but does not have a measurable boiling point, because when heated below its boiling point it degrades thermally by dehydration.

Table 8.2: Physical properties of fructose

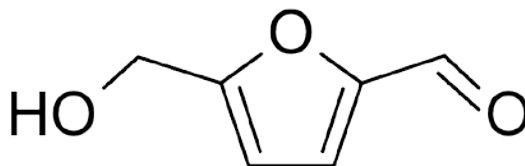
CAS number	57-48-7 Y
Molecular formula	C ₆ H ₁₂ O ₆
Molar mass	180.16 g mol ⁻¹
Density	1.694 g/cm ³
Melting point	103 °C; 217 °F;
Water solubility	778 mg/mL at 20 °C
Water solubility	1110 g/L
LogP	-2.45
LogP	-2.8
LogS	0.79
pKa (strongest acidic)	10.28
pKa (strongest basic)	-3
Hydrogen acceptor count	6
Hydrogen donor count	5
Polar surface area	110.38 Å ²
Rotatable bond count	2
Refractivity	36.36
Polarizability	16.52
Formal charge	0
Physiological charge	0

Rennovia intellectual property

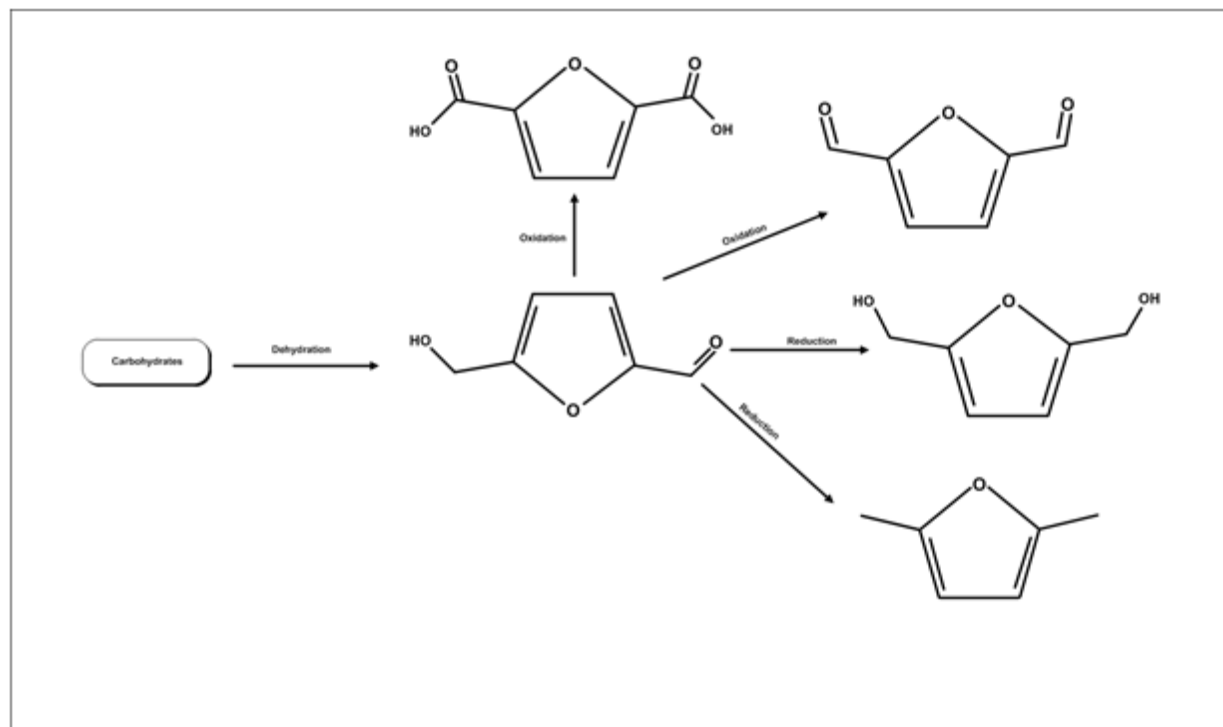
The Rennovia bio-HMDA process starts with HFCS-90 as feedstock, and dehydrates it to 5-hydroxymethylfurfural (HMF). This is accomplished by Rennovia with in-house technology, although there is substantial industry literature describing this process, although different sources often provide contradictory claims. In the second step of the process, the HMF is hydrogenated to 1,2,6-hexanetriol, which is then further hydrogenated in the 3rd step to 1,6-hexanediol (HDO), also using Rennovia in-house technology. The hydrogenations of HMF and 1,2,6-hexanetriol can be conducted in the same reactor, as reactor processing conditions (temperature, pressure, LHSV, and catalyst composition) are similar. In the 4th and final step, HDO is reacted with ammonia to form HMDA directly, using Rennovia in-house technology that updates the established and patented Celanese process technology.

Rennovia's key patent claims for producing HMDA from fructose are disclosed in US Patent Application 2013 0184 495 (18 July 2013), entitled 'Process for the production of hexamethylenediamine from carbohydrate containing materials and intermediates therefor'. The Rennovia abstract for this patent application is presented below:

Processes are disclosed for the conversion of a carbohydrate source to hexamethylenediamine (HMDA) and to intermediates useful for the production of hexamethylenediamine and other industrial chemicals. HMDA is produced by direct reduction of a furfural substrate to 1,6-hexanediol in the presence of hydrogen and a heterogeneous reduction catalyst comprising Pt or by indirect reduction of a furfural substrate to 1,6-hexanediol wherein 1,2,6-hexanetriol is produced by reduction of the furfural substrate in the presence of hydrogen and a catalyst comprising Pt and 1,2,6-hexanediol is then converted by hydrogenation in the presence of a catalyst comprising Pt to 1,6 hexanediol, each process then proceeding to the production of HMDA by known routes, such as amination of the 1,6 hexanediol. Catalysts useful for the direct and indirect production of 1,6-hexanediol are also disclosed.

Figure 8.5: Molecular structure of 5-hydroxymethylfurfural (HMF)

Rennovia technology focuses on hydrogenating HMF to 1,2,6-hexanetriol, and then further hydrogenating the 1,2,6-hexanetriol to 1,6-hexanediol, via a ring opening mechanism. However, HMF is an active molecule that is amenable to a variety of chemical reactions that retain the furanic ring structure, and could also potentially lead to other attractive industrial products, as shown in the figure below.

Figure 8.6: Reaction options with 5-hydroxymethylfurfural (HMF)

A conventional method of dehydrating bio-based chemicals is treatment with acid (to remove hydroxyl groups in the form of water), followed by extraction with a polar solvent such as MEK (methylethyl ketone) or MIBK (methylisobutyl ketone). Ionic liquids enhance the conversion of HFCS to HMF. Chromous chloride is a conventional catalyst for the dehydration reaction.

HFCS is almost impossible to purify by distillation, because it thermally degrades at elevated temperature. HMF is amenable to fractional distillation (under vacuum conditions), and to other conventional separation and purification unit processes that require elevated temperature.

At atmospheric conditions, HMF is a yellow solid that is highly soluble in water. HMF physical properties are presented in the table below.

Table 8.3: 5-Hydroxymethylfurfural physical properties

Parameter	Value
Boiling point	114–116 °C (1 mbar)
Boiling point	351-354 °C at 760 mmHg
Melting point	32-35 °C
Specific gravity	1.206
ACD/LogP:	-0.45±0.27
ACD/LogD (pH 5.5):	-0.45
ACD/BCF (pH 5.5)	1
ACD/KOC (pH 5.5)	13.52
#H bond acceptors	3
#Freely rotating bonds	3
Index of refraction	1.563
Molar volume	97.7±3.0 cm ³
Surface tension	50.0±3.0 dyne/cm
Flash point	79.444 °C
# of rule of 5 violations:	0
ACD/LogD (pH 7.4)	-0.45
ACD/BCF (pH 7.4)	1
ACD/KOC (pH 7.4)	13.52
#H bond donors	1
Polar surface area	50.44 Å ²
Molar refractivity	31.8±0.3 cm ³
Polarizability	12.6±0.5 10 ⁻²⁴ cm ³
Density	1.3±0.1 g/cm ³
Enthalpy of vaporization	56.1±3.0 kJ/mol
Vapour pressure	0.0±0.6 mmHg at 25°C

Rennovia's published patent application does not claim discoveries or intellectual property for the process of converting HFCS and/or precursor glucose to HMF by dehydration. Instead, the Rennovia patent application lists other patents granted to others that claim to accomplish the dehydration. These patent listings are provided in the table below.

Table 8.4: Patents claiming dehydration of glucose/fructose to HMF

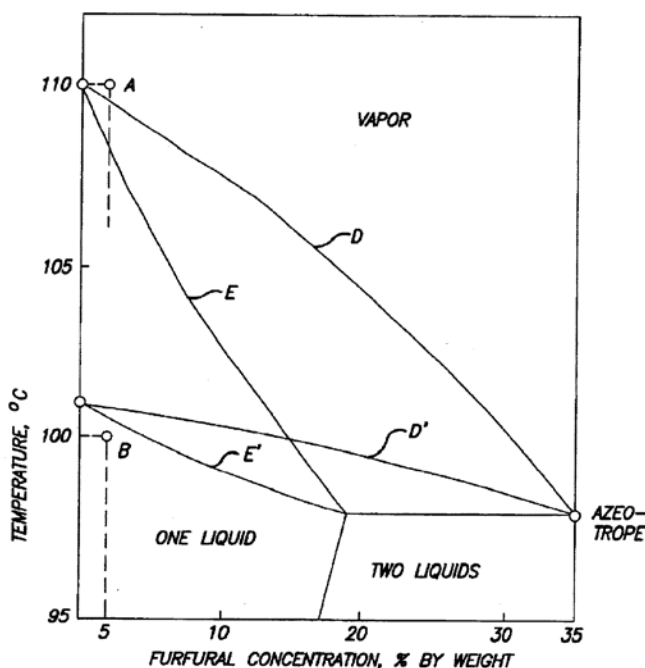
Patent #	Patent #
USP 6743928	USP 2917520
USP 6518440	USP 2750394
USP 4971657	GB 876463
USP 4912237	GB 600871
USP 4740605	GB 591858
USP 4590283	FR 2669635
USP 4533743	FR 2664273
USP 4339387	FR 2663933
USP 3118912	CA 2097812
USP 2929823	

US Patent 6743928 (International Furan Technology)

Rennovia cites USP 6743928 (1 June 2004, assigned to IFT- International Furan Technology) that describes a batch process for converting a pentose (C_5 monosaccharide carbohydrate) to furfural at virtually 100% conversion. According to the IFT patent, pentose is dissolved in a 12% hydrochloric acid solution that is saturated in sodium chloride (NaCl), resulting in an elevated boiling temperature for the solution. The patent claims that conventional furfural processes only achieve 60% conversion because they are conducted at a temperature in which furfural remains in the liquid solution as it is formed, and thus reacts with the pentose feedstock to produce furfural pentose. The proposed process described in the patent injects live steam into the pentose solution in aqueous HCl at elevated pressure, and then gradually de-pressures the mixture causing furfural to vaporize as it is formed. Since there is no pentose in the vapor phase under these conditions, there is no formation of furfural pentose.

The IFT patent provides a vapor-liquid equilibrium curve (shown in the figure below) of furfural in two different solutions: A) a pentose solution in aqueous 12% HCl saturated with NaCl that boils at 110 °C when there is no furfural present, and B) a pentose solution in water that boils at 100 °C when there is no furfural present. As furfural begins to form in the (A) HCl solution, the solution boiling temperature of 110 °C, is above the furfural boiling point, such that furfural as formed is immediately vaporized. The vapor phase has no pentose in it, and therefore conversion of pentose to furfural proceeds at 100% selectivity, because there is no chance of forming furfural pentose.

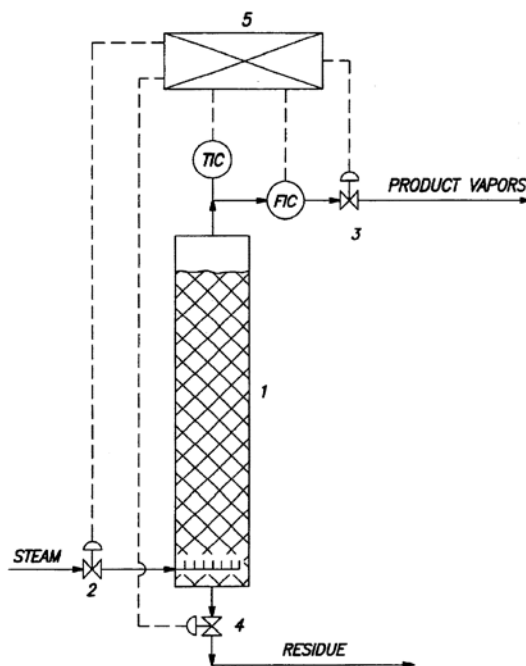
Figure 8.7: Furfural solutions vapor-liquid equilibrium curves (USP 6743928)



In the (B) aqueous solution of pentose, furfural is formed with the solution remaining below its boiling temperature of 100 °C. Under these conditions, since furfural is formed in the liquid phase and remains in the liquid phase, it has ample opportunity to mix with pentose to form furfural pentose, rather than furfural. As a result, the selectivity to furfural is only 60%.

The IFT patent also describes a device (shown in the figure below) for effecting the dehydration of pentose to furfural at 100% selectivity. A pentose solution in aqueous 12% HCl saturated with NaCl is used to fill a reactor vessel at elevated pressure (approximately 450 psia). Live steam is injected at a temperature between 170 – 230°C. Once the temperature reaches 230°C, an overhead valve slowly opens, slowly depressurizing the reactor vessel and causing the solution to boil. At boiling conditions, furfural formed by the dehydration reaction will vaporize, and be removed from the pressure vessel. The other component of the vapor phase will be steam. The solution will remain boiling until all of the pentose has been converted to furfural. The combined overhead vapor product stream can be condensed in a downstream heat exchanger, and directed to a distillation train for purification.

Figure 8.8: Furfural generating device at 100% selectivity (USP 6743928)



The operating procedure for the device, from the IFT patent, is described below:

‘A thermally well insulated reactor 1 charged with raw material acidified or not, is heated to a temperature T.sub.1 by admitting steam through valve 2 while the valves 3 and 4 are closed. During the very short heating process, the steam condenses, thus increasing the moisture content of the charge. Then, valve 2 is closed and a leak valve 3 is opened so as to produce a steady small flow of product vapor by gradual depressurization. This causes a slow drop in temperature. When in this fashion a suitably chosen temperature T.sub.2 is reached, the leak valve 3 is closed to terminate the first "gradual depressurization". If at the end of this period no more furfural was obtained, the digestion is completed by opening valve 4 to discharge the residue. If, however, furfural was still obtained, the reactor is reheated and submitted to another "gradual depressurization" period. This procedure can be arbitrarily repeated. All valve operations are governed by an automatic control unit 5. By an appropriate choice of the temperatures T.sub.1 and T.sub.2, and by an appropriate choice of the acid concentration, it is possible, if desired, to complete the process in a single depressurization period since high

temperature and high acidity permit a short reaction time. Needless to say, designing such an operation is complicated as the furfural reaction takes place over a wide range of temperatures (e.g. from 230.degree. C. to 160.degree. C.), but once calculated, the practical realization of the process is extremely simple. As due to the continuous leak stream the reaction medium is maintained in a state of boiling throughout the reaction period, the furfural yield corresponds to that of the analytical furfural processes by lying in the order of 100%.'

US Patent 6518440 (Lightner)

USP 6518440 (11 Feb 2003, Lightner), also cited in the Rennovia patent application, presents a continuous process for producing HMF from cellulose, which is a more difficult feedstock to process than fructose. Like the IFT patent above (USP 6743928), an aqueous and boiling sulfuric acid solution is used to hydrolyze cellulose to glucose, which is further dehydrated to HMF. The benefit of this intellectual property to the project is the provision of methods for purifying the acid solution containing HMF following the hydrolysis reactions, for the purpose of recovering high purity HMF. Like the patent above, HMF and water formed during the dehydration reaction are vaporized from the acidic aqueous solution in the reactor.

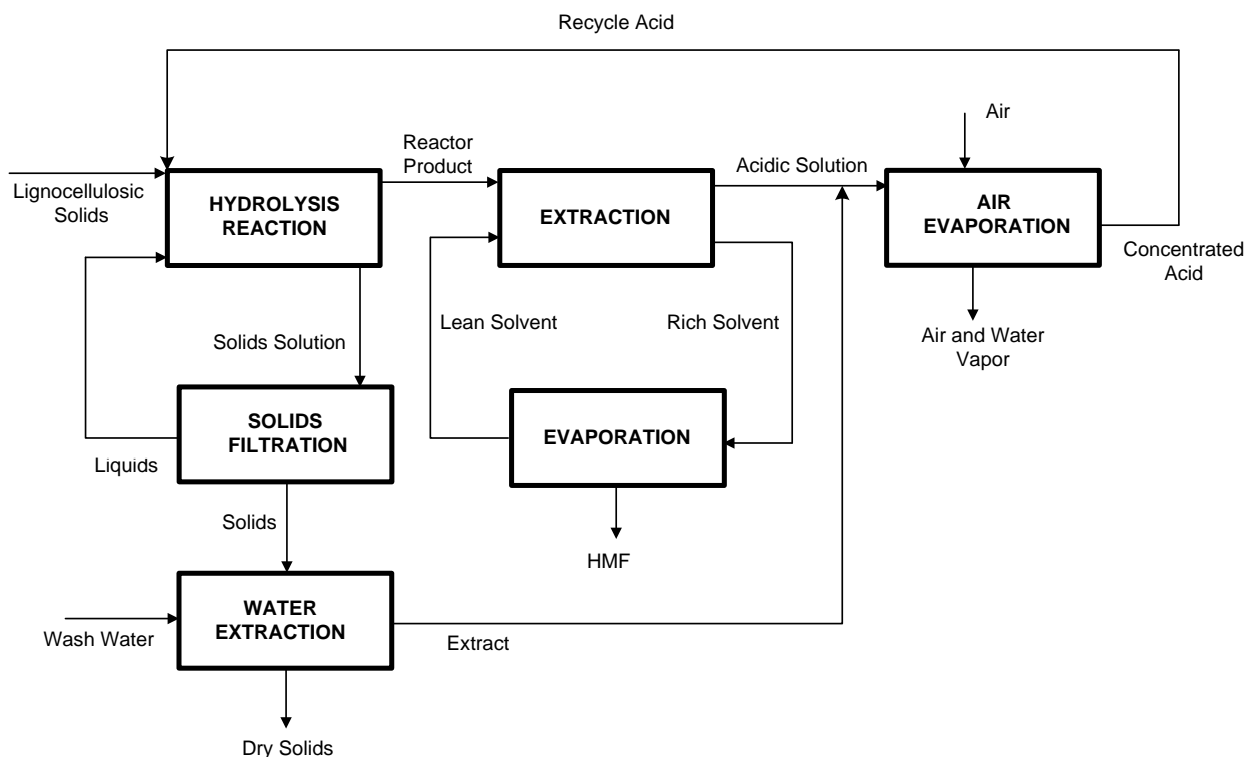
The dehydration reaction forming furfural from pentose (hemicellulose derived) is presented below.



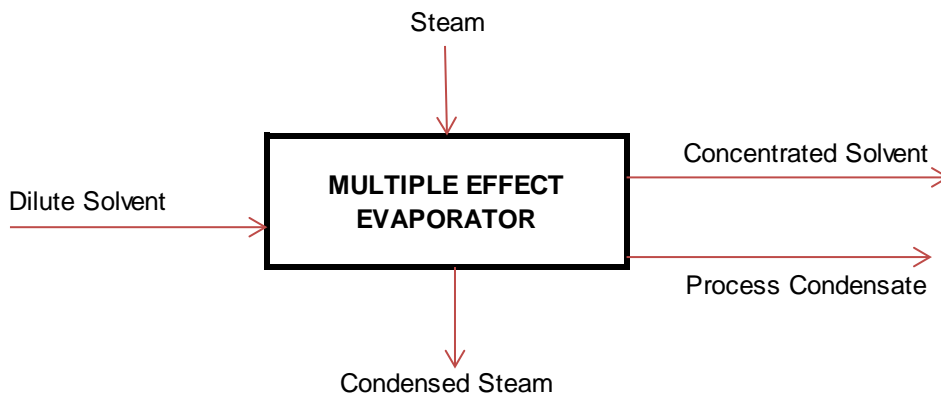
The dehydration reaction forming 5-hydroxymethylfurfural (HMF) from glucose (cellulose derived) is presented below.



A block flow diagram from the patent is presented below. The feedstock used is not HFCS, but a mixed composition of lignocellulosic solids (such as wood, paper, or municipal solid waste) containing both hemi-cellulose and cellulose. The feedstock is combined with a hot aqueous sulfuric acid solution in the hydrolysis reactor, which is boiling. HMF is produced in this reactor as a vapor product, along with water vapor and acid mist. The vapor phase reactor product stream is combined with a solvent in which HMF is highly soluble, but water and acid mist is not soluble. The composition of such solvent is not disclosed in the patent. The combined stream of solvent, HMF, water vapor and acid mist is thoroughly mixed and directed to a settling drum, in which the upper layer is solvent plus HMF, while the lower layer is water plus acid mist. The solvent layer containing HMF is processed through an evaporator, which separates high purity HMF product from solvent. The solvent, now free of HMF, is recycled to the extraction drum. The acid solution, which is now free of HMF, has been significantly diluted in water which was produced by the hydrolysis reaction. The now dilute acid stream is processed through an air evaporator, which removes some of the water, thus re-concentrating the acid solution. The concentrated acid solution is recycled to the hydrolysis reactor.

Figure 8.9: HMF by hydrolysis in acid solution (USP 6518440)

The method used to recover high purity HMF from the rich solvent from the extraction unit is further described in USP 6518440 in a figure, which is reproduced below. The rich solvent solution is passed through a conventional, industrial multi-stage evaporation unit. These modular process units usually operate using 3 - 4 stages at different pressures, such that the evaporation conducted in a higher pressure vessel (at a higher temperature) can be used to evaporate the feed being processed through an evaporation stage at a lower temperature and lower pressure. Such units are offered at industrial scale by companies such as Alfa Laval, GEA and HPD.

Figure 8.10: HMF recovery from rich solvent (USP 6518440)

IHS HMF production design approach

Using the information identified by Rennovia in the three non-Rennovia patents, we have developed a commercial scale, continuous processing scheme for making HMF using insights from the patents described above. The key process characteristics of the proposed process are listed below:

- 1 Pre-heating both HFCS feed and acid solution to reactor temperature of 200°C
- 2 Using a reacting solvent system of dilute (0.1%) HCl (hydrochloric acid), consistent with high temperature and boiling conditions, combined with an HMF extracting solvent (MIBK)
3. Operating the reaction system at a pressure of 250 psia in order to maintain the reacting system as a liquid in a slight boiling state. Under these conditions, as HMF is formed by the dehydration of HFCS, some of it vaporizes and leaves the reactor in a mixed vapor stream containing water vapor and residual acid mist, while free of feedstock HFCS
- 4 Using live steam injection into the hydrolysis reactor bottom to maintain the reactor in the boiling state
- 5 Condensing the HMF reactor product vapor stream and liquid product stream, and extracting HMF from water and dilute hydrochloric acid solution using the MIBK solvent
- 6 Separating HMF from MIBK by conventional fractional distillation
- 7 Processing the water produced by the dehydration reaction in a multi-stage distillation system to recover the hydrochloric acid and maintain the acid solution at the desired concentration when recycled to the HMF reactors

In determining a reactor temperature regime that was hot enough to substantially convert all of the HFCS to HMF, a concern addressed was the reality that the hydrolysis reaction produces substantial amounts of by-product water, diluting the hydrochloric acid (CAS: 7647-01-0) solution. Commercial grade 23° Baume HCl solution (38% HCl concentration) will be purchased as fresh make-up for our process. The physical properties of HCl solutions are presented in the table below.

Table 8.5: Commercial grade hydrochloric acid solution properties

Concentration			Density	Molarity	pH	Viscosity	Specific heat	Vapour pressure	Boiling point	Melting point
kg HCl/kg	kg HCl/m ³	Baumé	kg/L	mol/dm ³		mPa·s	kJ/(kg·K)	kPa	°C	°C
10%	104.8	6.6	1.048	2.87	-0.5	1.16	3.47	1.95	103	-18
20%	219.6	13	1.098	6.02	-0.8	1.37	2.99	1.4	108	-59
30%	344.7	19	1.149	9.45	-1.0	1.7	2.6	2.13	90	-52
32%	370.88	20	1.159	10.17	-1.0	1.8	2.55	3.73	84	-43
34%	397.46	21	1.169	10.9	-1.0	1.9	2.5	7.24	71	-36
36%	424.44	22	1.179	11.64	-1.1	1.99	2.46	14.5	61	-30
38%	451.82	23	1.189	12.39	-1.1	2.1	2.43	28.3	48	-26

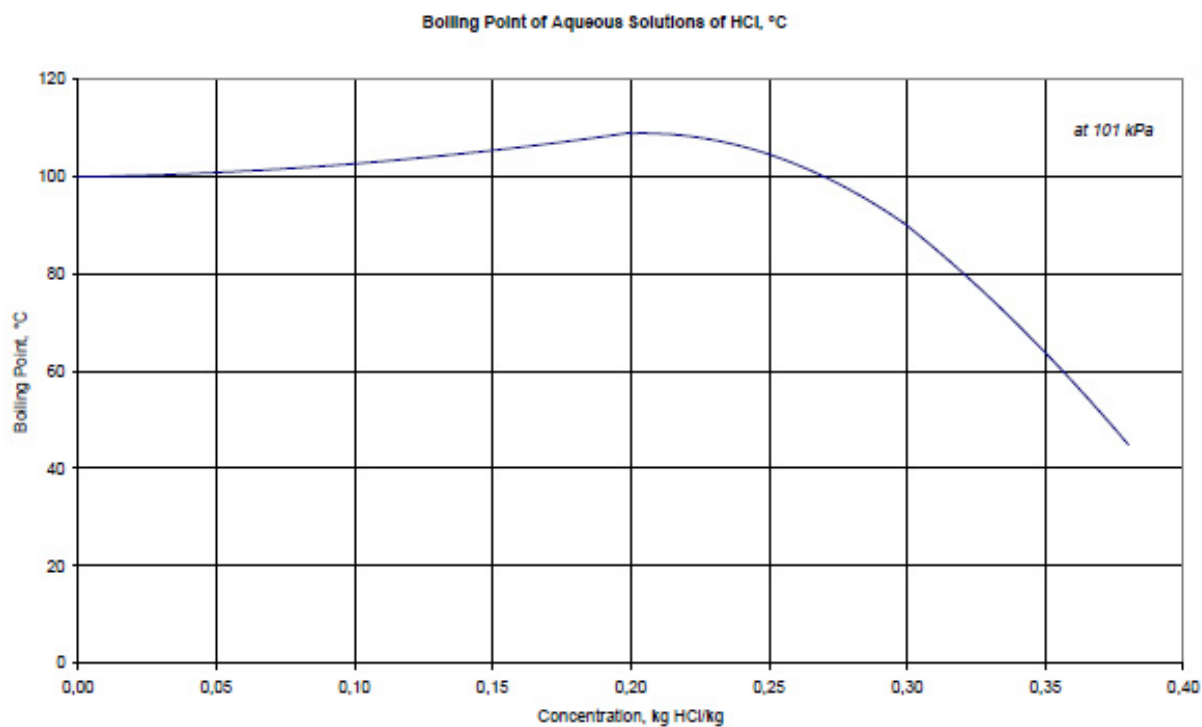
Source: Wikipedia

Note from the HCl solution boiling point curve below that the boiling point of an HCl solution increases only slightly as the concentration of HCl increases from zero to 22%, and then slowly decreases thereafter. Although the hydrochloric acid boiling curve shown below presents a classic azeotropic

distillation dilemma, the dilution of acid from its initial 0.1% concentration by water produced during the dehydration reaction allows the solution to be re-concentrated before reaching the azeotropic temperature peak. Since the proposed design only needs diluted hydrochloric acid to be re-concentrated to 0.1%, conventional distillation is suitable for this purpose within this acid concentration range.

An economic optimization would determine whether acid recovery is desirable at all, versus simply purging a portion of the diluted acid solution to the wastewater treatment plant, in order to avoid the capital and operating costs associated with multi-stage HCl acid recovery.

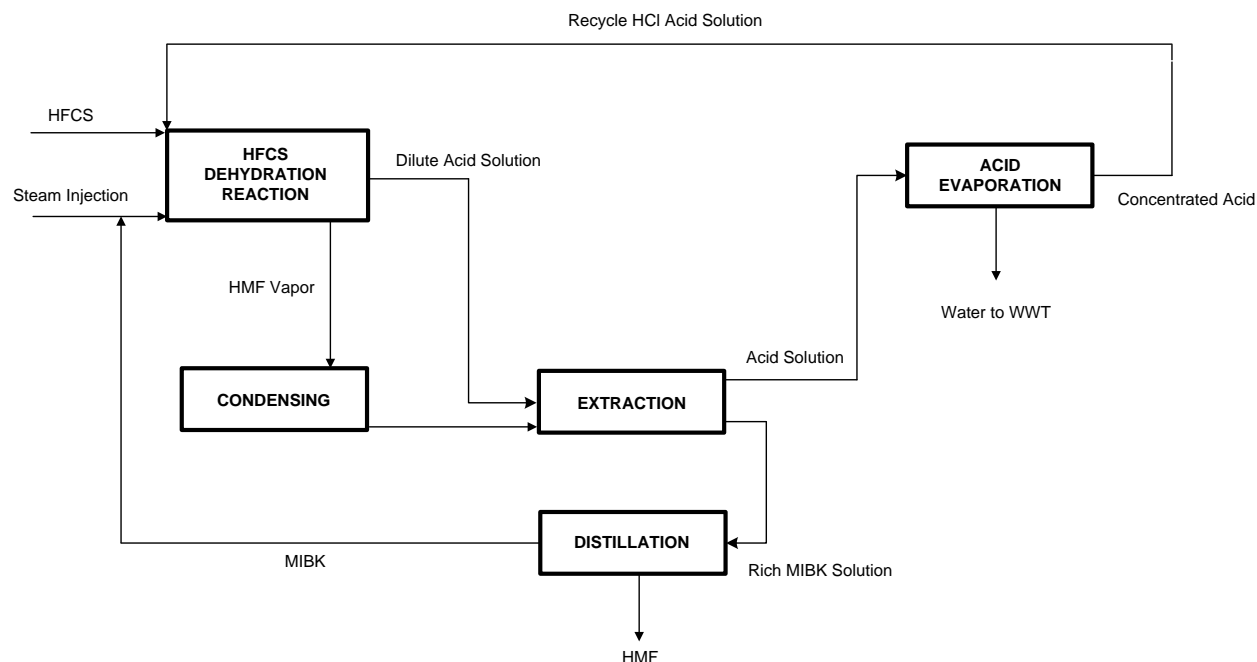
Figure 8.12: Hydrochloric acid solution boiling point curve



Source: Solvay

A block flow diagram for the proposed system is shown in the figure below.

Figure 8.13: IHS HMF from HFCS hydrolysis processing scheme



The rationale for using MIBK as the HMF extraction solvent is shown below with its physical and performance characteristics.

- Slightly soluble in water and miscible with most organic solvents
- High solvency power
- Low viscosity
- Viscosity reducer

Physical properties of MIBK used as the extracting solvent are presented in the table below. Un-converted HFCS feedstock in the hydrolysis reactor product stream is insoluble in MIBK, and will remain in the diluted hydrochloric acid liquid phase throughout the MIBK extraction process.

Table 8.6: Physical properties of MIBK solvent

Parameter	Value
CAS number	108-10-1
• Chemical formula	• $C_6H_{12}O$
Appearance	Colorless Liquid
Molecular weight	100.16
Boiling point	117.4°C
Vapor pressure	16 Torr at 20°C
Freezing point	-84°C
Refractive index	1.3957 at 20°C
Density	0.8008 g/mL (6.683 lb/gal) at 20°C
Density	0.7961 g/mL (6.643 lb/gal) at 25°C
Dielectric constant	13.11 at 25°C
Solvent group	6
Polarity index (P')	4.2
Eluotropic value on alumina	0.43
Viscosity	0.58 cP at 20°C
Surface tension	23.64 dyn/cm at 20°C
Solubility in water	1.7% at 20°C
Solubility of water in methyl isobutyl ketone	1.9% at 25°C
DOT hazard class	3, Flammable Liquid
Packing group	II
UN Identification Number	UN1245
Flash point	64°F (18°C) by closed cup
Lower explosive limit	1.20%
Upper explosive limit	8.00%
Time-weighted average	50 ppm ACGIH
Autoignition temperature	460°C
Evaporation rate in	
(n-butyl acetate = 1)	1.6
(ether = 1)	7.2
Specific heat @ 20°C	2.14 kJ/kg/°C
Heat of vaporization @ T _{boil}	364 kJ/kg
Heat of combustion (Net) @ 25°C	35000 kJ/kg
Conductivity @ 20°C	3*10 ⁻⁷ pS/m

A typical sales specification for commercial MIBK from Shell Oil is presented below.

Table 8.7: Shell Oil MIBK sales specification

Property	Unit	Min	Max	Method
Purity	% m/m	99.5		ASTM D3329
Dimethylketone	mg/kg		1000	ASTM D3329
Methyl isobutyl carbinol	mg/kg		1000	ASTM D3329
Mesityloxiide + Isomesityloxiide	mg/kg		1000	ASTM D3329
Water	%m/m		0.05	ASTM D1364
Acidity as Acetic acid	%m/m		0.005	ASTM D1613
Appearance	Clear and free from suspended matter			ASTM D4176
Color	Pt-Co		10	ASTM D1209
Density @ 20 oC	g/ml	0.799	0.802	ASTM D4052
Refractive Index @ 20 oC		1.395	1.397	ASTM D1218
Non Volatile Matter	g/100ml		0.002	ASTM D1353
Distillation, IBP	°C	114		ASTM D1078
Distillation, DP	°C		117	ASTM D1613

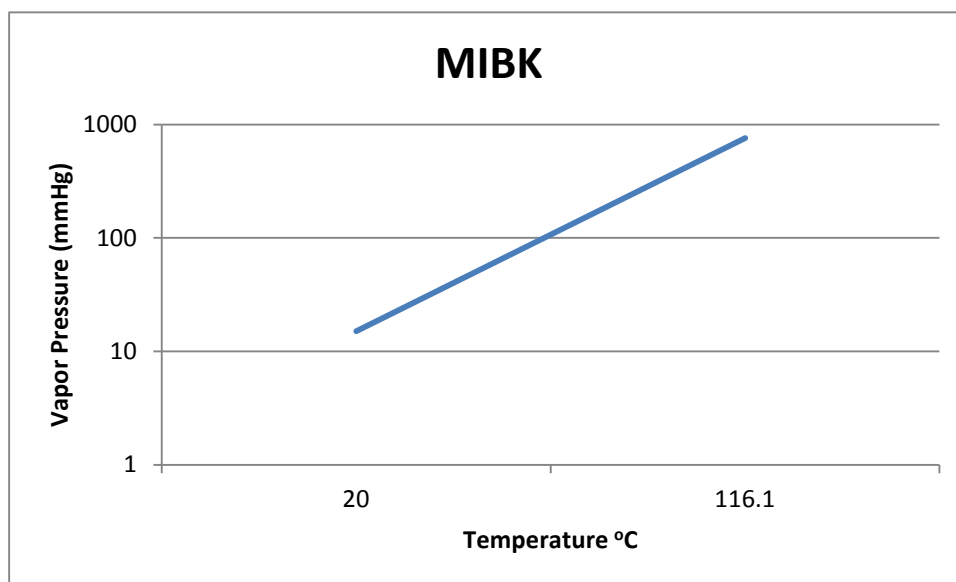
Source: Shell Oil [31C59]

The IHS design basis table for converting HFCS to HMF is provided below.

Table 8.8: Design basis table: HFCS to HMF

Parameter	Value
Reaction phase	Liquid
Feedstock conversion %	95
Product selectivity %	100
Design Temp °C	200
Design pressure psia	250
Residence time (min)	15
Catalyst	HCl in water

Since HMF boils at 351-354°C at atmospheric pressure, while solvent MIBK boils at only 117°C, fractional distillation is an effective way to separate and purify HMF from MIBK solvent. However, to minimize the potential thermal degradation of HMF at distillation temperatures, our design conducts the distillation under vacuum conditions, which allows the distillation to proceed effectively at significantly lower temperature. The vapor pressure curve for MIBK, useful for determining suitable vacuum conditions for fractional distillation, is presented below.

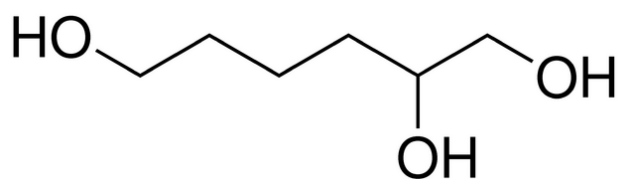
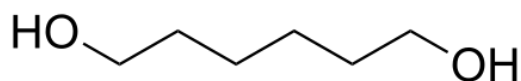
Figure 8.14: MIBK vapor pressure curve

Source: Computer Aided Data Book of Vapor Pressure [31C60] and Shuzo Ohe (www.s-ohe.com)

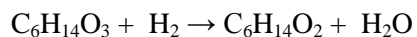
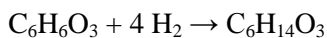
In summary for the dehydration reaction and extraction, adding MIBK to the dehydration reactor both dilutes the HMF formed, and also causes the HMF formed to preferentially migrate from the aqueous phase where it is formed to the solvent (MIBK) phase, minimizing the chance for the HMF to either re-hydrolyze, or oligomerize to form the humins and heavier tars and polymers documented by Kuster et al., [31C61, 31C62]

Hydrogenation of HMF to 1,2,6-Hexanetriol and 1,6-Hexanediol

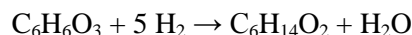
HMF produced by the dehydration of HFCS is hydrogenated to a combination of 1,2,6-hexanetriol, and subsequently 1,6-hexanediol, using Rennovia patented intellectual property. The molecular structure of 1,2,6-hexanetriol, and 1,6-hexanediol are shown in the figures below.

Figure 8.15: Molecular structure of 1,2,6-Hexanetriol**Figure 8.16: Molecular structure of 1,6-Hexanediol**

Rennovia's USPA 2013 / 0184495 A1 discloses a process for the hydrogenation of HMF over a platinum /tungsten active metal catalyst on zirconium oxide substrate at elevated temperature (60 – 200°C) and elevated pressure (200 – 2000 psia). The stoichiometric equations for the hydrogenation of HMF to 1,2,6-hexanetriol, and the subsequent hydrogenation of 1,2,6-hexanetriol to 1,6-hexanediol, are shown below.

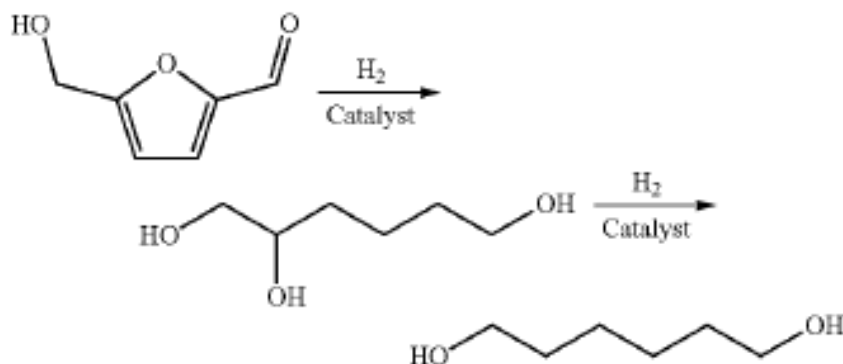


The overall equation for converting HMF to 1,6-hexanediol is shown below.



The molecular pathway from HMF to 1,6-HDO is shown in the figure below.

Figure 8.17: Molecular pathway from HMF to HDO



Yield of 1,6-HDO as high as 60% is reported in the patent application. Physical properties of 1,6-hexanediol and 1,2,6-hexanetriol are presented in the table below.

Table 8.9: Physical properties of hexanediol and hexanetriol (USPA 2013 / 0184495 A1)

Property	1,6-Hexanediol	1,2,6-Hexanetriol
Physical form	Colorless solid, sold as flakes	Light yellow viscous liquid
CAS number	629-11-8 Y	106-69-4
Molecular formula	C ₆ H ₁₄ O ₂	C ₆ H ₁₄ O ₃
Molar mass	118.17 g mol ⁻¹	134.17
Melting point	42 °C; 108 °F; 315 K	-20 °C
Boiling point at 760 mmHg	208 °C; 406 °F; 481 K	405-408 @ °C
Boiling point at 9.75 mmHg	141 °C	167 °C @ 2 mmHg
Boiling point at 5 mmHg		178
Solubility in water	5000 g/L	miscible
Solubility	soluble in ethanol and acetone, slightly soluble in diethyl ether, insoluble in benzene. ^[2]	
Density at 50 °C (kg/l)	1.116	
Density at 20 °C (kg/l)	0.96	1.109
Heat of fusion Btu/lb	74.34	
Heat of vaporization	306 Btu/lb	65 kJ/mol
Flash Point		191
Tagged closed cup	135 °C	
Pensky-Martens	147 °C	
Solubility in water	0.1 mg/l	
Water solubility in.....	500 mg/l	
Vapor pressure at 20 °C		<0.01 mmHg
Refractive index n ₂₀ /D		1.476

Although 1,6-hexanediol in this process is used only as an intermediate for the subsequent ammoniation to HMDA, our design is intended to produce a 1,6-hexanediol product purity that could be sold into the marketplace at industry accepted specifications. Below is a standard commercial industry specification for 1,6-hexanediol sold by BASF.

Table 8.10: BASF commercial sales specification for 1,6-hexanediol

Specification	Value	Test Method
Assay, % min	96.0	GC
Hexanediols, % min	99.0	GC
Cyclohexanediols, % max	3.0	GC
Acid number, mg KOH/g max	0.1	DIN EN 3682
Water, % max	0.3	DIN 51 777
Color, APHA max	15.0	DIN EN 1557

The Rennovia patent application discloses the use of a solvent to enhance the hydrogenation of HMF to 1,6-hexanediol, and uses water as the preferred solvent. For our process, our intent is to feed a 20% aqueous solution of HMF to the hydrogenation reaction section. The design basis for the HMF hydrogenation section is presented in the table below.

Table 8.11: Design basis table: HMF to 1,6-HDO

Parameter	Value
HMF to 1,2,6-Hexanetriol	
Reaction phase	Liq in H ₂ trickle bed Rx
Feedstock	20% HMF in H ₂ O
Feedstock conversion %	90
Product selectivity %	100% HTO+HDO
Design Temp °C	120
Design Pressure psia	1000
Residence time (min)	10
Catalyst	Pt/Mo on AlO
1,2,6-Hexanetriol to 1,6-Hexanediol	
Reaction phase	Liq in H ₂ trickle bed Rx
Feedstock conversion %	95
Product selectivity %	70
Design Temp °C	150
Design Pressure psia	1000
Residence time (min)	10
Catalyst	Pt/W on ZrO

As noted in the table above, our design assumes 60% selectivity of HMF to 1,6-hexanediol. The selectivity to the other 40% of by-products, documented in the Rennovia patent application, includes the following by product materials:

1,5-hexanediol
 1,2,5 hexanetriol
 1,2,5,6-hexanetetrol
 1-hexanol
 2-hexanol

These materials will be recovered in our design as a mixed C₆ alcohol by product stream that can be used as a commercial solvent and plasticizer feedstock. The Rennovia patent application claims that these C₆ alcohols can be separated from the desired 1,6-hexanediol via fractional distillation under vacuum conditions. Below are boiling point and melting point properties of these C₆ materials at standard conditions, as well as the claimed vacuum distillation temperature range documented in the Rennovia patent application.

Table 8.12: Hydrogenation reactor product properties

Chemical	Mol Wt	BP °C	MP °C	Vacuum distillation range °C
1,6-hexanediol	118	208	42	90 - 110
1,2,6-hexanetriol	134	405	-20	150 - 175
1,5-hexanediol	118	259	1.85	
1,2,5 hexanetriol	134	315	39	
1,2,5,6-hexanequatrol	150	na	na	
1-hexanol	102	157	-52	100 - 125
2-hexanol	102	139	-23	100 - 125
1,2-hexanediol	118	223	45	100 - 125

From the table above, it is feasible to purify 1,6-hexanediol from the reactor mixed product stream by vacuum distillation, while using the distillation train to also separate and recycle 1,2,6-hexanetriol and unconverted HMF. BASF's sales brochure on 1,6-hexanediol [31C63] provides the following boiling point and vapor pressure data.

1,6-Hexanediol Boiling Point

760 mmHg	253-260 °C
9.75 mmHg	141-142 °C

1,6-Hexanediol Vapor Pressure

20 °C	0.54 mmHg
100 °C	0.75mmHg
150 °C	15.00 mmHg

From the above BASF physical property data, we can estimate that a vacuum distillation temperature of approximately 141-142°C will require that 1,6-hexanediol be distilled at an operating pressure of 9.75 mmHg.

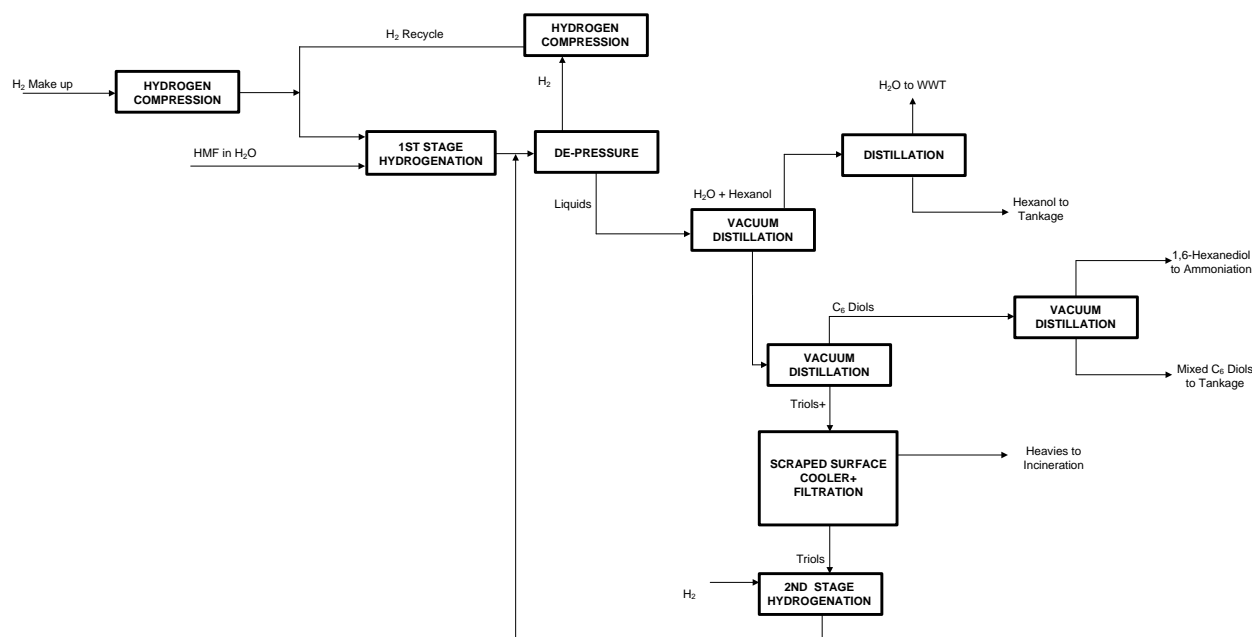
Our approach to designing the HMF hydrogenation section is to dissolve high purity HMF in distilled water, pre-heat the stream to reaction temperature, and conduct a 2-stage hydrogenation reaction using high pressure, catalyst packed reactors operating adiabatically.

The examples provided in the Rennovia patent application describe hydrogenating HMF to 1,6-hexanediol in a single hydrogenation reaction, or conducting the reaction in two stages. The first stage hydrogenates HMF to 1,2,6-hexanetriol, while the 2nd stage hydrogenates 1,2,6-hexanetriol to 1,6-hexanediol. From our interpretation of the example results, it appears more effective to operate the process in two distinct hydrogenation steps. The hydrogenation of HMF to 1,2,6-hexanetriol was shown experimentally to be conducted with nearly 100% conversion to a nearly 50:50 mix of 1,2,6-hexanetriol and 1,6-hexanediol using platinum-molybdenum catalyst on an alumina substrate. A separate hydrogenation of 1,2,6-hexanetriol to 1,6-hexanediol was conducted experimentally to achieve 95% conversion at a selectivity to 1,6-hexanediol of 68% using a platinum-tungsten catalyst on zirconium oxide substrate.

Our design intent is to conduct the 1st stage hydrogenation of HMF to a mixture of 1,6-hexanediol and 1,2,6-hexanetriol. Reactor liquid product from 1st stage hydrogenation is passed through the distillation purification train to recover 1,6-hexanediol as intermediate product to tankage, while purifying the 1,2,6-hexanetriol so that it can be processed through the 2nd stage hydrogenation reactor for conversion to 1,6-hexanediol.

The proposed distillation train sequence is shown in the block flow diagram below. HMF feedstock dissolved in water is hydrogenated at high pressure in packed catalyst bed reactors to produce primarily a mixture of 1,6-hexanediol and 1,2,6-hexanetriol, plus water of hydrogenation. HMF feedstock conversion is nearly 100%. The high pressure mixed phase reactor product (liquid + vapor) is de-pressured to release and recycle dissolved hydrogen vapor. The de-pressured reactor product is distilled under vacuum to take an overhead product stream containing water of hydrogenation plus mono-alcohols. The overhead stream is further distilled to remove water (sent to wastewater treatment), and produce a mixed C₆ mono-alcohol by-product stream, which is sent to tankage. The bottoms stream from the first vacuum distillation column contains primarily C₆ diols plus heavier material (triols, quatrols, polymer and tars). This stream is vacuum distilled to remove the C₆ diols as the overhead product stream. This stream is further distilled to take 1,6-hexanediol as the overhead product, and a mixture of 1,2-hexanediol and 1,5-hexanediol as the bottoms product. The bottoms product is sent to by-product tankage. The 1,6-hexanediol is the desired intermediate product that will be subsequently ammoniated to produce HMDA.

Figure 8.18: Proposed HMD hydrogenation product distillation sequence



The triols + heavies stream is cooled in a scraped surface heat exchanger which solidifies the material heavier than triols, allowing them to subsequently be filtered and incinerated. Consideration of either burning this material as plant fuel, or selling this material as commercial product was taken, but in our judgment the environmental permitting requirements for combustion would be excessive given the small quantity of material generated (0.34 mt/stream hour). The small quantity generated, in our opinion, does not justify the cost of producing and marketing a commercial product such as animal feed. The triols stream is directed to the 2nd stage of hydrogenation where the most prominent component (1,2,6-hexanetriol) is hydrogenated to 1,6-hexanediol. The product stream from the 2nd stage hydrogenation

reactor is recycled to the de-pressuring drum to recycle excess dissolved hydrogen gas, and fractionate the stream for 1,6-hexanediol recovery and purification.

An alternative approach to 1,6-hexanediol purification is patented by Ube Industries (USP 8304585, 8513472). Ube takes the mixed C₆ mono and di-alcohol streams from its reactor (producing 1,6-HDO via cyclohexane oxidation), and reacts the mixed stream with an alcohol (preferentially methanol) to produce the corresponding esters from contained by-product monocarboxylic and dicarboxylic acids, conducting the separation of esters by distillation, and de-esterifying the desired product via hydrogenation in a separate reactor. The boiling point range of the various esters produced are substantially wider than the range of boiling points of the mono and di-alcohols, making distillation of esters lower cost than distillation of alcohols.

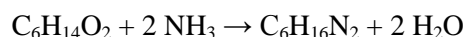
Ammoniation of 1,6-hexanediol to HMDA

The Rennovia patent application does not offer discovery information for producing HMDA from 1,6-hexanediol. Instead, it cites four older US patents by others that, in aggregate, establish the prevailing science for conducting this chemistry. As of year-end 2013, Rennovia indicated that it has developed its own proprietary process technology and catalysis to improve upon the prior patent claims for 1,6-hexanediol ammoniation to HMDA, but at this time their know how has not been published or patented, although we have been informed by Rennovia that a patent application has been filed. The relevant patents by others that are cited by Rennovia are listed below.

Table 8.13: Cited patents for ammoniation of 1,6-hexanediol to HMDA

Patent #	Date	Title	Assignee
3270059	30-Aug-66	Production of diamino alkanes	BASF
3268588	23-Aug-66	Process for producing hexamethylenediamine from 1,6-hexanediol	Celanese
3215742	2-Nov-65	Process for the preparation of alkylene diamines	Celanese
2754330	10-Jul-56	Manufacture of aliphatic diamines	DuPont

The chemical reaction stoichiometry for the ammoniation of 1,6-HDO to HMDA is shown below.

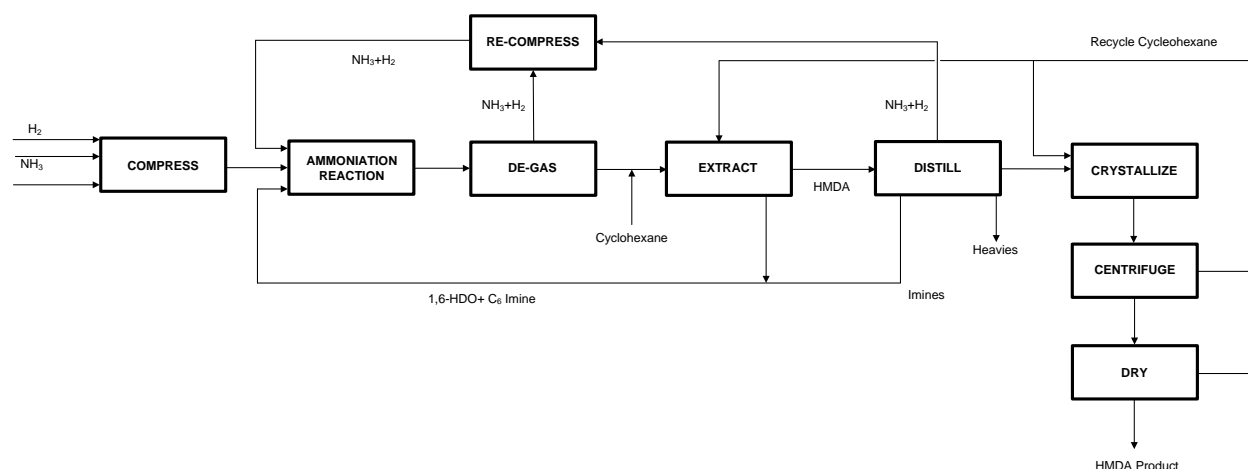


Based upon our review of the patents listed in Table 8.13, and the identification of subsequent patents that also describe the ammoniation of 1,6-hexanediol to produce HMDA, we have developed what we believe is a viable commercial continuous process using existing art and science. The design basis for our approach is provided in the table below.

Table 8.14: Ammoniation reaction design basis table

Parameter	Value
Reaction phase	Liq + Vapor
Feedstock conversion %	15%
Product selectivity %	90%
Design Temp °C	200
Design Pressure psia	3000
Residence time (min)	10
Catalyst	Raney nickel

The overall process scheme we propose is shown in the figure below.

Figure 8.19: Proposed ammoniation of 1,6-hexanediol to HMDA

1,6-hexanediol and ammonia are pre-heated to 200°C and pressurized to 3000 psig, and react in a packed bed plug flow reactor filled with Raney nickel catalyst. A small amount of hydrogen is supplied with the ammonia to enhance reaction kinetics and selectivity. Per pass conversion is 15%, and selectivity to HMDA is 90%. Reactor product is de-gassed, with the overhead vapor ($\text{NH}_3 + \text{H}_2$) re-compressed and recycled to the reactor.

The liquid product from the de-gassing drum contains un-converted 1,6-hexanediol, product HMDA, heavy polymer products, hexamethylene imine, 6-aminohexanol-1, cyclohexylamine, 1,2-diaminocyclohexane, and 1,4-diaminocyclohexane. Since 1,6-hexanediol and HMDA have nearly identical boiling and melting points (see table below), conventional distillation or crystallization are unable to separate them effectively.

Table 8.15: Ammoniation reaction component properties

Component	Boiling point (°C)	Melting point (°C)
1,6-Hexanediol	208	42
Hexamethylene diamine	205	41
Cyclohexane	81	6
Hexamethylene imine	138	-37
6-amino hexanol-1	137	56
Cyclohexylamine	135	-18
1,4-Diaminocyclohexane	197	71
1,2-Diaminocyclohexane	80	15

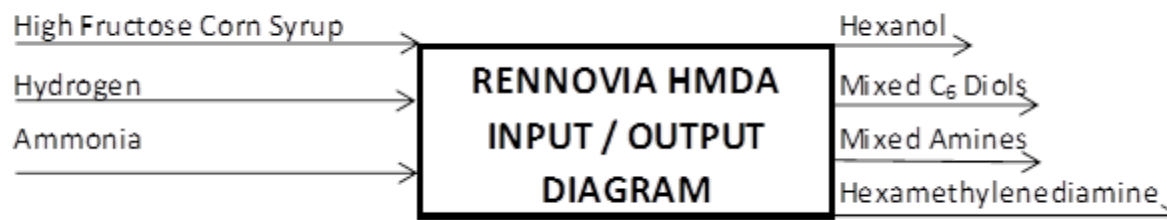
Since HMDA is highly soluble in cyclohexane, while 1,6-hexanediol is nearly insoluble in cyclohexane, cyclohexane is a suitable liquid-liquid extraction solvent. When added to the ammoniation reactor product stream, and allowed to settle in a decanter, an upper oil phase will form containing cyclohexane, HMDA, and other non-polar components. A lower polar phase will form containing un-converted 1,6-hexanediol and other intermediate mono-hydric and di-hydric alcohols. The lower polar-phase stream containing primarily un-converted 1,6-hexanediol is recycled to the ammoniation reactors.

The upper phase stream from the decanting drum is directed to a distillation train designed to purify HMDA. The lightest liquid component is solvent cyclohexane, which is taken as an overhead distillate and used in the subsequent crystallization step. A small quantity of H₂ and NH₃ gas will not condense in the overhead section of this column, and will be directed as a vapor from the condenser's receiving drum to the ammonia recycle compressor for recycle to the ammoniation reactors. Intermediate mono-amines and imines will also be recycled to the ammoniation reactors to complete the ammoniation reaction to produce HMDA. Heavy polymer will be incinerated.

Although most by products from the upper oil phase can be separated from HMDA by distillation, 1,4-diaminocyclohexane boils at nearly the same temperature as HMDA, and cannot be effectively removed by distillation. For this reason, the HMDA stream from distillation is re-dissolved in cyclohexane solvent, and crystallized at ambient pressure at reduced temperature (10°C). Under these conditions, HMDA will preferentially form crystals that can be subsequently centrifuged and dried to product specifications. The cyclohexane rich liquor from the centrifuge and dryer is recycled back to the dissolving drum. A small portion of this stream is distilled to remove accumulated 1,2-diaminocyclohexane and 1,4-diaminocyclohexane, which can be sold into the polyurethane market.

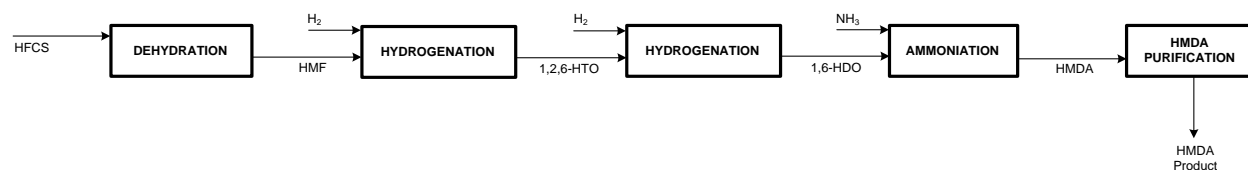
Rennovia input/output and block flow diagrams

Based upon the process as proposed above, we have summarized the essential feedstocks and products for the aggregated process. These are shown on the input/output diagram below.

Figure 8.20: Rennovia Input/Output diagram

High fructose corn syrup (HFCS) is the basic feedstock for the Rennovia HMDA process, and is dehydrated to 5-hydroxymethylfurfural (HMF). HMF is hydrogenated to 1,2,6-hexanetriol, purified by distillation, and further hydrogenated to 1,6-hexanediol. The hydrogenation reactions produce by products consisting primarily of C₆ mono-alcohols (1-hexanol and 2-hexanol), and C₆ di-alcohols. 1,6-hexanediol is finally ammoniated to produce HMDA product, plus by-product mixed amines.

We have chosen to segment the process into five process sections, as shown in the figure below.

Figure 8.21: Rennovia block flow diagram

Process description

We have segmented the Rennovia process into five plant sections, as listed below.

Section 100 – 5-Hydroxymethylfurfural from HFCS by Dehydration

Section 200 – Hydrogenation of HMF to 1,2,6-Hexanetriol

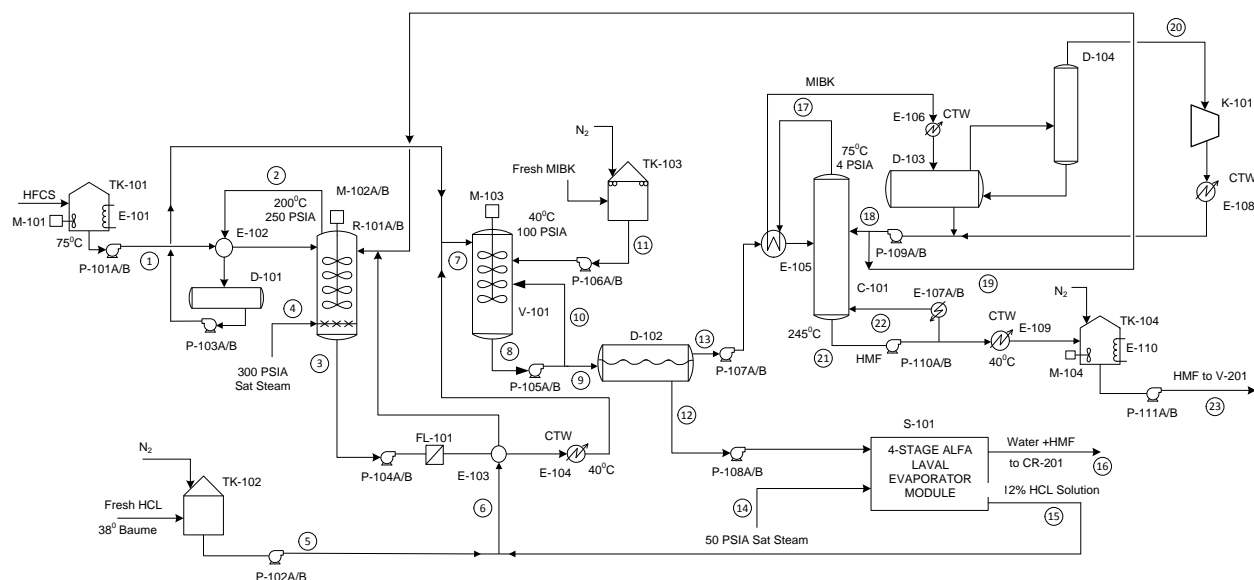
Section 300 – Hydrogenation of 1,2,6-Hexanetriol to 1,6-Hexanediol

Section 400 – Ammoniation of 1,6-Hexanediol to HMDA

Section 500 – HMDA Purification

Section 100 – Hydroxymethylfurfural from HFCS by dehydration

Figure 8.22: Section 100 PFD – HFCS hydrolysis to HMF



High fructose corn syrup (HFCS) is purchased as a viscous liquid, and stored in a well-mixed, heated and insulated day tank (Tk-101). HFCS is pre-heated in E-102, and pumped into dehydration reactors R-101 A/B. Also entering R-101 A/B is heated 0.1% hydrochloric acid solution. Bulk purchases of 23° Baume hydrochloric acid (38% concentration) are used as fresh make-up to the process. A commercial specification for 23° Baume hydrochloric acid from Axiall is presented in the table below.

Table 8.16: Axiall 23° Baume hydrochloric acid commercial specification

Item Specification APHA	Value
Color, max	15
Degrees Baume DEG Baume @60F	23.0-23.4
Arsenic, max (AS)	0.1
Bromide, max (BR)	50
Calcium, max (CA)	2
Free chlorine, max (CL2)	3
Fluoride, max (F)	2
Iron, max (FE)	0.5
Non-volatile residue, max (NVR)	15
Organics, max	1
Lead, max (PB)	0.2
Sulfate, max % by wWeight	10
Hydrogen chloride % weight	37.1-38.0

Source: Axiall

Since the dehydration reaction produces water, the hydrochloric acid becomes diluted during processing, and must be re-concentrated before being recycled back to the R-101 A/B hydrolysis reactors. Physical properties of hydrochloric acid solutions at different concentration levels are provided in the table below.

Table 8.17: Hydrochloric acid solution properties

	-5°C	0°C	10°C	20°C	40°C	60°C	80°C	100°C
Concentration (% Weight)	Density (kg/L)							
1	1.0048	1.0052	1.0048	1.0032	0.9970	0.9881	0.9768	0.9636
2	1.0104	1.0106	1.0100	1.0082	1.0019	0.9930	0.9819	0.9688
4	1.0213	1.0213	1.0202	1.0181	1.0116	1.0026	0.9919	0.9791
6	1.0321	1.0319	1.0303	1.0279	1.0211	1.0121	1.0016	0.9892
8	1.0428	1.0423	1.0403	1.0376	1.0305	1.0215	1.0111	0.9992
10	1.0536	1.0528	1.0504	1.0474	1.0400	1.0310	1.0206	1.0090
12	1.0645	1.0634	1.0607	1.0574	1.0497	1.0406	1.0302	1.0188
14	1.0754	1.0741	1.0711	1.0675	1.0594	1.0502	1.0398	1.0286
16	1.0864	1.0849	1.0815	1.0776	1.0692	1.0598	1.0494	1.0383
18	1.0975	1.0958	1.0920	1.0878	1.0790	1.0694	1.0590	1.0479
20	1.1087	1.1067	1.1025	1.0980	1.0888	1.0790	1.0685	1.0574
22	1.1200	1.1177	1.1131	1.1083	1.0986	1.0886	1.0780	1.0668
24	1.1314	1.1287	1.1238	1.1187	1.1085	1.0982	1.0874	1.0761
26	1.1426	1.1396	1.1344	1.1290	1.1183	1.1076	1.0967	1.0853
28	1.1537	1.1505	1.1449	1.1392	1.1280	1.1169	1.1058	1.0942
30	1.1648	1.1613	1.1553	1.1493	1.1376	1.1260	1.1149	1.1030
32	1.1814	1.1763	1.1674	1.1593	1.1471	1.1359	1.1246	1.1126
34	1.1929	1.1876	1.1781	1.1691	1.1566	1.1452	1.1339	1.1216
36	1.2043	1.1988	1.1889	1.1789	1.1661	1.1544	1.1432	1.1305
38	1.2156	1.2100	1.1996	1.1885	1.1754	1.1635	1.1525	1.1393
40				1.1980				

Source: Axiall

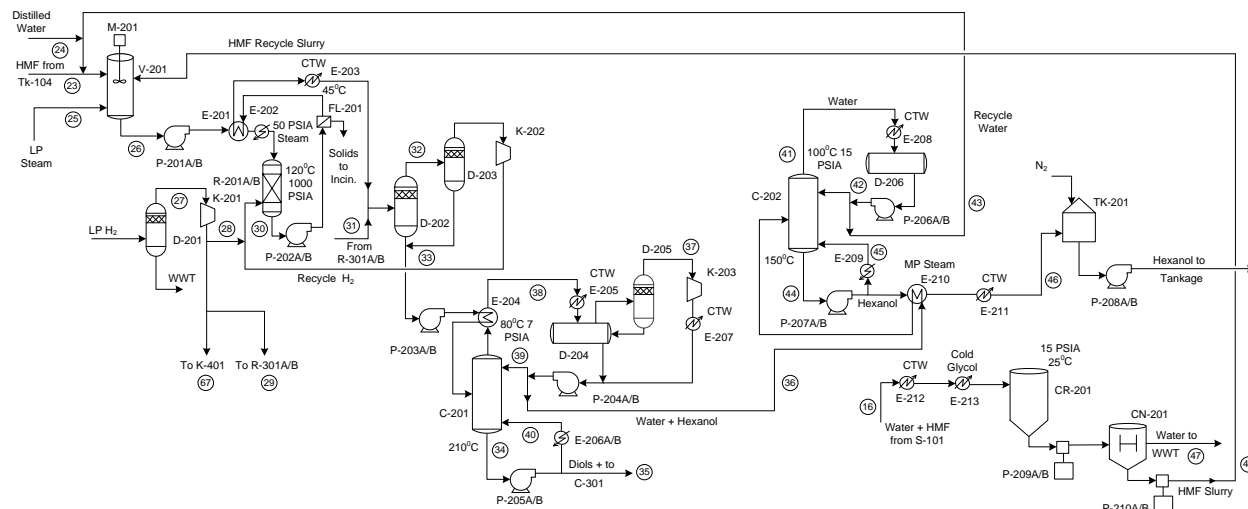
HFCS and dilute hydrochloric acid enter near the top of the reactor, and proceed downward. The dehydration reactors operate at 200°C and 250 psia. 300 psia saturated steam is distributed into the reactor near its bottom, and flows upward causing the reactor contents to boil mildly. HFCS is dehydrated to crude 5-hydroxymethylfurfural (HMF) in the dehydration reactor, and the liquid reactor product exits the bottom of the reactor vessels. MIBK solvent is added to the reactors to pull produced HMF from the aqueous phase into the MIBK solvent phase. The low solubility of fructose in MIBK minimizes the oligomerization of produced HMF with fructose to form humins.

The crude HMF mixed stream is pumped through a feed/product heat exchanger, and a cooler before entering the extraction mixing tank V-101, where it is well mixed with more MIBK and very dilute 0.1% concentration hydrochloric acid from the reactor. The extraction tank operates at 40°C and 100 psia. The feed enters V-101 at the top, and exits at the bottom, where it is pumped to extraction settling tank D-102. A 2-phase liquid forms in the settling drum, with MIBK extracting nearly all of the HMF produced by dehydration/hydrolysis and settling as the upper phase. The bottom phase contains the hydrochloric acid solution, which has been diluted by the water formed by the dehydration reaction, plus a small amount of HMF. The hydrochloric acid is re-concentrated in a 4-stage multi-effect evaporator module provided by Alfa Laval S-101 (or equivalent). The water and residual HMF removed from the dilute acid is directed to the HMF crystallizer (CR-201), which is designed to recover residual HMF from the water phase.

The HMF/MIBK upper oil layer from settling tank D-102 is pumped to a distillation column (C-101) that is designed to re-concentrate MIBK as the overhead distillate, and produce concentrated HMF as the bottoms product. The distillation column operates under vacuum (4 psia), with an overhead temperature of 75°C, and a bottoms temperature of 245°C. Concentrated HMF is cooled in E-109, and stored in a day tank (Tk-104) that contains an immersion heater (E-110) and agitator (M-104).

Section 200 – Hydrogenation of HMF to 1,2,6-Hexanetriol

Figure 8.23: Section 200 PFD – Hydrogenation of HMF to 1,2,6-hexanetriol



HMF is diluted with water to a concentration of 20% in mixing vessel V-201, heated, and pumped to hydrogenation reactors R-201 A/B, which are designed to produce a mixture of 1,2,6-hexanetriol and 1,6-hexanediol. Hydrogen from offsites (purchased hydrogen) is compressed to 1250 psia in K-201, and directed to a vapor distributor in the bottom of R-201 A/B. HMF aqueous solution is fed to the top of the packed catalyst bed reactors, while hydrogen is fed to the bottom of the reactors. The reactors operate at 120°C and 1000 psia. Reactor product is pumped through a dual basket filter (FL-201), which removes solid tars and heavy polymer for discharge to incineration.

Downstream of the dual basket filters, the reactor product is directed to a 3-stage degassing drum (D-202) that operates at 50 psia, for the purpose of degassing hydrogen for recycle. Recycle hydrogen compressor K-202 is provided for that purpose.

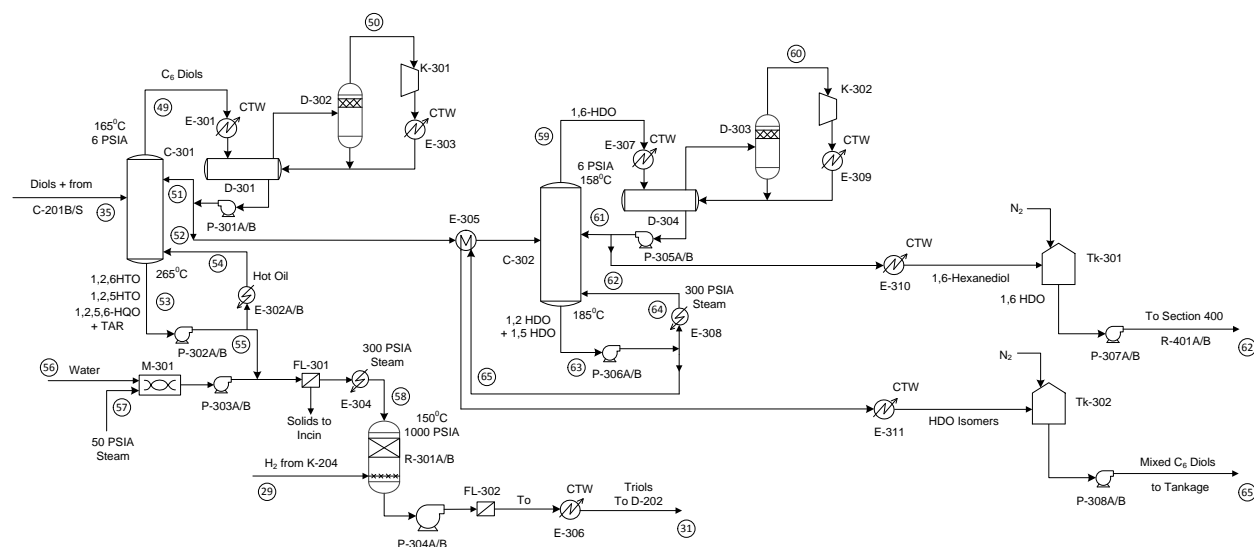
De-gassed reactor product is distilled under vacuum conditions in C-201, for the purpose of removing water plus mono-hexanols (1-hexanol, 2-hexanol) as the overhead distillate. The column operates at vacuum (7 psia), in order to minimize the thermal degradation of produced C₆ diols and triols. The overhead distillate from C-201 is directed to column C-202, which takes water as the overhead distillate product for recycle to the mixing vessel V-201. The bottoms product stream from C-202 is a mixture of 1-hexanol and 2-hexanol, which is cooled in E-211, and directed to a day tank (TK-201), for eventual disposition to offsites tankage for sales as a mixed hexanol by-product stream.

The bottoms product stream from C-201 contains C₆ diols plus heavier material (triols, un-converted HMF), which is pumped to section 300 for subsequent reaction to hydrogenate C₆ triols to C₆ diols.

A dilute stream of un-converted HMF in water is recovered from the 4-stage HCl acid concentrator (S-101), and chilled to 25°C in E-213 for the purpose of crystallizing the HMF out of aqueous solution. The HMF crystal solution is concentrated to 20% solids in crystallizer CR-201, and further concentrated to 80% solids slurry in centrifuge CN-201. The concentrated slurry is recycled to the dehydration reactors (R-101 A/B), while the liquor product from the centrifuge is discharged to the plant's wastewater treatment plant.

Section 300 – Hydrogenation of 1,2,6-Hexanetriol to 1,6-Hexanediol

Figure 8.24: Section 300 PFD – Hydrogenation of 1,2,6-hexanetriol to 1,6-hexanediol

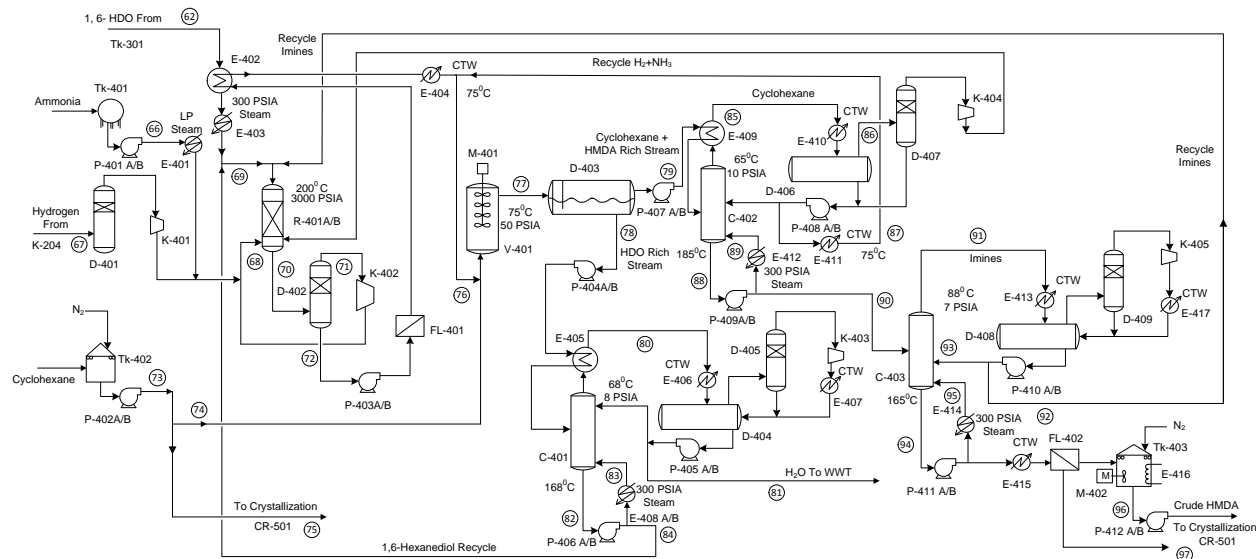


C₆ Diols distilled from the R-201 A/B HMF hydrogenation reactors are further distilled in C-301 for the purpose of separating diols from triols. C-301 operates under vacuum conditions, with a design pressure of 6 psia, an overhead temperature of 165°C, and a bottoms temperature of 265°C. The overhead distillate stream is a mixed diol stream containing primarily 1,6-hexanediol, 1,2-hexanediol, and 1,5-hexanediol. This distillate stream is directed to C-302, which is the 1,6-hexanediol column, and is designed to produce high purity 1,6-hexanediol as the overhead distillate product. The distillate product stream is cooled and stored in day tank Tk-301. The bottom stream product from C-302 is a mixture of 1,2-hexanediol and 1,5-hexanediol, which is sold as a commercial by-product. The bottoms stream is cooled and stored in day tank Tk-302, before being pumped to offsites bulk storage tankage.

The bottoms stream from C-301 is primarily C₆ triols, plus heavier materials such as polymer and tars. This stream is diluted to 20% in hot water, and fed to triols hydrogenation reactors R-301 A/B. These reactors are designed to convert primarily 1,2,6-hexanetriol to 1,6-hexanediol, but they will also hydrogenate other triols to their corresponding diols. Water is heated with live steam injection through a Kenics (or equal) static mixer M-301, and combines with the bottoms diols stream from C-301. The diluted stream is filtered to remove solids, precipitated tars and polymer in FL-302, heated to 150°C reaction temperature in E-304, and fed to the top of R-301 A/B, which operates at 150°C, and 1000 psia. Hydrogen pressured to 1250 psia in K-201 is fed to the bottom of R-301 A/B through a gas distribution manifold, and hydrogenates triols to diols using a packed bed catalyst reactor. The R-301 A/B bottoms liquid product stream is cooled in E-306, and directed back to the Section 200 distillation train for the purpose of de-gassing hydrogen, and then separating diols from triols via distillation.

Section 400 – Ammoniation of 1,6-Hexanediol to HMDA

Figure 8.25: Section 400 PFD – Ammoniation of 1,6-hexanediol to HMDA



The intent of section 400 is to react 1,6-hexanediol with ammonia to produce crude HMDA, plus water of reaction. 1,6-hexanediol from Tk-301 is reacted with ammonia to produce HMDA in reactors R-401 A/B. Liquid ammonia stored in sphere Tk-401 is pressured by P-401 A/B to 3250 psia and vaporized in E-401, before being fed to the ammoniation reactors. A small amount of hydrogen is also mixed with the ammonia vapor, and also fed to R-401 A/B through a bottoms vapor distribution manifold. Since R-401 A/B is designed to operate at 200°C and 3000 psia, 1250 psi hydrogen from K-201 must be boosted by K-401 to 3250 psia. Also fed to R-401 A/B is recycle mixed C₆ imines from the downstream distillation train.

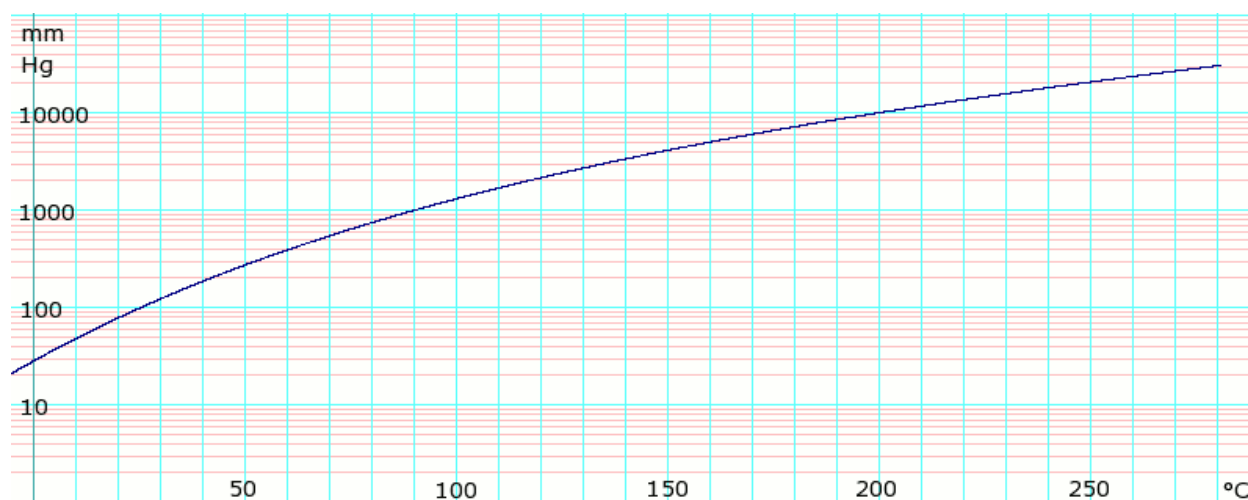
Ammoniation reactor liquid product from R-401 A/B is degassed in D-402, with the overhead vapor of primarily hydrogen and ammonia recompressed in K-402, and recycled to the reactors. The degassed liquid product containing primarily produced HMDA and un-converted feedstock HDO is then separated from crude HMDA via liquid-liquid extraction. Since product HMDA and feedstock 1,6-hexanediol boil and melt at nearly identical temperatures, separation by distillation or crystallization is not economically feasible.

HMDA and 1,6-hexanediol can be separated by liquid-liquid extraction using a non-polar solvent. We have chosen cyclohexane, since it has a relatively high boiling temperature (81°C), is highly miscible in HMDA, but nearly immiscible in 1,6-hexanediol. Physical properties of cyclohexane are presented in the table below.

Table 8.18: Cyclohexane physical property table

Property	Value
CAS number	110-82-7 Y
Formula	C ₆ H ₁₂
Molar mass	84.16 g/mol
Appearance	colorless liquid
Odor	sweet, gasoline-like
Density	0.7781 g/mL, liquid
Melting point	6.47 °C; 43.65 °F; 279.62 K
Boiling point	80.74 °C; 177.33 °F; 353.89 K
Solubility in water	Immiscible
Solubility	soluble in ether, alcohol, acetone miscible with olive oil
Refractive index (nD)	1.42662
Viscosity	1.02 cP at 17 °C
Std enthalpy of formation $\Delta_f H^\circ_{298}$	-156 kJ/mol
Std enthalpy of combustion $\Delta_c H^\circ_{298}$	-3920 kJ/mol
vapor density :	2.9 (vs air)
vapor pressure :	168.8 mm Hg (37.7 °C)
$\Delta_f H^\circ_{\text{liquid}}$, kJ/mol	-157.7 \pm 1.8
$\Delta_c H^\circ_{\text{liquid}}$, kJ/mol	-3930. \pm 20.
S°_{liquid} , J/mol °K	203.89
$C_{p,\text{liquid}}$ (J/mol*K) @ 298 °K	156
Flash point	-18 °C
Autoignition temperature	260 °C
Lower explosion limit	1.30%
Upper explosion limit	8%

Cyclohexane has a boiling temperature of 81°C, which enhances separation by distillation since the use of vacuum distillation (to minimize degradation of components in the bottom of the column) allows the overhead cyclohexane distillate to still be condensed with cooling water. Below is the vapor pressure curve for cyclohexane.

Figure 8.26: Cyclohexane vapor pressure curve

Source: Wikipedia

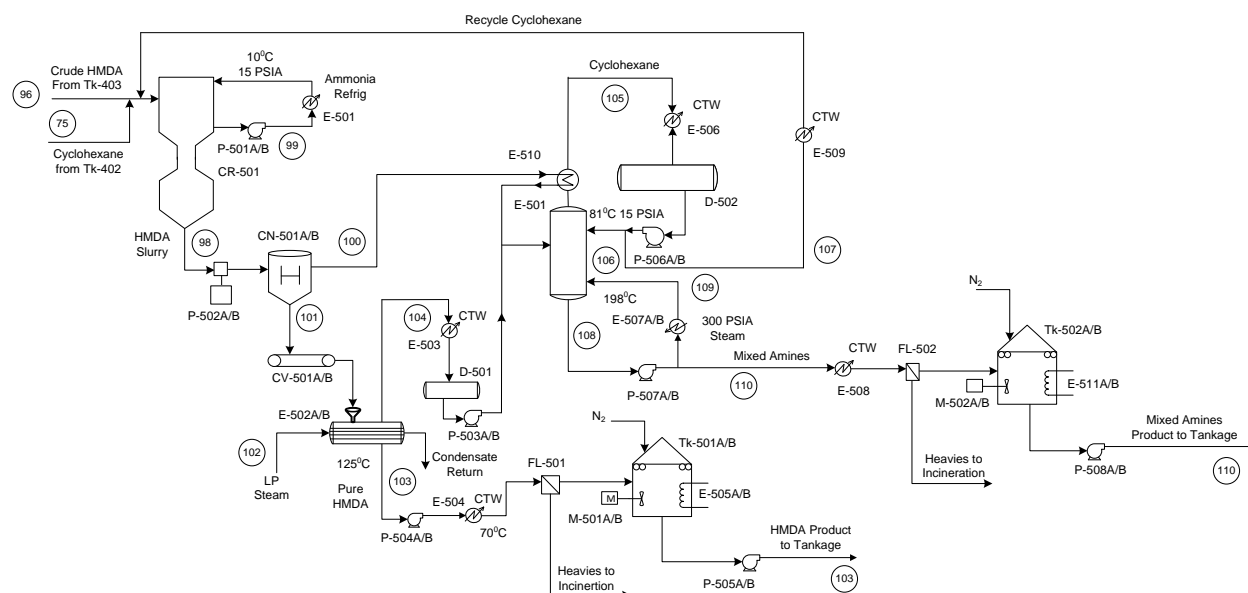
Both HMDA and 1,6-hexanediol are highly soluble in water, eliminating the possibility of using water as an extraction solvent. Fresh (from Tk-402) and recycle cyclohexane are mixed with the reactor product liquid in extraction vessel V-401, and allowed to phase separate in D-403. Un-converted 1,6-hexanediol, other by product mono and di-alcohols, and water produced by the reaction form a lower aqueous layer in D-403, while the cyclohexane extraction solvent and HMDA (plus other amines and imines) form an upper oil layer.

The lower aqueous layer from D-403 is pumped to dewatering distillation column C-401, which operates at 8 psi vacuum. Water produced by the reaction is taken as the overhead distillate product, while hexanol and other polar hydrocarbons are removed as the bottoms product stream, and recycled back to the R-401 A/B ammoniation reactors.

The upper oil layer from D-403 is pumped to C-402 distillation column, for the purpose of recovering as overhead distillate product at high purity cyclohexane solvent. The cyclohexane stream from reflux pumps P-408 A/B is cooled through exchanger E-411, and recycled to the extraction vessel V-401. The bottoms product stream from C-402 is fed to distillation column C-403 for the purpose of recovering at high purity in the overhead distillate product stream a mixed imine stream, which is recycled back to the R-401 A/B ammoniation reactors for further conversion to crude HMDA. The bottoms product stream from C-403 is primarily crude HMDA, plus heavy by-products such as oligomers, polymers, and tar. The bottoms product stream is cooled to near ambient temperature in E-415, and filtered through FL-402 to remove precipitated solids such as polymer and tar. The polymers and tar heavy material is sent to incineration. The filtered stream represents crude HMDA, which is stored temporarily in day tank Tk-403. Due to HMDA's relatively high crystallization temperature (39 - 42°C), Tk-403 is provided with an internal immersion heater E-416 and side entering mixer M-402, in order to maintain its contents in the liquid phase.

Section 500 – HMDA Purification

Figure 8.27: Section 500 PFD – HMDA purification



The purpose of section 500 is to purify crude HMDA to product specifications. HMDA is sold commercially at 99.9% purity (or greater) for nylon 66 fiber applications, and in technical grades of lower purity, usually in aqueous solutions of 60% to 90% HMDA. Since pure HMDA at standard conditions is a crystalline solid, aqueous solutions provide the benefit of handling HMDA as a liquid. Impurities found in fiber grade HMDA include 2-aminomethylcyclopentylamine, 1,2-diamonocyclohexane, 6-aminocapronitrile, and tetrahydroazepine.

HMDA purified by distillation from Tk-403 is diluted to a 20% concentration in cyclohexane, and pumped into Oslo crystallizer CR-501. The crystallizer operates at atmospheric pressure and 10°C. To achieve these sub-ambient temperatures, the crystallizer contents are pumped around external cooler E-501, which is supplied with ammonia refrigerant from a modular package refrigeration unit. Chilling the crystallizer to 10°C will cause the HMDA to crystallize, while maintaining nearly all of the other contaminants dissolved in the cyclohexane solvent.

The Oslo crystallizer CR-501 is designed to concentrate crystallized HMDA in a 20% slurry at the bottom of the crystallizer. The HMDA slurry is pumped by P-502 A/B to puller centrifuges CN-501 A/B, which concentrate the HMDA slurry to an 80% solids filter cake. Cyclohexane rich liquor from the centrifuges is pumped to distillation column C-501 for cyclohexane purification and recovery.

The filter cake from the centrifuges are conveyed (via CV-501 A/B) to rotary dryers E-502 A/B for the purpose of removing residual cyclohexane from the HMDA. The dryers are equipped with internal heating tubes through which low pressure steam condenses, causing the crystallized HMDA to liquefy, while boiling off residual cyclohexane. The now purified HMDA is cooled to nearly ambient temperature in E-504, filtered of any residual solids in FL-501, and sent to HMDA product day tanks Tk-501 A/B, before being pumped via P-505 A/B to bulk product tankage in the offsites area of the plant. Tk-501 A/B are equipped with immersion heaters (E-505 A/B) and side entering mixers (M-501 A/B) to keep the HMDA in liquid phase.

Residual cyclohexane boiled off HMDA filter cake in the rotary dryers exits the dryers as an overhead vapor stream, is condensed in E-503, and pumped to distillation column C-501 for the purification and recycle of cyclohexane solvent. C-501 operates at atmospheric pressure, with an overhead temperature of 81°C and bottoms temperature of 198°C. Cyclohexane is purified as the overhead distillate in C-501, while by-product mixed amines concentrate in the column bottoms stream. The mixed amine stream is pumped through cooler E-508, filtered in FL-502, and discharged to by product day tanks Tk-502 A/B, prior to being pumped offsites (P-508 A/B) to bulk by product tankage. To prevent crystallization in the mixed amines day tanks, they are equipped with immersion heaters (E-509 A/B) and side entering mixers (M-502 A/B).

Stream by stream material balance

We have prepared a stream-by-stream material balance in metric tons per hour for this process, assuming annual HMDA production of 250 kty at a 90% capacity utilization factor. A summary of major stream flows, expressed in mt/hr and kty, is presented in the table below.

Table 8.19: Rennovia material balance summary

Component	Stream #	mt/hr	kty
HFCS feedstock	1	61.31	483
5-HMF intermediate product	23	37.76	298
H ₂ feedstock	27	2.51	20
Mixed Hexanol by-product	46	1.51	12
Mixed Diols by-product	65	2.10	17
1,6-Hexanediol intermediate product	62	35.62	281
Ammonia feedstock	66	10.23	81
Mixed Amines by-product	110	2.62	21
HMDA product	103	31.74	250

The stream by stream material balance is presented below in units of mt/hr.

Table 8.20: Rennovia stream by stream material balance (mt/hr)

Stream number	MW	Boiling point (°C)	1	2	3	4	5	6
Label			HFCS	R-101 O/H Vapor	R-101 B/S Liquids	300 psia steam	HCL 23° Baume	Recycle HCl acid
From			Tk-101	R-101	R-101	OSBL	Tk-102	E-103
To			R-101 AB	V-101	V-101	R-101 A/B	R-101 A/B	R-101 A/B
Temp (°C)			200	200	200	214	140	160
Pres (psia)			300	250	250	300	300	300
Phase			Liq	Vap	Liq	Vap	Liq	Liq
Total flow (mt/hr)			61.31	28.62	711.16	6.50	0.92	339.14
<u>Components</u>								
Hydrogen	2	-253						
Ammonia	17	-33						
Water	18	100		6.50	228.00	6.50	0.57	186.57
Hydrogen chloride	36	-85		0.002	0.188		0.002	0.190
Cyclohexane	84	81						
Hexamethyleneimine	99	138						
Cyclohexylamine	99	135						
Methyl isobutyl ketone (MIBK)	100	118		4.85	334.63			35.40
2-hexanol	102	139						
1-hexanol	102	157						
1,2-Diaminocyclohexane	114	80						
1,4-Diaminocyclohexane	114	197						
Mixed diamines	115	200						
HMDA	116	205						
6-Aminohexanol-1	117	137						
1,6-hexanediol	118	208						
1,2-hexanediol	118	223						
1,5-hexanediol	118	259						
5-Hydroxymethyl furfural	126	115		3.67	38.59			
1,2,5-hexanetriol	134	315						
1,2,6-hexanetriol	134	405						
1,2,5,6-hexanequatrol	150	>405						
Fructose	180	decomp	55.13		3.01			2.60
Dextrose	180	decomp	5.21		0.25			0.22
Higher saccharides in HFCS	240	decomp	0.95		0.95			
Humins	500+	decomp						
Heavy polymer and tar	na	na			4.96			
Ash in HFCS	na	na	0.02		0.02			

Table 8.20 (continued): Rennovia stream by stream material balance (mt/hr)

Stream number	7	8	9	10	11	12	13	14
Label	Extraction feed	Extraction product	Settling drum feed	Extraction pump around	MIBK Make-Up	Extraction drum acid	Rich MIBK solvent	50 psia steam
From	R-101 A/B	V-101	V-101	V-101	Tk-103	D-102	D-102	OSBL
To	V-101	D-102	D-102	V-101	M-103	S-101	C-101	S-101
Temp (°C)	40	40	40	40	20	40	40	138
Pres (psia)	125	100	100	100	125	100	100	50
Phase	Liq	Liq	Liq	Liq	Liq	Liq	Liq	Vap
Total flow (mt/hr)	734.25	1109.38	739.58	369.80	0.37	366.14	373.44	4.30
<u>Components</u>								
Hydrogen								
Ammonia								
Water	234.50	351.75	234.50	117.25		202.90	31.60	4.30
Hydrogen chloride	0.19	0.31	0.19	0.12		0.19		
Cyclohexane								
Hexamethyleneimine								
Cyclohexylamine								
Methyl isobutyl ketone (MIBK)	339.48	509.78	339.85	169.93	0.37	35.77	304.08	
2-hexanol								
1-hexanol								
1,2-Diaminocyclohexane								
1,4-Diaminocyclohexane								
Mixed diamines								
HMDA								
6-Aminohexanol-1								
1,6-hexanediol								
1,2-hexanediol								
1,5-hexanediol								
5-Hydroxymethyl furfural	42.26	63.39	42.26	21.13		4.50	37.76	
1,2,5-hexanetriol								
1,2,6-hexanetriol								
1,2,5,6-hexanequatrol								
Fructose	2.60	3.90	2.60	1.30		2.60		
Dextrose	0.22	0.33	0.22	0.11		0.22		
Higher saccharides in HFCS	0.82	1.23	0.82	0.41		0.82		
Humins								
Heavy polymer and tar		7.44	4.96	2.48		4.96		
Ash in HFCS	0.02	0.03	0.02	0.01		0.02		

Table 8.20 (continued): Rennovia stream by stream material balance (mt/hr)

Stream number	15	16	17	18	19	20	21	22
Label	HCl recycle solution	Water + HMF	C-101 O/H vapor	C-101 Reflux	C-101 distillate product	D-103 offgas	C-101 B/S	C-101 reboil
From	S-101	S-101	C-101	D-103	D-103	D-103	C-101	E-107 A/B
To	R-101 A/B	CR-201	D-103	C-101	R-101 A/B	K-101	P-110 A/B	C-101
Temp (°C)	80	105	75	75	75	75	245	245
Pres (psia)	300	40	4	4	4	4	4	4
Phase	Liq	Liq	Vap	Liq	Liq	Vap	Liq	Vap
Total flow (mt/hr)	338.21	22.12	672.18	335.68	335.68	40.28	341.76	304.00
<u>Components</u>								
Hydrogen								
Ammonia								
Water	186.00	16.90	63.20	31.60	31.60	3.79		
Hydrogen chloride	0.19	0.002						
Cyclohexane								
Hexamethyleneimine								
Cyclohexylamine								
Methyl isobutyl ketone (MIBK)	35.40	0.37	608.16	304.08	304.08	36.49		
2-hexanol								
1-hexanol								
1,2-Diaminocyclohexane								
1,4-Diaminocyclohexane								
Mixed diamines								
HMDA								
6-Aminohexanol-1								
1,6-hexanediol								
1,2-hexanediol								
1,5-hexanediol								
5-Hydroxymethyl furfural		4.50					341.76	304.00
1,2,5-hexanetriol								
1,2,6-hexanetriol								
1,2,5,6-hexanequatrol								
Fructose	2.60							
Dextrose	0.22							
Higher saccharides in HFCS								
Humins			0.82					
Heavy polymer and tar								
Ash in HFCS								

Table 8.20 (continued): Rennovia stream by stream material balance (mt/hr)

Stream number	23	24	25	26	27	28	29	30	31
Label	C-101 B/S product	Distilled water	LP Steam	HMF solution	Hydrogen feed	Hydrogen feed	Hydrogen feed	R-201 A/B product stream	R-301 A/B bottom stream
From	C-101	OSBL	OSBL	V-201	OSBL	K-201	K-201	R-201 A/B	R-301
To	Tk-104	V-201	V-201	R-201 A/B	K-201	R-201 A/B	R-301 A/B	D-202	D-202
Temp (°C)	40	40	138	120	40	160	160	120	150
Pres (psia)	50	50	50	1000	500	1250	1250	1000	1000
Phase	Liq	Liq	Vap	Liq	Vap	Vap	Vap	Liq	Vap
Total flow (mt/hr)	37.76	1.05	0.35	126.88	2.51	1.01	1.27	210.38	94.06
<u>Components</u>									
Hydrogen					2.51	1.01	1.27	9.09	1.01
Ammonia									
Water		1.05	0.35	80.83				86.23	69.36
Hydrogen chloride									
Cyclohexane									
Hexamethyleneimine									
Cyclohexylamine									
Methyl isobutyl ketone (MIBK)									
2-hexanol				2.69				3.63	2.17
1-hexanol				5.60				7.55	4.52
1,2-Diaminocyclohexane									
1,4-Diaminocyclohexane									
Mixed diamines									
HMDA									
6-Aminohexanol-1									
1,6-hexanediol								21.12	14.50
1,2-hexanediol								1.15	0.05
1,5-hexanediol								0.26	0.64
5-Hydroxymethyl furfural	37.76			37.76					
1,2,5-hexanetriol								0.64	0.27
1,2,6-hexanetriol								14.42	1.48
1,2,5,6-hexanequatrol								0.13	0.06
Fructose									
Dextrose								48.90	
Higher saccharides in HFCS									
Humins									
Heavy polymer and tar								0.34	
Ash in HFCS									

Table 8.20 (continued): Rennovia stream by stream material balance (mt/hr)

Stream Number	32	33	34	35	36	37	38	39
Label	D-202 O/H gas	D-202 B/S liquid	C-201 bottoms	C-201 B/S product	C-201 distillate product	D-204 vapor	C-201 O/H vapor	C-201 reflux
From	D-202	D-202	C-201	C-201	C-201	D-204	C-201	P-204 A/B
To	K-202	C-201	E-206	C-301	C-202	K-203	E-205	C-201
Temp (°C)	120	120	210	210	80	80	80	80
Pres (psia)	50	50	7	50	50	7	7	50
Phase	Vap	Liq	Liq	Liq	Liq	Vap	Vap	Liq
Total flow (mt/hr)	27.02	227.14	550.60	55.06	172.08	25.81	516.25	344.17
<u>Components</u>								
Hydrogen	10.10							
Ammonia								
Water		155.59			155.59	23.34	466.77	311.18
Hydrogen chloride								
Cyclohexane								
Hexamethyleneimine								
Cyclohexylamine								
Methyl isobutyl ketone (MIBK)								
2-hexanol		5.35			5.35	0.80	16.06	10.70
1-hexanol		11.14			11.14	1.67	33.42	22.28
1,2-Diaminocyclohexane								
1,4-Diaminocyclohexane								
Mixed diamines								
HMDA								
6-Aminohexanol-1								
1,6-hexanediol		35.62	356.20	35.62				
1,2-hexanediol		1.20	12.00	1.20				
1,5-hexanediol		0.90	9.00	0.90				
5-Hydroxymethyl furfural								
1,2,5-hexanetriol		0.91	9.10	0.91				
1,2,6-hexanetriol		15.90	159.00	15.90				
1,2,5,6-hexanequatrol		0.19	1.90	0.19				
Fructose								
Dextrose								
Higher saccharides in HFCS								
Humins								
Heavy polymer and tar		0.34	3.40	0.34				
Ash in HFCS								

Table 8.20 (continued): Rennovia stream by stream material balance (mt/hr)

Stream Number	40	41	42	43	44	45	46	47
Label	C-201 reboil	C-202 overhead gas	C-202 reflux	C-202 distillate product	C-202 B/S liquid	C-202 reboil	C-202 B/S product	CN-201 water liquor
From	E-206 A/B	C-202	P-206 A/B	P-206 A/B	C-202	E-209	C-202	CN-201
To	C-201	E-208	C-202	V-201	P-207 A/B	C-202	Tk-201	WWT
Temp (°C)	210	100	100	100	150	150	150	25
Pres (psia)	50	15	50	50	15	50	50	50
Phase	Vap	Vap	Liq	Liq	Liq	Vap	Liq	Liq
Total flow (mt/hr)	495.54	60.40	45.30	14.24	46.81	45.30	1.51	16.42
<u>Components</u>								
Hydrogen								
Ammonia								
Water		54.36	40.77	14.24				15.70
Hydrogen chloride								0.002
Cyclohexane								
Hexamethyleneimine								
Cyclohexylamine								
Methyl isobutyl ketone (MIBK)								0.37
2-hexanol		1.96	1.47		15.19	14.70	0.49	
1-hexanol		4.08	3.06		31.62	30.60	1.02	
1,2-Diaminocyclohexane								
1,4-Diaminocyclohexane								
Mixed diamines								
HMDA								
6-Aminohexanol-1								
1,6-hexanediol	320.58							
1,2-hexanediol	10.80							
1,5-hexanediol	8.10							
5-Hydroxymethyl furfural								
1,2,5-hexanetriol	8.19							
1,2,6-hexanetriol	143.10							
1,2,5,6-hexanequatrol	1.71							
Fructose								
Dextrose								
Higher saccharides in HFCS								
Humins								
Heavy polymer and tar	3.06							
Ash in HFCS								

Table 8.20 (continued): Rennovia stream by stream material balance (mt/hr)

Stream number	48	49	50	51	52	53	54	55
Label	HMF water slurry	C-301 O/H vapor	D-301 degas	C-301 reflux	C-301 distillate product	C-301 bottoms liquid	C-301 reboil	C-301 B/S product
From	CN-201	C-301	D-301 O/H	P-301 A/B	C-301 O/H	C-301	E-302 A/B	C-301
To	V-201	E-301	K-301	C-301	C-302	P-302 A/B	C-301	R-301 A/B
Temp (°C)	25	165	165	165	165	265	265	265
Pres (psia)	50	6	6	6	6	6	50	50
Phase	Slurry	Vap	Vap	Liq	Liq	Liq	Vap	Liq
Total flow (mt/hr)	5.70	150.88	7.54	113.16	37.72	130.07	112.73	17.34
<u>Components</u>								
Hydrogen								
Ammonia								
Water	1.20							
Hydrogen chloride								
Cyclohexane								
Hexamethyleneimine								
Cyclohexylamine								
Methyl isobutyl ketone (MIBK)								
2-hexanol								
1-hexanol								
1,2-Diaminocyclohexane								
1,4-Diaminocyclohexane								
Mixed diamines								
HMDA								
6-Aminohexanol-1								
1,6-hexanediol		142.48	7.12	106.86	35.62			
1,2-hexanediol		4.80	0.24	3.60	1.20			
1,5-hexanediol		3.60	0.18	2.70	0.90			
5-Hydroxymethyl furfural	4.50							
1,2,5-hexanetriol						6.83	5.92	0.91
1,2,6-hexanetriol						119.25	103.35	15.90
1,2,5,6-hexanequatrol						1.43	1.24	0.19
Fructose								
Dextrose								
Higher saccharides in HFCS								
Humins								
Heavy polymer and tar						2.56	2.22	0.34
Ash in HFCS								

Table 8.20 (continued): Rennovia stream by stream material balance (mt/hr)

Stream number	56	57	58	59	60	61	62	63
Label	Distilled water	50 psia steam	R-301 A/B feed	C-302 O/H vapor	E-304 degas	C-302 reflux	C-302 distillate product	C-302 bottoms stream
From	OSBL	OSBL	E-304	C-302	D-304	P-304 A/B	P-304 A/B	C-302
To	R-301 A/B	R-301 A/B	R-301 A/B	E-307	K-302	C-302	Tk-301	E-308
Temp (°C)	150	138	150	158	158	158	158	185
Pres (psia)	1000	50	1000	6	6	50	50	6
Phase	Liq	Vap	Liq	Vap	Vap	Liq	Liq	Liq
Total flow (mt/hr)	69.81	6.24	93.05	356.20	17.81	320.58	35.62	321.30
<u>Components</u>								
Hydrogen								
Ammonia								
Water	63.12	6.24	69.36					
Hydrogen chloride								
Cyclohexane								
Hexamethyleneimine								
Cyclohexylamine								
Methyl isobutyl ketone (MIBK)								
2-hexanol	2.17		2.17					
1-hexanol	4.52		4.52					
1,2-Diaminocyclohexane								
1,4-Diaminocyclohexane								
Mixed diamines								
HMDA								
6-Aminohexanol-1								
1,6-hexanediol				356.20	17.81	320.58	35.62	
1,2-hexanediol								183.60
1,5-hexanediol								137.70
5-Hydroxymethyl furfural								
1,2,5-hexanetriol			0.91					
1,2,6-hexanetriol			15.90					
1,2,5,6-hexanequatrol			0.19					
Fructose								
Dextrose								
Higher saccharides in HFCS								
Humins								
Heavy polymer and tar								
Ash in HFCS								

Table 8.20 (continued): Rennovia stream by stream material balance (mt/hr)

Stream number	64	65	66	67	68	69	70	71
Label	C-302 reboil	C-302 B/S product	Ammonia make-up	Hydrogen feed	R-401 A/B vapor feed	R-401 A/B liq feed	R-401 A/B liq product	Recycle gas
From	E-308	P-306 A/B	Tk-401	K-201	K-401	Tk-301	R-401 A/B	D-402
To	C-302	Tk-302	R-401 A/B	K-401	R-401 A/B	R-401 A/B	D-402	K-402
Temp (°C)	185	185	200	250	200	200	200	150
Pres (psia)	50	50	3250	1250	3250	3250	3000	50
Phase	Vap	Liq	Vap	Vap	Vap	Liq	Vap/Liq	Vap
Total flow (mt/hr)	319.20	2.10	10.23	0.23	66.16	236.69	333.56	49.13
Components								
Hydrogen				0.23	4.86		1.15	1.15
Ammonia			10.23		61.30		54.73	44.50
Water							10.83	
Hydrogen chloride								
Cyclohexane								
Hexamethyleneimine							27.06	
Cyclohexylamine							0.36	
Methyl isobutyl ketone (MIBK)								
2-hexanol								
1-hexanol								
1,2-Diaminocyclohexane							0.30	
1,4-Diaminocyclohexane							0.06	
Mixed diamines							1.65	
HMDA							31.71	
6-Aminohexanol-1							0.13	
1,6-hexanediol						236.69	201.07	
1,2-hexanediol	182.40	1.20						
1,5-hexanediol	136.80	0.90						
5-Hydroxymethyl furfural								
1,2,5-hexanetriol								
1,2,6-hexanetriol								
1,2,5,6-hexanequatrol								
Fructose								
Dextrose								
Higher saccharides in HFCS								
Humins								
Heavy polymer and tar							1.03	
Ash in HFCS								

Table 8.20 (continued): Rennovia stream by stream material balance (mt/hr)

Stream number	72	73	74	75	76	77	78	79
Label	Degassed liquid	Fresh Cyclohexane	Cyhex to extraction	Cyhex to crystallization	Combined extraction feed	Extraction product	D-403 bottom layer	D-403 top layer
From	D-402	Tk-402	Tk-402	Tk-402	R-401 A/B	V-401	D-403	D-403
To	V-401	V-401	V-401	CR-501	V-401	D-403	C-401	C-402
Temp (°C)	75	45	45	45	75	75	75	75
Pres (psia)	50	75	75	75	75	75	70	70
Phase	Liq	Liq	Liq	Liq	Liq	Liq	Liq	Liq
Total flow (mt/hr)	277.85	0.50	0.35	0.15	462.28	462.63	212.25	250.38
<u>Components</u>								
Hydrogen								
Ammonia	3.65				3.65	3.65		3.65
Water	10.83				10.83	10.83	10.83	
Hydrogen chloride								
Cyclohexane		0.50	0.35	0.15	184.40	184.75	0.35	184.40
Hexamethyleneimine	27.06				27.06	27.06		27.06
Cyclohexylamine	0.36				0.36	0.36		0.36
Methyl isobutyl ketone (MIBK)								
2-hexanol								
1-hexanol								
1,2-Diaminocyclohexane	0.30				0.30	0.30		0.30
1,4-Diaminocyclohexane	0.06				0.06	0.06		0.06
Mixed diamines	1.65				1.65	1.65		1.65
HMDA	31.71				31.71	31.71		31.71
6-Aminohexanol-1	0.13				0.13	0.13		0.13
1,6-hexanediol	201.07				201.07	201.07	201.07	
1,2-hexanediol								
1,5-hexanediol								
5-Hydroxymethyl furfural								
1,2,5-hexanetriol								
1,2,6-hexanetriol								
1,2,5,6-hexanequatrol								
Fructose								
Dextrose								
Higher saccharides in HFCS								
Humins								
Heavy polymer and tar	1.03				1.06	1.06		1.06
Ash in HFCS								

Table 8.20 (continued): Rennovia stream by stream material balance (mt/hr)

Stream number	80	81	82	83	84	85	86	87
Label	C-401 O/H vapor	C-401 distillate product	C-401 bottoms	C-401 reboil	C-401 B/S product	C-402 O/H vapor	D-406 degas	C-402 distillate product
From	C-401	C-401 O/H	C-401	E-408 A/B	C-401 B/S	C-402	D-406	P-408 A/B
To	E-406	WWT	E-408 A/B	C-401	R-401 A/B	E-410	K-404	V-401
Temp (°C)	68	68	168	168	168	65	65	65
Pres (psia)	8	50	8	8	8	10	10	10
Phase	Vap	Liq	Liq	Vap	Liq	Vap	Vap	Liq
Total flow (mt/hr)	55.88	11.18	250.24	49.17	201.07	564.15	3.65	184.40
<u>Components</u>								
Hydrogen								
Ammonia						10.95	3.65	
Water	54.13	10.83						
Hydrogen chloride								
Cyclohexane	1.75	0.35				553.20		184.40
Hexamethyleneimine								
Cyclohexylamine								
Methyl isobutyl ketone (MIBK)								
2-hexanol								
1-hexanol								
1,2-Diaminocyclohexane								
1,4-Diaminocyclohexane								
Mixed diamines								
HMDA								
6-Aminohexanol-1								
1,6-hexanediol			250.24	49.17	201.07			
1,2-hexanediol								
1,5-hexanediol								
5-Hydroxymethyl furfural								
1,2,5-hexanetriol								
1,2,6-hexanetriol								
1,2,5,6-hexanequatrol								
Fructose								
Dextrose								
Higher saccharides in HFCS								
Humins								
Heavy polymer and tar								
Ash in HFCS								

Table 8.20 (continued): Rennovia stream by stream material balance (mt/hr)

Stream number	88	89	90	91	92	93	94	95
Label	C-402 bottoms	C-402 reboil	C-402 B/S product	C-403 O/H vapor	C-403 distillate product	C-403 reflux	C-403 bottoms	C-403 reboil
From	C-402	E-412	C-402 B/S	C-403	C-403	P-410 A/B	C-403	E-414
To	E-412	C-402	C-403 Feed	E-413	R-401 A/B	C-403	E-414	C-403
Temp (°C)	185	185	185	88	88	88	165	165
Pres (psia)	10	10	10	7	7	7	7	7
Phase	Liq	Vap	Liq	Vap	Liq	Liq	Liq	Vap
Total flow (mt/hr)	461.22	398.89	62.33	108.24	27.06	81.18	119.90	84.63
<u>Components</u>								
Hydrogen								
Ammonia								
Water								
Hydrogen chloride								
Cyclohexane								
Hexamethyleneimine	200.24	173.18	27.06	108.24	27.06	81.18		
Cyclohexylamine	2.66	2.30	0.36				1.22	0.86
Methyl isobutyl ketone (MIBK)								
2-hexanol								
1-hexanol								
1,2-Diaminocyclohexane	2.22	1.92	0.30				1.02	0.72
1,4-Diaminocyclohexane	0.44	0.38	0.06				0.20	0.14
Mixed diamines	12.21	10.56	1.65				5.61	3.96
HMDA	234.65	202.94	31.71				107.81	76.10
6-Aminohexanol-1	0.96	0.83	0.13				0.44	0.31
1,6-hexanediol								
1,2-hexanediol								
1,5-hexanediol								
5-Hydroxymethyl furfural								
1,2,5-hexanetriol								
1,2,6-hexanetriol								
1,2,5,6-hexanetetrol								
Fructose								
Dextrose								
Higher saccharides in HFCS								
Humins								
Heavy polymer and tar	7.84	6.78	1.06				3.60	2.54
Ash in HFCS								

Table 8.20 (continued): Rennovia stream by stream material balance (mt/hr)

Stream number	96	97	98	99	100	101	102	103
Label	C-403 B/S product	C-403 heavies	CR-501 B/S slurry	CR-501 pump around	CN-501 A/B liquor	CN--501 A/B cake	50 psia steam	Dried HMDA
From	C-403	FL-402	CR-501	P-501 A/B	CN-501 A/B	CN-501 A/B	OSBL	E-502 A/B
To	Tk-403	Incineration	CN-501 A/B	E-501	CR-501	E-502 A/B	E-502 A/B	Tk-501 A/B
Temp (°C)	165	165	10	10	10	10	138	70
Pres (psia)	7	7	50	50	50	50	50	50
Phase	Liq	Solid	Slurry	Slurry	Liq	Cake	Vap	Liq
Total flow (mt/hr)	34.21	1.06		339.64	134.59	35.23	1.01	31.74
<u>Components</u>								
Hydrogen								
Ammonia								
Water							1.01	
Hydrogen chloride								
Cyclohexane			135.61	271.22	132.12	3.49		
Hexamethyleneimine								
Cyclohexylamine		0.36	0.36	0.72	0.36			
Methyl isobutyl ketone (MIBK)								
2-hexanol								
1-hexanol								
1,2-Diaminocyclohexane		0.30	0.30	0.60	0.30			
1,4-Diaminocyclohexane		0.06	0.06	0.12	0.03	0.03		0.03
Mixed diamines		1.65	1.65	3.30	1.65			
HMDA		31.71	31.71	63.42		31.71		31.71
6-Aminohexanol-1		0.13	0.13	0.26	0.13			
1,6-hexanediol								
1,2-hexanediol								
1,5-hexanediol								
5-Hydroxymethyl furfural								
1,2,5-hexanetriol								
1,2,6-hexanetriol								
1,2,5,6-hexanequatrol								
Fructose								
Dextrose								
Higher saccharides in HFCS								
Humins								
Heavy polymer and tar		1.06						
Ash in HFCS								

Table 8.20 (continued): Rennovia stream by stream material balance (mt/hr)

Stream number	104	105	106	107	108	109	110	111
Label	Dryer O/H vapor	C-501 O/H vapor	C-501 reflux	C-501 distillate product	C-501 bottoms	C-501 reboil	C-501 B/S product	D-404 O/H gas
From	E-502 A/B	C-501	E-506	P-506 A/B	C-501	E-507 A/B	C-501	D-404
To	E-503	E-506	C-501	CR-501	E-507 A/B	C-501	Tk-502	K-403
Temp (°C)	125	84	84	84	198	198	70	68
Pres (psia)	30	15	15	50	15	15	50	8
Phase	Vap	Vap	Liq	Liq	Liq	Vap	Liq	Vap
Total flow (mt/hr)	3.49	66.69	44.46	22.23	55.02	52.40	2.62	2.24
<u>Components</u>								
Hydrogen								
Ammonia								
Water								2.17
Hydrogen chloride								
Cyclohexane	3.49	66.69	44.46	22.23	3.15	3.00	0.15	0.07
Hexamethyleneimine								
Cyclohexylamine					7.56	7.20	0.36	
Methyl isobutyl ketone (MIBK)								
2-hexanol								
1-hexanol								
1,2-Diaminocyclohexane					6.30	6.00	0.30	
1,4-Diaminocyclohexane					0.63	0.60	0.03	
Mixed diamines					34.65	33.00	1.65	
HMDA								
6-Aminohexanol-1					2.73	2.60	0.13	
1,6-hexanediol								
1,2-hexanediol								
1,5-hexanediol								
5-Hydroxymethyl furfural								
1,2,5-hexanetriol								
1,2,6-hexanetriol								
1,2,5,6-hexanequatrol								
Fructose								
Dextrose								
Higher saccharides in HFCS								
Humins								
Heavy polymer and tar								
Ash in HFCS								

Table 8.20 (completed): Rennovia stream by stream material balance (mt/hr)

Stream number	112	113	114	115	116	117	118
Label	C-401 reflux	D-408 degas	Mixed amine	CN-501 A/B liquor recycle	Heavies from hydrogenation	Water purge to WWT	Heavy purge
From	D-404	D-408	CN-501 A/B	CN-501 A/B	FL-301	P-206 A/B	S-101
To	C-401	K-405	C-501	CR-501	Incineration	WWT	Incineration
Temp (°C)	68	88	89	89	200	100	125
Pres (psia)	8	7	50	50	1250	50	50
Phase	Liq	Vap	Liq	Liq	Solid	Liq	Liq
Total flow (mt/hr)	44.70	5.41	21.31	113.98	0.34	86.52	5.80
<u>Components</u>							
Hydrogen							
Ammonia							
Water	43.30					78.23	
Hydrogen chloride							
Cyclohexane	1.40		18.84	113.98			
Hexamethyleneimine		5.41					
Cyclohexylamine			0.36				
Methyl isobutyl ketone (MIBK)							
2-hexanol						2.69	
1-hexanol						5.60	
1,2-Diaminocyclohexane			0.30				
1,4-Diaminocyclohexane			0.03				
Mixed diamines			1.65				
HMDA							
6-Aminohexanol-1			0.13				
1,6-hexanediol							
1,2-hexanediol							
1,5-hexanediol							
5-Hydroxymethyl furfural							
1,2,5-hexanetriol							
1,2,6-hexanetriol							
1,2,5,6-hexanetetrol							
Fructose							
Dextrose							
Higher saccharides in HFCS							0.82
Humins							
Heavy polymer and tar					0.34		4.96
Ash in HFCS							0.02

Equipment List

By combining PFD information with the stream by stream material balance, we have prepared in the table below an equipment list for major ISBL process equipment, including duty specifications.

Table 8.21: ISBL equipment list with duty specifications

	Buildings	Floor area (ft2)	# above ground stories	Sidewall materials / insulated?	Roof type / insulated?	Fit for occupancy?	HVAC (scfm)	Heating Duty (MM-Btu/hr)	Refrig Duty (tons/hr)
B-101	Process control building	5000	1	Reinf concrete	Reinf concrete + membrane	Yes	400	0.75	35
B-102	Compressor building	5000	2	no	removable	No	No	No	No
	<u>Distillation columns</u>	<u># installed</u>	<u>Materials of construction</u>	<u>L x D (ft)</u>	<u>DesP (psia)</u>	<u>DesT (°C)</u>	<u># of trays</u>	<u>Internals details</u>	
C-101	MIBK column	1	304 SS	68 x 8	full vac	270	24	struc packing	
C-201	Lites column	1	304 SS	68 x 10	full vac	235	24	struc packing	
C-202	Hexanol column	1	304 SS	80 x 3	full vac	235	30	struc packing	
C-301	Diols splitter	1	CS	92 x 5	full vac	290	36	struc packing	
C-302	1,6-HDO column	1	CS	140 x 8	full vac	210	60	struc packing	
C-401	Dewatering column	1	304 SS	92 x 4	full vac	200	36	struc packing	
C-402	Lites column	1	CS	68 x 10	full vac	210	24	struc packing	
C-403	Imines column	1	304 SS	80 x 5	full vac	190	30	struc packing	
C-501	Cyclohexane column	1	304 SS	68 x 4	30	225	24	sieve trays	
	<u>Centrifuges</u>	<u># installed</u>	<u>Materials of construction</u>	<u>L x D (ft)</u>	<u>DesP (psia)</u>	<u>DesT (°C)</u>	<u>Duty (BHP)</u>	<u>Type (bowl or screen)</u>	<u>Screen opening (mm)</u>
CN-201	HMF Slurry centrifuge	1	304 SS	8 x 6	30	25	100	Screen	0.5
CN-501 A/B	HMDA centrifuges	2	304 SS	8 x 4	30	25	40	Screen	0.5
	<u>Crystallizers</u>	<u># installed</u>	<u>Materials of construction</u>	<u>L x D (ft)</u>	<u>DesP (psia)</u>	<u>DesT (°C)</u>	<u>Duty (MM-btu/hr)</u>	<u>Suspension or Draft Tube?</u>	
CR-201	HMF Recovery crystallizer	1	304SS	18 x 3	30	25	0	Suspension	
CR-501	HMDA centrifuges	1	304SS	36 x 8	30	25	0	Suspension	
	<u>Solid conveyors</u>	<u># installed</u>	<u>Materials of construction</u>	<u>L x W (ft)</u>	<u>DesP (psia)</u>	<u>DesT (°C)</u>	<u>Mass flow (lbs/hr)</u>	<u>Belt, pneumatic, or screw?</u>	<u>Motor HP</u>
CV-501 A/B	HMDA cake slurry	2	304 SS	50 x 4	15	25	38841	Covered belt	35

Table 8.21 (continued): ISBL equipment list with duty specifications

	Drums	# installed	Materials of construction	Vol (ft3)	L x D (ft)	DesP (psia)	DesT (°C)	Orientation (ASME B31.3 spec)
D-101	102 receiver	1	304 SS	167	13.3 x 4	325	250	Hor
D-102	xtraction settler	1	304 SS	12845	64 x 16	125	65	Hor
D-103	106 receiver	1	304 SS	5880	52 x 12	full vac	125	Hor
D-104	101 K/O drum	1	304 SS	25	8 x 1	full vac	125	Vert
D-201	201 K/O drum	1	304 SS	402	32 x 4	1250	250	Vert
D-202	2 degassing drum	1	304 SS	402	32 x 4	1250	250	Vert
D-203	202 3-stage flash drum	1	304 SS	170	24 x 3	100	250	Vert
D-204	205 receiver	1	304 SS	4517	45 x 11	full vac	105	Hor
D-205	203 K/O drum	1	304 SS	50	16 x 2	full vac	105	Vert
D-206	208 receiver	1	304 SS	529	18.7 x 6	30	125	Hor
D-301	301 receiver	1	CS	1320	26 x 8	full vac	190	Hor
D-302	301 K/O drum	1	CS	25	8 x 1	full vac	125	Vert
D-303	302 K/O drum	1	CS	50	16 x 2	full vac	105	Vert
D-304	307 receiver	1	CS	3117	40 x 10	full vac	183	Hor
D-401	401 K/O drum	1	304 SS	402	32 x 4	3250	250	Vert
D-402	401 3-stage flash drum	1	304 SS	1018	36 x 6	3250	250	Vert
D-403	xtraction settling drum	1	304 SS	8096	52 x 14	100	125	Hor
D-404	406 receiver	1	304 SS	489	25 x 5	full vac	93	Hor
D-405	403 K/O drum	1	304 SS	25	8 x 1	full vac	125	Vert
D-406	410 receiver	1	CS	4936	44 x 12	full vac	90	Hor
D-407	404 K/O drum	1	CS	50	16 x 2	full vac	105	Vert
D-408	413 receiver	1	CS	947	28.5 x 6.5	full vac	113	Hor
D-409	405 K/O drum	1	CS	25	8 x 1	full vac	125	Vert
D-501	503 receiver	1	CS	25	8 x 1	30	50	Hor
D-502	506 receiver	1	CS	584	21 x 6	30	106	Hor
	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	Tk101 tank heater	1	304 SS	5.0	500	75	150	Tank immersion
E-102	HFCS feed/product exchanger	1	Incoloy800 /Incoloy800	15.8	1600	300/300	250/250	S&T-API650
E-103	Acid heater	1	Incoloy800 /Incoloy800	157.0	15700	300/300	250/250	S&T-API650
E-104	Reaction cooler	1	304SS/ Incoloy800	125.0	10454	300/100	250/100	S&T-API650
E-105	C101 feed / product exchanger	1	CS/CS	40.4	3360	100/vac	125/125	S&T-API650
E-106	C101 condenser	1	CS/304SS	445.0	37100	100/vac	100/100	S&T-API650
E-107 A/B	C101 reboilers	2	CS/CS	234.0	19500	100/vac	300/300	S&T-API650
E-108	K101 condenser	1	CS/304SS	26.6	2220	100/30	100/105	S&T-API650
E-109	HMF product cooler	1	CS/304SS	16.6	1390	100/100	100/300	S&T-API650
E-110	Tk104 heater	1	304 SS	5.0	500	75	150	Tank immersion
E-201	R201 feed/prod exchanger	1	CS/CS	5.7	480	1250/150	145/145	S&T-API650
E-202	R201 heater	1	CS/CS	5.9	492	1250/100	150/150	S&T-API650
E-203	R201 cooler	1	304SS/304SS	23.2	1930	1250/100	145/100	S&T-API650
E-204	C201 feed heater	1	CS/CS	50.1	4175	50/vac	105/105	S&T-API650
E-205	C201 condenser	1	304SS/CS	342.0	28500	100/vac	75/105	S&T-API650
E-206 A/B	C201 reboilers	2	CS/CS	179.6	14970	100/vac	300/300	S&T-API650
E-207	K203 condenser	1	CS/304SS	17.1	14200	75/vac	100/105	S&T-API650

Table 8.21 (continued): ISBL 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 (°C) tube/shell	HX configuration
E-208	C202 condenser	1	304SS/304SS	39.9	3330	75/30	100/150	S&T-API650
E-209	C202 reboiler	1	CS/CS	41.9	3490	325/30	300/200	S&T-API650
E-210	Hexanol exchanger	1	CS/304SS	0.5	42	75/75	100/200	S&T-API650
E-211	Hexanol cooler	1	CS/304SS	0.3	21	75/75	100/175	S&T-API650
E-212	HMF solution CW cooler	1	304SS/304SS	4.9	410	75/75	100/100	S&T-API650
E-213	HMF solution Glycol cooler	1	304SS/CS	3.7	305	75/75	100/100	S&T-API650
E-301	C301 condenser	1	CS/304SS	99.8	8317	75/vac	100/190	S&T-API650
E-302 A/B	C301 reboilers	2	vac/CS	52.4	4366	325/vac	300/300	S&T-API650
E-303	K301 condenser	1	CS/304SS	5.0	416	75/30	100/190	S&T-API650
E-304	Reactor Feed Heater	1	CS/304SS	30.8	2565	1250/325	175/250	S&T-API650
E-305	C302 Feed Pre-Heater	1	CS/CS	0.7	58	75/75	230/190	S&T-API650
E-306	R301 product cooler	1	304SS/CS	41.5	3457	1250/75	200/100	S&T-API650
E-307	C302 condenser	1	304SS/CS	236.0	19600	75/vac	100/185	S&T-API650
E-308	C302 reboiler	1	CS/CS	248.0	20650	325/vac	250/230	S&T-API650
E-309	K302 condenser	1	CS/304SS	11.8	982	75/vac	100/185	S&T-API650
E-310	1,6-HDO cooler	1	CS/304SS	7.9	655	75/75	100/100	S&T-API650
E-311	Mixed Diol cooler	1	CS/304SS	1.4	116	75/75	100/100	S&T-API650
E-401	Ammonia vaporizer	1	CS/CS	13.5	1128	1250/75	250/250	S&T-API650
E-402	HDO feed / product exchanger	1	CS/CS	61.3	5106	3250/75	250/250	S&T-API650
E-403	Cyclohexane heater	1	CS/CS	73.6	6130	3250/325	250/300	S&T-API650
E-404	R401 product cooler	1	CS/304 SS	38.6	3217	3250/100	250/100	S&T-API650
E-405	C401 feed / product heater	1	304SS / 304SS	14.8	1232	75/vac	100/100	S&T-API650
E-406	C401 condenser	1	304SS / 304SS	66.1	5550	75/vac	100/100	S&T-API650
E-407	K403 condenser	1	304SS / 304SS	5.7	462	75/30	100/100	S&T-API650
E-408 A/B	C401 reboilers	2	CS/CS	35.1	2913	325/vac	250/190	S&T-API650
E-409	C402 feed heater	1	CS/CS	149.3	12440	75/vac	100/100	S&T-API650
E-410	C402 condenser	1	CS/CS	224.0	18663	75/vac	100/100	S&T-API650
E-411	C402 distillate cooler	1	CS/CS	18.7	1555	75/vac	100/100	S&T-API650
E-412	C402 reboiler	1	CS/CS	264.0	21989	325/vac	250/210	S&T-API650
E-413	C403 condenser	1	CS/304SS	71.6	5967	75/vac	100/115	S&T-API650
E-414	C403 reboiler	1	CS/CS	75.2	6265	325/vac	250/190	S&T-API650
E-415	HMDA cooler	1	CS/304SS	7.5	629	75/75	190/100	S&T-API650
E-416	Tk-403 tank heater	1	304 SS	5.0	500	75	150	Tank immersion
E-417	K405 condenser	1	CS/304SS	3.6	298	75/vac	100/115	S&T-API650
E-501	Ammonia cooler	1	CS/CS	15.0	2496	75/30	100/100	S&T-API650
E-502 A/B	HMDA dryers	2	304 SS	1.2	100	75/30	150/125	Rotary dryer
E-503	E502 condenser	1	CS/304SS	2.4	200	75/30	75/125	S&T-API650
E-504	HMDA cooler	1	CS/304SS	1.7	140	75/75	75/100	S&T-API650
E-505 A/B	Tk501 immersion heaters	2	304 SS	5.0	500	75	150	Tank immersion
E-506	C501 condenser	1	CS/304SS	44.1	3676	75/vac	75/105	S&T-API650
E-507 A/B	C501 reboilers	2	CS/CS	23.2	1929	325/30	250/220	S&T-API650
E-508	Amines cooler	1	CS/304SS	0.2	19	75/75	100/225	S&T-API650

Table 8.21 (continued): ISBL equipment list with duty specifications

		#	Materials of	Duty	Surf area	DesP	DesT	HX		
Heat exchangers		installed	construction shell side / tube side	(MM-btu/hr)	(ft2)	(psia) tube/shell	(°C) tube/shell	configuration		
E-509	Cyclohexane cooler	1	CS/304SS	4.9	408	30/75	100/105	S&T-API650		
E-510	C501 feed heater	1	CS/CS	1.1	95	75/75	105/105	S&T-API650		
E-511 A/B	Tk502 immersion heaters	2	304 SS	0.5	50	75	150	Tank immersion		
Filters		#	Materials of	Flow rate	DesP	DesT	Opening			
		installed	construction	(k-lbs/hr)	(psia) tubes	(°C)	size (microns)			
FL-101	R101 Dual Basket Filter	1	304 SS	1565	275	250	0.5			
FL-201	R201 Dual BasketFilters	1	304 SS	465	1250	145	0.5			
FL-301	R301 Dual Basket Filters	1	304 SS	205	1250	175	0.5			
FL-302	P303 Dual Basket Filter	1	304 SS	207	1250	175	0.5			
FL-401	P403 Dual Basket Filter	1	304 SS	613	150	250	0.5			
FL-402	HMDA Duel Basket Filter	1	304 SS	75.4	75	190	0.5			
FL-501	HMDA Dual Basket Filters	1	304 SS	70	75	175	0.5			
FL-502	Amines Dual Basket Filter	1	304 SS	5.8	75	250	0.5			
Compressors		#	Fluid	BHP	SCFM	Pin	Pout	Des T	Matl of	Machine
		installed				(psia)	(psia)	(°C)	construction / design details	type
K-101	C101 Vacuum Pump	1	MIBK	677.3	5701.3	4	15	100	CS	Sliding Vane Vac Pump
K-201	LP H2 Compressor	1	H2	2813.7	17763.3	250	1250	250	316L SS	Centrif
K-202	H2 Recycle Compressor	1	H2	5661.1	71478.0	500	1250	250	316L SS	Centrif
K-203	C201 Vacuum Pump	1	H2O	1377.2	20287.5	7	15	130	Gray Iron	Sliding Vane Vac Pump
K-301	C301 Vacuum Pump	1	HDO	71.6	904.4	6	15	190	CS	Sliding Vane Vac Pump
K-302	C302 Vacuum Pump	1	HDO	169.2	2136.3	6	15	183	CS	Sliding Vane Vac Pump
K-401	H2 HP Compressor	1	H2	134.1	1627.7	1250	3250	250	316L SS	Centrif
K-402	NH3 Recycle Compressor	1	NH3	2408.2	38007.8	1625	3250	250	316L SS	Centrif
K-403	C401 Vacuum Pump	1	H2O	104.6	1761.4	8	15	100	Gray Iron	Sliding Vane Vac Pump
K-404	C402 Vacuum Pump	1	Cyclohexane	29.2	615.0	10	15	100	CS	Sliding Vane Vac Pump
K-405	C403 Vacuum Pump	1	NH3	305.8	4504.3	7	15	115	316L SS	Sliding Vane Vac Pump
MIXERS & AGITATORS		#	Materials of	BHP	DesT	Liquid	Viscosity	Mixer type		
		installed	construction		(°C)		(cs)			
M-101	Tk101 Agitator	1	316L SS	85	100	HFCS	50	Side entering		
M-102 A/B	R101 Mixers	2	316L SS	124	250	H2O+MIBK	10	Top entering		
M-103	Extraction Mixer	1	316L SS	250	70	H2O+MIBK	10	Top entering		
M-104	Tk104 Agitator	1	316L SS	53	80	HMF	10	Side entering		
M-201	V201 Mixer	1	316L SS	7.5	100	H2O+HMF	2.5	Top entering		
M-301	P303 Static Mixer	1	316L SS	6 inch pipeline	200	H2O	1	Kenics static mixer		
M-401	V401 Mixer	1	316L SS	27	125	HMDA + Cyhex	5	Top entering		

Table 8.21 (continued): ISBL equipment list with duty specifications

Mixers & agitators		# installed	Materials of construction	BHP	DesT (°C)	Liquid	Viscosity (cs)	Mixer type	
M-402	Tk403 Mixer	1	316L SS	50	100	HMDA	10	Side entering	
M-501 A/B	Tk501 Mixers	2	316L SS	25	100	HMDA	10	Side entering	
M-502 A/B	Tk502 Mixers	2	316L SS	4	100	Amines	10	Side entering	
Pumps		# installed	Materials of construction	gpm x hd (ft)	Liquid	DesP (psia)	DesT (°C)	Type ump	Pump BHP
P-101 A/B	HFCS Feed Pumps	2	CS	270 x 621	HFCS	275	250	API 610-Centrif	65.0
P-102 A/B	HCl Acid Feed Pumps	2	PVDF	4 x 621	HCl soln	275	250	API 685-Canned	1.0
P-103 A/B	Reactor O/H pumps	2	Incoloy 800	126 x 250	HCl-MIBK soln	275	250	API 610-Centrif	12.2
P-104 A/B	Reactor B/S Pumps	2	Incoloy 800	3135 x 250	HCl-MIBK soln	275	250	API 610-Centrif	304.5
P-105 A/B	Extraction Pumps	2	Incoloy 800	4890 x 150	HCl soln	150	100	API 610-Centrif	285.0
P-106 A/B	MIBK Pumps	2	CS	1 x 250	MIBK	150	100	API 675-Metering	0.1
P-107 A/B	Extract Pumps	2	316L SS	1650 x 150	MIBK soln	150	100	API 610-Centrif	96.2
P-108 A/B	Dilute Acid Pumps	2	Incoloy 800	1615 x 150	Dilute HCl	150	100	API 610-Centrif	94.1
P-109 A/B	C101 Reflux Pumps	2	316L SS	2964 x 150	MIBK + H2O	75	100	API 610-Centrif	172.7
P-110 A/B	C101 B/S Pumps	2	Incoloy 800	1507 x 150	Dilute HCl	75	270	API 610-Centrif	87.8
P-111 A/B	HMF Product Pumps	2	CS	167 x 150	HMF	75	100	API 610-Centrif	9.7
P-201 A/B	HMF Feed Pumps	2	316L SS	560 x 2500	HMF+H2O	1250	100	API 610-Centrif	543.9
P-202 A/B	R201 B/S Pumps	2	316L SS	928 x 150	HDO Soln	75	150	API 610-Centrif	54.1
P-203 A/B	C201 Feed Pumps	2							
P-204 A/B	C201 Reflux Pumps	2	316L SS	2277 x 150	HDO Soln	75	130	API 610-Centrif	132.7
P-205 A/B	C201 B/S Pumps	2	CS	2428 x 150	HDO	75	260	API 610-Centrif	141.5
P-206 A/B	C202 Reflux Pumps	2	316L SS	266 x 150	H2O	75	150	API 610-Centrif	15.5
P-207 A/B	C202 B/S Pumps	2	CS	206 x 150	Hexanol	75	200	API 610-Centrif	12.0
P-208 A/B	Tk201 Pumps	2	CS	7 x 150	Hexanol	75	100	API 610-Centrif	0.4
P-209 A/B	HMF Light Slurry Pumps	2	316L SS	98 x 150	HMF Slurry	75	100	API 676-Moyno	5.7
P-210 A/B	HMF Heavy Slurry Pumps	2	316L SS	98 x 150	HMF Slurry	75	100	API 676-Moyno	5.7
P-301 A/B	C301 Reflux Pumps	2	CS	665 x 150	Diols	75	215	API 610-Centrif	38.8
P-302 A/B	C301 B/S Pumps	2	CS	573 x 2500	Triols	1250	200	API 610-Centrif	556.5
P-303 A/B	HP Water Pumps	2	Cl	335 x 2500	H2O	1250	200	API 610-Centrif	325.4
P-304 A/B	R301 Product Pumps	2	CS	415 x 150	Triols	75	200	API 610-Centrif	24.2
P-305 A/B	C302 Reflux Pumps	2	CS	1571 x 150	HDO	75	210	API 610-Centrif	91.6
P-306 A/B	C302 B/S Pumps	2	CS	1415 x 150	Mixed Diol	75	235	API 610-Centrif	82.5
P-307 A/B	Tk301 Pumps	2	CS	157 x 7000	HDO	3250	100	API 610-Centrif	427.0
P-308 A/B	Tk302 Pumps	2	CS	10 x 150	Mixed Diol	75	100	API 610-Centrif	0.6
P-401 A/B	Ammonia feed pumps	2	316L SS	45 x 7000	Ammonia	3250	100	API 610-Centrif	17.5
P-402 A/B	Cyclohexane Feed Pumps	2	CS	2.2 x 200	Cyclohexane	100	100	API 675-Metering	0.2
P-403 A/B	R401 Product Pumps	2	316L SS	1225 x 200	HMDA Soln	100	250	API 610-Centrif	95.2
P-404 A/B	D403 B/S Pumps	2	316L SS	936 x 150	HDO Soln	100	125	API 610-Centrif	54.5
P-405 A/B	C401 Reflux Pumps	2	Cl	246 x 150	H2O	50	125	API 610-Centrif	14.3

Table 8.21 (continued): ISBL equipment list with duty specifications

		# installed	Materials of construction	gpm x hd (ft)	Liquid	DesP (psia)	DesT (°C)	Type pump	Pump BHP
P-406 A/B	C401 B/S Pumps	2	CS	1104 x 7000	HDO	3250	250	API 610-Centrif	3002.3
P-407 A/B	D403 O/H Pumps	2	CS	1104 x 150	Cyhex Soln	75	125	API 610-Centrif	64.3
P-408 A/B	C402 Reflux Pumps	2	CS	2488 x 200	Cyclohexane	100	125	API 610-Centrif	193.3
P-409 A/B	C402 B/S Pumps	2	316L SS	2034 x 150	HMDA	75	235	API 610-Centrif	118.5
P-410 A/B	C403 Reflux Pumps	2	316L SS	477 x 7000	Imines	3250	125	API 610-Centrif	1297.2
P-411 A/B	C403 B/S Pumps	2	CS	529 x 150	Heavies	75	220	API 610-Centrif	30.8
P-412 A/B	Tk403 Pumps	2	316L SS	151 x 150	HMDA	75	100	API 610-Centrif	8.8
P-501 A/B	Circulating Pumps	2	316L SS	1498 x 150	HMDA Soln	75	100	API 676-Moyno	87.3
P-502 A/B	HMDA Slurry Pumps	2	316L SS	749 x 150	HMDA Soln	75	100	API 676-Moyno	43.6
P-503 A/B	C501 Feed Pumps	2	CS	15 x 150	Cyclohexane	75	175	API 610-Centrif	0.9
P-504 A/B	HMDA Dryer Pumps	2	316L SS	140 x 150	HMDA	75	175	API 610-Centrif	8.2
P-505 A/B	Tk501 Pumps	2	316L SS	140 x 150	HMDA	75	175	API 610-Centrif	8.2
P-506 A/B	C501 Reflux Pumps	2	CS	294 x 150	Cyclohexane	75	135	API 610-Centrif	17.1
P-507 A/B	C501 B/S Pumps	2	316L SS	243 x 150	Mixed Amine	75	250	API 610-Centrif	14.2
P-508 A/B	Tk502 Pumps	2	316L SS	12 x 150	Mixed Amine	75	100	API 610-Centrif	0.7
Reactors		# installed	Materials of construction	Vol (ft3)	L x D (ft)	DesP (psia)	DesT (°C)	Internals	
R-101 A/B	Hydrolysis Reactor	2	Incoloy 800	3111	62 x 8	275	250	baffling	
R-201 A/B	H2 HMF Reactors	2	316L SS	613.7	40 x 5	1250	170	Packed catalyst	
R-301 A/B	H2 Triol Reactors	2	316L SS	274.3	28 x 3.5	1250	170	Packed catalyst	
R-401 A/B	Ammoniation Reactors	2	316L SS	973	50 x 5	3250	250	Packed catalyst	
Specially packaged equipment				# installed	Duty		Details		
S-101	4-stagel Acid Concentrator			1	5 MM-Btu/hr		Incoloy 800		
S-102	Ammonia chiller system			1	1250 tons				
S-103	Glycol chiller system			1	400 tons				
S-104	Solids incinerator w steam production			1	20 MM-Btu/hr				
S-105	Liquids incinerator			1	50 MM-Btu/hr				
S-106	2-flare system with blowdown drums & header			1	250 MM-Btu/hr + 12 in LP header		John Zink or equiv		
S-107	Process computer control system			1	1200 loops at 5 operator stations		Honeywell Experion or equiv		
S-108	Dowtherm Hot Oil System			1	300 MM Btu/hr duty				
Steam turbine drivers		# installed	Mechanical or electrical?	BHP	KW	Inlet steam (pres/ temp)	Outlet steam (pres/ temp)	Steam turbine details	
ST-201	K-201 ST Driver	1	Mech	3100	2313	1350	50	Centrif Back Pres	
ST-202	K-202 ST Driver	1	Mech	6250	4663	1350	50	Centrif Back Pres	
ST-203	K-203 ST Driver	1	Mech	1400	1044	1350	50	Centrif Back Pres	
ST-401	K-402 ST Driver	1	Mech	2700	2014	1350	50	Centrif Back Pres	

Table 8.21 (continued): ISBL equipment list with duty specifications

	Storage tanks	# installed	Materials of construction	Vol (ft3)	L x D (ft)	DesP (psia)	DesT (°C)	Type tank w details (API?)
TK-101	HFCS Tank	1	FRP	17167	17 x 35	ATM	60	ASTM 3299
TK-102	HCl Fresh Acid Tank	1	FRP	258	4 x 9	ATM	60	ASTM 3299 + ex scrubber
TK-103	MIBK Tank	1	CS	208	7.5 x 3	ATM	100	API 650-floating roof
TK-104	HMF Tank	1	CS	10573	15 x 30	ATM	100	API 650
TK-201	Hexanol Tank	1	CS	846	11 x 10	ATM	100	API 650
TK-301	1,6-HDO Tank	1	CS	9974	14 x 30	ATM	100	API 650
TK-302	Mixed Diol Tank	1	CS	1176	12 x 11	ATM	100	API 650
TK-401	Ammonia sphere	1	304 SS	5729	13.5 dia	350	150	API 2510
TK-402	Cyclohexane Tank	1	CS	280	7 x 7	ATM	100	API 650
TK-403	Crude HMDA Tank	1	304 SS	9579	23 x 23	ATM	100	API 650-floating roof
Tk-501 A/B	HMDA Product Tanks	2	304 SS	4790	19 x 18	ATM	100	API 650-floating roof
Tk-502 A/B	Amines Day Tanks	2	304 SS	734	10 x 10	ATM	100	API 650-floating roof
	Pressure vessels (API 510-ASME BPVC)	# installed	Materials of construction	Vol (ft3)	L x D (ft)	Orientation	DesP (psia)	DesT (°C)
V-101	Extraction Mixing Tank	1	Incoloy 800	6469	80 x 10	Vert	125	100
V-201	HMF Mixing Tank	1	304 SS	740	15 x 8	Vert	50	150
V-401	Extraction Vessel	1	304 SS	8091	53 x 14	Horiz	100	125

Itemized capital cost estimate

We have prepared an itemized capital cost estimate of the ISBL process equipment portion of the plant using the equipment list and the IHS PEPCOST computer program. The PEPCOST index used is 1164. These costs represent the year 2013 estimated FOB purchase price of process equipment, plus the direct installation costs for this equipment. We have segmented the ISBL process equipment costs by section of the plant, as shown in the table below.

Table 8.22: Itemized ISBL capital cost estimate by plant section (\$US-k)

Description	Installed cost (\$US-k)
Section 100 – Hydroxymethylfurfural from HFCS by Hydrolysis	56,135
Section 200 – Hydrogenation of HMF to 1,2,6-Hexanetriol	62,740
Section 300 – Hydrogenation of 1,2,6-Hexanetriol to 1,6-Hexanediol	20,154
Section 400 – Ammoniation of 1,6-Hexanediol to HMDA	53,856
Section 500 – HMDA purification	9,939
Special Purpose equipment	77,415
Sum	280,239

Significant direct ISBL capital costs are created by the gas phase reactions: Section 200/300 hydrogenation of HMF to 1,6-hexanediol, and the Section 400 ammoniation of 1,6-hexanediol to HMDA. Since the patent and trade data did not provide optimized residence time (LHSV) data, we used a conservative 10 minutes liquid residence time for hydrogenation and 15 minutes for the ammoniation reactions.

In the case of the section 200 hydrogenation of HMF to 1,6-hexanediol, the combination of residence time (10 minutes), feedstock dilution in water (30% concentration), high pressure operation (1000 psia), and excess feed of hydrogen above stoichiometric (8:1) resulted in the design necessity of physically large

high pressure alloy reactors (614 ft³ apiece), and large capacity hydrogen recycle compressor (5,661 BHP). In hydraulic terms, the feed to the hydrogenation reactor is approximately 22,000 bbl/day, so it is not surprising that the capex approximates that of a refinery hydro--cracker. We would expect that a process specific optimization should be able to accomplish the same reaction results in less than 10 minutes residence time, with an excess hydrogen ratio of 5:1 rather than 8:1. Such standard operating conditions for commercial hydrogenation units would reduce process unit capex by nearly half.

A similar situation exists with the section 400 ammoniation of 1,6-hexanediol to HMDA. This reaction occurs at even higher pressure (3000 psia), is designed for 15 minute residence time, and uses an excess ammonia ratio of 5:1.

We have also segmented the ISBL process equipment costs by type of process equipment, as shown in the table below.

Table 8.23: Itemized ISBL capital cost estimate by type of equipment (\$US-k)

	FOB (1 unit)	FOB (all units)	Install (1 unit)	Install (all units)	Installed cost (all units)
Buildings	750	750	1,250	1,250	2,000
Distillation columns	2,418	2,418	4,690	4,690	7,108
Centrifuges	809	1,112	399	702	1,815
Crystallizers	1,020	1,020	149	149	1,169
Solids conveyors	125	250	185	370	620
Drums	5,596	5,596	1,535	1,535	7,132
Heat exchangers	28,705	30,580	4,526	5,038	35,618
Solids filters	3,653	3,653	2,586	2,586	6,239
Compressors	17,577	17,577	33,622	33,622	51,200
Mixers & agitators	712	885	186	232	1,116
Pumps	6,839	13,678	19,967	39,935	53,613
Reactors	3,540	7,080	1,033	2,065	9,145
Special package equip	29,655	29,655	47,760	47,760	77,415
Steam turbine drivers	7,087	7,087	12,200	12,200	19,286
Storage tanks	3,014	3,563	923	1,004	4,567
Pressure vessels	1,937	1,937	260	260	2,197
Sum	113,437	126,842	131,271	153,397	280,239

As presented above, the design basis for the hydrogenation and ammoniation reactions results in high capex for the required process compressors, and their steam turbine drivers. High pressure reaction also requires high head feed pumps, and large dimension heavy wall alloy reactors. The itemized ISBL cost estimates by tagged process equipment label are presented in the table below.

Table 8.24: Itemized ISBL capital cost estimate (\$US-k)

	Buildings	Floor area (ft2)	FOB (1 unit)	FOB (all units)	Install (1 unit)	Install (all units)	Installed cost (all units)
B-101	Process control building	5000	500.0	500.0	750.0	750.0	1250.0
B-102	Compressor building	5000	250.0	250.0	500.0	500.0	750.0
	Distillation columns	# installed	FOB (1 unit)	FOB (1 unit)	FOB (all units)	Install (1 unit)	Install (all units)
C-101	MIBK column	1	269.1	269.1	537.8	537.8	806.9
C-201	Lites column	1	365.2	365.2	574.9	574.9	940.1
C-202	Hexanol column	1	190.4	190.4	460.2	460.2	650.6
C-301	Diols splitter	1	189.8	189.8	477.7	477.7	667.5
C-302	1,6-HDO column	1	471.4	471.4	646.2	646.2	1117.6
C-401	Dewatering column	1	272.3	272.3	499.5	499.5	771.8
C-402	Lites column	1	255.2	255.2	529.8	529.8	785.0
C-403	Imines column	1	237.7	237.7	501.0	501.0	738.7
C-501	Cyclohexane column	1	167.0	167.0	462.4	462.4	629.4
	Centrifuges	# installed	FOB (1 unit)	FOB (1 unit)	FOB (all units)	Install (1 unit)	Install (all units)
CN-201	HMF slurry centrifuge	1	505.6	505.6	95.5	95.5	601.1
CN-501 A/B	HMDA centrifuges	2	303.4	606.7	303.4	606.7	1213.4
	Crystallizers	# installed	FOB (1 unit)	FOB (all Units)	Install (1 unit)	Install (all units)	Installed cost (all units)
CR-201	HMF recovery crystallizer	1	329.0	329.0	48.0	48.0	377.0
CR-501	HMDA centrifuges	1	690.9	690.9	100.8	100.8	791.7
	Solids conveyors	# installed	FOB (1 unit)	FOB (all units)	Install (1 unit)	Install (all units)	Installed cost (all units)
CV-501 A/B	HMDA cake slurry	2	125.0	250.0	185.0	370.0	620.0
	Drums	# installed	FOB (1 unit)	FOB (all units)	Install (1 unit)	Install (all units)	Installed cost (all units)
D-101	E102 receiver	1	55.1	55.1	51.0	51.0	106.1
D-102	Extraction settler	1	796.6	796.6	151.0	151.0	947.6
D-103	E106 receiver	1	473.2	473.2	74.5	74.5	547.7
D-104	K101 K/O drum	1	25.1	25.1	44.6	44.6	69.7
D-201	K201 K/O drum	1	301.4	301.4	62.8	62.8	364.2
D-202	H2 degassing drum	1	301.4	301.4	62.8	62.8	364.2
D-203	K202 3-stage flash drum	1	45.5	45.5	48.6	48.6	94.1
D-204	E205 receiver	1	195.3	195.3	68.6	68.6	263.9
D-205	K203 K/O drum	1	31.1	31.1	45.7	45.7	76.8
D-206	E208 receiver	1	60.6	60.6	54.2	54.2	114.8
D-301	E301 receiver	1	64.0	64.0	57.5	57.5	121.5
D-302	K301 K/O drum	1	22.4	22.4	43.4	43.4	65.8
D-303	C302 K/O drum	1	26.3	26.3	44.5	44.5	70.8
D-304	E307 receiver	1	99.5	99.5	63.7	63.7	163.2
D-401	K401 K/O drum	1	718.8	718.8	75.8	75.8	794.6
D-402	R401 3-stage flash drum	1	1650.0	1650.0	103.9	103.9	1753.9

Table 8.24 (continued): Itemized ISBL capital cost estimate (\$US-k)

	DRUMS	# installed	FOB (1 unit)	FOB (all units)	Install (1 unit)	Install (all units)	Installed cost (all units)
D-403	Extraction settling drum	1	354.8	354.8	75.1	75.1	429.9
D-404	E406 receiver	1	58.3	58.3	53.8	53.8	112.1
D-405	K403 K/O drum	1	25.1	25.1	44.6	44.6	69.7
D-406	E410 receiver	1	125.0	125.0	67.7	67.7	192.7
D-407	K404 K/O drum	1	26.3	26.3	44.5	44.5	70.8
D-408	E413 receiver	1	55.5	55.5	55.5	55.5	111.0
D-409	K405 K/O drum	1	22.4	22.4	43.4	43.4	65.8
D-501	E503 receiver	1	18.0	18.0	45.0	45.0	63.0
D-502	E506 receiver	1	44.6	44.6	53.1	53.1	97.7
	Heat exchangers	# installed	FOB (1 unit)	FOB (all units)	Install (1 unit)	Install (all units)	Installed cost (all units)
E-101	Tk101 tank heater	1	34.3	34.3	54.1	54.1	88.4
E-102	HFCS feed/ product exchanger	1	1021.5	1021.5	105.6	105.6	1127.1
E-103	Acid heater	1	7126.0	7126.0	180.4	180.4	7306.4
E-104	Reaction cooler	1	5176.5	5176.5	90.1	90.1	5266.6
E-105	C101 feed / product exchanger	1	155.3	155.3	55.6	55.6	210.9
E-106	C101 condenser	1	2497.5	2497.5	286.5	286.5	2784.0
E-107 A/B	C101 reboilers	2	614.6	1229.2	136.9	273.8	1503.0
E-108	K101 condenser	1	213.4	213.4	61.3	61.3	274.7
E-109	HMF product cooler	1	151.2	151.2	58.4	58.4	209.6
E-110	Tk104 heater	1	34.6	34.6	54.2	54.2	88.8
E-201	R201 feed/prod exchanger	1	51.3	51.3	46.7	46.7	98.0
E-202	R201 heater	1	52.1	52.1	46.8	46.8	98.9
E-203	R201 cooler	1	218.6	218.6	63.0	63.0	281.6
E-204	C201 feed heater	1	201.1	201.1	61.5	61.5	262.6
E-205	C201 condenser	1	929.4	929.4	195.4	195.4	1124.8
E-206 A/B	C201 reboilers	2	469.7	939.4	102.9	205.8	1145.2
E-207	K203 condenser	1	963.9	963.9	116.3	116.3	1080.2
E-208	C202 condenser	1	303.8	303.8	64.5	64.5	368.3
E-209	C202 reboiler	1	167.1	167.1	57.5	57.5	224.6
E-210	Hexanol exchanger	1	18.1	18.1	49.5	49.5	67.6
E-211	Hexanol cooler	1	16.9	16.9	48.9	48.9	65.8
E-212	HMF solution CW cooler	1	58.7	58.7	53.5	53.5	112.2
E-213	HMF solution glycol cooler	1	44.1	44.1	44.6	44.6	88.7
E-301	C301 condenser	1	593.8	593.8	74.3	74.3	668.1
E-302 A/B	C301 reboilers	2	380.3	760.6	68.7	137.4	898.0
E-303	K301 condenser	1	58.0	58.0	53.6	53.6	111.6
E-304	Reactor feed heater	1	262.8	262.8	65.5	65.5	328.3
E-305	C302 feed pre-heater	1	17.0	17.0	40.9	40.9	57.9
E-306	R301 product cooler	1	178.8	178.8	59.3	59.3	238.1
E-307	C302 condenser	1	615.0	615.0	129.2	129.2	744.2
E-308	C302 reboiler	1	621.4	621.4	136.0	136.0	757.4
E-309	K302 condenser	1	114.4	114.4	56.4	56.4	170.8
E-310	1,6-HDO cooler	1	83.2	83.2	54.9	54.9	138.1
E-311	Mixed Diol cooler	1	21.9	21.9	50.8	50.8	72.7
E-401	Ammonia vaporizer	1	85.8	85.8	50.4	50.4	136.2
E-402	HDO feed / product exchanger	1	226.3	226.3	65.8	65.8	292.1

Table 8.24 (continued): Itemized ISBL capital cost estimate (\$US-k)

		# installed	FOB (1 unit)	FOB (all units)	Install (1 unit)	Install (all units)	Installed cost (all units)
Heat exchangers							
E-403	Cyclohexane heater	1	258.6	258.6	68.6	68.6	327.2
E-404	R401 product cooler	1	320.8	320.8	69.1	69.1	389.9
E-405	C401 feed / product heater	1	139.7	139.7	57.5	57.5	197.2
E-406	C401 condenser	1	445.3	445.3	69.3	69.3	514.6
E-407	K403 condenser	1	64.5	64.5	53.9	53.9	118.4
E-408 A/B	C401 reboilers	2	149.2	298.4	55.8	111.6	410.0
E-409	C402 feed heater	1	404.1	404.1	88.8	88.8	492.9
E-410	C402 condenser	1	614.3	614.3	135.0	135.0	749.3
E-411	C402 distillate cooler	1	97.2	97.2	49.8	49.8	147.0
E-412	C402 reboiler	1	711.3	711.3	156.3	156.3	867.6
E-413	C403 condenser	1	461.2	461.2	70.1	70.1	531.3
E-414	C403 reboiler	1	241.0	241.0	64.1	64.1	305.1
E-415	HMDA cooler	1	80.6	80.6	54.8	54.8	135.4
E-416	Tk-403 tank heater	1	34.3	34.3	27.0	27.0	61.3
E-417	K405 condenser	1	44.5	44.5	52.7	52.7	97.2
E-501	Ammonia cooler	1	130.4	130.4	52.9	52.9	183.3
E-502 A/B	HMDA dryers	2	95.5	191.0	53.8	107.6	298.6
E-503	E502 condenser	1	32.3	32.3	51.8	51.8	84.1
E-504	HMDA cooler	1	24.5	24.5	51.2	51.2	75.7
E-505 A/B	Tk501 immersion heaters	2	34.3	68.6	27.0	54.0	122.6
E-506	C501 condenser	1	318.4	318.4	65.1	65.1	383.5
E-507 A/B	C501 reboilers	2	115.4	230.8	52.5	105.0	335.8
E-508	Amines cooler	1	16.8	16.8	48.8	48.8	65.6
E-509	Cyclohexane cooler	1	57.1	57.1	53.5	53.5	110.6
E-510	C501 feed heater	1	18.1	18.1	41.6	41.6	59.7
E-511 A/B	Tk502 immersion heaters	2	16.8	33.6	14.5	29.0	62.6
Filters							
FL-101	R101 dual basket filter	1	1783.3	1783.3	1262.3	1262.3	3045.6
FL-201	R201 dual basket filters	1	529.9	529.9	375.1	375.1	904.9
FL-301	R301 dual basket filters	1	233.6	233.6	165.3	165.3	398.9
FL-302	P303 dual basket filter	1	235.9	235.9	167.0	167.0	402.8
FL-401	P403 dual basket filter	1	698.5	698.5	494.4	494.4	1192.9
FL-402	HMDA dual basket filter	1	85.9	85.9	60.8	60.8	146.7
FL-501	HMDA dual basket filters	1	79.8	79.8	56.5	56.5	136.2
FL-502	Amines dual basket filter	1	6.6	6.6	4.7	4.7	11.3
Compressor							
K-101	C101 vacuum pump	1	1386.0	1386.0	1561.0	1561.0	2947.0
K-201	LP H2 compressor	1	2546.0	2546.0	4450.8	4450.8	6996.8
K-202	H2 Recycle compressor	1	5284.4	5284.4	9994.5	9994.5	15278.9
K-203	C201 vacuum pump	1	2377.0	2377.0	3189.0	3189.0	5566.0
K-301	C301 vacuum pump	1	252.4	252.4	1057.0	1057.0	1309.4
K-302	C302 vacuum pump	1	483.1	483.1	1221.0	1221.0	1704.1
K-401	H2 HP compressor	1	404.9	404.9	1162.0	1162.0	1566.9
K-402	NH3 recycle compressor	1	3622.3	3622.3	7443.4	7443.4	11065.7

Table 8.24 (continued): Itemized ISBL capital cost estimate (\$US-k)

Compressors		# installed	FOB (1 unit)	FOB (all units)	Install (1 unit)	Install (all units)	Installed cost (all units)
K-403	C401 vacuum pump	1	336.2	336.2	1113.0	1113.0	1449.2
K-404	C402 vacuum pump	1	127.1	127.1	982.7	982.7	1109.8
K-405	C403 vacuum pump	1	758.0	758.0	1448.0	1448.0	2206.0
Mixers & agitators		# installed	FOB (1 unit)	FOB (all units)	Install (1 unit)	Install (all units)	Installed cost (all units)
M-101	Tk101 agitator	1	96.2	96.2	25.2	25.2	121.4
M-102 A/B	R101 mixers	2	140.4	280.7	36.7	73.4	354.1
M-103	Extraction mixer	1	283.0	283.0	74.0	74.0	357.0
M-104	Tk104 agitator	1	60.0	60.0	15.7	15.7	75.7
M-201	V201 mixer	1	8.5	8.5	2.2	2.2	10.7
M-301	P303 static mixer	1	3.5	3.5	1.2	1.2	4.7
M-401	V401 mixer	1	30.6	30.6	8.0	8.0	38.6
M-402	Tk403 mixer	1	56.6	56.6	14.8	14.8	71.4
M-501 A/B	Tk501 mixers	2	28.3	56.6	7.4	14.8	71.4
M-502 A/B	Tk502 mixers	2	4.5	9.1	1.2	2.4	11.4
Pmps		# installed	FOB (1 unit)	FOB (all units)	Install (1 unit)	Install (all units)	Installed cost (all units)
P-101 A/B	HFCS feed pumps	2	33.7	67.4	153.5	307.0	374.4
P-102 A/B	HCl acid feed pumps	2	19.0	38.0	63.3	126.6	164.6
P-103 A/B	Reactor O/H pumps	2	61.1	122.2	126.1	252.2	374.4
P-104 A/B	Reactor B/S pumps	2	792.0	1584.0	1800.6	3601.2	5185.2
P-105 A/B	Extraction pumps	2	1188.0	2376.0	2700.9	5401.8	7777.8
P-106 A/B	MIBK pumps	2	18.5	37.0	37.5	75.0	112.0
P-107 A/B	Extract pumps	2	161.1	322.2	452.9	905.8	1228.0
P-108 A/B	Dilute acid pumps	2	236.8	473.6	498.7	997.4	1471.0
P-109 A/B	C101 reflux pumps	2	297.4	594.8	843.4	1686.8	2281.6
P-110 A/B	C101 B/S pumps	2	129.8	259.6	318.3	636.6	896.2
P-111 A/B	HMF product pumps	2	12.8	25.6	46.8	93.6	119.2
P-201 A/B	HMF feed pumps	2	470.8	941.6	1264.8	2529.6	3471.2
P-202 A/B	R201 B/S pumps	2	62.2	124.4	187.1	374.2	498.6
P-203 A/B	C201 Feed Pumps	2	0.0	0.0	0.0	0.0	0.0
P-204 A/B	C201 reflux pumps	2	118.9	237.8	346.3	692.6	930.4
P-205 A/B	C201 B/S pumps	2	64.8	129.6	309.0	618.0	747.6
P-206 A/B	C202 reflux pumps	2	30.6	61.2	89.7	179.4	240.6
P-207 A/B	C202 B/S pumps	2	14.0	28.0	52.9	105.8	133.8
P-208 A/B	Tk201 pumps	2	5.3	10.6	17.4	34.8	45.4
P-209 A/B	HMF light slurry pumps	2	78.0	156.0	122.7	245.4	401.4

Table 8.24 (continued): Itemized ISBL capital cost estimate (\$US-k)

	Pumps	# installed	FOB (1 unit)	FOB (all units)	Install (1 unit)	Install (all units)	Installed cost (all units)
P-210 A/B	HMF heavy slurry pumps	2	78.0	156.0	122.7	245.4	401.4
P-301 A/B	C301 reflux pumps	2	26.1	52.2	109.3	218.6	270.8
P-302 A/B	C301 B/S pumps	2	197.1	394.2	982.4	1964.8	2359.0
P-303 A/B	HP water pumps	2	216.8	433.6	1080.6	2161.2	2594.8
P-304 A/B	R301 product pumps	2	19.9	39.8	79.0	158.0	197.8
P-305 A/B	C302 reflux pumps	2	46.4	92.8	219.6	439.2	532.0
P-306 A/B	C302 B/S pumps	2	43.1	86.2	195.6	391.2	477.4
P-307 A/B	Tk301 pumps	2	175.8	351.6	832.0	1664.0	2015.6
P-308 A/B	Tk302 pumps	2	5.6	11.2	18.2	36.4	47.6
P-401 A/B	Ammonia feed pumps	2	51.4	102.8	235.7	471.4	574.2
P-402 A/B	Cyclohexane feed pumps	2	35.4	70.9	71.2	142.4	213.3
P-403 A/B	R401 product pumps	2	92.2	184.4	260.9	521.8	706.2
P-404 A/B	D403 B/S pumps	2	76.0	152.0	220.6	441.2	593.2
P-405 A/B	C401 reflux pumps	2	12.7	25.4	46.4	92.8	118.2
P-406 A/B	C401 B/S pumps	2	492.8	985.6	2354.0	4708.0	5693.6
P-407 A/B	D403 O/H pumps	2	36.2	72.4	163.1	326.2	398.6
P-408 A/B	C402 reflux pumps	2	86.9	173.8	391.4	782.8	956.6
P-409 A/B	C402 B/S pumps	2	108.8	217.6	321.0	642.0	859.6
P-410 A/B	C403 reflux pumps	2	751.8	1503.6	1492.5	2985.0	4488.6
	PUMPS	# installed	FOB (1 unit)	FOB (all units)	Install (1 unit)	Install (all units)	Installed cost (all units)
P-411 A/B	C403 B/S pumps	2	22.8	45.6	94.6	189.2	234.8
P-412 A/B	Tk403 pumps	2	23.6	47.2	63.6	127.2	174.4
P-501 A/B	Circulating pumps	2	213.4	426.8	533.2	1066.4	1493.2
P-502 A/B	HMDA slurry pumps	2	122.4	244.8	338.5	677.0	921.8
P-503 A/B	C501 feed pumps	2	6.1	12.2	19.1	38.2	50.4
P-504 A/B	HMDA dryer pumps	2	22.9	45.8	62.4	124.8	170.6
P-505 A/B	Tk501 pumps	2	22.9	45.8	62.4	124.8	170.6
P-506 A/B	C501 reflux pumps	2	16.6	33.2	66.2	132.4	165.6
P-507 A/B	C501 B/S pumps	2	29.3	58.6	78.0	156.0	214.6
P-508 A/B	Tk502 pumps	2	11.2	22.4	21.2	42.4	64.8
	REACTORS	# installed	FOB (1 unit)	FOB (all units)	Install (1 unit)	Install (all units)	Installed cost (all units)
R-101 A/B	Hydrolysis reactor	2	1468.0	2936.0	384.8	769.6	3705.6
R-201 A/B	H2 HMF reactors	2	850.0	1700.0	248.9	497.8	2197.8

Table 8.24 (continued): Itemized ISBL capital cost estimate (\$US-k)

Reactors		# installed	FOB (1 unit)	FOB (all units)	Install (1 unit)	Install (all units)	Installed cost (all units)
R-301 A/B	H2 Triol reactors	2	425.0	850.0	124.4	248.8	1098.8
R-401 A/B	Ammoniation reactors	2	796.9	1593.8	274.5	549.0	2142.8
Specially packaged equipment		# installed	FOB (1 unit)	FOB (all units)	Install (1 unit)	Install (all units)	Installed cost (all units)
S-101	4-stagel acid concentrator	1	675.0	675.0	1350.0	1350.0	2025.0
S-102	Ammonia chiller system	1	1000.0	1000.0	1400.0	1400.0	2400.0
S-103	Glycol chiller system	1	250.0	250.0	350.0	350.0	600.0
S-104	Solids incinerator w steam production	1	3600.0	3600.0	2000.0	2000.0	5600.0
S-105	Liquids incinerator	1	4500.0	4500.0	2500.0	2500.0	7000.0
S-106	2-flare system with blowdown drums & header	1	4309.0	4309.0	11234.0	11234.0	15543.0
S-107	Process computer control system	1	6800.0	6800.0	11600.0	11600.0	18400.0
S-108	Dowtherm hot oil system	1	8521.0	8521.0	17326.0	17326.0	25847.0
Steam turbine drivers		# installed	FOB (1 unit)	FOB (all units)	Install (1 unit)	Install (all units)	Installed cost (all units)
ST-201	K-201 ST driver	1	1803.9	1803.9	3201.3	3201.3	5005.2
ST-202	K-202 ST driver	1	3100.4	3100.4	5502.0	5502.0	8602.4
ST-203	K-203 ST driver	1	933.0	933.0	1279.5	1279.5	2212.5
ST-401	K-402 ST driver	1	1249.3	1249.3	2217.0	2217.0	3466.3
Storage tanks		# installed	FOB (1 unit)	FOB (all units)	Install (1 unit)	Install (all units)	Installed cost (all units)
TK-101	HFCS tank	1	190.3	190.3	161.7	161.7	352.0
TK-102	HCl fresh acid tank	1	25.1	25.1	11.8	11.8	36.9
TK-103	MIBK tank	1	23.6	23.6	11.1	11.1	34.7
TK-104	HMF tank	1	139.7	139.7	118.7	118.7	258.4
TK-201	Hexanol tank	1	61.6	61.6	29.0	29.0	90.6
TK-301	1,6-HDO tank	1	133.8	133.8	113.7	113.7	247.5
TK-302	Mixed Diol tank	1	69.1	69.1	32.5	32.5	101.6
TK-401	Ammonia sphere	1	1362.0	1362.0	233.6	233.6	1595.6
TK-402	Cyclohexane tank	1	41.8	41.8	19.7	19.7	61.5
TK-403	Crude HMDA tank	1	417.3	417.3	110.8	110.8	528.1
Tk-501 A/B	HMDA product tank	2	361.8	723.6	53.1	106.2	829.8
Tk-502 A/B	Amines day tank	2	187.5	375.0	27.5	55.0	430.0
Pressure vessels (API 510-ASME BPVC)		# installed	FOB (1 unit)	FOB (all units)	Install (1 unit)	Install (all units)	Installed cost (all units)
V-101	Extraction mixing tank	1	1425.0	1425.0	99.9	99.9	1524.9
V-201	HMF mixing tank	1	81.3	81.3	56.6	56.6	137.9
V-401	Extraction vessel	1	430.8	430.8	103.8	103.8	534.6
Sum			113436.5	126842.1	131271.0	153397.2	280239.3

Total fixed capital cost estimate

Incorporating the itemized ISBL capital cost estimate values into the standard PEP template for estimating total project capital cost, and providing additional factored estimates for the required OSBL utility and infrastructure investments, we have estimated the total fixed capital cost estimate for the project. The components of the TFC estimate are presented in the table below.

Table 8.25: Total fixed capital cost estimate (\$US-k)

Capacity: 250,000 MT/YR			
AT 0.90 stream factor			
PEP Cost Index: 1164			
		Capacity exponent	
Battery limits equipment, FOB	Cost (\$US-K)	Up	Dpwn
Buildings	750	0.55	0.53
Distillation columns	2,418	0.70	0.60
Centrifuges	1,112	0.61	0.58
Crystallizers	1,020	0.67	0.62
Solids conveyors	250	0.67	0.62
Drums	5,596	0.65	0.63
Heat exchangers	30,580	0.63	0.60
Solids filters	3,653	0.62	0.60
Compressors	17,577	0.69	0.60
Mixers & agitators	885	0.67	0.62
Pumps	13,678	0.85	0.85
Reactors	7,080	0.65	0.65
Special package equip	29,655	0.70	0.70
Steam turbine drivers	7,087	0.85	0.85
Storage tanks	3,563	0.55	0.53
Pressure vessels	1,937	0.65	0.65
Total BLE	126,842		
Direct installation costs	153,397	0.66	0.62
Indirect costs	115,048	0.63	0.59
Unscheduled equipment, 20%	30,679	0.65	0.62
Battery limits, installed	425,966	0.65	0.62
BLI contingency, 25%	106,492	0.65	0.62
Battery limits investment	532,458	0.65	0.62
Off-sites, installed			
Cooling water	21,298	0.65	0.62
Process water	2,556	0.65	0.62
Boiler feedwater	8,519	0.65	0.62
Process steam	63,895	0.55	0.53
Fuel gas system	3,408	0.55	0.53
Inert gas & instrument AIR	2,556	0.55	0.53
Off-sites tankage	28,500		
Utilities & storage	130,732	0.65	0.62
General service facilities	21,298	0.65	0.62
Wastewater treatment	51,116	0.65	0.62
Total off-sites	203,146	0.65	0.62
Off-sites contingency 25%	50,787	0.65	0.62
Off-sites capital investment	253,933	0.65	0.62
Total fixed capital	786,391	0.65	0.62

HMDA production cost

Variable raw material production cost

By combining the consumption of raw materials with unit raw material prices documented in the design basis section of the report, we have developed an estimate of the variable costs of production, which are presented in the table below.

Table 8.26: Rennovia variable raw material costs

Raw materials	Unit cost		Consumption		\$/mt
High fructose corn syrup	450	\$US/mt	1.932	mt/mt	869.4
Hydrochloric Acid 23° Baume	198	\$US/mt	0.02899	mt/mt	5.7
Ammonia	600	\$US/mt	0.3223	mt/mt	193.4
Hydrogen	872	\$US/mt	0.0791	mt/mt	69.0
Cyclohexane solvent	1550	\$US/mt	0.01575	mt/mt	24.4
MIBK solvent	1750	\$US/mt	0.01167	mt/mt	20.4
Pt/W on ZrO catalyst					25.0
Raney nickel catalyst					15.0
By-product credits					
Mixed Hexanol	900	\$US/mt	-0.0476	mt/mt	-42.8
Mixed Amines	750	\$US/mt	-0.08255	mt/mt	-61.9
Net raw material cost					1117.6

The largest single raw material cost contributor to the process is feedstock high fructose corn syrup. Each metric ton of HMDA produced consumes nearly 2 metric tons of HFCS feedstock. Fortunately, the relatively low unit price for HFCS (\$450/mt) allows this level of unit consumption without creating undue burden on overall production cost. Other significant feedstock cost components are ammonia for converting 1,6-hexanediol to HMDA, and hydrogen for converting 5-hydroxymethylfurfural (HMF) to 1,6-hexanediol (HDO).

Modest variable cost contributors include the solvents consumed during the extraction unit operations. Methylisobutyl ketone (MIBK) is used in the hydrolysis/dehydration reaction that converts HFCS to HMF. As HMF is formed in the liquid reactor, it has a propensity to react with remaining HFCS to form humins, oligomers, tars and polymers. For this reason, our process adds MIBK directly to the reactors for the purpose of quickly migrating the formed HMF away from the hydrochloric acid solution phase in which it is formed, and into the MIBK phase, which is essentially free of HFCS.

Although the extraction itself does not consume MIBK, the subsequent re-purification of MIBK via distillation requires that contaminants accumulating in the solvent be periodically removed. The purging of contaminants also results in the loss of small amounts of MIBK.

In the ammonialysis reaction that converts 1,6-hexanediol (HDO) to HMDA, reactor products include unconverted HDO. Since HDO and HMDA have nearly the same boiling points and melting points, separation via conventional distillation or crystallization is not economically practical. For our design, we separate HDO from HMDA using cyclohexane solvent, with the re-purification of cyclohexane causing small losses due to contaminant build-up.

Catalysts used in the process include dilute hydrochloric acid, platinum/tungsten on zirconium oxide substrate for HMF hydrogenation, and Raney nickel for ammonialysis. We have included in our economics minor debits for catalyst consumption, although it is expected that spent catalysts will be re-

processed to recover the active metals, and converted back into fresh catalyst. As a result, the cost debit represents precious catalyst re-processing costs, rather than metal purchase costs.

Our process recovers small amounts of by-product mixed hexanol (1-hexanol and 2-hexanol), as well as mixed amines for commercial sale. The combined credit for both by products is approximately \$100/mt of produced HMDA.

Variable utility production cost

Our production cost estimate for the contribution of utility and related energy costs is presented in the table below. The design requires significant consumption of process steam to drive distillation column reboilers, which then requires significant consumption of cooling water for the overhead condensers. The proposed design dissolves the HFCS feedstock in dilute hydrochloric acid, and uses large amounts of MIBK for liquid-liquid extraction. These unit operations require subsequent recovery and re-purification of the hydrochloric acid and solvent via distillation. The hydrogenation of HMF to 1,6-hexanediol is also conducted in a dilute water solution, requiring large distillation columns in the downstream purification stages. The ammoniation of 1,6-hexanediol to HMDA uses a large quantity of cyclohexane as HMDA extracting solvent, again requiring large distillation columns in the recovery section.

Table 8.27: Rennovia variable utility costs

Utilities	Unit cost		Consumption		\$/mt
Process water	0.350211	\$US/m3	12.84	m3/mt	4.5
Cooling water	0.041004	\$US/m3	656	m3/mt	26.9
Electricity	5.93	¢US/kwh	269.56	kwh/mt	16.0
Process steam	16.758	\$US/mt	14.5	mt/mt	243.0
Fuel gas	218.0304	\$US/mt	0.1328	mt/mt	29.0
Net utility cost					319.3

Fixed production costs

Using standard PEP assumptions (presented in the table below), we developed fixed costs of production to include direct plant operating and maintenance costs, indirect plant overhead, property tax and depreciation values, and corporate SG&A costs.

Table 8.28: Rennovia fixed cost assumption values

Value	Parameter
1.5	Maintenance Materials (% of BLI)
10	Operating Supplies (% of op labor)
46.23	Operating Labor Rate (\$/manhour)
1.5	Maintenance Labor (% of BLI)
20	Control Laboratory (% of op labor)
60	Plant Overhead (% of total labor)
2	Taxes & Insurance (% of TFC)
10	Depreciation (% of TFC)
25	Product Value Premium (Production Cost + % TFC)
4	Number of operators per shift
1	G&A, Sales, R&D (% of product price)

When the fixed costs assumptions are combined with the variable cost parameters, the result is our estimate of total HMDA production costs for the Rennovia technology. These are provided at three different production capacity levels (125 kty, 250 kty, 500 kty). The result of these is provided in the table below.

Table 8.29: Rennovia HMDA estimated production cost

Capacity	MT/Y	125	250	500
Production	MT/Y	125	250	500
Investment (\$US millions)				
Battery limits		321.0 (0.73)	532.5	883.2
Off-sites		<u>180.8</u> (0.49)	<u>253.9</u>	<u>356.6</u>
Total fixed capital		501.8	786.4	1239.8
Production cost (\$/MT)				
		<u>\$/mt</u>	<u>\$/mt</u>	<u>\$/mt</u>
Net raw materials		1117.6	1117.6	1117.6
Net utilities		<u>319.3</u>	<u>319.3</u>	<u>319.3</u>
Variable costs		1436.9	1436.9	1436.9
Direct costs				
Maintenance materials		38.5	31.9	26.5
Operating supplies		1.3	0.6	0.3
Operating labor		13.0	6.5	3.2
Maintenance labor		38.5	31.9	26.5
Control laboratory		<u>2.6</u>	<u>1.3</u>	<u>0.6</u>
Total direct costs		1530.8	1509.2	1494.1
Plant overhead		30.9	23.1	17.8
Taxes & insurance		80.3	62.9	49.6
Depreciation		<u>401.4</u>	<u>314.5</u>	<u>248.0</u>
Plant gate cost		2043.4	1909.7	1809.5
G&A, sales, R&D		29.0	29.0	29.0
Total production cost				
AT 100% capacity		2072.4	1938.7	1838.5
AT 75% capacity		2284.3	2106.0	1972.3
AT 50% capacity		2707.9	2440.6	2240.1
Product value (cost + 25%/YR ROI before taxes)				
AT 100% capacity		3077.8	2723.3	2453.9
AT 75% capacity		3287.9	2892.4	2592.2
AT 50% capacity		3711.6	3226.9	2860.0
Cash cost		1670.97	1624.19	1590.53
Cash cost profitability		1229.04	1275.83	1309.48
Total cost profitability		827.60	961.28	1061.53

The combination of segmented variable and fixed production costs are presented in the table below, following the conventional PEP production cost sheet format.

Table 8.30: Rennovia HMDA estimated production cost

					<u>\$/mt</u>
					2900.0
		Unit Cost		HMDA market price Consumption	\$/mt
Raw materials					
High fructose corn syrup	450	\$US/mt	1.932	mt/mt	869.4
Hydrochloric Acid 23° Baume	198	\$US/mt	0.02899	mt/mt	5.7
Ammonia	600	\$US/mt	0.3223	mt/mt	193.4
Hydrogen	872	\$US/mt	0.0791	mt/mt	69.0
Cyclohexane solvent	1550	\$US/mt	0.01575	mt/mt	24.4
MIBK solvent	1750	\$US/mt	0.01167	mt/mt	20.4
Pt/W on ZrO catalyst					25.0
Raney Nickel catalyst					15.0
By-product credits					
Mixed Hexanol	900	\$US/mt	-0.0476	mt/mt	-42.8
Mixed Amines	750	\$US/mt	-0.08255	mt/mt	-61.9
Net raw material cost					1117.6
Utilities		Unit cost		Consumption	\$/mt
Process water	0.350211	\$US/m3	12.84	m3/mt	4.5
Cooling water	0.041004	\$US/m3	656	m3/mt	26.9
Electricity	5.93	¢US/kwh	269.56	kwh/mt	16.0
Process steam	16.758	\$US/mt	14.5	mt/mt	243.0
Fuel gas	218.0304	\$US/mt	0.1328	mt/mt	<u>29.0</u>
Net utility cost					319.3
Variable costs					1436.9
Value	Parameter				
1.5	Maintenance materials (% of BLI)				
10	Operating supplies (% of op labor)				
46.23	Operating labor rate (\$/manhour)				
1.5	Maintenance labor (% of BLI)				
20	Control laboratory (% of op labor)				
60	Plant overhead (% of total labor)				
2	Taxes & insurance (% of TFC)				
10	Depreciation (% of TFC)				
25	Product value premium (production cost + % TFC)				
4	Number of operators per shift				
1	G&A, sales, R&D (% of product price)				

Table 8.30 (continued): Rennovia HMDA estimated production cost

Capacity	MT/Y	125	250	500
Production	MT/Y	125	250	500
Investment (\$US millions)				
Battery limits		321.0 (0.73)	532.5	883.2
Off-sites		<u>180.8</u> (0.49)	<u>253.9</u>	<u>356.6</u>
Total fixed capital		501.8	786.4	1239.8
Production cost (\$/MT)				
		<u>\$/mt</u>	<u>\$/mt</u>	<u>\$/mt</u>
Net raw materials		1117.6	1117.6	1117.6
Net utilities		<u>319.3</u>	<u>319.3</u>	<u>319.3</u>
Variable costs		1436.9	1436.9	1436.9
Direct costs				
Maintenance materials		38.5	31.9	26.5
Operating supplies		1.3	0.6	0.3
Operating labor		13.0	6.5	3.2
Maintenance labor		38.5	31.9	26.5
Control laboratory		<u>2.6</u>	<u>1.3</u>	<u>0.6</u>
Total direct costs		1530.8	1509.2	1494.1
Plant overhead		30.9	23.1	17.8
Taxes & insurance		80.3	62.9	49.6
Depreciation		<u>401.4</u>	<u>314.5</u>	<u>248.0</u>
Plant gate cost		2043.4	1909.7	1809.5
G&A, sales, R&D		29.0	29.0	29.0
Total production cost				
AT 100% capacity		2072.4	1938.7	1838.5
AT 75% capacity		2284.3	2106.0	1972.3
AT 50% capacity		2707.9	2440.6	2240.1
Product value (cost + 25%/YR ROI before taxes)				
AT 100% capacity		3077.8	2723.3	2453.9
AT 75% capacity		3287.9	2892.4	2592.2
AT 50% capacity		3711.6	3226.9	2860.0
Cash cost		1670.97	1624.19	1590.53
Cash cost profitability		1229.04	1275.83	1309.48
Total cost profitability		827.60	961.28	1061.53

Economic analysis

When compared to the conventional routes to HMDA practiced by Invista/DuPont (from butadiene), and Ascend/Monsanto (from acrylonitrile), the Rennovia HMDA process shows potentially significant feedstock cost advantages, driven primarily by using low cost HFCS as the starting material. In the

absence of Rennovia process patents disclosing key technical parameters (solvent to feed ratios, optimized reactor residence times, excess hydrogen and ammonia feed ratios), we used the information that was provided, which was most likely determined to satisfy laboratory experimental requirements, rather than to represent potentially commercial values. The result is what we believe to be a technically viable integrated process, although surely not an economically optimum integrated process.

Conventional petrochemical hydrogenations, although operated at very high pressure, have reactor residence times measured in seconds, or at most minutes, rather than the 1 hour used in our process design for dehydration, and 10 minutes for hydrogenation. As a result, our process requires very large (and very expensive) heavy wall alloy reactor vessels. The large excess feed ratio of hydrogen and ammonia results in very large recycle gas compressors, contributing to both high capex and high energy consumption to drive them. Lastly, the feed dilution and solvent addition ratios are very high, resulting in large and energy intensive downstream distillation columns to purify products and recycle solvents.

If conventional petrochemical processing parameter values could be applied to the Rennovia design without degrading chemical performance (kinetics, selectivity and conversion), we estimate that the capital cost could be reduced from approximately \$786 million for a 250 kty plant to about \$600 MM. Such a capex reduction would result in substantially lower utility costs, and provide overall economics that potentially would be superior to the conventional routes to HMDA from butadiene via hydrocyanation, and from acrylonitrile via electro-dimerization.

Appendix A: Patent summary table

Patent summary

Reference number (patent)	Assignee	Earliest date shown
Process for the separation of mono and di-carboxylic acid compounds		
2013 0345473	Rennovia	12/26/2013
The present disclosure relates to processes for the separation of at least one di-carboxylic acid compound and/or at least one mono-carboxylic acid compound from a mixture. The separation processes involve contacting the mixture with an ion exchange medium to cause at least one of the mono- and/or di-carboxylic acid compounds to be retained by the medium, eluting at least one of the mono-carboxylic acid compound or the di-carboxylic acid compound using an eluent to form an eluate, wherein the eluate is enriched in at least one of the mono-carboxylic acid compound or di-carboxylic acid relative to the concentration of such eluted acid in the mixture having contacted the medium and wherein the eluent comprises an organic acid. The process has particular utility in the production of di-carboxylic acid compounds from glucose.		
Process for making nitriles		
2013 0167728	Invista	10/10/2013
Adiponitrile is made by reacting 3-pentenitrile with hydrogen cyanide. The 3-pentenitrile is made by reacting 1,3-butadiene with hydrogen cyanide and by isomerizing 2-methyl-3-butenitrile. Both reactions take place in the presence of a catalyst comprising zero valent nickel and a phosphorus-containing ligand. The ligand is partially degraded by hydrolysis or oxidation. Phosphorus-containing ligand degradation products are removed during the production of 3-pentenitrile and adiponitrile.		
High purity 1,6-hexanediol and process for preparing the same		
8513472	Ube Industries	8/20/2013
There is provided a process for preparing 1,6-hexanediol by esterifying a carboxylic acid mixture resulted from oxidation of cyclohexane with oxygen, and then hydrogenating the esters, which substantially does not contain a compound leading to a high ester value. A process for preparing 1,6-hexanediol from a carboxylic acid mixture containing adipic acid and 6-hydroxycaproic acid, the carboxylic acid mixture is obtained as a by-product in oxidization of cyclohexane to cyclohexanone/cyclohexanol using oxygen or an oxygen-containing gas, the process comprises esterifying the acids with an alcohol, followed by hydrogenation, and the process is characterized by comprising the following steps of: a) separating a component having a boiling point lower than that of water and the alcohol used in the esterification from a mixture obtained by the hydrogenation in a first distillation step; b) separating an EV component having a boiling point higher than that of 1,6-hexanediol further in a second distillation step; c) separating an EV component having a boiling point lower than that of 1,6-hexanediol further in a third distillation step; and then d) obtaining 1,6-hexanediol in a fourth distillation step, in this order.		
Production of adipic acid and derivatives from carbohydrate-containing materials		
8501989	Rennovia	8/6/2013
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.		
Process for production of hexamethylenediamine from carbohydrate-containing materials and intermediates therefor		
2013 0184495	Rennovia	7/18/2013
Processes are disclosed for the conversion of a carbohydrate source to hexamethylenediamine (HMDA) and to intermediates useful for the production of hexamethylenediamine and other industrial chemicals. HMDA is produced by direct reduction of a furfural substrate to 1,6-hexanediol in the presence of hydrogen and a heterogeneous reduction catalyst comprising Pt or by indirect reduction of a furfural substrate to 1,6-hexanediol wherein 1,2,6-hexanetriol is produced by reduction of the furfural substrate in the presence of hydrogen and a catalyst comprising Pt and 1,2,6-hexanediol is then converted by hydrogenation in the presence of a catalyst comprising Pt to 1,6 hexanediol, each process then proceeding to the production of HMDA by known routes, such as amination of the 1,6 hexanediol. Catalysts useful for the direct and indirect production of 1,6-hexanediol are also disclosed.		

Patent summary

Reference number (patent)	Assignee	Earliest date shown
Separation of 6-aminocapronitrile and hexamethylenediamine from a mixture comprising hexamethylenediamines, 6-aminocapronitrile and tetrahydroazepine		
EP 1786758	Invista	6/26/2013
The invention relates to the field of separation by distillation of 6-aminocapronitrile (ACN) and hexamethylenediamine (HMD) from a mixture comprising ACN, HMD, tetrahydroazepine (THA), adiponitrile (ADN) and low boilers (LB). Also disclosed is a method for producing a distillate stream comprising HMD; a side draw stream comprising ACN, THA and low levels of dimers of ACN and HMD; and a tails stream comprising ACN, THA and substantially higher levels of dimers of ACN and HMD than found in the side draw stream. The side draw stream is particularly suitable for use in the production of caprolactam since the low levels of dimers of ACN and HMD do not greatly affect the catalyst life in the caprolactam production process. The tails stream can be further distilled to produce a distillate stream comprising ACN and THA, which can be recycled back to the first distillation column, further increasing recovery of ACN from the feed stream. Process conditions of the method of the invention disfavor the production of 2-cyanocyclopentylideneimine (CPI).		
Process for making nitriles		
2013 0150610	Invista	6/13/2013
A hydrocyanation reaction is used to react 1,3-butadiene with hydrogen cyanide in the presence of a catalyst to produce pentenenitriles, as well as reaction byproducts, such as methylglutaronitrile (MGN). The effluent from the hydrocyanation reaction is distilled in a particular manner to produce a pentenenitrile-enriched stream, a catalyst-enriched stream and a stream enriched in methylglutaronitrile (MGN). At least a portion of the catalyst enriched stream may be recycled to the hydrocyanation reaction. 3-pentenenitrile may be recovered and, optionally, further reacted with HCN to make adiponitrile (ADN).		
Calcination and reduction process including a fluidizing bed reactor		
2013 0144079	Invista	6/6/2013
These disclosures relate to preparing nickel metal (Ni(0)) suited for use in catalyst systems, such as nickel complexes with phosphorus-containing ligands, useful to catalyze the hydrocyanation of ethylenically unsaturated compounds. The methods described herein can include use of steam during reduction of nickel.		
Metal ligand catalyst formation		
2013 0143730	Invista	6/6/2013
As described herein, nickel treated with sulfur provides a surprisingly effective source of nickel atoms for generating nickel-phosphorus-containing ligand complexes useful as hydrocyanation catalysts.		
Purification of impure hexamethylenediamines		
8436212	Rhodia	5/7/2013
Impure hexamethylenediamines and more particularly those hexamethylenediamines containing contaminating amounts of tetrahydroazepine (THA), or more generally contaminating amounts of imines, are purified by distillation carried out with a short retention time of the impure hexamethylenediamine in the distillation column; the hexamethylenediamine obtained has a very low concentration of THA.		
Separation of 6-aminocapronitrile and hexamethylenediamine from a mixture comprising hexamethylenediamine, 6-aminocapronitrile and tetrahydroazepine		
EP 2581264	Invista	4/17/2013
The invention relates to the field of separation by distillation of 6-aminocapronitrile (ACN) and hexamethylenediamine (HMD) from a mixture comprising CAN, HMD, tetrahydroazepine (THA), adiponitrile (ADN) and low boilers (LB). Also disclosed is a method for producing a distillate stream comprising HMD; a side draw stream comprising ACN, THA and low levels of dimers of ACN and HMD; and a tails stream comprising ACN, THA and substantially higher levels of dimers of ACN and HMD than found in the side draw stream. The side draw stream is particularly suitable for use in the production of caprolactam since the low levels of dimers of ACN and HMT do not greatly affect the catalyst life in the caprolactam production process. The tails stream can be further distilled to produce a tails distillate stream comprising CAN and THA, which can be recycled back to the first distillation column, further increasing recovery of CAN from the feed stream. Process conditions of the method of the invention disfavor the production of 2-cyanocyclopentylideneimine (CPI).		
Recovery of aromatic carboxylic acids and oxidation catalyst		
2013 0079551	Invista	3/28/2013
The present invention relates to a process for recovery of catalyst, aromatic polycarboxylic acids and aromatic monocarboxylic acids from a residue stream from manufacture of an aromatic polycarboxylic acid.		

Patent summary

Reference number (patent)	Assignee	Earliest date shown
Hydrocyanation of 2-pentenitrile		
8394981	Invista	3/12/2013
The invention provides a process for hydrocyanation, comprising: contacting 2-pentenitrile with hydrogen cyanide at a temperature in the range of about 0.degree. C. to about 150.degree. C. in the presence of at least one Lewis acid promoter and a catalyst precursor composition, wherein the catalyst precursor composition comprises a zero-valent nickel and at least one bidentate phosphite ligand selected from a member of the group represented by Formula I and Formula II, in which all like reference characters have the same meaning, except as further explicitly limited: ##STR00001## wherein R.sub.1 and R.sub.5 are independently selected from the group consisting of C.sub.1 to C.sub.5 hydrocarbyl; and R.sub.2, R.sub.3, R.sub.4, R.sub.6, R.sub.7 and R.sub.8 are independently selected from the group consisting of H and C.sub.1 to C.sub.4 hydrocarbyl.		
Production process of 1,6-hexanediol		
8304585	Ube Industries	11/6/2012
A method is provided for producing highly pure 1,6-hexanediol in which the contents of impurities such as 1,4-cyclohexanediol, 1,5-hexanediol, 1,2-cyclohexanediol, 1,7-pentanediol, 1,5-pentanediol and high boiling point components are significantly reduced. The process contains the steps of (1) treating an aqueous extraction concentrate of a reaction mixture obtained by oxidation of cyclohexane with a lower alcohol to esterify monocarboxylic acids and dicarboxylic acids contained in the extract, and simultaneously removing and separating by distillation water, excess lower alcohols and carboxylic acid esters; (2) converting oligomer esters contained in the bottom liquid to carboxylic acid esters by depolymerizing the oligomer esters at a high temperature and high pressure in the presence of a lower alcohol and a catalyst; and (3) hydrogenating the carboxylic acid esters distilled off in step (1) and the carboxylic acid esters obtained in step (2) either respectively or collectively to convert to 1,6-hexanediol.		
Process for preparing hexamethylenediamine and polyamides therefrom		
WO 2012 / 141993 A1	Amyris	10/18/2012
Provided herein are processes for preparing hexamethylenediamine from one or more of the cis,cis-, cis,trans- and trans,trans-double-bond isomers of muconate diester. The muconate diester can contain carbon atoms derived from biomass containing detectable ¹⁴ C content determined according to ASTM D6866 and optionally containing a ¹⁴ C content up to 0.0000000001%. The process converts one or more of the cis,cis-, cis,trans- and trans,trans- double-bond isomers of muconate diester to the one or more of the cis,cis-, cis,trans- and trans,trans- double-bond isomers of muconamide. The isomer(s) of muconamide is then either: 1) directly converted by reduction to hexamethylenediamine; or 2) dehydrated to one or more of the cis,cis-, cis,trans- and trans,trans- double-bond isomers of mucononitrile which is then reduced to the hexamethylenediamine; or 3) reduced to adipamide, which is dehydrated to adiponitrile, and which is converted to hexamethylenediamine. Hexamethylenediamine so prepared can be used to make various polyamides.		
Preparation of polyamides		
2012 0264907	Invista	10/18/2012
A process for making a polyamide polymer, said process comprising heating, in one or more ionic liquid(s), one or more polyamide precursor(s) selected from: (i) one or more free dicarboxylic acid(s) or ester(s) thereof, with one or more diamine(s); or (ii) one or more salt(s) of a dicarboxylic acid with a diamine; or (iii) one or more lactam(s); or (iv) mixtures of any of the foregoing precursors (i) to (iii).		
Process for the removing of hydrogen cyanide and ammonia from synthesis gas		
8258193	Shell Oil	9/4/2012
The invention provides a process for removal of HCN and NH.sub.3 from synthesis gas, the process comprising the steps of: (a) contacting feed synthesis gas comprising HCN with a HCN hydrolysis sorbent in the presence of water, thereby obtaining synthesis gas comprising NH.sub.3; (b) contacting the synthesis gas comprising NH.sub.3 with an acidic cation exchange resin in the presence of water to remove NH.sub.3, thereby obtaining purified synthesis gas.		
Reactor and the use thereof for producing cyanides		
8133458	EICPROC	3/13/2012
A reactor for converting methane, ammonia and oxygen and alkaline or alkaline earth hydroxides into alkaline or alkaline earth cyanides by two-stage reactions comprising a first stage with a gas inlet, wherein the first stage is formed by a cone with distribution plates providing an even gas distribution over the catalyst material wherein the distribution plates are located between the gas inlet of the reactor and catalyst material and the distribution plates being perforated with a number of holes, with the distribution plates spaced from each other in the flow direction of the gas, the first distribution plate(s) functioning mainly to distribute the gas, whereas the last distribution plate works as a heat radiation shield and as a distribution plate facing the catalyst material, and wherein the catalyst material is present in the form of catalyst gauze fixed by catalyst weights.		

Patent summary

Reference number (patent)	Assignee	Earliest date shown
Process for improving adiponitrile quality		
8101790	Invista	1/24/2012
A process and apparatus for reacting deleterious impurities contained in adiponitrile (ADN) comprises feeding ADN and an ozone containing gas into a co-current plug flow reactor containing static mixer elements, to oxidize at least a portion of the impurities, thereby producing a reactor discharge, which is processed to produce an ozone-treated ADN product.		
Hydrocyanation of pentenenitriles		
8088943	Invista	1/3/2012
The invention provides a hydrocyanation process to produce adiponitrile and other dinitriles having six carbon atoms, in the presence of catalyst composition comprising a zero-valent nickel and at least one bidentate phosphorus-containing ligand wherein the bidentate phosphorus-containing ligand gives acceptable results according to at least one protocol of the 2-Pentenitrile Hydrocyanation Test Method.		
Preparation of caprolactone, caprolactam, 2,5-tetrahydrofuran-dimethanol, 1,6-hexanediol or 1,2,6-hexanetriol from 5-hydroxymethyl-2-furfuraldehyde		
WO 2011 / 149339	NA	12/1/2011
The present invention relates to a method for preparing caprolactone, comprising converting 5-hydroxymethyl-2-furfuraldehyde by hydrogenation into at least one intermediate compound selected from the group of 2,5-tetrahydrofuran-dimethanol, 1,6-hexanediol and 1,2,6-hexanetriol, and preparing caprolactone from said intermediate compound. Further, the invention relates to a method for preparing 1,2,6-hexanetriol comprising preparing 5-hydroxymethyl-2-furfuraldehyde from a renewable source, converting 5-hydroxymethyl-2-furfuraldehyde into 2,5-tetrahydrofuran-dimethanol and converting 2,5-tetrahydrofuran-dimethanol into 1,2,6-hexanetriol. Further, the invention relates to a method for preparing 1,6-hexanediol from 1,2,6-hexanetriol, wherein 1,2,6-hexanetriol is subjected to a ring closure reaction, thereby forming (tetrahydro-2H-pyran-2-yl)methanol, and the (tetrahydro-2H-pyran-2-yl)methanol is hydrogenated, thereby forming 1,6-hexanediol.		
Reactor for preparing hydrogen cyanide by the andrussow process		
20110171101 A1	Evonik / Degussa	7/14/2011
The present invention relates to a reactor (1) for preparing hydrogen cyanide by the Andrussow process, comprising a reactor vessel (2), at least one gas inlet (3) which opens into a gas inlet region (4), an outlet for the reaction products (5) and a catalyst (6), wherein at least one mixing element (7) and at least one gas-permeable intermediate layer (8) are provided within the reactor vessel (2) between the gas inlet region (4) and the catalyst (6), the mixing element (7) being arranged between the gas inlet region (4) and the gas-permeable intermediate layer (8).		
Preparation of primary diamines		
7939691	Rhodia	5/10/2011
Primary diamines are prepared by hydrogenation of a dinitrile compound in the presence of a catalyst, in particular hexamethylenediamine is prepared by hydrogenation of adiponitrile; the product diamines are recovered by distillation in several distillation columns mounted in series and the heavy impurities are separated from the second distillation.		
Process of hydrocyanation of unsaturated carboxylic acid derivatives		
2011 0092729	Invista	4/21/2011
The present invention is directed to compositions of specific carboxylic acid, fatty acid or oil derivatives containing nitrile groups and methods of their preparation. The preparation involves a hydrocyanation reaction. A method of hydrogenating the nitrile containing carboxylic acid acids obtained by above hydrocyanation to produce amine containing carboxylic acids is also disclosed in this invention.		
Separation of 6-aminocapronitrile and hexamethylenediamine from a mixture comprising hexamethylenediamine, 6-aminocapronitrile and tetrahydroazepine		
EP 1786760 B1	Invista	3/9/2011
The invention relates to the field of separation by distillation of 6-aminocapronitrile (ACN) and hexamethylenediamine (HMD) from a mixture comprising ACN, HMD, tetrahydroazepine (THA), adiponitrile (ADN) and low boilers (LB). A method for producing a distillate stream comprising HMD is disclosed, which is suitable for the production of Nylon-6,6. The tails stream from the distillation of the mixture can be further distilled to produce a distillate comprising ACN and THA, which is particularly suitable for use in the production of caprolactam and Nylon-6 from the caprolactam. Process conditions of the method of the invention disfavor the production of 2-cyanocyclopentylideneimine (CPI).		

Patent summary

Reference number (patent)	Assignee	Earliest date shown
Microorganisms and methods for the biosynthesis of adipate, hexamethylenediamine and 6-aminocaproic acid		
2010 0317069	NA	2010 0317069
The invention provides a non-naturally occurring microbial organism having a 6-aminocaproic acid, caprolactam, hexamethylenediamine or levulinic acid pathway. The microbial organism contains at least one exogenous nucleic acid encoding an enzyme in the respective 6-aminocaproic acid, caprolactam, hexamethylenediamine or levulinic acid pathway. The invention additionally provides a method for producing 6-aminocaproic acid, caprolactam, hexamethylenediamine or levulinic acid. The method can include culturing a 6-aminocaproic acid, caprolactam or hexamethylenediamine producing microbial organism, where the microbial organism expresses at least one exogenous nucleic acid encoding a 6-aminocaproic acid, caprolactam, hexamethylenediamine or levulinic acid pathway enzyme in a sufficient amount to produce the respective product, under conditions and for a sufficient period of time to produce 6-aminocaproic acid, caprolactam, hexamethylenediamine or levulinic acid.		
Highly selective process for producing organodiphosphites		
2010 0267991	Invista	10/21/2010
Disclosed is a method for making a diphosphite of Structure I,		
Process of catalytic ammoxidation for hydrogen cyanide production		
7763225	Ascend	7/27/2010
A process for the ammoxidation of an alcohol feed, such as methanol, or a nitrile feed, such as propionitrile, or a mixture thereof, to form hydrogen cyanide uses a modified Mn--P catalyst having the following empirical formula: Mn.sub.aP.sub.1A.sub.bO.sub.x where A=one or more of K, Ca, Mo, Zn, Fe or mixtures thereof; a=1 to 1.5; b=0.01 to 1.0 and x is a total number of oxygen atoms determined by the oxidation states of the other elements present.		
Process of catalytic ammoxidation for hydrogen cyanide production		
7763225	Ascend	7/27/2010
A process for the ammoxidation of an alcohol feed, such as methanol, or a nitrile feed, such as propionitrile, or a mixture thereof, to form hydrogen cyanide uses a modified Mn--P catalyst having the following empirical formula: Mn.sub.aP.sub.1A.sub.bO.sub.x where A=one or more of K, Ca, Mo, Zn, Fe or mixtures thereof; a=1 to 1.5; b=0.01 to 1.0 and x is a total number of oxygen atoms determined by the oxidation states of the other elements present.		
1,2-Diaminocyclohexane and chemical process		
2010 0125152	Invista	5/20/2010
Disclosed is a process for the preparation of 1,2-cycloaliphatic diamines from 1,2-aromatic diamines. In one embodiment, the process provides a method for making 1,2-diaminocyclohexane by the reaction of 1,2-phenylenediamine contained in a polar, protic solvent with hydrogen in the presence of a supported rhodium catalyst, ammonia, and a trialkylamine, and having enhanced overall conversion and selectivity.		
1,2-Diaminocyclohexane and chemical process		
2010 0125151	Invista	5/6/2010
Disclosed is a process for the preparation of 1,2-cycloaliphatic diamines from 1,2-aromatic diamines. In one embodiment, the process provides a method for making 1,2-diaminocyclohexane by the reaction of 1,2-phenylenediamine contained in a polar, protic solvent with hydrogen in the presence of a supported rhodium catalyst, ammonia, and an inorganic borohydride, and having enhanced overall conversion and selectivity.		
Hydrocyanation process with reduced yield losses		
7709674	Invista	5/4/2010
A hydrocyanation process produces adiponitrile and other dinitriles having six carbon atoms. The process involves forming a reaction mixture in the presence of at least one Lewis acid. The reaction mixture includes ethylenically unsaturated nitriles having five carbon atoms, hydrogen cyanide, and a catalyst precursor compositions. The reaction mixture is continuously fed while controlling the overall feed molar ratio of 2-pentenitriles to all unsaturated nitriles and the overall feed molar ratio of hydrogen cyanide to all unsaturated nitriles. In the reaction product mixture, including adiponitrile, the ratio of the concentration of 2-pentenitriles to the concentration of 3-pentenitriles from about 0.2/1 to about 10/1. Included in the catalyst precursor composition is a zero-valent nickel and at least one multidentate phosphorus-containing ligand. The multidentate phosphorus-containing ligand may be a phosphite, a phosphonite, a phosphinite, a phosphine, and a mixed phosphorus-containing ligand or a combination of such members.		

Patent summary

Reference number (patent)	Assignee	Earliest date shown
Hydrocyanation process with reduced yield losses		
7659422	Invista	2/9/2010
A hydrocyanation process produces adiponitrile and other dinitriles having six carbon atoms. The process involves forming a reaction mixture in the presence of at least one Lewis acid. The reaction mixture includes ethylenically unsaturated nitriles having five carbon atoms, hydrogen cyanide, and a catalyst precursor composition. The reaction mixture is continuously fed while controlling the overall feed molar ratio of 2-pentenitriles to all unsaturated nitriles and the overall feed molar ratio of hydrogen cyanide to all unsaturated nitriles. In the reaction product mixture, including adiponitrile, the ratio of the concentration of 2-pentenitriles to the concentration of 3-pentenitriles is from about 0.2/1 to about 10/1. Included in the catalyst precursor composition is a zero-valent nickel and at least one bidentate phosphite ligand.		
Method for the purification of triorganophosphites by treatment with a basic additive		
7629484	Invista	12/8/2009
One or more triorganophosphite components are separated from a crude phosphite mixture containing acidic hydrolysis products. The crude phosphite mixture is contacted with a basic additive to produce a second mixture comprising a first phase and a second phase. The first phase comprises the basic additive and acidic hydrolysis products. The second phase comprises one or more triorganophosphite components.		
Methods of making cyclododecatriene and methods of making laurolactone		
2009 0240068	Invista	9/24/2009
The present disclosure provides processes for the preparation of dodecanedioic acid (DDDA).		
Method for the production of dinitrile compounds		
2009 0099386	Rhodia	2009 0099386
The present invention relates to a process for the manufacture of dinitrile compounds by double hydrocyanation of an olefin. It relates particularly to a process for the manufacture of dinitrile compounds by double hydrocyanation of an olefin present in a mixture of hydrocarbons, such as a petroleum fraction and more particularly still a petroleum fraction known under the name of C4 fraction. The process of the invention comprises a sequence of stages for the separation of the various compounds which makes it possible to remove the byproducts, such as the products from the trimerization of alkynes, present in the C4 fraction and thus to prevent their accumulation in the hydrocyanation reactors.		
Continuous process for the hydrogenation of nitriles or nitro compounds to amines		
7453012	Rhodia	11/18/2008
A process for the hydrogenation of compounds comprising nitrile or nitro functional groups to amine, aminonitrile or aminonitro compounds is provided. The process can be a continuous process conducted in the presence of a heterogeneous hydrogenation catalyst in divided form and a basic compound. The reaction can be conducted in a stirred reactor comprising an external loop for circulating the reaction mixture, allowing one portion of the hydrogenated products to be separated without withdrawing the catalyst, by using tangential filtration. The process may be especially useful in the hydrogenation of adiponitrile to an aminocapronitrile/hexamethylenediamine mixture.		
Method for the Production of Adipodinitrile by Hydrocyanation of 1,3-Butadiene		
2008 0221351	BASF	9/11/2008
A process is described for preparing adiponitrile by hydrocyanating 1,3-butadiene over a catalyst, by, in a first process step, hydrocyanating 1,3-butadiene to 3-pentenitrile over at least one nickel(0) catalyst, and, in a second process step, hydrocyanating 3-pentenitrile to adiponitrile over at least one nickel(0) catalyst with addition of at least one Lewis acid, wherein at least one of the at least one nickel(0) catalysts used in the particular process steps is transferred into the other process step.		
Process for the preparation of dinitriles		
2007 0260086	Rhodia	11/8/2007
The present invention relates to a process for the preparation of dinitriles by hydrocyanation of unsaturated nitrile compounds in the presence of a catalyst based on a metal element in the zero oxidation state and on organophosphorus ligands; the invention relates more particularly to a process for the recovery from the hydrocyanation medium of a catalyst for the hydrocyanation of unsaturated nitrites to dinitriles. It consists in controlling the concentration of unsaturated nitrites in the reaction medium resulting from the hydrocyanation reaction in order to obtain a concentration by weight of unsaturated nitrites of less than 20% in the said medium, and in then feeding the said medium to a stage of settling into two upper and lower phases. The lower phase comprises most of the catalytic system, while the upper phase is composed essentially of the dinitriles.		

Patent summary

Reference number (patent)	Assignee	Earliest date shown
Process for producing hydrogen cyanide		
7063827	Rohm & Haas	6/20/2006
A conical reactor head for use in chemical processes or other systems is provided. The reactor head includes a robust internal insulator to boost efficiency while maintaining safety by allowing the reactor head to self-radiate at high temperatures. The reactor head also includes a plurality of support lugs to protect its bottom flange from scratches or other damage when the reactor head is set on the ground. The reactor head is adapted to connect to a catalyst-containing barrel which is specially designed to facilitate easy installation and removal of catalysts or other equipment from outside the barrel. The reactor may be coupled with a rotation vane to induce laminar flow at the inlet of the reactor to increase reactor efficiency and prolong catalyst life.		
Process for producing hexamethylenediamine and aminocapronitrile from adiponitrile, wherein the hexamethylenediamine contains less than 100 ppm tetrahydroazepine		
7060819	Invista	6/13/2006
Process for making both ACN and HMD from partial hydrogenation of ADN by using a combination of distillations resulting in the formation of a mixture of HMD and THA that can be hydrogenated to produce a mixture of HMD and HMI that can be separated easily by simple distillation		
Distillative method for separating hexamethylenediamine from a mixture comprising hexamethylenediamine, 6-aminocapronitrile and tetrahydroazepine		
6887352	Invista	5/3/2005
A method for recovering hexamethylene diamine (HMD) from a mixture comprising HMD, 6-aminocapronitrile (ACN) tetrahydroazepine (THA), and adiponitrile (ADN) is disclosed. The method includes introducing the mixture into a first distillation column, separating as a group the HMD, ACN and at least a portion of the THA as distillate from the ADN. The first distillation column is operated at a temperature and pressure to minimize isomerization of the ADN into 2-cyanocyclopentylideneimine(CPI). The distillate of the first distillation column is introduced into a subsequent distillation column and the HMD is separated from the ACN and THA.		
Method for removing ammonia from a gas comprising hydrogen cyanide, ammonia and water		
6872296	Invista	3/29/2005
A method for removing ammonia from a gas comprising HCN, ammonia and water, by first contacting the gas with aqueous ammonium phosphate to remove ammonia from the gas, and then passing the resulting ammonium phosphate solution through an electrolyzer to convert oxalates and formates into hydrogen and carbon dioxide.		
Distillative method for separating hexamethylenediamine from a mixture comprising hexamethylenediamine, 6-aminocapronitrile and tetrahydroazepine		
6887352	Invista	3/5/2005
A method for recovering hexamethylene diamine (HMD) from a mixture comprising HMD, 6-aminocapronitrile (CAN) tetrahydroazepine (THA), and adiponitrile (ADN) is disclosed.		
Process for the preparation of a nickel/phosphorous ligand catalyst		
6844289	Invista	1/18/2005
Process for preparing a nickel/ligand catalyst in which a crude ligand mixture is contacted with at least one member selected from the group consisting of (i) a weakly acidic organic resin, (ii) a weakly basic organic resin, (iii) a high-surface-area organic resin, (iv) activated carbon, (v) aluminosilicate zeolite, (vi) a two phase solvent system for liquid-liquid extraction and (vii) a Lewis acid; recovering a solution containing a ligand of the formula contacting the solution with nickel chloride in the presence of a nitrile solvent and a reducing metal which is more electropositive than nickel to produce the nickel/ligand catalyst.		
Methods for hydrogenating nitrile functions into amine functions		
6790994	Rhodia	9/14/2004
The present invention relates to a process for the hydrogenation of nitrile functional groups to amine functional groups. It relates more particularly to a process for the complete or partial hydrogenation of dinitrile compounds to diamine or aminonitrile compounds. The invention relates to a process for the hydrogenation of nitrile functional groups to amine functional groups using hydrogen in the presence of a hydrogenation catalyst and of a strong inorganic base preferably deriving from an alkali metal or alkaline earth metal. According to the invention, the process comprises a stage of conditioning the catalyst which consists in mixing the hydrogenation catalyst, a predetermined amount of strong inorganic base and a solvent in which the strong inorganic base is not very soluble. This solvent is an amine compound, such as hexamethylenediamine in the case of the hydrogenation of adiponitrile to HMD and/or aminocapronitrile.		

Patent summary

Reference number (patent)	Assignee	Earliest date shown
Process for the manufacture of furfural		
6743928	Intl Furan Technology	6/1/2004
<p>Process for the manufacture of furfural wherein a pentosan-containing raw material acidified or not, is heated to a temperature T.sub.1 by admitting steam through valve 2 while the valves 3 and 4 are closed. During the very short heating process, the steam condenses, thus increasing the moisture content of the charge. Then, valve 2 is closed and a leak valve 3 is opened so as to produce a steady small flow of product vapor by gradual depressurization. This causes a slow drop in temperature. When a suitably chosen temperature T.sub.2 is reached, the leak valve 3 is closed to terminate the first "gradual depressurization". If at the end of this period no more furfural was obtained, the digestion is completed by opening valve 4 to discharge the residue. If, however, furfural was still obtained, the reactor is reheated and submitted to another "gradual depressurization" period.</p>		
Phosphonite ligands and their use in hydrocyanation		
6737539	DuPont	5/13/2004
<p>Disclosed herein are processes for hydrocyanation and isomerization of olefins by using at least one multidentate phosphonite ligands, including organometallic phosphonite ligands with a Group VIII metal or Group VIII metal compound, and optionally, a Lewis acid promoter.</p>		
Method for eliminating organophosphorus compounds contained in a gas or liquid		
6656363	Rhodia	12/2/2003
<p>The invention concerns a method for eliminating organophosphorus compounds contained in a gas or liquid whereby said gas or liquid is contacted with alumina and/or titanium oxide. According to one aspect of the present invention, a process is provided for disposing of a trivalent and/or pentavalent organophosphorus compound which comprises at least one carbon atom and is contained in a liquid. The process comprises contacting the liquid with titanium oxide and/or alumina, the alumina having a specific surface of at least 70 m.sup.2 /g and a total pore volume of at least 0.3 cm.sup.3 /g. The alumina and/or titanium dioxide can be doped with alkaline metals, alkaline-earth metals and/or rare earths. The organophosphorus compound can include phosphines, phosphinites, phosphites, phosphonites, phosphinates and phosphonates. The liquid which is treated can originate from a dimerization reaction of acrylonitrile in the presence of catalysts containing phosphorus, or from a hydrocyanation reaction of butadiene in the presence of catalysts containing phosphorus.</p>		
Hydroxymethylfurfural derived from cellulose contained in lignocellulose solids		
6518440	Lightner	2/11/2003
<p>A method to produce hydroxymethylfurfural from cellulose contained within lignocellulose solids is disclosed. Hemicellulose contained in lignocellulose solids is converted to furfural. Lignocellulose solids, containing cellulose, is added to a vessel containing an aqueous acidic solution which is employed for hydrolysis of cellulose, contained within lignocellulose solids, to form glucose. Subjecting the glucose to additional hydrolysis to convert glucose and form hydroxymethylfurfural and removing hydroxymethylfurfural from the vessel are procedures applied. Solids remaining from hydrolysis containing lignins are filtered and then extracted with water to remove aqueous acidic solution contained within solids and form an extractate containing dilute aqueous acidic solution. The extractate is combined with a dilute solution of aqueous acidic solution removed from the vessel. Dilute solutions of aqueous acidic solution are treated to remove water and then the aqueous acidic solution is recycled to the vessel employed for hydrolysis of cellulose within lignocellulose solids.</p>		
Method of producing hexamethylene diamine		
6359178	BASF	3/19/2002
<p>A process for catalytic hydrogenation of adiponitrile to hexamethylenediamine at elevated temperature and elevated pressure in the presence of catalysts based on elemental iron as catalytically active component and ammonia as solvent comprises a) hydrogenating adiponitrile at from 70 to 220.degree. C. and from 100 to 400 bar in the presence of catalysts based on elemental iron as catalytically active component and ammonia as solvent to obtain a mixture comprising adiponitrile, 6-aminocapronitrile, hexamethylenediamine and high boilers until the sum total of the 6-aminocapronitrile concentration and the adiponitrile concentration is within the range from 1 to 50% by weight, based on the ammonia-free hydrogenation mixture, b) removing ammonia from the hydrogenation effluent, c) removing hexamethylenediamine from the remaining mixture, d) separating 6-aminocapronitrile and adiponitrile from high boilers individually or together, and e) returning 6-aminocapronitrile, adiponitrile or mixtures thereof into step a).</p>		
Method of producing hexamethylene diamine		
6348630	BASF	2/19/2002
<p>The level of an unsaturated cyclic imine (I) of the formula R1-(CH)=N where R1 is alkenyl having 3,4,5,6,7,8,9,10,11 carbon atoms belonging to the ring system, in a mixture comprising hexamethylenediamine and an imine (I) is reduced by electrochemical conversion of an imine (I) in a mixture comprising hexamethylenediamine and an imine (I) in the presence of solvated protons into a saturated cyclic amine of the formula (II)</p>		

Patent summary

Reference number (patent)	Assignee	Earliest date shown
Recovery of hexamethylenediamine (HMD) with low polarographically reducible impurities (PRI) from mixtures of HMD, aminocapronitrile and PRI		
6248926	DuPont	6/19/2001
A method for separating a mixture of hexamethylenediamine, aminocapronitrile and polarographically reducible impurities using fractional distillation in which the temperature in the rectifying zone of a distillation column varies sigmoidally along its length to force a major portion of the PRI to co-distill with the aminocapronitrile		
Process for simultaneously preparing 6-aminocapronitrile and hexamethylene diamine		
6207851	BASF	3/27/2001
A process for coproduction of 6-aminocapronitrile and hexamethylenediamine starting from adiponitrile comprises (1) partially hydrogenating adiponitrile in the presence of a catalyst to obtain a mixture comprising 6-aminocapronitrile, hexamethylenediamine and adiponitrile, (2) removing 6-aminocapronitrile and hexamethylenediamine from the mixture, (3) adding to the portion comprising essentially adiponitrile from 0.01 to 10% by weight of an acid, based on adiponitrile, or an acidic ion exchanger and removing the adiponitrile from the mixture, and (4) recycling the adiponitrile into step (1).		
Selective synthesis of organodiphosphite compounds		
6069267	DuPont	5/30/2000
A process for the preparation of organodiphosphites of the formula (R.sub.1 O).sub.2 P(OZO)P(OR.sub.1).sub.2 wherein R.sub.1 and Z are different substituted or unsubstituted aryl groups.		
Process for the production of 6-aminocapronitrile and/or hexamethylenediamine		
5986126	DuPont	11/16/1999
Process for producing 6-aminocapronitrile and/or hexamethylenediamine by hydroformylating 3-pentenitrile, isolating a formylvaleronitrile (FVN) mixture from the hydroformylation reaction product, reductively aminating the FVN mixture and isolating the desired product.		
Process for continuous hydrogenation of adiponitrile		
5900511	DuPont	5/4/1999
A process for continuous hydrogenation of adiponitrile (ADN) to hexamethylene diamine (HMD) and optionally to aminocapronitrile (ACN) involving the catalytic hydrogenation of adiponitrile at relatively low temperature (e.g., 75.degree. C.) and pressure (e.g., 500 psig) using a sponge cobalt catalyst (Raney.RTM. Co) in a reaction medium that is substantially free of caustic. In such a process periodic addition of water controls the production of side reaction products and the periodic addition of ammonium hydroxide rejuvenates the catalyst. Hexamethylene diamine is an important intermediate for the synthesis of polyamides such as Nylon-6,6 and aminocapronitrile is a potential intermediate of Nylon-6.		
Preparation of hydrogen cyanide		
5393393	DuPont	2/28/1995
Hydrogen cyanide is produced by reacting ammonia or urea and elemental carbon or a hydrocarbon while irradiating them with microwave energy.		
Process for producing hydrogen cyanide		
5439661	Mitsubishi Gas Chemical	8/8/1994
There is disclosed a process for efficiently producing hydrogen cyanide at a reaction temperature of preferably 250.degree. to 550.degree. C. by a catalytic dehydrative reaction of formamide which comprises employing as a catalyst, a manganese oxide (MnO) and/or a magnesium oxide (MgO) each modified with an alkali metal (Na, K, Rb, Cs, etc.). The above process is capable of producing hydrogen cyanide at an enhanced conversion efficiency of formamide and at a high selectivity while minimizing the by-production of ammonia. The use of the catalyst comprising as a principal component, MnO modified with an alkali metal is particularly effective in prolonging its service life and enables a long-term stable operation.		
Process for the separation of hydrogen cyanide from gases and waste gases		
5200161	Degussa	4/6/1993
A process is disclosed for the separation of hydrogen cyanide from gases and waste gases by a throughflow or circulation scrubbing, in which formaldehyde is added at a controlled rate to the aqueous scrubbing liquid to form glycol nitrile. This addition is controlled by measuring the HCN tension in a measuring stream which has been branched off and which is first treated with hydrogen peroxide so that free H.sub.2 O.sub.2 is still detectable after 1 to 100 seconds and the pH is adjusted to a constant value before measurement of the HCN tension is carried out. The process prevents overdosing with formaldehyde which could not always be prevented in previously known processes in which the addition of formaldehyde was regulated by measuring the cyanide specific redox potential.		

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Reference number (patent)	Assignee	Earliest date shown
Synthesis of non-cyclic, aliphatic polyamines		
5105015	WR Grace	4/14/1992
An improved process for selectively forming noncyclic, aliphatic polyamines from the corresponding aliphatic polynitriles by reacting the polynitrile with hydrogen at low temperature under a pressure of from 50 to 5,000 psi in a fixed bed reactor while continuously contacting the reactants with granular chromium and nickel promoted Raney.RTM. cobalt packed therein		
Acrylonitrile dimerization process and method of treating residual catalyst		
4952541	Monsanto	8/28/1990
Treatment of dicyanobutene to inactivate residual dimerization catalyst facilitates hydrogenation of the product to form adiponitrile		
Acrylonitrile dimerization process		
4841087	Monsanto	6/20/1989
Acrylonitrile dimerization is improved by increasing the proportions of catalyst used in the reaction mixture.		
Method for producing adiponitrile		
4789442	Asahi	12/6/1988
A method for producing adiponitrile through the electrohydrodimerization of acrylonitrile by electrolyzing an emulsion comprised of an aqueous phase and an organic phase in at least one undivided cell having a cathode of lead or a lead alloy, in which an ethyltributylammonium salt as a quaternary ammonium salt is included in the aqueous phase in a concentration of from 0.02 to 0.08 mol/liter. The method of the present invention is remarkably improved with respect to the prevention of the corrosion of the cathode.		
Preparation of hexamethylene 1,6-diisocyanate and/or isomeric diisocyanates where alkylene is of 6 carbon atoms		
4613466	BASF	9/23/1986
Hexamethylene 1,6-diisocyanate and/or isomeric aliphatic diisocyanates where alkylene is of 6 carbon atoms, preferably 2-methylpentamethylene 1,5-diisocyanates and/or 2-ethyltetramethylene 1,4-diisocyanate, are prepared by a process wherein the corresponding dialkylurethanes are vaporized, without decomposition, at from 220 ° to 300 ° C., advantageously under reduced pressure, the dialkylurethane vapors are subjected to thermal cleavage under reduced pressure, preferably from 0.1 to 200 mbar, and at above 300 ° C., preferably from 310 ° to 480 ° C. The cleavage products are fractionally condensed with the product obtained in the first condensation stage consisting predominantly of the diisocyanates, while that obtained in the second condensation stage is the alcohol.		
Molded catalyst materials containing reduced cobalt and/or nickel particles		
4598058	BASF	7/1/1986
Molded catalyst materials contain metallic cobalt and/or nickel particles and a lubricant, and said particles being obtained by reduction of cobalt oxide and/or nickel oxide particles containing less than 0.1% by weight of alkali metal oxides and/or alkaline earth metal oxides at equal to or less than 500 ° C., and the molded catalyst material having an indentation hardness greater than 300 kp/cm ² .		
Molded iron catalyst material and its preparation		
4587228	BASF	5/6/1986
A molded iron catalyst material which has an indentation hardness of from 850 to 1500 kp/cm ² and contains metallic iron particles, obtained from iron oxide particles by contact with hydrogen at less than 500 ° C., and a lubricant, its preparation and use.		
Preparation of zerovalent nickel complexes		
4416825	DuPont	11/22/1983
An improved, continuous process for the preparation of hydrocyanation catalysts comprising zerovalent nickel complexes with organophosphorus compounds (ligands) by controlling the temperature of the reaction relative to the amount of ligand and conducting the reaction in the presence of a chlorine ion and organic nitrile such as adiponitrile.		
Production and separation of amines		
4395573	Monsanto	7/26/1983
In the production of hexamethylenediamine from adiponitrile an inorganic base is used to facilitate separation of Raney nickel catalyst and crude hexamethylenediamine.		

Patent summary

Reference number (patent)	Assignee	Earliest date shown
Catalyst passivation in production of amines		
4359585	Monsanto	11/16/1982
This is an improvement in a process for the production of an amine such as hexamethylenediamine from a nitrile such as adiponitrile where the nitrile is hydrogenated under pressure in the presence of a Raney nickel catalyst, the reaction being conducted in a reactor from which is discharged a product stream containing both the amine and the Raney nickel catalyst. The improvement comprises charging to the process discharge stream containing the product amine and the Raney nickel catalyst, an inorganic base, whereby the Raney nickel catalyst is passivated and catalytic decomposition of the amine is substantially decreased.		
Process for the production of hydrogen cyanide		
4289741	Degussa	9/15/1981
The known hydrocyanic acid-methane-ammonia (BMA) process for the production of hydrogen cyanide can now be carried out with liquified gases namely through the presence of additional hydrogen at the beginning of the reaction. The atomic ratio of carbon to nitrogen and hydrogen is from 1:1.7:1 to 1:1.33:1.3. As additional hydrogen there is the portion of hydrogen present coming out of the reaction "hydrocarbon+NH ₃ ". Otherwise the reaction conditions are the same as in the known BMA process.		
Process for purifying hexamethylenediamine		
4282381	DuPont	8/4/1981
Hexamethylenediamine (HMD) is purified by dissolving ammonia in crude molten HMD under pressure, directing the solution thus prepared to a reduced pressure zone where the ammonia is vaporized thereby causing a portion of the HMD to crystallize following which the crystals in the slurry are washed with essentially pure HMD. This purified HMD is suitable for conversion into polyamide fibers.		
Pretreatment of cathodes in electrohydrodimerization of acrylonitrile		
4250001	Monsanto	2/10/1981
An improvement in the process of electrohydrodimerizing acrylonitrile to adiponitrile wherein metal-plated cathodes, which are employed in the process as a part of an electrolytic cell, are pretreated by wetting the cathodes with aqueous phosphoric acid thereby to significantly reduce fouling.		
Electrohydrodimerization process improvement and improved electrolyte recovery process		
4207151	Monsanto	6/10/1980
An improvement in an electrolytic hydrodimerization process for hydrodimerizing an olefinic compound such as acrylonitrile to form a dimerized product such as adiponitrile in which an aqueous electrolyte solution comprised of the olefinic compound, a directive salt (providing quaternary ammonium cations) and a conductive salt is electrolyzed in a reaction cell, the aqueous solution is purged from the reaction cell, and subjected to a series of steps involving the recovery of the product, the directive salt and the conductive salt, the recovered salts being used to reconstitute the aqueous solution, the improvement being a functionally coordinated evaporation step which permits a higher rate and more efficient recovery of product and salts, a higher purge rate and a substantially higher yield of the dimerized product. The invention also constitutes an improved electrolyte recovery process.		
Semi-continuous electro-hydrodimerization of acrylonitrile to adiponitrile with replating of cathode		
4155818	Monsanto	5/22/1979
An improvement in the process of electrohydrodimerizing acrylonitrile to adiponitrile wherein the plated electrodes, which are employed in the process as a part of an electrolytic cell, are, without removal from the cell, cleaned and replated.		
Process for making HCN		
4107278	DuPont	8/15/1978
In an Andrussov-type process for making HCN from methane and ammonia, activity of the catalyst is improved by adding CO ₂ to the reactants		
Hexamethylene diamine by hydrogenation of adiponitrile in presence of an activated iron oxide catalyst		
4064172	ICI	12/20/1977
Adiponitrile is hydrogenated to hexamethylene diamine in the presence of a fused and solidified iron oxide catalyst containing at least 96.5% of iron oxide, having an atomic ratio of oxygen to iron of 1.2:1 to 1.4:1, previously activated by heating in hydrogen.		
Manufacture of hexamethylene diamine		
3972938 A	DuPont	8/3/1976
A process for the catalytic hydrogenation of adiponitrile in the presence of ammonia, in which a portion of the reaction mixture is recycled and specific molar ratios of adiponitrile and ammonia are maintained.		

Patent summary

Reference number (patent)	Assignee	Earliest date shown
Manufacture of hexamethylene diamine		
3972938	BASF	8/3/1976
A process for the catalytic hydrogenation of adiponitrile in the presence of ammonia, in which a portion of the reaction mixture is recycled and specific molar ratios of adiponitrile and ammonia are maintained.		
Diaphragm cell having uniform and minimum spacing between the anodes and cathodes		
3960697	Olin	6/1/1976
A diaphragm cell is provided having a continuous net between the anodes and the diaphragm. The continuous net permits the minimum anode-cathode spacing to be employed while maintaining uniform anode-cathode spacing throughout the cell. In addition, the diaphragm is retained and prevented from adhering to the surface of the anodes. Employing the diaphragm cell of the present invention in the electrolysis of aqueous alkali metal halide brines results in lower electrical energy requirements and reduced operating costs.		
Hydrogenation of adiponitrile over alkali modified cobalt catalyst		
3773832	DuPont	11/20/1973
Hexamethylenediamine is prepared by hydrogenating adiponitrile in the presence of an excess of hydrogen at a total system pressure of from 3000 to 6000 psig in the presence of from about 200 to 800 % of ammonia, based on the weight of the adiponitrile, at a temperature of from about 85 ° C to about 185 ° C in the presence of a pelleted, sintered, reduced cobalt oxide catalyst on which is maintained from about 200 to less than 1000 parts per million of a strong base.		
Manufacture of adiponitrile		
3671566	BASF	6/20/1972
Production of adiponitrile by introducing adipic acid in solid powder form or in liquid form and simultaneously introducing ammonia into a fluidized bed of a usual catalyst at a temperature of from 250 ° to 420 ° C and recovering the adiponitrile from the reaction gases by fractional distillation wherein there is added to the reaction gas before entry into the distillation column sufficient water to make the molar ratio of water vapor to ammonia 0.8 to 1.5 in the mixture entering the column. Adiponitrile is an intermediate in the manufacture of synthetic fibers of, for example, nylon 6,6.		
Production of adiponitrile		
3642592	BASF	2/15/1972
Process for the production of adiponitrile by direct electrochemical hydrodimerization of acrylonitrile using a medium containing acrylonitrile, an electrolyte salt, water and, if desired, a solvent at a temperature of from 10.degree. to 60.degree. C. at a pH of from 1 to 10. In the process, electrolysis is carried out in a cell having a liquid cathode which is contacted by a solid anode which is not wetted by the liquid cathode or into which the solid anode is immersed to a depth of up to 20 mm. Adiponitrile is an important intermediate for synthetic fiber manufacture.		
Process for the production of adiponitrile		
3616321	UCB	10/26/1971
Process of hydrodimerization of acrylonitrile to adiponitrile by the direct electrolytic route, by passing a direct electrical current through an electrolytic cell having the anode and cathode in contact with the electrolytic medium, which comprises using an initial electrolysis medium consisting essentially of (a) acrylonitrile, (b) water, (c) at least one alkali salt selected from the group consisting of the alkali salts of condensed polyphosphoric acids of the formula $n \text{ H.sub.3 PO.sub.4} \cdot (n-1) \text{ H.sub.2 O}$ (I) in which n has a value of from 2 to 100, and the alkali salts of polymetaphosphoric acids of the formula $\text{H.sub.n P.sub.n O.sub.3n}$ (II) in which n has a value of from 2 to 100, (d) a surface-active substance, and (e) at least one acidic salt of an alkali metal and of a polyacid, the ratio by weight of (e) to (c) being comprised between 99.9/0.1 and 0/100.		
Catalytic isomerization of 2-methyl-3-butenitrile to linear pentenenitriles		
3536748	DuPont	10/27/1970
The present invention discloses the isomerization of 2-methyl-3-butenitrile to linear pentenenitriles by means of zero-valent nickel complexes used as catalysts at temperatures in the range 10-200 ° C. The linear pentenenitrile products are useful as intermediates to adiponitrile.		
Hydrogenation of adiponitrile		
3696153	DuPont	5/7/1970
Process for the catalytic hydrogenation of adiponitrile at elevated temperatures and pressures in the presence of a catalyst derived from an iron compound in granular form which has been activated with hydrogen at a temperature not exceeding 600.degree. C.		

Patent summary

Reference number (patent)	Assignee	Earliest date shown
Purification of hexamethylene diamine by recrystallization from cyclohexane		
3510522	Celanese	5/5/1970
Process for purifying hexamethylenediamine such as is produced by the reductive ammonolysis of 1,6-hexanediol, by crystallization and recrystallization from hydrocarbons of 5 to 12 carbon atoms		
Hydrocyanation of olefins using selected nickel phosphite catalysts		
3496215	DuPont	2/17/1970
Process for hydrocyanating olefinically unsaturated organic compounds at from -25 to 200 ° C using as catalyst a compound of the structure Ni(PXYZ) ₄ , where X is OR and Y and Z are or OR and R is an alkyl or aryl radical of up to 18 carbon atoms.		
Process for making hexamethylenediamine from adiponitrile		
3461167	DuPont	8/12/1969
Hydrogenation of adiponitrile to hexamethylene-diamine in the presence of ammonia and hydrogenation catalyst is conducted in a plurality of reaction zones arranged in series, with the ammonia present in the first reaction zone of the series being passed serially to each subsequent reaction zone.		
Amalgam reduction process for the production of adiponitrile		
3458559	ICI	7/29/1969
In the reduction of an organic compound with alkali metal or alkaline earth metal amalgam in aqueous medium, especially of acrylonitrile to adiponitrile, the residual aqueous liquid, after removing the reduced organic compound is electrolyzed using a mercury cathode so as to reduce the concentration of alkali or alkaline earth metal ions, to form alkali or alkaline earth metal amalgam with the mercury, and the so treated aqueous liquor is used as the aqueous medium in the further reduction of the organic compound.		
Manufacture of adiponitrile		
3325532	ICI	6/13/1967
This invention relates to the manufacture of adiponitrile and more particularly it relates to a process for the separation of adiponitrile from the mixed products of the high temperature reaction of adipic acid and ammonia		
Process for the manufacture of adiponitrile		
3325531	ICI	6/13/1967
This invention relates to a process for the manufacture of adiponitrile from adipic acid and ammonia		
Production of diamino alkanes		
3270059	BASF	8/30/1966
This invention relates to a process for the production of diamines from alkanediols, alkylene oxides, alkylidenamines or alkanolamines and ammonia or primary or secondary amines. More specifically, the invention relates to the use of certain catalysts for this reaction.		
Process for producing hexamethylenediamine from 1,6-hexanediol		
3268588	Celanese	8/23/1966
This invention relates to a process of making amines. It more particularly refers to a process particularly adapted to making hexamethylenediamine. It is well known that hexamethylenediamine has outstanding utility as one of the starting reagents for making so-called 6-6 nylon		
Purification of hexamethylene diamine		
3254126	Celanese	5/31/1966
This invention relates to purifying hexamethylenediamine. More particularly it relates to a process for removing 1,2-diaminocyclohexane from crude hexamethylenediamine		
Production of hydrogenation catalysts containing cobalt		
3232888	BASF	2/1/1966
This invention relates to a new and improved process for the production of hydrogenation catalysts and to the new hydrogenation catalysts themselves. More specifically the invention relates to a new process for the production of cobalt containing catalysts which also contain chromium and/or manganese.		
Process for the preparation of alkylene diamines		
3215742	Celanese	11/2/1965
This invention relates to the preparation of aliphatic amines. More particularly, it relates to the preparation of aliphatic diamines, e.g., hexamethylene diamine, from diols, e.g. 1,6-hexanediol, by reacting the diol with ammonia		

Patent summary

Reference number (patent)	Assignee	Earliest date shown
Process for the Production of Hexamethylene Diamine		
3048635	VGF AG	8/7/1962
This invention relates to an improved process for the production of hexamethylene diamine, and more particularly, to the improved continuous conversion of adiponitrile to hexamethylene diamine by catalytic hydrogenation		
Method for the preparation of HMX using boron trifluoride		
2941994	Celanese	6/21/1960
The present invention relates to the preparation of high explosives of the nitramine type. More particularly the invention pertains to an improved method for the preparation of the explosive known as HMX, in good yield and purity		
Reactor for making hydrogen cyanide		
2782107	DuPont	2/19/1957
This invention relates to a process and reactor for effecting chemical conversions in the vapor phase and more particularly to a process and reactor for producing hydrogen cyanide by means of such conversions.		
Manufacture of aliphatic diamines		
2754330	DuPont	7/10/1956
This invention relates to a process for the manufacture of saturated aliphatic diamines. More particularly, it relates to a catalytic process for the manufacture of saturated aliphatic diamines by the reaction of ammonia with glycols, or with hydroxyamines.		
Process for making nitriles		
2642454	Phillips Petroleum	6/16/1953
This invention relates to a process for the preparation of nitriles. In some of its more specific aspects, it relates to the preparation of acetonitrile and/or other nitriles by the interaction of ammonia with saturated hydrocarbons, i.e., paraffins and/or cycloparaffins (naphthenes), having not in excess of ten and not less than two carbon atoms per molecule		
Process for making aliphatic nitriles		
2481826	Allied Chemical	9/13/1949
This invention relates to the manufacture of nitriles and is particularly concerned with the production of aliphatic nitriles by reaction of ammonia with organic compounds		
Preparation of hexamethylene diisocyanate		
2374340	DuPont	4/24/1945
A process for the preparation of long chain isocyanates from acyclic primary amines, wherein the amino group or groups are attached to an acyclic hydrocarbon radical of at least six carbon atoms, by reacting said amine or a hydrohalide thereof with phosgene in the presence of a solvent for the reactants.		
Production of hydrogen cyanide		
2105831	IG Farben	1/18/1938
This invention relates to the production of hydrogen cyanide. It is known to produce hydrocyanic acid by passing a gaseous mixture containing ammonia, hydrocarbons, especially methane, and oxygen at elevated temperature over catalysts, especially those which favor the oxidation of ammonia. For this purpose noble metals, such as platinum metals or gold or silver or alloys of these metals with each other, or other metallic or oxidic catalysts are proposed		
Production of hydrocyanic acid		
2006981	IG Farben	7/2/1935
The present invention relates to the production of hydrocyanic acid, which comprises passing a gaseous mixture containing ammonia and at least one hydrocarbon over a hot oxidation catalyst while carrying out the reaction with a gaseous mixture containing from 0.2 molecular proportion of oxygen for a mixture of 1 molecular proportion each of ammonia and of hydrocarbon up to about 1 molecular proportion of oxygen per each carbon atom of said hydrocarbons plus 0.25 molecular proportion of oxygen for each atomic proportion of hydrogen present in hydrocarbon and ammonia.		

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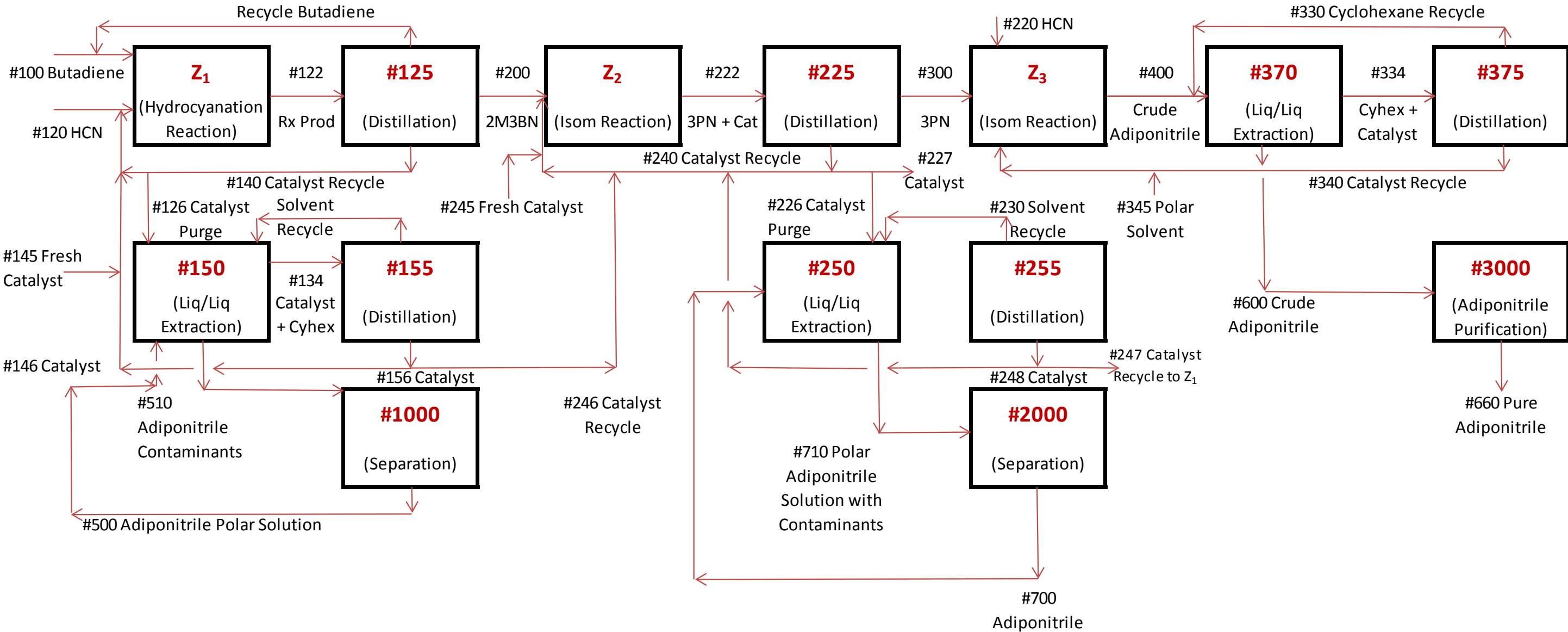
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Appendix C: Invista block flow diagram

Figure 6.12: Butadiene hydrocyanation process sequence (USPA 2013 0150610)



Appendix D: Process flow diagrams

Figure 6.Error! Reference source not found.23 (1 of 5): HMDA from butadiene by hydrocyanation

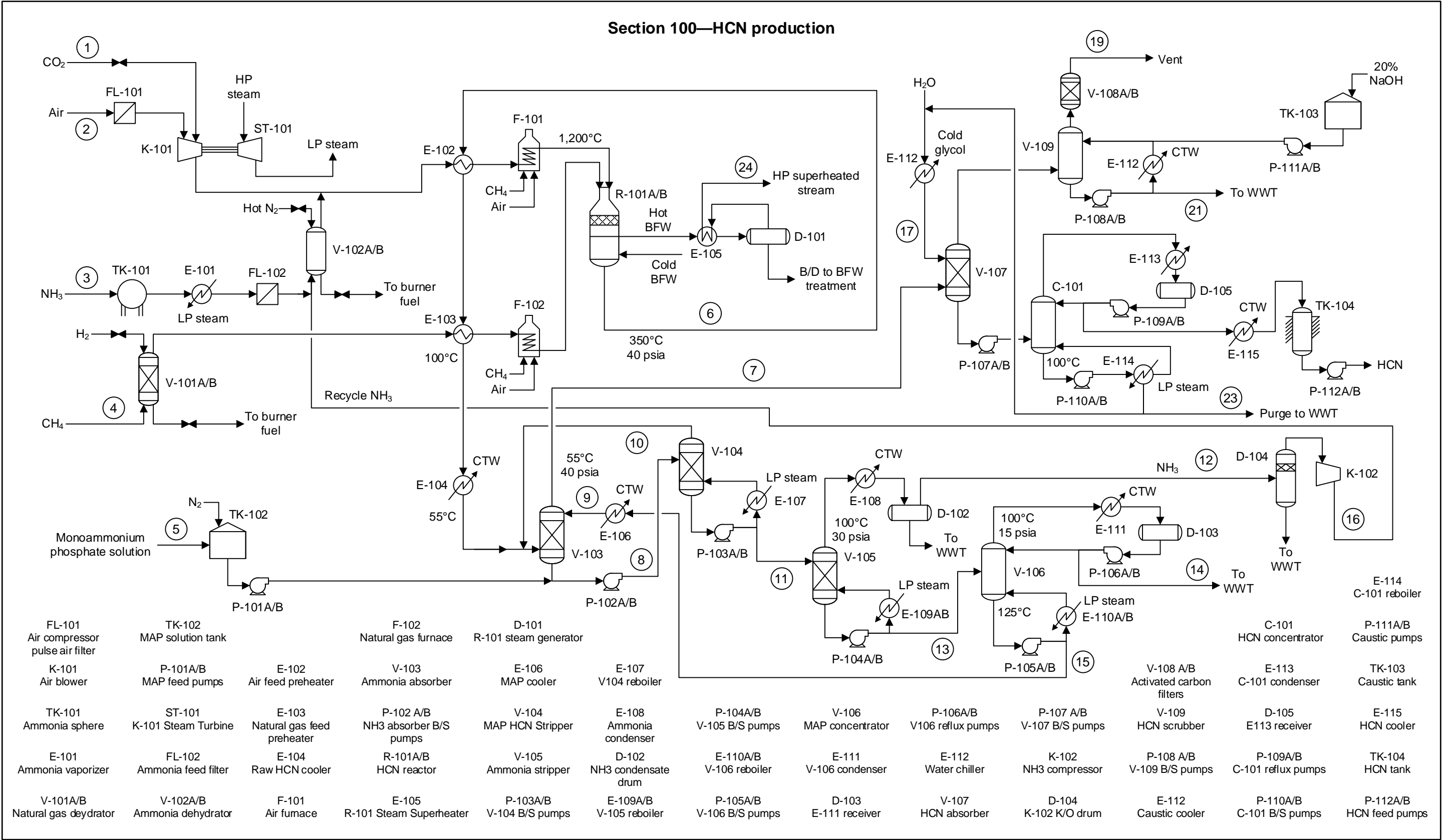


Figure 6.24 (2 of 5): HMDA from butadiene by hydrocyanation

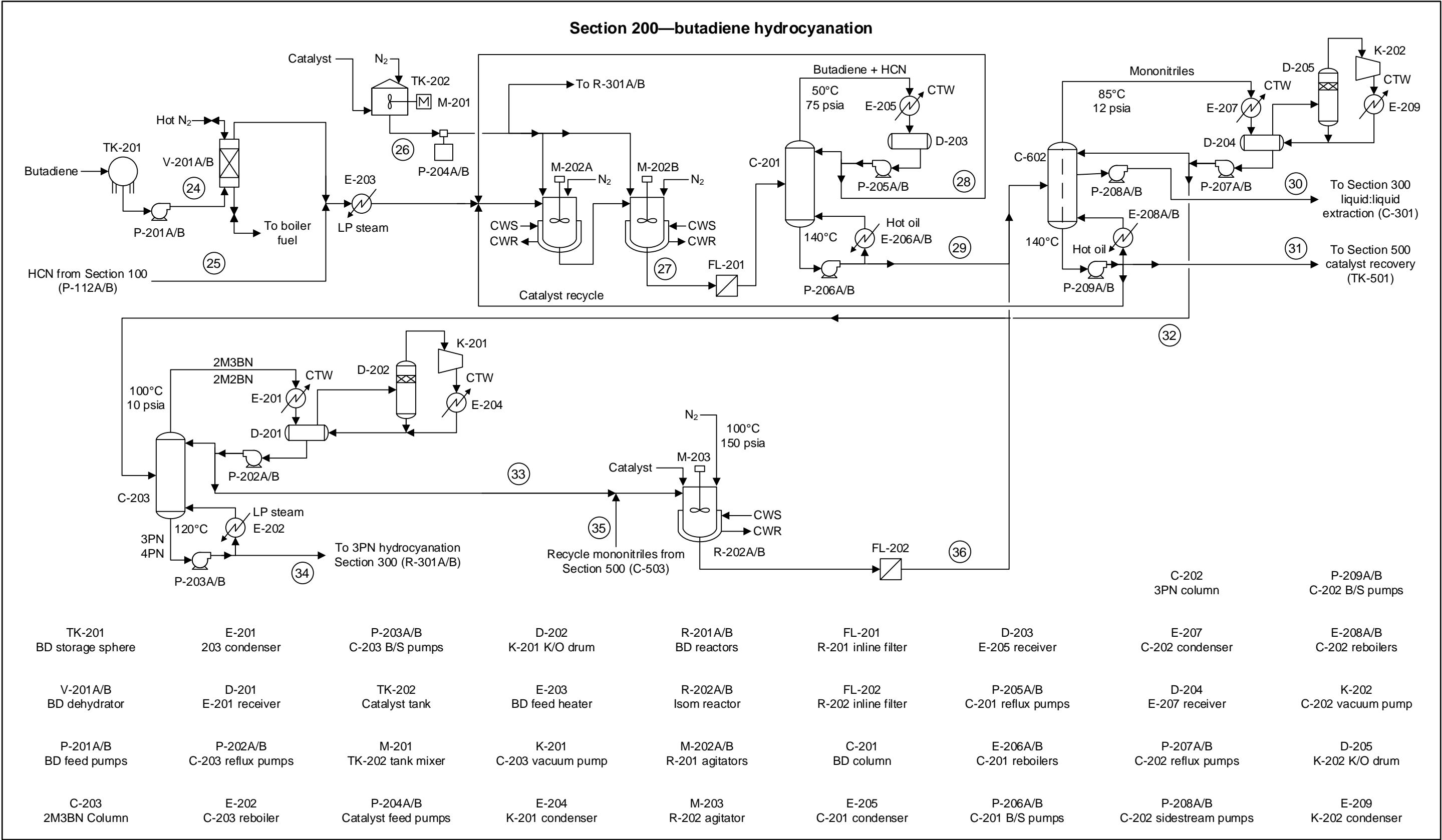


Figure 6.25 (3 of 5): HMDA from butadiene by hydrocyanation

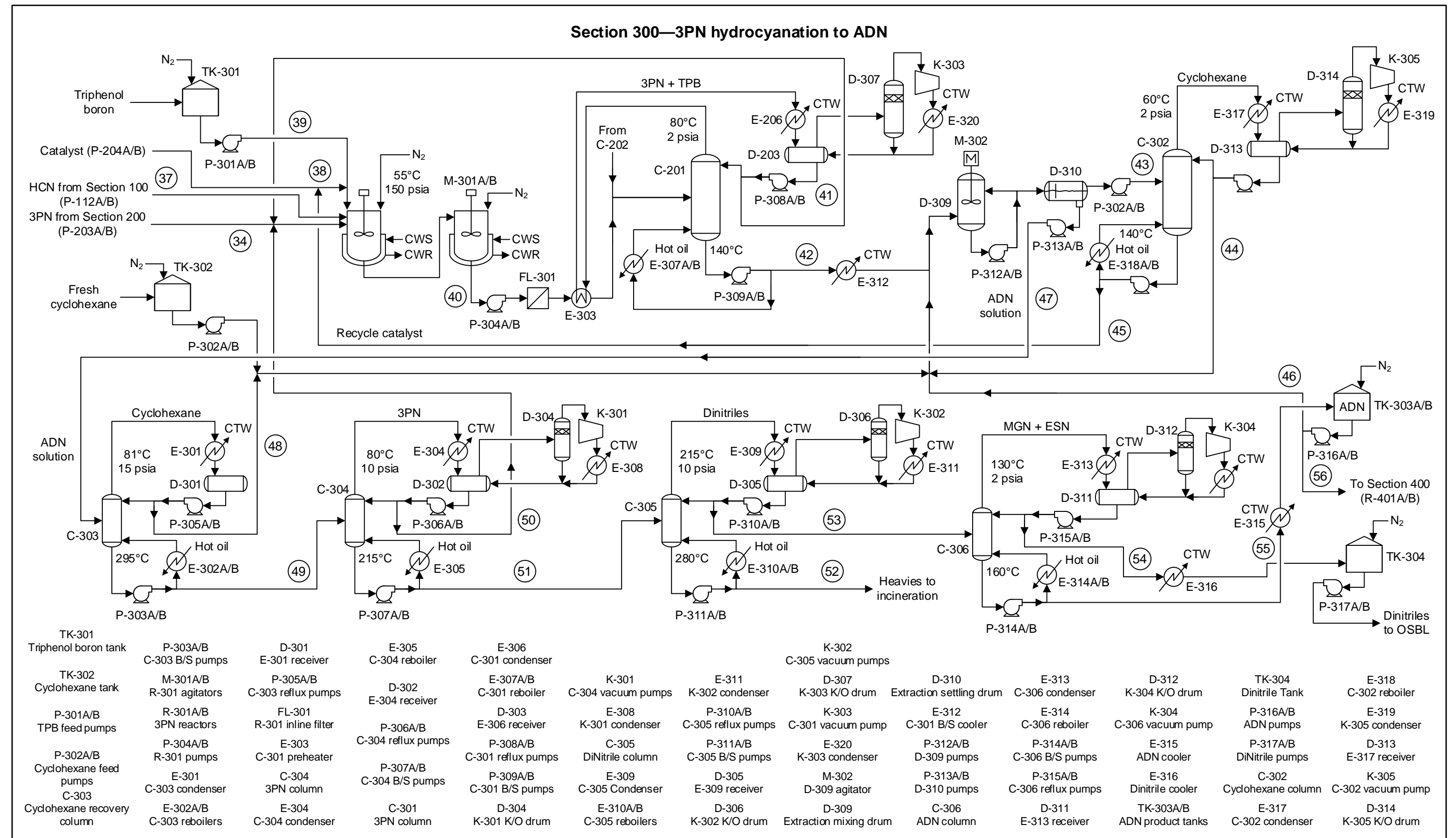


Figure 6.26 (4 of 5): HMDA from butadiene by hydrocyanation

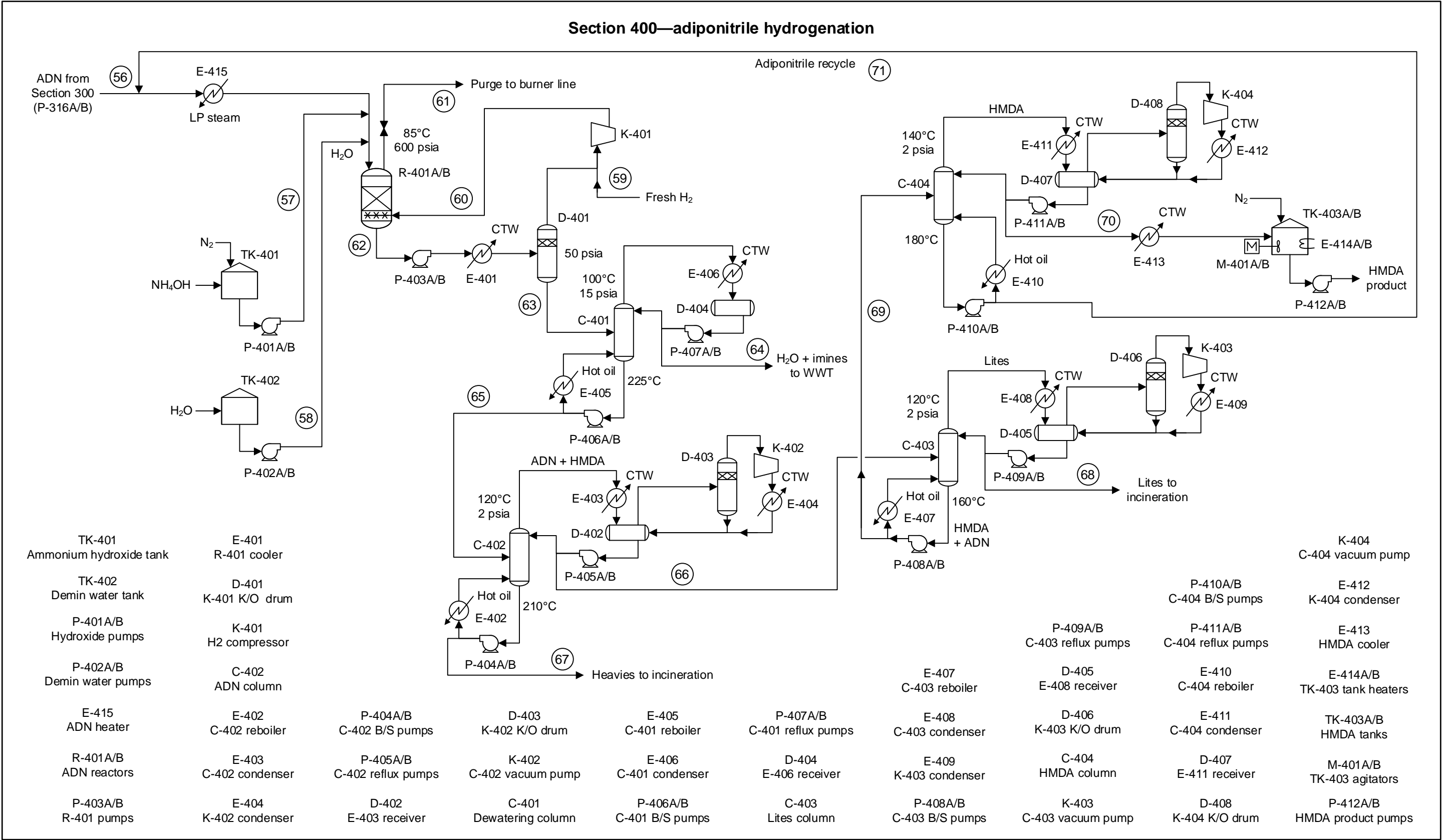


Figure 6.27 (5 of 5): HMDA from butadiene by hydrocyanation

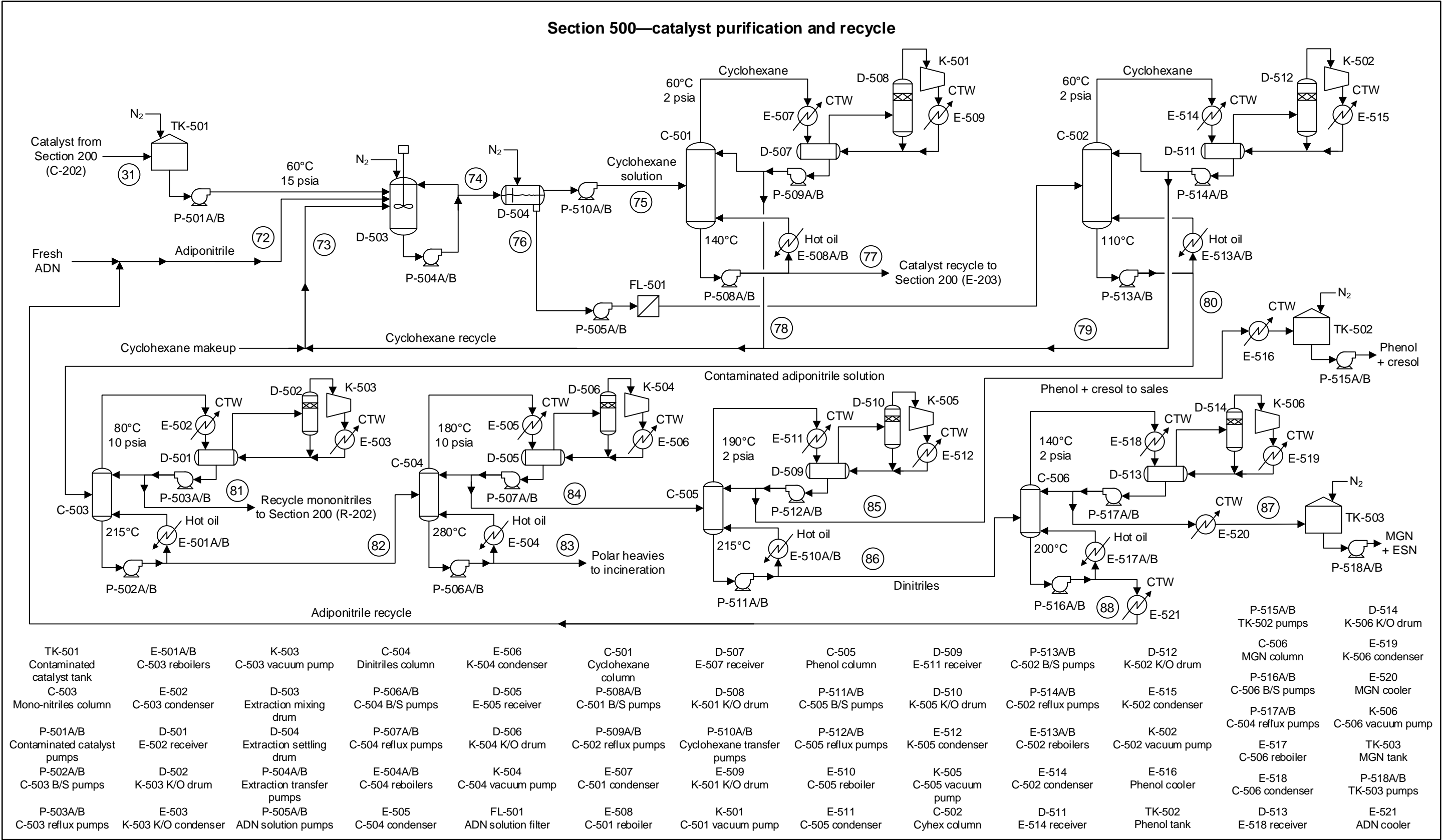


Figure 7.5 (1 of 3): HMDA from acrylonitrile by electrohydrodimerization

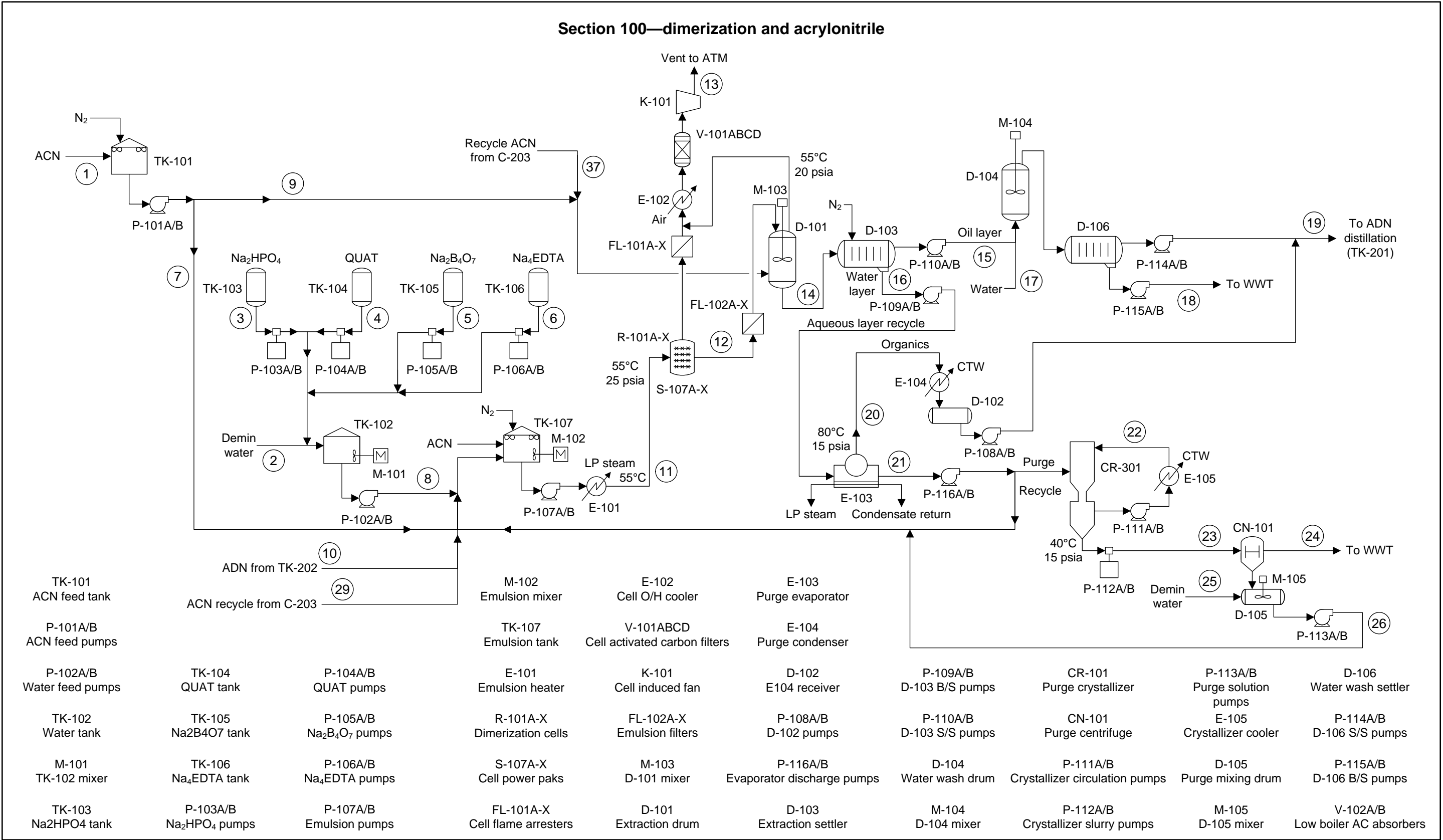


Figure 7.6 (2 of 3): HMDA from acrylonitrile by electrohydrodimerization

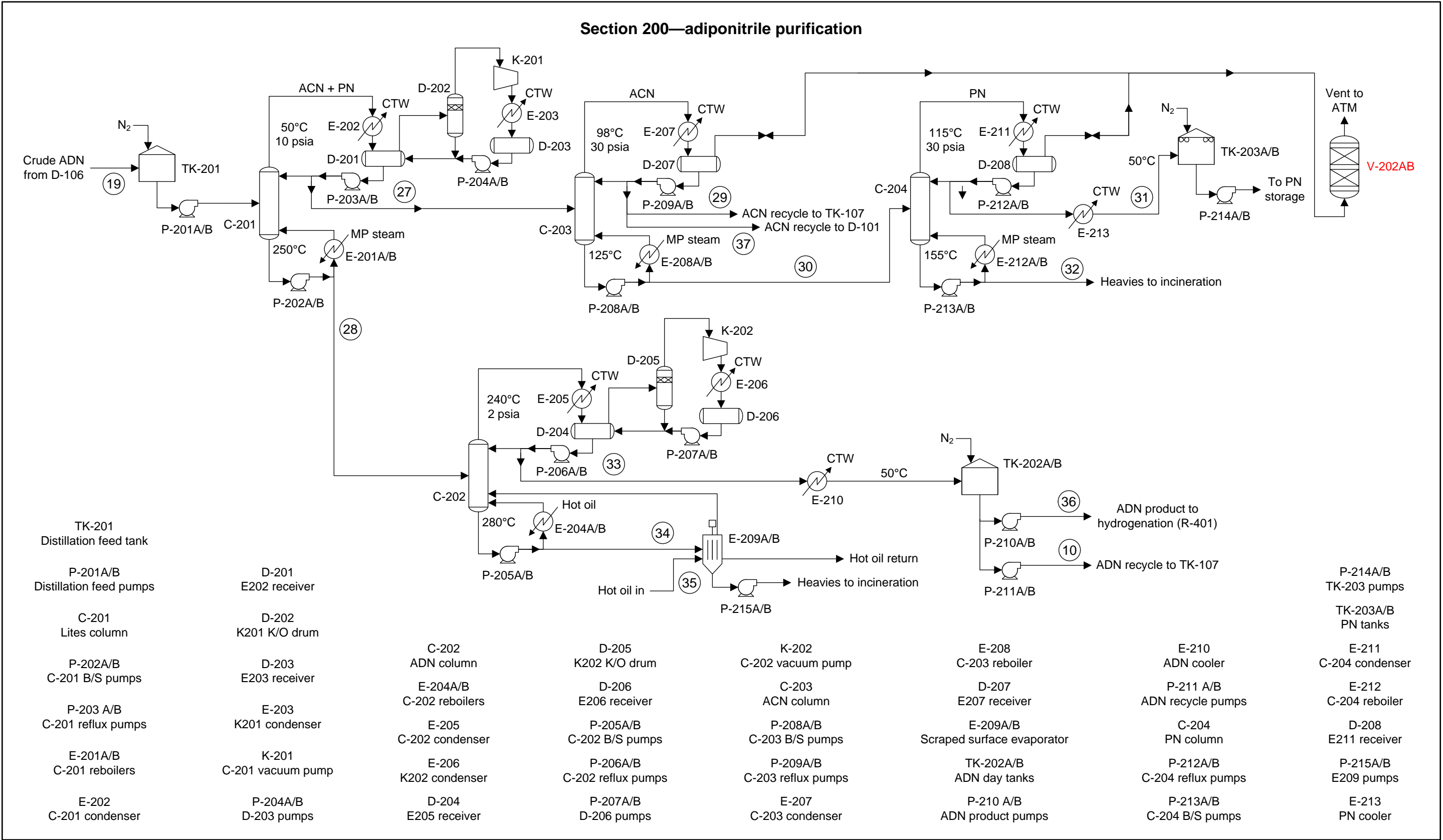


Figure 7.7 (3 of 3): HMDA from acrylonitrile by electrohydrodimerization

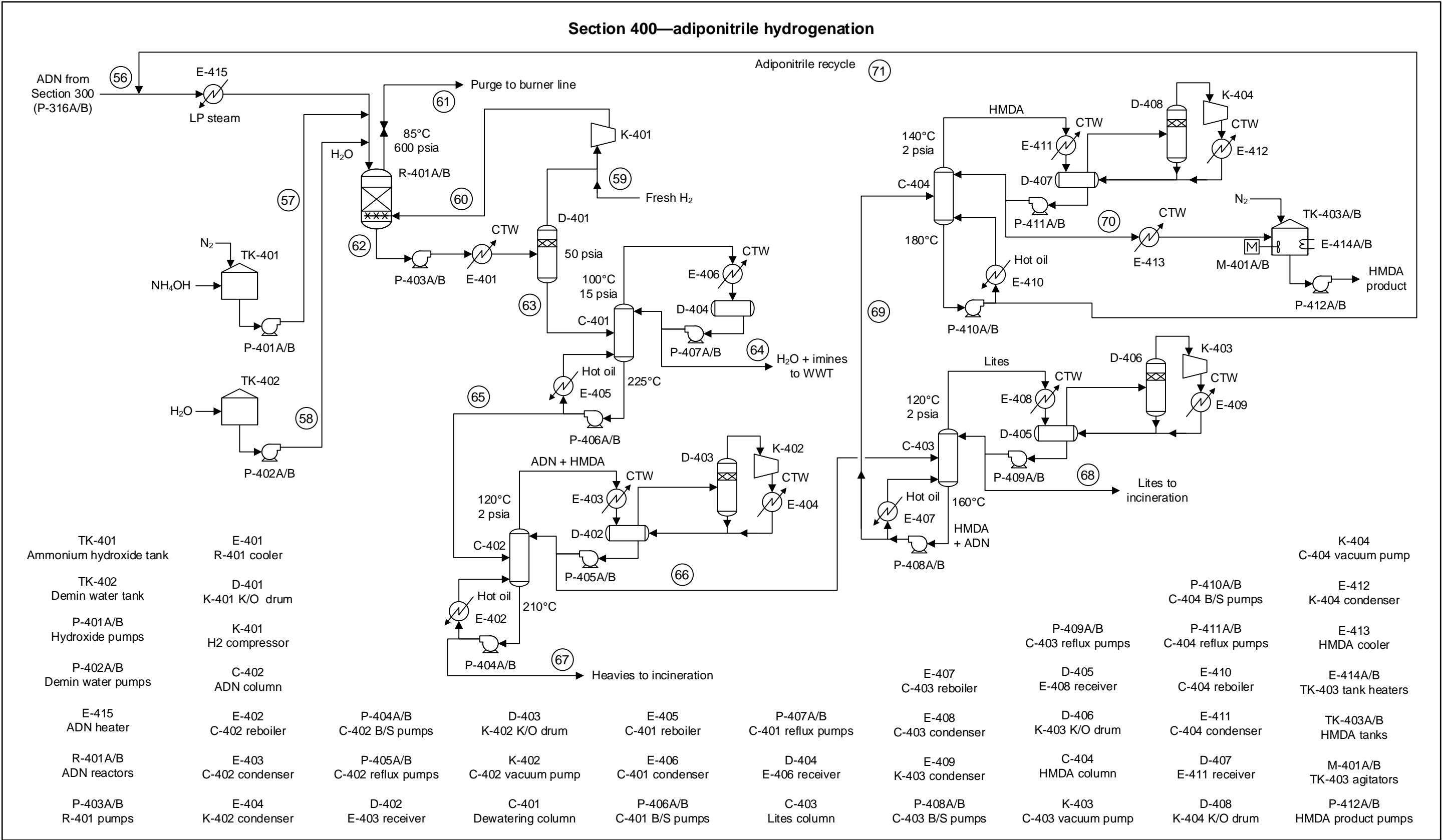


Figure 8.22 (1 of 5): HMDA from HFCS by Rennovia technology

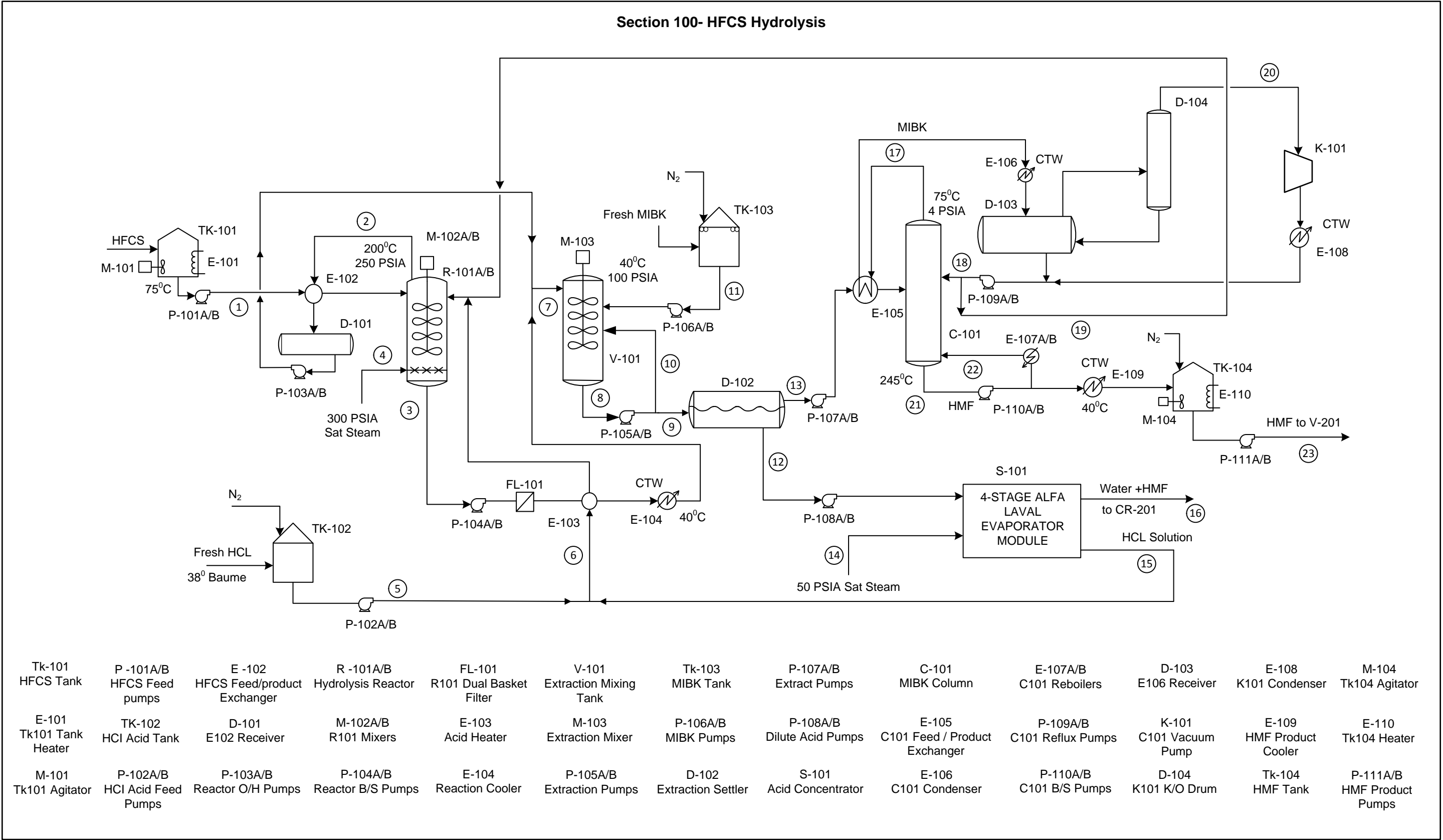


Figure 8.23 (2 of 5): HMDA from HFCS by Rennovia technology

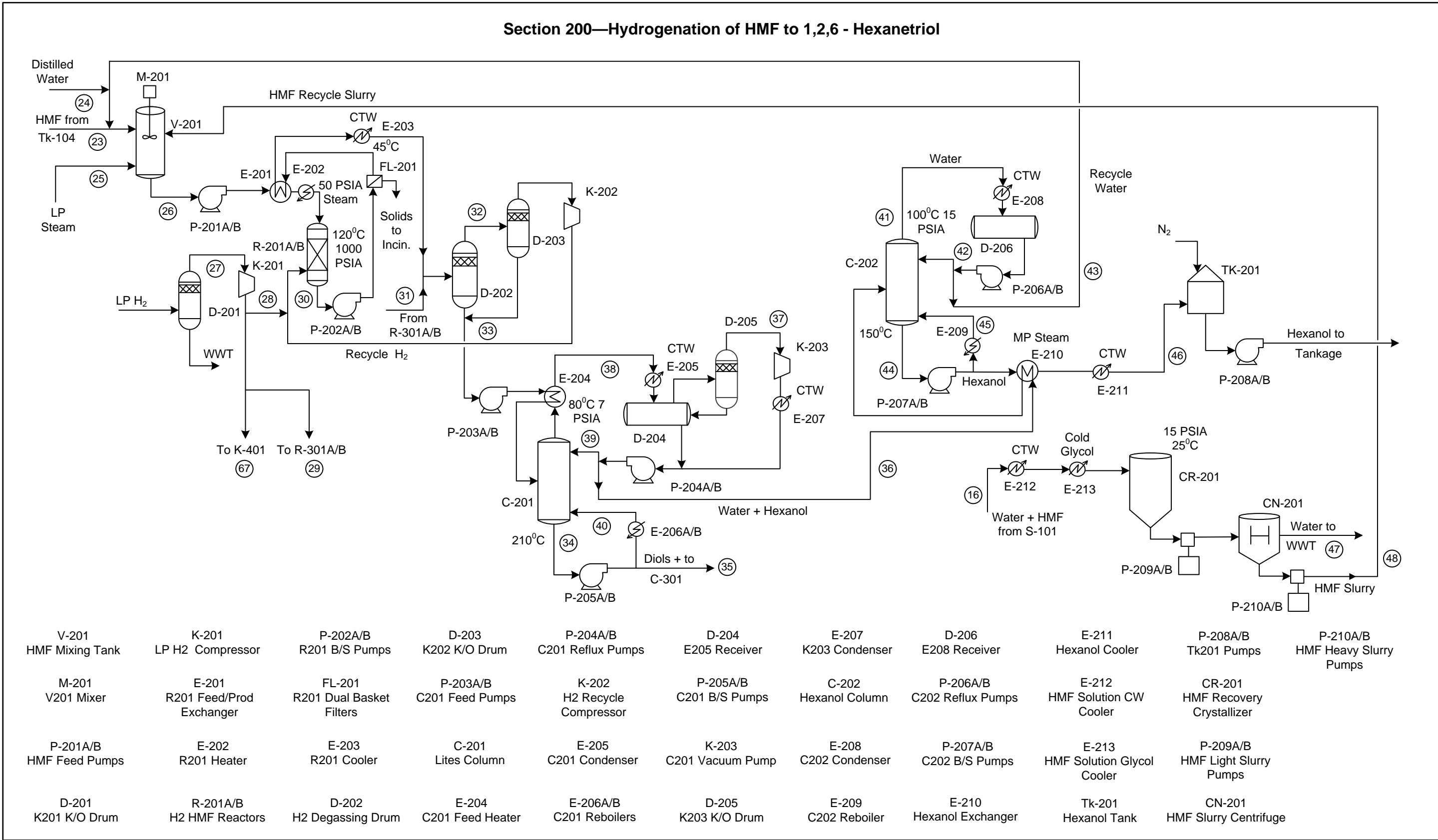


Figure 8.24 (3 of 5): HMDA from HFCS by Rennovia technology

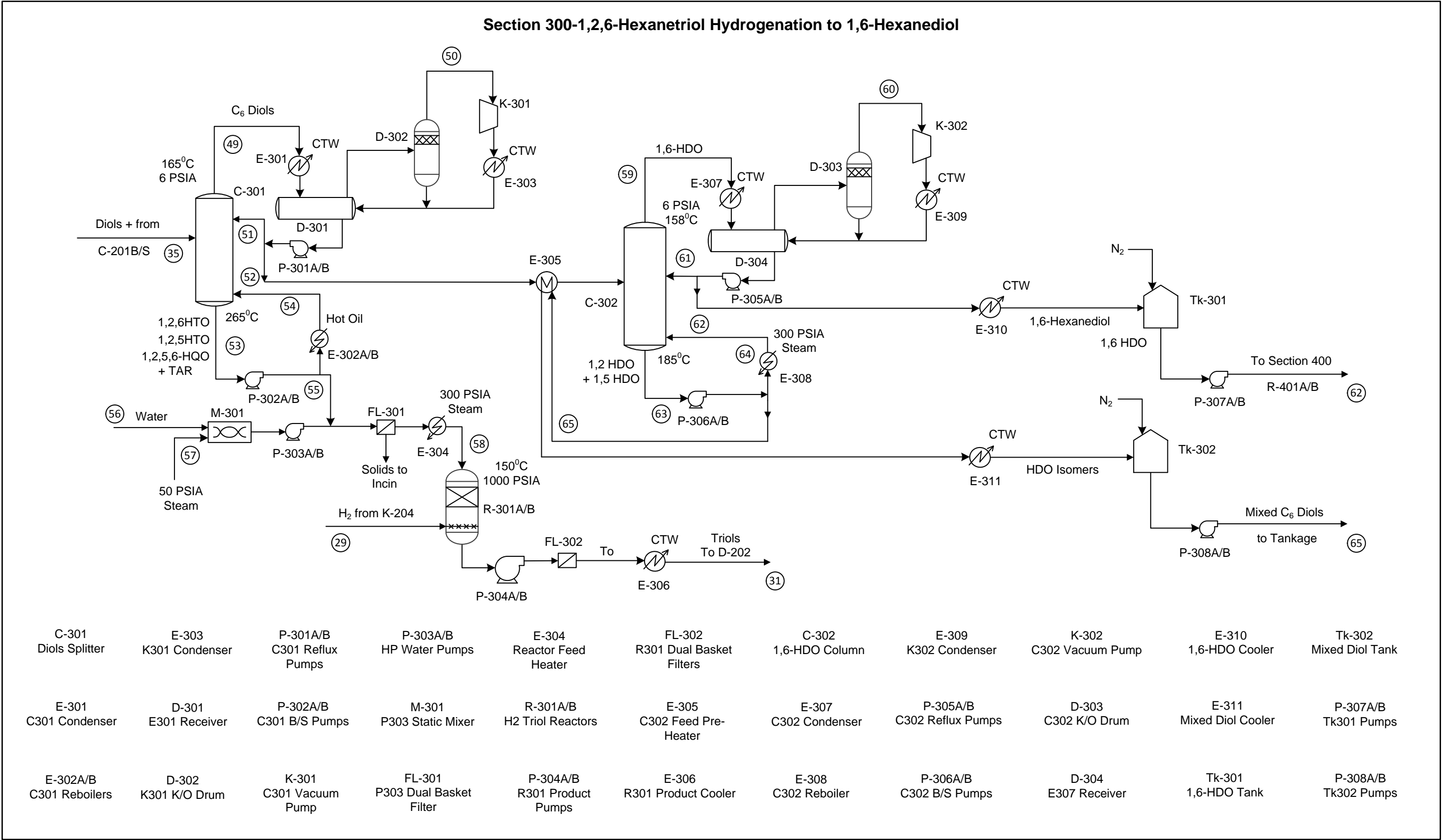


Figure 8.25 (4 of 5): HMDA from HFCS by Rennovia technology

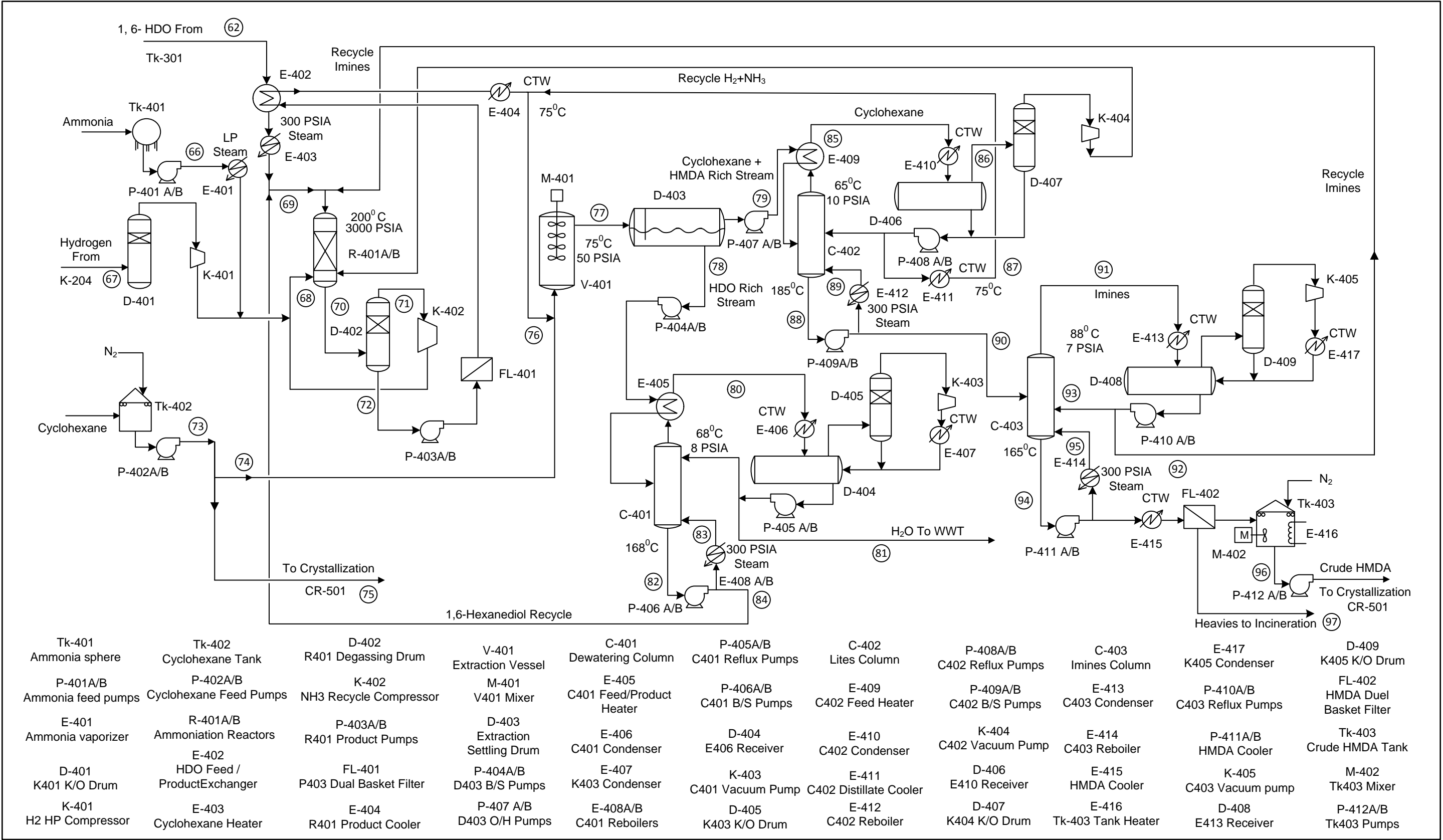


Figure 8.27 (5 of 5): HMDA from HFCS by Rennovia technology

