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SUSTAINABLE P2 DESIGN FOR BATCH-BASED SPECIALTY CHEMICAL MANUFACTURE

by

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Abstract

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2015-2016
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A case study has been conducted on the reduction of n-methyl-2-pyrrilodone (NMP) solvent waste in the manufacture of polyimide and polybenzoxazole precursors. The evaluation includes the environmental and economic assessment of solvent recovery and substitution strategies. A two-step distillation process proved effective in recovering 95% of the NMP at a purity of 99.97% from the aqueous solvent waste stream. Yearly operating costs were reduced by 83% and total life cycle emissions were reduced by 44%, due to reduction in virgin NMP use and hazardous waste disposal. With capital acquisition, the recovery option would still result in a net present value (NPV) at 10 years of $3,120,000. The reduction in life cycle emissions is limited by the thermodynamics of the system, in particular the large composition of water in the waste stream which requires significant energy to distill. Substitution of NMP with dimethyl sulfoxide (DMSO) and sulfolane reduces life cycle emissions by 44% and 47%, respectively, even without recovery, due to their greener manufacturing profile. Although, when the recovery system is integrated, no further reductions in the environmental impact are seen. This demonstrates the need for a complete analysis of a greener design, since the thermodynamic characteristics of the solvents are important to the life cycle assessment. Water reuse was also considered for the overall process, but is not recommended due to the high cost of treating the wastewater to ultrapure water standards.

Table of Contents

Table of Contents (Continued)

Table of Contents (Continued)

List of Figures

List of Tables

Chapter 1

Introduction

The following project focuses on the implementation of green engineering practices to more efficiently design and operate processes and facilities that manufacture specialty chemicals including: chemical additives, fine chemicals, performance chemicals, organic/inorganic intermediates, pharmaceutical intermediates, dyes/colorants, resins, coatings, consumer product ingredients, and precursor chemicals. An opportunity that was identified for improvement of this sector was optimization of the batch-based manufacturing platforms prevalent in specialty chemical manufacture. These batched-based systems have the drawbacks of high solvent and water use, greater potential for hazardous material emissions, and poor energy efficiency.

A test case for these green engineering efforts was performed at the DuPont Parlin, NJ plant where Cyrel® printing products, ChromaPro® colorants, Teflon® and Autograph® coatings, Pyralin® resin precursors, and other specialty chemicals have been produced. The batch Pyralin® resin precursor manufacturing process, where the solvent n-methyl-2-pyrrolidone (NMP) is used, was chosen for this case study because it generates significant solvent waste. The disposal of solvent waste, as well as the amount of virgin solvent used, poses a concern. The environmental burden is magnified since the resin precursor product must be washed of all contaminants in a water-intensive finishing step. Currently, the plant disposes of the solvent waste and wastewater. This project involved working with DuPont plant personnel to analyze the full extent of the current process inefficiencies and apply green engineering strategies for solvent recovery, solvent substitution, and water recovery.

This project includes the following work. An analysis of the background issues relevant to DuPont's resin precursor process was conducted, followed by an investigation of parallels to solvent use and waste issues of batch processes in the specialty chemical sector. Background information on the resin precursor process was investigated next. This included the goal, scope, and boundaries of the life cycle assessment (LCA); followed by the life cycle inventories of raw material manufacture, utility generation, and waste disposal. Once the background of the DuPont process and the broader specialty and performance chemical sector were known, approaches to solvent reduction for the resin precursor process were investigated. This required a preliminary solvent recovery design for a basic aqueous NMP waste stream, which would also have parallels to other industrial sectors. Possible solvent substitutes for NMP were also investigated and preliminary solvent recovery designs for aqueous systems containing these solvent substitutes were designed. After the preliminary designs were completed, a solvent recovery design for the actual DuPont resin precursor process solvent waste was investigated. Use of solvent substitutes in the resin precursor process was also investigated and recovery systems for these solvent substitutes were designed. Finally, water recovery from the wastewater generated by the resin precursor process was evaluated.

Environmental and design software, along with established protocols, were used to evaluate the preliminary solvent recovery designs and the solvent recovery designs for the resin precursor process. Aspen Plus® was used for process design for the project. This software tool is useful in determining separation system performance and operating requirements (e.g., utilities). SimaPro®, an LCA software tool, was used to calculate environmental impact reductions. Aspen Capital Cost Estimator was used to estimate the capital costs of recovery equipment. The environmental and economic impacts of all green alternative designs were compared to the current DuPont process, with the overall goal of improving the current DuPont process.

Chapter 2

Background

Inefficiencies in the Specialty Chemical Industry

The majority of specialty chemicals are made through inorganic and organic batch-based processes, in multipurpose or multiproduct plants (MPPs). These plants consist of versatile equipment for reaction, separation and purification, storage, effluent treatment, solvent recovery, and utilities. Specialty chemical MPPs can be adapted for different processes by changing the connections between units and by careful cleaning of the equipment. MPPs have lower investment and labor costs than dedicated plants, while maintaining the flexibility to meet changing demands. This is important in the specialty chemical industry because a great number of products, in limited quantity, are manufactured. The center of an MPP is a stirred tank reactor, commonly run in batch mode. Downstream of the reactors are equipment for crystallization, solid/liquid separation (i.e. filters and centrifuges), drying, fractionation for separation and purification of liquid products, and solvent recovery [1]. In many cases, the same reaction vessels are used not only for reaction, but also for batch separation processes such as extractions, distillations, and crystallizations [2, 3]. The specialty chemical MPPs are distinctly different than the large scale commodity chemical and petrochemical plants which are typically designed around a continuous production platform for large (greater than 10,000 metric tons per year) single product use, such as in the production of ethylene [1].

The specialty chemical sector can be further divided into fine chemicals and performance chemicals [4]. Fine chemicals are complex, single, pure chemical substances; that are produced in limited quantities [5]. They are used in final formulations and as intermediate and precursor chemicals in the agricultural, pharmaceutical, dye and pigment, and other consumer and specialty chemical sectors. Figure 1 shows the use of fine chemicals by sector. Fine chemical production is diverse, yet limited in quantity so versatile equipment is required. They are often manufactured using multipurpose batch processes. Batch stirred tank reactors and batch separation techniques such as distillation, extraction, and crystallization are often used [1].

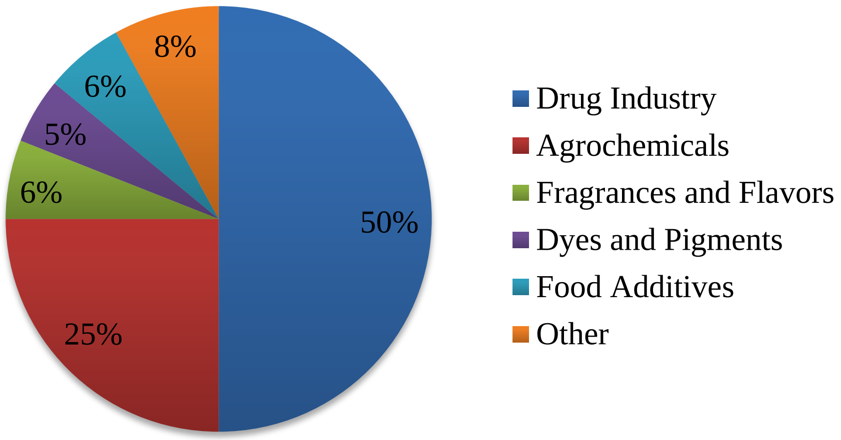


Figure 1. Fine chemical use by industry [1]

Performance chemicals are identified according to functional performance, rather than molecular qualities [4]. Performance chemicals are used in adhesives, resins, electronic chemicals, specialty polymers, and other specialty chemical applications. They are also used along with fine chemicals in applications including pharmaceuticals, agrochemicals, and dyes and pigments [5]. Similar to fine chemicals, resins are also manufactured using batch stirred tank reactors and batch separation and purification processes because it offers flexibility in product specification and production rate [6, 7].

Resin batch manufacturing is also energy intensive as reactions occur at high temperatures and are highly exothermic [7]. Organic dyes are typically synthesized using solvents in batch reactors; followed by separation using a filter press and drying batch processes [8, 9]. This process is labor intensive and causes inconsistencies in production quality [9]. Also, large quantities of wastewater are generated, which contain toxic organic residues [9]. Personal care products, such as cosmetics, utilize batch processing due to relatively small production volumes and the specialized chemistry involved. Batch operations in the cosmetic industry include distillation, centrifugation, classification, and high-shear dispersion [10]. Many raw ingredients used in personal care products are made through step-wise batch processes. For example, polymers represent a significant portion of raw materials in the personal care industry [11]. They are used as thickening agents, film formers, resinous powders, humectants [11]. Polymers are most commonly processed in batches, due equipment flexibility [12].

Specialty chemical manufacturing requires many sequential reaction steps, each followed by numerous separation and purification steps. At each of these steps, inefficiencies in chemical, water, and energy use may occur [13]. Addition of all inefficiencies of the process, results in high volumes of waste and high waste per unit product. The specialty chemical sector reported 5.6 billion lb of waste to the Toxic Release Inventory in 2013 [14]. This sector is represented by several NAICS codes, listed in Table 1, the waste profiles from which represent organic solvents and associated chemicals (acids, bases, precursor chemicals, etc.) used in manufacturing operations. An analysis of this sector is presented in the following section, “Sector Analysis.” The specialty chemical sector has one of the highest waste generation rates per kilogram of product produced (5-50 kg waste/kg product) which is comprised primarily of organic solvents. Other wastes include sludges, inorganic loads, and air emissions. However, wash water is another significant source of waste, but it is excluded from this data [15].

Table 1

Sectors included in specialty and performance chemicals

Sector	**NAICS Sector Code**
Inorganic Dye and Pigment Manufacturing	325131
Synthetic Organic Dye and Pigment Manufacturing	325132
Plastic, Resin, Rubber, and Synthetic Fibers and Filaments Manufacturing	3252 and 326
Pesticide, Fertilizer, and Other Agricultural Chemical Manufacturing	3253
Pharmaceutical and Medicinal Manufacturing	3254
Paint, Coating, and Adhesive Manufacturing	3255
Semiconductor and Other Electronic Components	3344
Printing Ink Manufacturing	325910
Explosives Manufacturing	325920
Purchased Resins Custom Compounding	325991
Photographic Film, Paper, and Plate Manufacturing	325992
Other Chemical Products and Manufacturing	325998

There are many reasons for the large quantities of waste produced in specialty chemical batch processes. High volumes of waste results from the large amounts of solvents and cleaning agents commonly used to meet strict product quality and purity specifications. In addition, complex reaction syntheses, that are not well understood, can cause formation of waste byproducts and low selectivity toward the desired product [3]. Complex reactions may also increase the difficulty of recycling solvents and other valuable components for reuse. Unlike commodity chemical operations, batch chemical operations rarely achieve a high level of process control. Since batch processes have less control, they produce a greater quantity of waste, consume more materials and energy per unit of product, and lead to reduced throughput and increased cycle time [16]. The discontinuous operation used in specialty chemical processing results in further consumption of energy and time [17]. In the past, batch chemical industries could tolerate high waste generation, due to the high value of final products. However, as environmental regulations become more stringent, it becomes more expensive to treat or dispose of waste. Hazardous waste, whether in solid, liquid, or vapor form is typically pretreated before release to a publically-owned treatment works (POTW) or pooled for off-site disposal by a private entity. Price competition provides incentives for batch industries to consider waste minimization [3, 18].

In batch specialty chemical processes, continuous utilization of multiple unit operations is extremely difficult and rarely achieved. The batch operation of equipment requires production to be stopped, and the equipment cleaned, reconfigured, and validated before changing to another batch or product. In addition, for many batch chemical operations, it is common for there to be long reaction times, lengthy periods of time at reflux, and long filtration and drying times. Each of these process steps lengthen the cycle time and lead to increased consumption of materials, energy, and labor. Cleaning procedures require large volumes of solvent and/or aqueous detergents [17]. Solvents are routinely used to clean reaction vessels in the pharmaceutical industry, due to strict limits on equipment cleanliness. The volume of solvents used for cleaning in the pharmaceutical industry is generally 2-3 times greater than the amount of solvent used in the reaction itself [19]. Usually these solvents are relatively green; however, their use significantly increases the emissions generated by the process [19]. These cleaning materials are often not considered part of a process, so their use is not optimized in the same way as other directly used raw materials and solvents.

Frequency of cleaning, length of cleaning time, volume of cleaning chemicals and water, energy use, and other factors are all important parameters that affect the real waste generation of a process, as well as cycle time and throughput [17]. Cleaning processes often generate a significant portion of a plant's wastewater [20]. Pharmaceutical facilities in the United Sates estimated an average daily generation of 260,000 gal of wastewater [21]. The semiconductor industry also generates significant waste water from cleaning of silicon wafer and microchips [22]. A single semiconductor plant generates up to 15,000 tons (3,600,000 gal) of wastewater each day, in addition to large amounts of isopropyl alcohol or other alcohol used as drying agent [23].

Green engineering efforts that have been proposed to improve the environmental footprint of cleaning operations include solvent replacement with supercritical CO_2 [24]. Supercritical CO_2 could be used to wash microelectronics and replace solvents in other production steps [23, 25, 26]. Another approach in reducing the impact of wash water is to recycle it for reuse in the cleaning process [27, 28, 29]. Optimization of cleaning processes and making increased use of dilute chemistries, hot water rinses, and megasonic cleaning have also reduced water use in the semiconductor industry [28].

Solvents are used in unit processes to facilitate reactions and in various separation and purification operations. Processes that generate liquid waste streams containing organic solvents include crystallization, distillation, extraction, washing and cleaning processes, as well as byproduct streams from inefficiencies in reactions [13]. Solvents represent 80 to 90% of the total mass in a typical specialty chemical batch process [30].

The top organic solvents used in the specialty chemicals industry include toluene, methanol, 1, 2-dicholoethane, dichloromethane, xylene, n-hexane, and other toxic and hazardous solvents like n-methyl-2-pyrrolidone [14]. These solvents have varying degrees of toxicity to humans and animals and some are known or possible carcinogens or developmental toxins [13]. The toxic chemicals used by the specialty chemical industry also pose significant environmental concerns regarding releases into the environment during their life cycle. The life cycle of chemicals extends beyond the plant boundaries and includes production and disposal, which significantly impact the environment [31]. The emissions generated to manufacture the average virgin solvent are approximately twice the mass of the solvent produced, and the emissions generated to incinerate solvent waste are slightly more than twice the mass of waste [32]. These emissions negatively impact air, water, and land through release of greenhouse gases, ozone-depleting substances, volatile organic compounds (VOCs), sulfur and nitrogen oxides, and aqueous organic matter [16].

Solvent waste can be released into the air as VOCs from the finished product drying processes and packaging operations, and from fugitive emissions from the manufacturing process [13]. Fugitive VOC emissions can be released during batch reactor charging, reactant addition, and reaction through the vacuum system, vent line, or manway. During vessel cleaning and subsequent drying, emissions can also be released [6]. VOCs react with nitrogen oxides in the troposphere to produce smog. Smog is responsible for short-term effects such as irritation of the respiratory tract, lung function reduction, increases in asthma symptoms, and inflammation of lung linings [16]. Solid waste that contains solvent is formed from filtration and centrifugation of final product and intermediate compounds. Throughout their life cycle, organic solvents negatively impact the environment through air, water, and soil pollution; thereby requiring approaches to reduction in use [18, 32, 33].

Solvent use has become so established in specialty chemical synthesis and manufacturing, that little attempt is made to minimize the quantity and/or number of solvents used. This is partly due to the fact that many reactions used today were developed during a time when toxic properties of many reagents and solvents were not known, and waste minimization and sustainability were not considered significant issues [15]. As a result, environmental impact of solvent use is still often ignored when developing a chemical manufacturing route. Solvent can be recovered, for reuse, using separation techniques such as distillation or pervaporation [31]. Solvent recovery or reduction can often reduce the emissions associated with the chemical process [32]. Also, it is often economically favorable to recover spent solvent and reduce solvent use, as solvents are relatively expensive. Typically solvent waste is incinerated and the heat produced is recovered. However, this is an expensive method of producing energy as the cheapest solvents have prices per BTU twice that of normal fuels [34]. Expensive solvents such as pyridine, tetrahydrofuran, n-methyl-2-pyrrolidone, and dimethylacetamide may be up to 10 or 20 times more costly per BTU [34]. These expensive solvents are also more likely to contain chlorine and nitrogen, which result in higher emissions of nitrogen oxides and hydrogen chloride from incineration, and therefore are less attractive fuels [34].

Specialty chemical processes can be further improved by reducing solvent use and/or making solvent recovery easier. Reaction sequences can be optimized to reduce the number of solvents used. This avoids the need for complex solvent separation and reduces the complexity of the synthesis (fewer separation steps). Unnecessary isolation of intermediates can be avoided by carrying out as much of the synthesis route as possible in a single reactor. Combination of synthesis steps in a single reactor may reduce the amount of solvent, wash steps, and intermediate filtration and drying. Solid state reactions, which do not require a solvent reaction media, can be investigated to completely eliminate solvent use in some reaction steps. The use of continuous reactors, separators, and crystallizers offers another potential strategy for reduction of solvent use [35]. Continuous processes typically allow for greater heat and mass transfer rates, which should lower the amount of solvent required compared to batch processes. Chemical properties and toxicity should be considered when choosing a solvent for a chemical process. For example, a solvent's boiling point reflects the energy required to separate it through distillation. Also, substitution to a less harmful solvent (based on health and safety factors) can reduce environmental impact [36].

Many specialty chemicals are manufactured through complex reaction syntheses, which may not be efficient. Waste, due to inefficiencies, can be reduced through use of catalyzed reactions. However, around 95% of all industrial heterogeneous catalysts are used in the production of bulk chemicals and 3-5% in the synthesis of specialty chemicals [37]. In current specialty chemical manufacturing processes, traditional stoichiometric chemistry or homogeneous catalysts are used. These processes lead to inefficiencies due to formation of byproducts, salts, and catalysts that cannot be regenerated. This results in costly disposal or treatment of hazardous waste. Use of heterogeneous catalysts can improve productivity through increased yield and selectivity, reduced cycle time, reduced variability, and increased reactor volume efficiency. Environmental impact can be reduced through elimination or reduction of solvent, reduction of by-products, avoided salt formation, and elimination of catalyst waste [15, 37]. Biocatalytic routes can be used in specialty chemical manufacturing to lessen the environmental impact, through reduction in the number of processing steps, amount of waste, and in-process energy [35, 38].

The batch-based nature of specialty chemical manufacturing causes additional inefficiencies. Batch reactors do not use energy efficiently and lose reaction efficiency due to size constraints. The efficiency of most chemical reactions is dependent on mixing and/or heat transfer. Small chemical reactors have an advantage over larger volume reactors because they have a higher ratio of heat transfer area to volume, making reactor temperature more controllable. They can also deliver more mixing energy per unit volume, without damaging the agitator, resulting in uniform concentration throughout the reactor. The improved efficiency of small reaction vessels can substantially lower capital and operating costs. However, small batch vessels are impractical at the industrial scale since hundreds or even thousands of process cycles would be required for commercial throughputs [39]. Therefore, energy and reaction inefficiencies will always be present in traditional batch reactors. More efficient reactor designs are seldom implemented because existing batch reactors with supporting unit operations are rarely replaced. Existing in-ground capital equipment that has been paid for many times over is difficult to stop using unless the gains in efficiency or the reduction in costs are overwhelming [17]. It is very difficult to implement new technologies to improve energy and reaction efficiency, because older technologies are frequently retained. Older technologies are frequently retained because companies are more comfortable with those existing methods. Companies often feel that these older technologies are better understood, have performed reliably over the years, and are hesitant to change.

The *FY 2011-2015 EPA Strategic Plan* Goal 4, Objective 4.2 specifically asks for industries to reduce hazardous materials, CO_2 emissions, and water and energy use. This project will assist industry to "prevent pollution and waste before generation by implementing conservation techniques, promoting efficient re-use of materials, making production process more sustainable, and promoting the use of safer substances" [40]. The *FY 2014-2018 EPA Strategic Plan* Goal 4, Objective 4.2 states that "fostering the development of P2 innovations: … promoting green chemistry and engineering" and "promoting increased use of P2 innovations: … providing technical assistance on manufacturing" are critical to the Agency's mission [41]. This project assisted industry in advancing these objectives.

Even though the Principles of Green Chemistry and Green Engineering have been publicized for well over a decade, the application and assimilation of these in the design process and operation of commercial facilities is lacking [42, 43, 44]. The Principles of Green Chemistry and Green Engineering can be seen in Table 2. Both sets of principles will be applied to design alternative processes to the current DuPont resin precursor process. The Principles of Green Engineering will mainly be used when designing solvent recovery processes and Green Chemistry principles will mainly be used when investigating possible solvent substitutes.

Table 2

Twelve Principles of Green Chemistry and Green Engineering

	The Twelve Principles of Green Chemistry [42]	**The Twelve Principles of Green Engineering** [43]
1	It is better to prevent waste than to treat or clean up waste after it is formed.	Designers need to strive to ensure that all material and energy inputs and outputs are inherently nonhazardous as possible
2	Synthetic methods should be designed to maximize the incorporation into the final product of all materials used in the process.	It is better to prevent waste than to treat or clean up waste after it is formed
3	Wherever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment	Separation and purification operations should be designed to minimize energy consumption and materials use.
4	Chemical products should be designed to preserve efficacy of function while reducing toxicity.	Products, processes, and systems should be designed to maximize mass, energy, space, and time efficiency.
5	The use of auxiliary substances (e.g., solvents, separation agents) should be made unnecessary whenever possible and innocuous when used.	Products, processes, and systems should be "output pulled" rather an "input pushed" through the use of energy and materials
6	Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.	Embedded entropy and complexity must be viewed as an investment when making design choices on recycle, reuse, or beneficial disposition.
7	A raw material feedstock should be renewable rather than depleting whenever technically and economically practical.	Targeted durability, not immortality, should be a design goal.
8	Unnecessary derivatization (blocking group, protection-deprotection, temporary modification or physical/chemical processes) should be avoided whenever possible	Design for unnecessary capacity or capability (e.g., "one size fits all") solutions should be considered a design flaw
9	Catalytic products should be designed so that at the end of their function they do not persist in the environment and break down into innocuous degradation products.	Material diversity in multicomponent products should be minimized to promote disassembly and value retention.
10	Chemical products should be designed so that at the end of their function they do not persist in the environment and break down into innocuous degradation products.	Design of products, processes, and systems must include integration and interconnectivity with available energy and material flows.
11	Analytical methodologies need to be further developed to allow for real-time in-process monitoring and control prior to the formation of hazardous substances.	Products, processes, and systems should be designed for performance in a commercial "afterlife".
12	Substances and the form of a substance used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosions, and fires.	Material and energy inputs should be renewable rather than depleting.

Analysis of the Specialty Chemical Sector

As mentioned in the previous section, batch-based production platforms cause inefficiencies from an environmental and operational standpoint. Solvent and associated waste issues are present which can be addressed through green engineering practices. In order to fully understand the specialty chemical sector, an evaluation of the Toxic Release Inventory (TRI) data and investigation of representative manufacturing cases was undertaken. The specialty chemical sector is represented by several NAICS codes; previously listed in Table 1. These codes were chosen based on sectors that manufacture specialty chemicals of interest. The sectors chosen include dyes and pigments, plastics, resins, rubbers, agrochemicals, pharmaceuticals, coatings and adhesives, electronic chemicals, and other specialty chemical industries. Batch processing is prevalent in all of these industries [1].

A TRI analysis was performed to determine the type and quantity of waste generated in the specialty chemical sector. As seen in Table 3, the specialty chemical sector reported 5.6 billion lb of waste in 2013 [14]. The waste includes organic solvents, acids, bases, precursor chemicals, refrigerants, and other chemicals used in manufacturing operations. However, the TRI only includes chemicals that cause cancer or other chronic human health effects, significant adverse acute human health effects, and/or significant adverse environmental effects [45]. For example, chemicals such as isopropyl alcohol and acetone are not included in the TRI. Solvent use is actually higher than in the reported TRI values since isopropyl alcohol, tetrahydrofuran, acetone, and ethanol that are commonly used solvents in this sector are not reported in the TRI.

Table 3

Specialty chemical sector TRI for 2013 [14]

Chemical	**Waste (lb/yr)**	**Percentage of Sector Waste (%)**	**Chemical**	**Waste (lb/yr)**	**Percentage of Sector Waste (%)**
Toluene	873,938,776	15.53	Acetonitrile	45,016,395	0.800
Hydrogen Sulfide	396,114,826	7.04	Styrene	42,815,162	0.761
1,2-Dichloroethane	320,265,441	5.69	Chlorine	39,959,259	0.710
Ethylene Glycol	314,023,232	5.58	Formic Acid	37,940,627	0.674
Ethylene	313,424,297	5.57	1,1,2-Trichloroethane	37,326,205	0.663
Freon 113	306,041,337	5.44	Sulfuric Acid	36,771,382	0.653
Ammonia	302,042,509	5.37	Titanium Tetrachloride	35,233,046	0.626
Acrylonitrile	293,071,966	5.21	Nitric Acid	34,717,682	0.617
Methanol	271,523,078	4.82	Formaldehyde	33,835,026	0.601
Hydrochloric Acid	230,420,410	4.09	Hydrogen Fluoride	31,249,537	0.555
Propylene	193,519,631	3.44	N-Methyl-2-Pyrrolidone	29,812,316	0.530
Nitrate Compounds	162,261,958	2.88	Certain Glycol Ethers	29,647,488	0.527
Xylene	122,922,866	2.18	N,N-Dimethylformamide	27,470,810	0.488
Dichloromethane	96,892,427	1.72	N-Butyl Alcohol	26,196,321	0.465
Methyl Isobutyl Ketone	70,226,664	1.25	Vinyl Chloride	25,840,821	0.459
Phenol	69,846,517	1.24	Ethylbenzene	22,193,180	0.394
Benzene	63,664,131	1.13	1,3-Butadiene	21,516,156	0.382
N-Hexane	63,307,916	1.12	Naphthalene	21,392,680	0.380
Hydrogen Cyanide	59,203,751	1.05	Other	469,722,258	8.35
Cyclohexane	57,355,747	1.02	Total	5,628,723,830	100

The waste generated by each sector within the specialty chemical sector, can be seen in Figure 2 and Table 4. From this analysis it was found that the plastic, resin, rubber, and synthetic fiber and filament industry generates the most waste in the specialty chemical sector. This industry is attributed with almost half of the waste generated in the specialty chemical sector. The agrochemical industry generated the second most waste, as it was responsible for about a quarter of the waste generated within the specialty chemical sector. The other chemical products industry also generated significant waste, as it represented 15% of the waste generated in the specialty chemical sector. The combination of all the other sectors represented less than 15% of the waste generated in the specialty chemical sector. However, as mention previously, the TRI only includes chemicals that are deemed to have significant impact on human health and/or the environment. This means that the actual quantity of waste generated in the specialty chemical industry is much higher. As previously stated in this report, solvent is used to facilitate reactions and separations/purifications and is not consumed in these processes, so it exits the process as waste. Therefore, the TRI waste generation values are indicative of the usage rates of those solvents in the particular manufacturing sector.

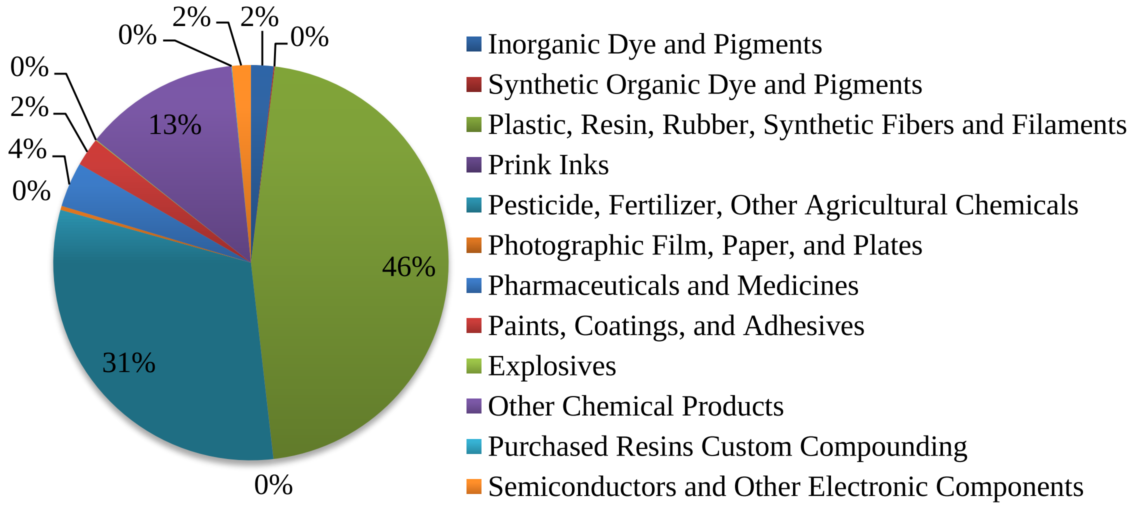


Figure 2. TRI for sectors within the specialty chemical sector (2013) [14]

Table 4

TRI for sectors within the specialty chemical sector (2013) [14]

NAICS Code	Sector	Waste Generated in 2013 (lb)	Percentage of Sector Waste (%)
325131	Inorganic Dye and Pigment Manufacturing	103,996,145	1.85
325132	Synthetic Organic Dye and Pigment Manufacturing	4,908,505	0.0872
3252 & 326	Plastic, Resin, Rubber, and Synthetic Fibers and Filaments Manufacturing	2,602,612,319	46.2
325910	Printing Ink Manufacturing	520,453	0.00925
3253	Pesticide, Fertilizer, and Other Agricultural Chemical Manufacturing	1,752,184,685	31.13
352992	Photographic Film, Paper, and Plate Manufacturing	18,394,294	0.327
3254	Pharmaceutical and Medicinal Manufacturing	206,595,152	3.67
3255	Paint, Coating, and Adhesive Manufacturing	130,587,397	2.32
325920	Explosives Manufacturing	3,245,139	0.0577
325998	Other Chemical Products and Manufacturing	716,247,092	12.72
325991	Purchased Resins Custom Compounding	2,694,116	0.0479
3344	Semiconductor and Other Electronic Components	86,738,532	1.54
Total		5,628,723,830	100

The trends of the most widely used chemicals found in the TRI for the specialty chemical sector, over the past ten years, were analyzed. In Table 5, it is seen that the top ranked chemicals have remained relatively consistent. For the past ten years, toluene has been ranked as the highest chemical waste. Other chemicals such as methanol, ethylene, 1, 2-dichloroethane, and ethylene glycol have consistently been in the top ten, in terms of waste generation, for the past ten years. Propylene and ammonia have remained close to the top ten over the past ten years. Freon 113 and acrylonitrile do not consistently rank high over the past ten years, as their waste has recently increased. This analysis shows that the chemical waste throughout the past ten years has remained relatively consistent.

This means that similar chemicals have been used by the specialty chemical industry throughout the past ten years.

Table 5

TRI rank of chemical waste in the specialty chemical sector [14]

	2012	**2010**	**2008**	**2006**	**2004**	**2002**
Toluene	1	1	1	1	1	1
Freon 113	2	3	3	6	124	143
Methanol	3	6	4	2	3	2
Acrylonitrile	4	64	58	53	62	55
Ethylene	5	4	5	3	7	6
1,2-Dichloroethane	6	2	6	7	5	4
Propylene	7	10	8	8	10	13
Hydrochloric Acid	8	5	2	4	2	8
Ethylene Glycol	9	8	7	5	4	3
Ammonia	10	7	13	9	6	5

An analysis of solvent waste throughout the past ten years was conducted to determine trends in use. The trends for the six solvents with highest waste generation can be seen in Figure 3. Trends for eight other solvents with lower, but still significant, waste generations were plotted in Figure 4. Figure 3 shows that the most common solvents, in specialty chemical waste, have remained constant throughout the past ten years. However, toluene waste has increased and glycol ether waste has decreased. It is also seen that methanol, 1, 2-dichloroethane, dichloromethane, and xylene wastes have decreased since 2002, but these numbers are beginning to rise. Figure 4 shows that the waste of each solvent fluctuates from year to year; however they are overall relatively consistent throughout the past ten years. Figure 3 and Figure 4 show that the specialty chemical sector has reported significant waste from the same common solvents, throughout the past ten years. The analysis shows that organic solvent continues to be a large source of waste in the specialty chemical sector. Also, the types of solvent have not changed much throughout the past decade.

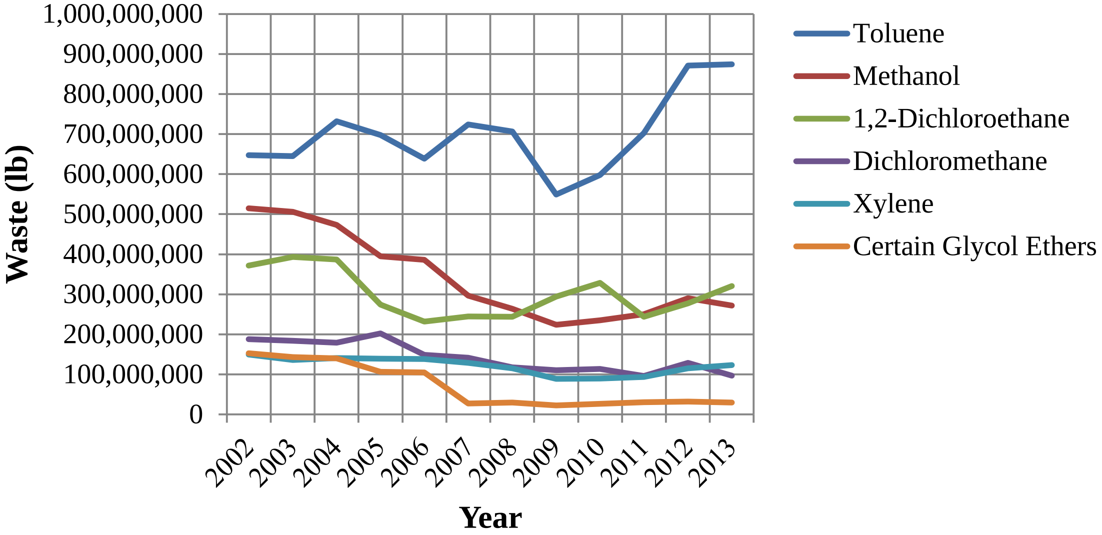


Figure 3. TRI data for the most common solvents used in the specialty chemical sector [14]

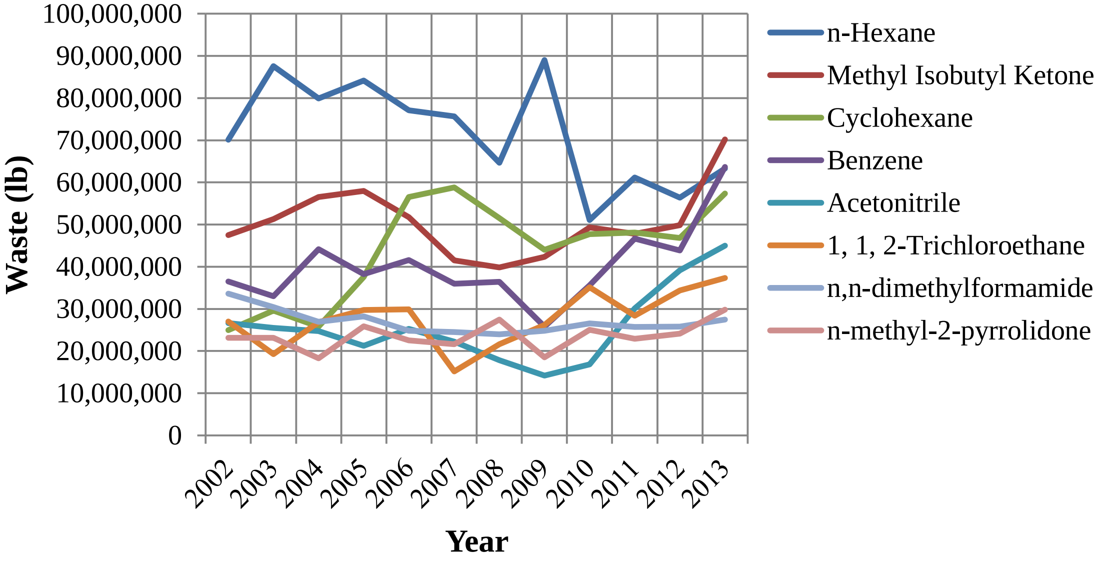


Figure 4. TRI for other significant solvents used in the specialty chemical sector [14]

Resin Precursor Industry

The DuPont plant in Parlin, NJ has manufactured many specialty chemicals, including Cyrel® printing products, ChromaPro® colorants, Teflon® and Autograph® coatings, and Pyralin® resin precursors [46, 47]. As mentioned previously, the manufacture of Pyralin® resin precursors was chosen for this case study, as NMP solvent reduction and recovery opportunities were recognized. The Pyralin® resin precursors manufactured by DuPont are liquid polyimide (PI) or polybenzoxazole (PBO) precursors [48]. They are called precursors because the product sold by DuPont is an intermediate that is thermally cured by the customer (final product manufacturer) to form a PI or PBO resin. PI and PBO resins are sold as precursors because PI and PBO resins have low solubility in common solvents and have high softening temperatures, making their processing difficult and expensive [49]. The PI and PBO precursors are soluble, so the customer can apply and cure the PI or PBO precursor to meet their needs. PI and PBO resins are performance polymers used in many technical fields including aerospace, microelectronics, and microelectromechanical systems [50]. Their applications include fibers, films, molding powders, coatings, and composite pre-impregnated materials. The main advantage of PI and PBO resins are their high heat resistance [50].

The liquid PI and PBO precursors manufactured by DuPont at the Parlin Plant are used in microelectronic applications. DuPont is the world’s largest supplier of PI and PBO precursor resins for microelectronic applications [51]. PI resins are often used in microelectronic applications due to their physical and chemical properties. PI resins are made of linear aromatic rings which results in rigid chains with strong interactions between chains. This provides PI resins with chemical resistance to organic solvents, mechanical strength, thermal stability, and dielectric properties [49]. PBOs are similar to PIs but use aqueous developers, reducing the use of solvent. PBOs have similar mechanical, chemical, and dielectric properties as polyimides. They also have decreased water absorption, lower thermal curing temperatures, and lower thermal stability when compared to PIs [52, 53]. In microelectronics, PIs and PBOs are used as passivation layers for silicon wafers or insulation materials [49]. PI and PBO resins are also used in flip chip packaging and devices [54]. There are two main types of PI and PBO precursors, photodefinable and non-photodefinable. The type of PI and PBO precursors, affects the application process. Photodefinable resin precursors react when exposed to UV light, while non-photodefinable precursors require the addition of photoresist chemicals and adhesion promoters [55].

As mentioned previously, PI and PBO resins are produced through two main steps. In the first step, PI or PBO precursor is synthesized. The precursor is then cured to produce the final PI or PBO resin [56]. The DuPont plant in Parlin, NJ is only responsible for manufacturing the PI or PBO precursor; while their customers are responsible for applying and curing the precursor. The customers are the manufacturing plant for the microelectronic device, which in turn is sold to a consumer. PI and PBO precursors are manufactured through solution polymerization [56]. This synthesis takes place in a dipolar aprotic solvent [56, 57]. The most commonly used solvents in the manufacture of PI and PBO precursors are n, n-dimethylformamide (DMF), n, n-dimethylacetamide (DMAc), n-methyl-2-pyrrolidone (NMP), and dimethyl sulfoxide (DMSO) [57]. NMP is frequently chosen as solvent because it has been shown to produce precursors with the highest molecular weight, thus producing polyimide resins with high molecular weight after curing [57]. The molecular weight of polyimide resins is important as it affects mechanical properties and chemical resistance. Dipolar aprotic solvents are used because of their basicity, as they are Lewis bases. Use of a basic solvent results in a strong exothermic acid-base reaction which is the most important driving force in the reaction. The rate of formation of PI or PBO precursor is faster in more basic and more polar solvents [57].

PI and PBO precursors are synthesized in a jacketed stirred tank reactor, blanketed with inert gas [57]. This synthesis is performed in a semibatch mode, using either one or two reactors [57, 58]. The semibatch reactors operate very similar to batch reactors, except some reactants are added over time instead of all at the same time at beginning of the process. PI precursor (polyamic acid) is formed from the reaction of a dianhydride, such as pyromellitic dianhydride (PMDA), and an aromatic diamine, mainly oxydianiline (ODA) [50, 56, 57, 58]. Photosensitivity is added to the polymer by attaching an unsaturated monomer, usually an acrylate such as hydroxyethyl methacrylate (HEMA), to the backbone of the polymer [59]. The synthesis is carried out in the presence of dipolar aprotic solvent, at temperatures below 50ºC. Initially, the diamine is dissolved in the dry solvent. Then 95% of the stoichiometric quantity of dianhydride is added rapidly to the reaction mixture. Additional dianhydride, dissolved in solvent, is added incrementally until the maximum viscosity is reached [57, 58]. In some cases, this process is carried out in a second reactor [58]. PBO precursor (polyhydroxyamide) is synthesized in a similar manner to PI precursor. However, PBO precursor has phenolic hydroxyl groups in its polymer backbone, so the precursor is soluble in aqueous base [52, 60]. This reduces the use of organic solvent in the PBO application process because an aqueous alkaline developer can be used [52, 60]. After the PI or PBO precursor is formed, it is precipitated and washed using DI water. The cleaned precursor is then dissolved in solvent (typically dipolar aprotic) with desired additives, such as adhesion promoters [61]. This product is then used by the microelectronic industry.

The precipitation and cleaning process generates significant waste. In this process, the solvent that was used in the reaction is removed, generating organic solvent waste. This waste also contains water from the cleaning process. Most commonly NMP is found in the waste streams since it is normally used as solvent in the resin precursor synthesis [59]. However, other dipolar aprotic solvents such as DMAc and DMF can be used as solvent, and therefore are the primary waste solvent. These dipolar aprotic solvents (NMP, DMAc, and DMF) are not favorable due to their human reproductive risks and negative impact on the environment [19]. These dipolar aprotic solvents negatively impact the environment through their disposal. Typically waste containing these solvents also contains large quantities of water, as is the case for the PI and PBO precursor waste. The solvent is generally not separated from the aqueous waste stream due to high capital costs and high energy input. The preferred method of disposal is incineration which requires additional fuel due to the high content of water. Incineration also causes generation of the greenhouse gas pollutants CO_2 and NO_x [19]. Use of dipolar aprotic solvents such as NMP, DMAc, and DMF has been identified by the pharmaceutical industry as a problem due the associated health and environmental risks [19, 30, 62]. The American Chemical Society Green Chemistry Institute Pharmaceutical Roundtable has identified greener alternatives to dipolar aprotic solvents as a key green chemistry research area [19].

Chapter 3

Analysis of NMP Use

Health Impact of NMP

As mentioned in the previous section, there is significant NMP use and waste generation in the resin precursor industry. This is true of the case study resin precursor process at the DuPont Parlin, NJ Plant. However; Table 3 shows that NMP use and waste generation is common throughout the entire specialty chemical sector. NMP is a dipolar aprotic solvent, typically used as a reaction medium, an extraction/purification solvent, a carrier solvent, and a stripping solvent [63]. NMP use is wide spread due to its strong solvating power which allows it to dissolve materials that will not dissolve in many other solvents. NMP is also important in applications that require a dipolar aprotic solvent [19]. However, there are problems associated with NMP use and waste generation, as NMP is harmful to humans and the environment.

In 2001, California listed NMP as a reproductive toxicant. In the following years, NMP has been placed under more scrutiny and most recently the European Union has begun to regulate NMP in sectors where it poses an inhalation hazard [64]. The major health concern associated with NMP is its reproductive toxicity. A study testing the reproductive effects of NMP found that NMP exposure caused multiple developmental problems in rats. NMP exposure reduced litter size, reduced postnatal survival and pup weight, decreased the number of viable fetuses, and decreased fetal body weight [65]. In addition, reduction of fertility in both males and females was observed. These health problems can occur without any maternal signs of toxicity. In an NMP developmental toxicity study on rabbits, it was found that NMP exposure negatively affected the health of the fetus [65]. However, there were no signs of maternal toxicity (death, food consumption, body weight, and uterus weight) or local effects at the application site. In addition to the negative health effects associated with NMP, it also negatively impacts the environment through emissions from manufacture and disposal.

TRI Analysis of NMP Waste Generation

The TRI data for NMP were analyzed to determine its use throughout the country as well as its use throughout different sectors of industry. Table 6 shows the quantity of NMP waste generated throughout the NACIS sectors in 2013 [14]. The sectors with the highest NMP waste generation in 2013 are Chemicals (18,697,534 lb); Computer and Electronics Products (10,171,889 lb); Plastics and Rubber Products (6,876,969 lb); and Electrical Equipment, Appliance, and Components (2,300,404 lb). The "other" sector (5,952,734 lb) combines NMP waste from the remaining TRI sectors, which individually have much lower quantities of NMP waste generation. The distribution of NMP waste in 2013, the most recent year of record, can be seen in Figure 5 [14].

Table 6

TRI of NMP in 2013 by sector [14]

Sector	**NMP Waste (lb)**	**Percentage (%)**
Chemicals	18,697,534	42.5
Computer and Electronic Products	10,171,889	23.1
Plastics and Rubber Products	6,876,969	15.6
Electrical Equipment, Appliance, Components	2,300,404	5.2
Other	5,952,734	13.5
Total	43,999,531	100

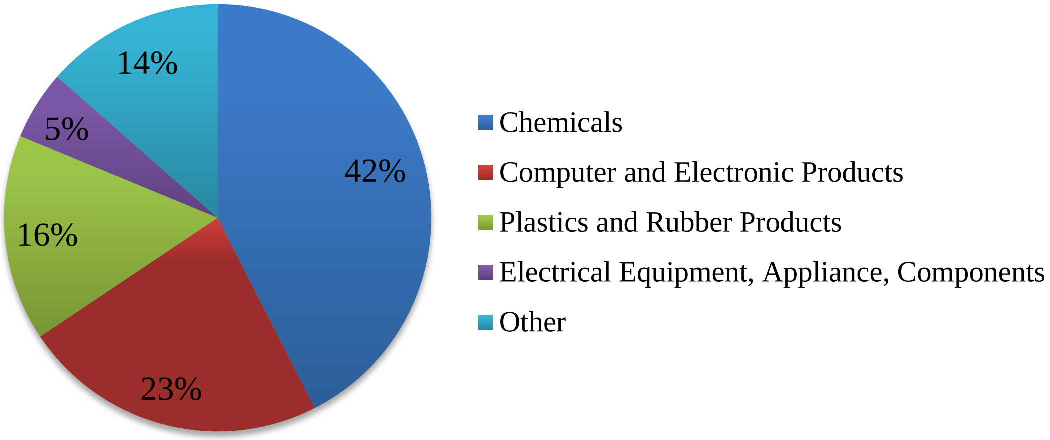


Figure 5. TRI of NMP in 2013 by sector [14]

The sectors where NMP is used were further investigated, by analyzing NAICS subsectors. These subsectors were analyzed to determine the quantity of waste NMP generated, as well as the significance of NMP waste in comparison to all toxic waste released by the subsector. In Table 7, subsectors of the Chemicals Sector are shown with the total quantity of NMP waste generated in 2013, the percentage of NMP in the waste of that subsector, and the rank of NMP compared to all other toxic chemicals released in that subsector [14]. This further investigation of the TRI data determined which subsectors of the chemical industry had high NMP waste. In terms of quantity, the All Other Basic Organic Chemicals Subsector had the highest NMP waste generation in 2013, with 4,700,869 lb of NMP waste. However, NMP accounts for only 0.155% of the total amount of waste generated by the subsector. This trend is the same for the Plastics Materials and Resins Subsector where the 4,421,275 lb of NMP waste only accounts for 0.239% of the total waste. In contrast, the Agrochemical and Pharmaceutical Subsectors generated 2,331,231 and 765,701 lb of NMP waste, respectively, with NMP use rankings of 20. Another subsector where NMP is a more significant portion of the waste is the

Printing Ink Subsector. In this subsector, 5,192 lb of NMP waste was generated. However, NMP is the 11th ranked chemical and it accounts for 0.998% of the total waste for the industry.

Table 7

TRI for NMP in the Chemical Sector for 2013 [14]

Subsector	NMP Waste (lb)	NMP in Total Subsector Waste (%)	NMP Ranking Among Waste
All Other Basic Organic Chemicals	4,700,869	0.155	64
Plastics Material and Resins	4,421,275	0.239	39
All Other Miscellaneous Chemical Product and Preparation	3,231,131	0.451	20
Pesticide and Other Agricultural Chemicals	2,331,231	0.289	20
Paint and Coating Manufacturing	771,997	0.662	9
Pharmaceutical and Medicine	765,701	0.371	20
Noncellulosic Organic Fibers	649,539	2.45	5
Custom Compounding of Purchased Resins	534,493	19.8	2
Photographic Film, Paper, Plate and Chemicals	433,073	2.35	5
Adhesive Manufacturing	216,580	1.55	11
Petrochemicals	191,849	0.0199	84
All Other Basic Inorganic Chemicals	97,403	0.0382	45
Synthetic Organic Dye and Pigment	49,782	1.01	9
Printing Ink	5,192	0.998	11
Fertilizer	2,710	0.221	7
Soap and Other Detergent Manufacturing	1,044	0.0791	25

Table 7 shows that NMP is more widely used in some subsectors than others. The total volume of waste for some subsectors may be lower than the All Other Basic Organic Chemicals or Plastics Material and Resins Subsectors, but NMP is a much more prominent chemical in these sectors. The Custom Compounding of Purchased Resins

(534,493 lb) and Photographic Film, Paper, Plate, and Chemicals (433,073 lb) Subsectors are two of the best examples of this situation. For these two subsectors, NMP accounts for a high percentage of waste, 19.8% and 2.35%, respectively. NMP is also one of the top ranking chemicals in each of these sectors. These sectors have smaller quantities of waste but NMP accounts for a larger majority of the waste in these industries. Some of these subsectors with high and/or significant NMP waste, and other subsectors listed in Table 7, are part of the specialty chemical sector, listed previously in Table 1.

The other sectors shown in Table 6 were also further investigated by analyzing NMP waste generation in NAICS subsectors. Table 8 shows NMP waste generation by subsectors within the Electronic Products Sector. NMP use in this sector is the second highest of all sectors analyzed. However, the Semiconductor and Related Devices Subsector generated 7,774,006 lb of NMP waste in 2013, highest of any NAICS subsector. NMP ranked second in this subsector, in terms of quantity of waste generated. Within the Electronic Products Sector, there are two subsectors which have NMP as the top ranking chemical in the waste. Other Electronic Components had 1,546,866 lb of NMP waste in 2013 and Computer Storage Devices had 681,437 lb which accounted for 26% and 93% of the waste in that subsector, respectively. The Analytical Laboratory Instruments Subsector generated 116,260 lb of NMP, accounting for 5.2% of the subsector’s waste. NMP ranks third in the Computer and Electronic Products Sector; accounting for 10% of the sector’s waste. The Semiconductor and Other Electronic Components Subsectors are part of the specialty chemical sector.

Table 8

TRI for NMP in the Computer and Electronic Products Sector for 2013 [14]

Subsector	**NMP Waste (lb)**	**NMP in Total Subsector Waste (%)**	**NMP Ranking Among Waste**
Semiconductor and Related Devices	7,774,006	14.9	2
Other Electronic Components	1,546,866	26.0	1
Computer Storage Devices	681,437	92.9	1
Analytical Laboratory Instruments	116,260	5.21	4
Bare Printed Circuit Boards	53,320	0.813	12

Table 9 shows an analysis of the subsectors within the Plastics and Rubber Products Sector. The Rubber Products for Mechanical Use Subsector generated the largest quantity of NMP waste throughout the Plastics and Rubber Products Sector, in 2013. This subsector generated 3,589,731 lb of NMP waste, accounting for 43% of the total waste in that subsector. The Laminated Plastics Plate, Sheet, and Shape Manufacturing and the Plastics Packaging Film and Sheets Subsectors generated 1,622,020 lb and 770,525 lb of NMP waste, respectively. NMP represented a significant portion of the toxic waste generated in these subsectors, accounting for 5% and 24% of the total waste, respectively. In these applications, NMP is used as a solvent in synthesis, separation, and purification processes. The subsectors within the Plastics and Rubber Products Sector are part of the specialty chemical sector. Other TRI subsectors that are not relevant to this project were not analyzed further.

Table 9

TRI for NMP in the Plastics and Rubber Products Sector for 2013 [14]

Subsector	NMP Waste (lb)	NMP in Total Subsector Waste (%)	NMP Ranking Among Waste
Rubber Products for Mechanical Use	3,589,731	43.2	1
Laminated Plastics Plate, Sheet (except Packaging), and Shape Manufacturing	1,622,020	5.18	6
Plastics Packaging Film and Sheets (including Laminated)	770,525	23.9	2
All Other Plastics Products	484,940	1.49	11
Unlaminated Plastics Film and Sheets (except Packaging)	376,506	0.434	21
All Other Rubber Products	18,493	0.102	20
Urethane and Other Foam Products (except Polystyrene)	14,755	0.171	14

TRI data were analyzed for the Parlin, NJ chemical plant to see the quantity and significance of NMP waste. NMP accounts for the largest amount of waste, as seen in Table 10. The total yearly quantity of NMP waste for the Parlin facility is 396,481 lb. This accounts for over 96% of all of the waste generated at the Parlin Plant. Taken in context of the national TRI values for the Plastics and Resins Subsection, shown in Table 7, the NMP waste generated at the Parlin Plant represents 9% of the sector. This shows that the Parlin Plant is a major use site for NMP.

Table 10

TRI for the Parlin Plant for 2013 [14]

Chemical	**Name**	**City**	**Total Waste (lb)**
Acrylonitrile	DuPont Parlin Plant	Parlin	894
Butyl acrylate	DuPont Parlin Plant	Parlin	392
Certain glycol ethers	DuPont Parlin Plant	Parlin	3,843
Methyl isobutyl ketone	DuPont Parlin Plant	Parlin	9,434
N-methyl-2-pyrrolidone	DuPont Parlin Plant	Parlin	396,481
Triethylamine	DuPont Parlin Plant	Parlin	430

Table 11 shows NMP use across DuPont in 2013. It is assumed that the NMP waste generation values from the TRI data is indicative of the yearly rate of NMP use at these facilities. This was done to see if there are other possible locations where recycled NMP could be sent or sold to. Due to the fact that DuPont requires high purity NMP (electronics grade), it might be difficult to reuse recovered NMP in their process. If the NMP recovery and purification system can purify the NMP to a high purity, but not electronic grade, it could be sent to one of the other seven DuPont facilities that report NMP waste.

Table 11

TRI for NMP at DuPont facilities for 2013 [14]

Name	**State**	**Total NMP Waste (lb)**
DuPont Spruance Plant	Virginia	649,539
DuPont Parlin Plant	New Jersey	396,481
DuPont Electronic Polymers	Ohio	183,070
DuPont Pontchartrain Works	Louisiana	143,944
DuPont EKC Technology	California	7,864
DuPont Sabine River Works	Texas	6,076
DuPont Towanda Plant	Pennsylvania	3,191
DuPont Circleville Plant	Ohio	2,212

TRI data from the past decade were analyzed to determine historical trends in NMP use, in the specialty and performance chemical sector. The TRI data was compiled from 2001 to 2013 for each of the subsectors within the specialty chemicals sector. Figure 6 shows the quantity of NMP waste generated by each subsector over the past 12 years. The pharmaceutical and medicine subsector (code 3254) has shown the largest decline in NMP waste. This decline of about 20.6% is due to the increased use of green engineering practices and green chemistry as well as for increased protection for workers and consumers. The use of NMP in the Plastic, Resin, Rubber, and Synthetic Fibers and Filaments Subsector (code 3252 and 326) and the Semiconductor and Other Electronic Components Subsector (code 3344) have been rising by 180% and 80%, respectively. This is due to the increased popularity of technology and electronic devices which are comprised of many types of plastics and electrical components.

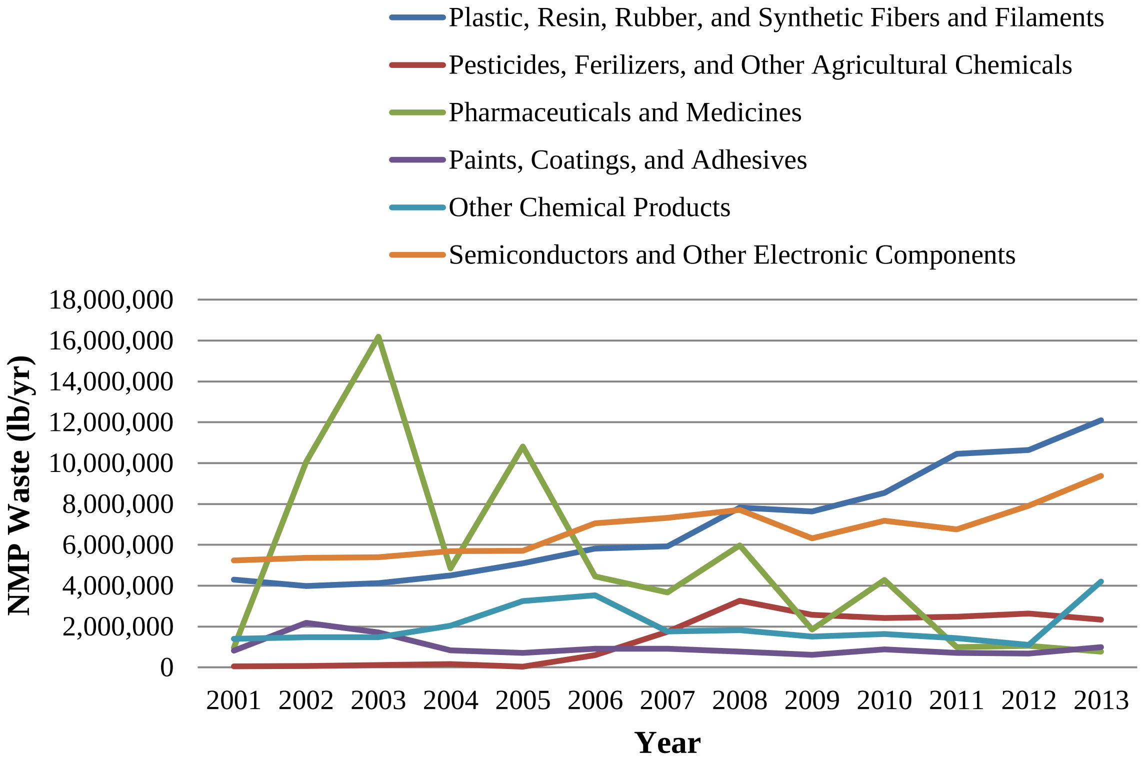


Figure 6. NMP waste generation in the specialty chemical sector from 2001-2013 [14]

Overall, NMP waste in industry has been rising during the past decade, as seen in Figure 7. It is assumed that the waste generation values from the TRI data for these sectors is proportional to the total NMP used in the industrial processes. This rise in NMP use is about 500,000 lb/yr. This gradual increase in use of NMP comes from the decreased use of NMP in some industries and increased use in others. Between 2001 and 2003 every industry was increasing its use of NMP. Then while the other industries continued to increase NMP use, the pharmaceutical industry began to use more environmentally friendly processes and lowered their use of NMP. From 2007 to 2012 every sector began to reduce the overall NMP use except the Plastic, Resin, Rubber, and Synthetic Fibers and Filaments Subsector (code 3252 and 326) and the Semiconductor and Other Electronic Components Subsector (3344) which continued to rise due to increased demand for electronic products.

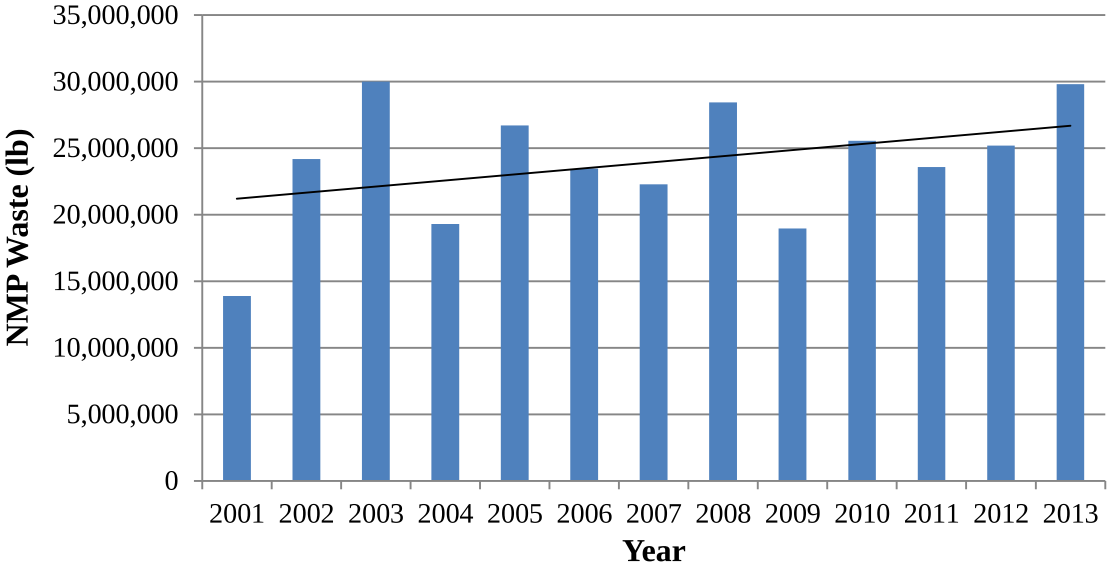


Figure 7. NMP TRI from 2001-2013 with trend line [14]

From an analysis of the TRI data for NMP, it is seen that NMP plays a significant role in the specialty chemical industry and other chemical related industries. NMP also plays a significant role in the waste generated by the Parlin Plant, and more broadly in EPA Region 2 and throughout DuPont. However, this is problem as NMP has environmental implications. This widespread use of NMP throughout the specialty chemical sector, Region 2, and DuPont shows that the NMP reduction efforts for this project will potentially benefit many other industries.

NMP Use in Industrial Sectors

Plastic materials and resins. The TRI analysis of NMP use showed that there is high NMP waste generation in the plastics, resins, and other related polymer industries. These industries include plastics and resins; paint and coating manufacturing; noncellulosic organic fibers; custom compounding of purchased resins; photographic film, paper, plate and chemicals; adhesives; and plastics and rubbers. From observing Table 7 and Table 9, it is seen that the Plastics Material and Resins Subsector had the highest NMP waste generation in 2013 of all polymer manufacturing related industries, at 4,421,275 lb. This industry is related to the polyimide precursor product manufactured by DuPont because the polyimide precursor is used to make polyimide resins. The paints and coatings industry is also related to the polyimide precursor because the polyimide precursor is used to create polyimide coatings. The Paints and Coatings Subsector reported 771,997 lb of NMP waste in 2013, where NMP is ranked as the 9th highest chemical waste. The polymer manufacturing industries related to the polyimide precursor product manufactured by DuPont were further investigated to determine the cause for high NMP waste generation.

NMP is a thermally and chemically stable polar compound, with powerful solvent abilities. Due to its beneficial solvent properties, NMP is used in the manufacture of polymers for membranes, coatings, resins, plastics, and rubbers. Commonly, NMP is used as a solvent for the synthesis and/or processing of thermoresistant polymers [66]. Thermoresistant polymers such as polyamides, polyimides, polyethersulfones, and polyarylene ethers are synthesized in NMP, due to their high solubility [49, 57, 59, 66, 67, 68, 69]. NMP is also as a solvent in the synthesis of polyurethanes [70]. Since NMP is not consumed in these syntheses, it exits the process as waste. This causes harm to the environment because NMP disposal and virgin NMP manufacture create pollutants.

NMP is also important in the processing of polymeric membranes [71]. A challenge in making polymeric membrane processing more sustainable is replacing the harmful solvents used in the manufacturing process, including NMP [71]. The solid membrane is washed in solvent to remove the polymer-lean phase and the membrane is sent to post treatment. Any NMP used in the formation process results in waste. Many polymeric membranes are manufactured using NMP. NMP is used as a solvent in the production of polysulfone and polyethersulfone membranes for ultrafiltration applications [72, 73, 74]. NMP is also widely used as a solvent for the processing of sulfonated aromatic polymeric membranes; where it is used to dissolve the polymer prior to casting [75].

Resins and coatings are prepared using similar methods to polymeric membranes and their manufacture also generates NMP waste [76, 77, 78]. In the microelectronics industry, spin coating is used to form photoresist and polyimide coatings. Polyamic acid, dissolved in NMP, is spin coated and cured to form a polyimide coating [79]. Polyamide, polyaniline, and polyoxadiazole coatings are also processed using NMP as solvent [67, 68, 80, 81]. Also, as with membrane processing, the NMP used as solvent for the coating process becomes waste. After the polymer-solvent solution is coated, the solvent is removed through evaporation, generating VOC solvent waste.

Pharmaceuticals and fine chemicals. The TRI analysis of NMP use showed that there is high NMP waste generation in the pharmaceutical and fine chemical industries. These industries include pharmaceuticals, pesticides agricultural chemicals, and dyes and pigments. From observing Table 7, it is seen that these NAICS subsectors report significant NMP waste. The pesticides and other agrochemicals subsector reported 2,331,231 lb of NMP waste in 2013, while the pharmaceuticals and medicines subsector reported 765,701 lb of NMP waste. NMP was ranked as the 20th highest chemical waste in these two subsectors, in 2013. The synthetic and organic dyes and pigments subsector reported 49,782 lb of NMP waste, where NMP ranked 9th. The pharmaceutical and fine chemical industries were further investigated to determine the cause for high NMP waste generation.

NMP has multiple uses in the pharmaceutical and fine chemical industries. In these industries, NMP is most commonly used as a reaction solvent. However, it is also used in extractions, recrystallizations, and purifications of different pharmaceutical drugs [63]. In all of these uses, NMP is not consumed by the reaction so it ends up as waste after it is separated from the product. Ashcroft *et al.* surveyed the use of dipolar aprotic solvents in literature for pharmaceutical and fine chemical synthesis [62]. They found that nearly 50% of dipolar aprotic solvent usage is for nucleophilic substitution reactions. Nucleophilic substitution reactions are much faster in dipolar aprotic solvents than in protic solvents. Also, dipolar aprotic solvents are useful in dissolving polar heterocyclic molecules, inorganic reagents, and salts [62]. In their survey, Ashcroft *et al.* found that NMP was the fourth most commonly used dipolar aprotic solvent; after acetonitrile, DMF, and DMSO. However, they found that NMP use is increasing over time [62]. For NMP specifically, more than 50% of its use in the pharmaceutical and fine chemical industries is for nucleophilic substitution reactions. About 25% of its use is for its solubility. NMP is used to a lesser extent in amide formation and workup [62].

A literature review of NMP use in the pharmaceutical and fine chemical industries further confirmed that NMP is commonly used as a solvent in substitution reactions. In one case, NMP is used to host the synthesis of an intermediate which is used to produce an active pharmaceutical ingredient used to treat high blood pressure [82]. NMP is also used as a solvent in the synthesis of antimalarial drugs and antivirals intended to treat viruses such as HIV, coxsackievirus, and Hepatitis C [83, 84, 85, 86, 87]. NMP is also used in the synthesis of drugs used to treat a variety of other illnesses including: diabetes, tuberculosis, schizophrenia, Alzheimer's, and the common cold [88, 89, 90, 91, 92]. In addition, NMP has been used to synthesize fine chemicals that could be used as intermediates in future drugs [93, 94].

NMP is also used as a solvent in the synthesis of different types of molecules used in the pharmaceutical and fine chemical industries. NMP is used as a solvent in the synthesis of nitriles from aldehydes. Nitriles are common organic compounds used as intermediates in a wide range of applications; including pharmaceuticals, pesticides, and dyes [95, 96]. Another example of NMP use in this sector is in the synthesis of heterocycles, which are intermediates for drugs and dyes [97]. In all of these examples, NMP is used as a reaction medium and is removed as waste during the synthesis procedure. This generates significant waste, as solvent can account for 80-90% of the total mass in the process [30, 35].

Chapter 4

Life Cycle Assessment

Life Cycle Boundaries

A life cycle assessment (LCA) is a cradle to grave analysis of the environmental impact associated with all stages of a product's life. This can include raw material extraction and product manufacturing, use, and disposal; depending on how the boundaries are selected. The overall goal of the LCA conducted in this report is to find an alternative process that reduces the environmental impact of the DuPont process and ultimately present these findings to DuPont. This will be done by quantitatively comparing the environmental impact of alternative processes to the current DuPont process, which will be referred to as the base case. The current DuPont process, shown in Figure 8, includes a reactor for resin precursor synthesis, a tank for precipitation and washing of the resin precursor, a filter press for drying of the solid resin precursor, and an ultrapure water production unit to produce ultrapure for washing. The washing process generates hazardous waste which contains water, significant quantities of NMP, and small quantities of resin precursor reagents. Non-hazardous wastewater is also generated which contains mostly water, with small quantities of NMP and regents. The DuPont process produces dried, solid resin precursor which is sent to a final formulation process. The final formulation involves dissolving the solid resin precursor in NMP with desired additives, such as adhesion promoters.

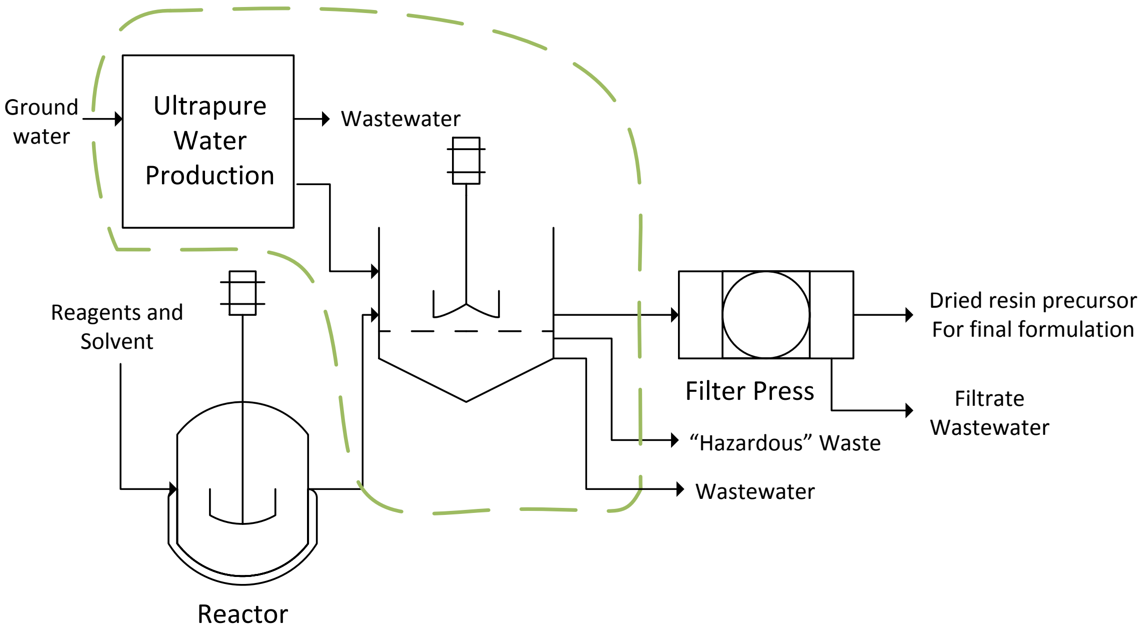


Figure 8. Current DuPont process with LCA boundaries

The boundaries of the LCA, outlined in Figure 8, include the inlet and outlet streams of the wash tank used to precipitate and wash the resin precursor. The ultrapure water production unit is also included within the LCA boundaries. Defining specific boundaries for the LCA is necessary in determining which impacts will be included. The current boundaries were chosen to focus on the solvent use and waste issues, which is of primary concern to DuPont. This method of process analysis of solvent use has been peer-reviewed on numerous occasions and is a valid approach for solvent issues, since the solvent is the main waste issue [18, 33, 32]. The LCA boundaries also allow for analysis of water use and waste issues associated with this process.

The reactor is outside of the LCA boundaries because DuPont is not open to changing their resin precursor syntheses procedure. The filter press is also outside of the

LCA boundaries since it is not relevant to solvent use. All solvent is removed from the resin precursor prior to drying in the filter press. Also, little wastewater is generated from filter press operation. Increasing the LCA boundary to include the entire resin precursor process could potentially allow for further opportunities to reduce environmental impact; however, the solvent use/waste issue is the best opportunity to reduce environmental impact. Also, this type of analysis is outside the scope of this project. Therefore, modifications of the synthesis process and filter press operation will not be made.

The current LCA boundaries shown in Figure 8 include the impact associated with the use of all chemicals entering the wash tank. This means that all emissions and resources used to manufacture raw materials: n-methyl-2-pyrrolidone (NMP), trifluoroacetic acid (TFA), hydroxyethyl methacrylate (HEMA), hydrochloric acid (HCl), and ultrapure water are included in the LCA. The impact of the disposal of the wash waste (hazardous waste and non-hazardous wastewater) is also included inside the LCA boundaries. The emissions and resources used from the resin precursor washing process are also accounted for in the LCA. The washing process requires utilities to agitate the wash tank, pump the reaction mass and ultrapure water into the wash tank, and pump the waste and solid resin precursor from the wash tank. The emissions and resource use from utility use impact the LCA of the process. However, the same utilities are also used in all alternative processes. This means that the emissions and resource use, due to utility use during the washing process, do not change for alternative processes. However, alternative processes will have additional utility use from operation of recovery equipment (e.g. distillation column or membrane pervaporation unit). This additional utility use will be included in the LCA of the alternative processes.

The material use and waste generated for the base case (current DuPont process) is shown in Table 12. These values are representative of annual process flows which will be used to perform this case study. The current DuPont process uses 404,000 lb/yr of virgin NMP and 9,062,000 lb/yr of ultrapure water. This process also uses 36,000 lb/yr of minor reagents, which includes HEMA, HCl, and TFA. This process generates 2,375,000 lb/yr of hazardous solvent waste and 7,126,000 lb/yr of non-hazardous wastewater. The composition of the hazardous solvent waste and non-hazardous wastewater is shown in Table 13. As mentioned previously, the utilities used during the washing process do not change for alternative processes. The annualized quantities of raw materials and waste will be used to calculate the LCA of the current DuPont process (base case). This LCA will be compared to the LCA of the alternative process, to see if there is a reduction in emissions and resource use.

Table 12

Raw material use, utility use, and waste generation for the current DuPont process

	Quantity (lb/yr)
NMP	404,000
Minor Reagents	36,000
HEMA	12,000
TFA	12,000
HCl	12,000
Ultrapure Water	9,062,000
Hazardous Waste	2,375,000
Wastewater	7,126,000
Process Steam	Constant for all processes
Electricity	Constant for all processes
Other Reagents	Outside of boundaries

Table 13

Hazardous waste and wastewater compositions

Component	Hazardous Solvent Waste Composition	Non-hazardous Wastewater Composition
Water	81.5 wt.%	99.835
NMP	17 wt.%	0.15 wt.%
HEMA	0.5 wt.%	50 ppm
TFA	0.5 wt.%	50 ppm
HCl	0.5 wt.%	50 ppm

Life Cycle Inventories

The first step in this study was an analysis of the life cycle inventory of each input and output. A life cycle inventory (LCI) is a summary of all the emissions associated with a given process. In this case, the LCI for the manufacture or disposal of a chemical or utility was determined on a certain basis, such as 1 lb or 1 MJ. This summary consists of all emissions released to soil, water, and air; from the manufacture or disposal process. In addition to emission data, the LCI contains data on water and energy use. The cumulative energy demand (CED) is used to express energy use of the process. The CED is the overall energy required for the defined manufacture or disposal process [98]. The LCI data was used to perform an LCA, for comparison of the environmental impact of alternative processes to the current DuPont resin precursor process (base case).

LCIs of the manufacture of chemicals and utilities used in the DuPont resin precursor process were generated. These chemicals include NMP, TFA, HEMA, HCl, and ultrapure water. The utilities included steam and electricity. Disposal of the 17% hazardous solvent waste is modeled as incineration and disposal of the 0.15% NMP wash water waste is modeled as being sent to a wastewater treatment plant. LCIs for the incineration of the hazardous waste and treatment of the non-hazardous wastewater were also found. All LCIs were found using SimaPro® Version 8. SimaPro® is an LCA software, which contains databases of LCI data. This software quantifies raw material use, energy use, and emissions for processes in its databases. These processes include the manufacture of certain chemicals and utilities, and the disposal of some materials [99]. The SimaPro® databases contain data for common products and processes, so they do not contain the LCI data for the manufacture of all chemicals. LCIs for compounds not in the SimaPro® databases were modeled through synthesis of compounds within the database or by product substitutions. These methods are discussed later in the report. The LCIs generated in SimaPro® were exported to Microsoft® Excel, where a Microsoft® Excel template was used to organize the data. The template was used to calculate the total emissions and the emissions to air, water, and soil for the process. In addition, the emissions of common pollutants were calculated. These pollutants include CO_2, CO, CH_4, NO_X, non-methane volatile organic compounds (NMVOC), particulates, and SO_2

emissions released into the air, and VOC emissions released into the water. The water use and CED were also calculated using the template.

N-methyl-2-pyrrolidone. The NMP used as solvent in the DuPont process is electronics grade. Electronics grade NMP has a purity of 99.85 wt.% and a water composition of 0.03 wt.%, with the remaining impurities consisting of reagents used in the manufacturing process [100]. The SimaPro® database contains a process to model the manufacture of NMP. The NMP produced by the process modeled in SimaPro® is 99.5% pure, which is very close to the purity of the NMP used in the DuPont process. Within SimaPro®, the manufacture of NMP is modeled by the condensation of butyrolactone with methylamine, as seen in in Equation 1 [101]. This is the current commercial route for synthesizing NMP [102]. The SimaPro® model for NMP manufacture was created using the LCI data for butyrolactone and methyl amine, assuming a 95% yield [101]. The SimaPro® model also includes additional data based on cooling water use, energy use, and transportation. This information was obtained from chemical manufacturing plants in Europe.

$$C_4H_6O_2 + CH_5N \rightarrow C_5H_9NO + H_2O \tag{1}$$

The LCI for the manufacture of NMP was calculated on a 1 lb basis, using SimaPro®. In Table 14, it is shown that 4.22 lb of total emissions is generated from the manufacture of 1 lb of NMP. These emissions consist mostly of emissions to air, which total 3.77 lb or 89% of the total emissions. CO_2 contributes to 99% of the air emissions released from NMP manufacture. The remaining 1% of air emissions is mainly CH_4,

NO_X, and SO_2. Emissions to water contribute to 11% of the total emissions, while emissions to soil are trace. The amount of water and energy used to manufacture 1 lb of NMP is very high, at 11,300 lb and 41 MJ, respectively.

Table 14

LCI for the manufacture of 1 lb of generic solvent and NMP

	Generic Solvent	**NMP**
Water Used (lb)	1.67E+03	1.13E+04
Total Air Emissions (lb)	1.91E+00	3.77E+00
CO_2 (lb)	1.87E+00	3.72E+00
CO (lb)	2.25E-03	2.38E-03
CH_4 (lb)	1.29E-02	9.68E-03
NO_X (lb)	4.47E-03	5.73E-03
NMVOC (lb)	1.98E-03	1.88E-03
Particulate (lb)	1.26E-03	2.08E-03
SO_2 (lb)	5.90E-03	7.45E-03
Total Water Emissions (lb)	1.49E-01	4.51E-01
VOCs (lb)	7.44E-07	4.69E-06
Total Soil Emissions (lb)	2.20E-04	1.44E-03
Total Emissions (lb)	**2.05E+00**	**4.22E+00**
CED (MJ)	2.99E+01	4.07E+01

The LCI of the manufacture of NMP was compared to the LCI of the manufacture of “generic solvent” shown in Table 14. The “generic solvent” is an equal mixture of the 15 most commonly used industrial solvents. It consists of 1-butanol, methanol, acetone, toluene, xylene, styrene, nitrobenzene, isopropanol, cumene, ethyl benzene, ethylene glycol, cyclohexanol, methyl ethyl ketone, dichloromethane, and tetrachloroethylene. It was found that the total emissions released from the manufacture of NMP were double the emissions released from the manufacture of generic solvent. The CO_2 emissions generated from NMP manufacture were also double those generated from the manufacture of generic solvent. All types of emissions were generated in higher quantities in the manufacture of NMP, in comparison to the manufacture of generic solvent, except CH_4 and NMVOC (non-methane volatile organic compounds) emissions which were slightly higher for the generic solvent. The CED of NMP was also compared to the CED for an average solvent. The CED for NMP (41 MJ) is about 35% greater than the CED for an average solvent, which is 30 MJ. This comparison shows that the manufacture of NMP has a high environmental impact, even when compared to other commonly used organic solvents.

Trifluoroacetic acid. The manufacture of TFA is not modeled within the SimaPro® databases. However, the compounds used to manufacture TFA are modeled in SimaPro®. TFA is synthesized using a two-step process [103]. In the first step, shown in Equation 2, acetic anhydride is reacted with hydrogen fluoride to produce trifluoroacetyl fluoride, oxygen difluoride, and hydrogen. In the second step, shown in Equation 3, trifluoroacetyl fluoride is hydrolyzed to produce TFA and hydrogen fluoride [103]. Using stoichiometry, it was calculated that 0.448 lb of acetic anhydride, 0.877 lb of hydrogen fluoride, and 0.158 lb of deionized water are required to synthesize 1 lb of TFA. These quantities of acetic anhydride, hydrogen fluoride, and deionized water were used to create a process for TFA manufacture in SimaPro®.

$$C_4H_6O_3 + 10HF \rightarrow 2C_2F_4O + OF_2 + 8H_2 \qquad (2)$$

$$C_2F_4O + H_2O \rightarrow C_2F_3O_2H + HF \qquad (3)$$

The energy required for these reactions was also estimated using the enthalpy of reaction for the first and second reactions. Both reactions are endothermic, so the enthalpy of reaction is the energy absorbed by the reaction. Enthalpy of reaction was calculated using Equation 4. The values used for enthalpy of formation (ΔH_f^o) are shown in Table 15. It was calculated that 691 kJ is required to synthesize 1 mol of trifluoroacetyl fluoride, and 57 kJ is required to hydrolyze 1 mol of trifluoroacetyl fluoride into TFA. Overall, 748 kJ is required to synthesize 1 mol of TFA. The energy requirement to manufacture 1 lb of TFA was incorporated to the SimaPro® model by adding a process steam input of 3 MJ.

$$\Delta H_{reaction} = \sum \Delta H_f^{\circ}\, products - \sum \Delta H_f^{\circ}\, reactants \tag{4}$$

Table 15

Enthalpies of formation for products and reactants of TFA synthesis

Chemical	**ΔH_f^o (kJ/mol)**
Trifluoroacetyl fluoride	-1000 [104]
Oxygen difluoride	24.5 [105]
Hydrogen	0
Acetic anhydride	-625 [106]
Hydrogen fluoride	-273 [107]
Water	-286 [108]
Trifluoroacetic acid	-1070 [109]

In Table 16, it is shown that 4.80 lb of total emissions is generated from the manufacture of 1 lb of TFA. These emissions consist mostly of emissions to air, which total 4.29 lb or 89% of the total emissions. CO_2 contributes to 97% of the air emissions released from TFA manufacture; while the remaining 3% of air emissions is mainly CH_4, NO_X, and SO_2. Emissions to water contribute to 11% of the total emissions, while emissions to soil are trace. The amount of water and energy used to manufacture 1 lb of TFA are 18,400 lb and 42 MJ, respectively.

Table 16

LCI for the manufacture of 1 lb of TFA

Water Used (lb)	1.84E+04
Total Air Emissions (lb)	4.29E+00
CO_2 (lb)	4.16E+00
CO (lb)	6.15E-03
CH_4 (lb)	1.02E-02
NO_X (lb)	1.01E-02
NMVOC (lb)	1.28E-03
Particulate (lb)	3.92E-03
SO_2 (lb)	7.14E-02
Total Water Emissions (lb)	5.04E-01
VOCs (lb)	1.01E-05
Total Soil Emissions (lb)	2.83E-03
Total Emissions (lb)	**4.80E+00**
CED (MJ)	4.20E+01

Hydroxyethyl methacrylate. The manufacture of HEMA is also not modeled in the SimaPro® databases. However, the manufacture of a similar chemical, methyl methacrylate, is modeled in SimaPro®. The manufacture of HEMA was modeled after the manufacture of methyl methacrylate because their manufacturing processes are similar. Eastman Chemical Company and Dow Chemical Company both produce HEMA and methyl methacrylate using a three step process. The difference in manufacture occurs in the third step where methacrylic acid undergoes an esterification reaction to form methyl methacrylate, or methacrylic acid is reacted with ethylene oxide to form HEMA [110, 111]. This is the only step that differs in the manufacturing process, which allows us to say that the manufacturing processes are similar. It makes sense that the manufacturing routes are similar because the chemical structure of HEMA and methyl methacrylate are similar, as shown in Figure 9.

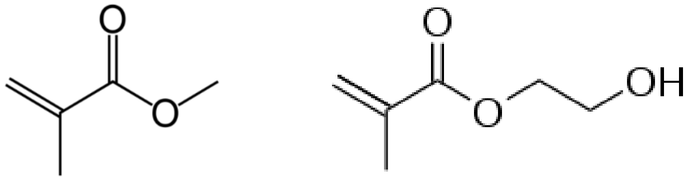


Figure 9. Molecular structure of methyl methacrylate (left) and HEMA (right)

The LCI for the manufacture of 1 lb of HEMA is listed in Table 17. The total emissions, 5.78 lb, are relatively large compared to the LCIs of the other chemicals used in the DuPont process. These emissions are mostly associated of emissions to the air, which constitute 5.70 lb or 99% of the total emissions from HEMA manufacture. The emissions to air are mostly CO_2, which accounts for 98% of the air emissions. The emissions to water represent 1% of the total emissions, while emissions to soil are trace. The CED for the manufacture of HEMA is also high, at 57 MJ. However, 129 lb of water is used to manufacture 1 lb of HEMA, which is low compared to NMP and HCl manufacture.

Table 17

LCI for the manufacture of 1 lb of HEMA

Water Used (lb)	1.29E+02
Total Air Emissions (lb)	5.70E+00
CO_2 (lb)	5.59E+00
CO (lb)	9.14E-03
CH_4 (lb)	4.44E-02
NO_X (lb)	1.23E-02
NMVOC (lb)	1.14E-02
Particulate (lb)	1.77E-03
SO_2 (lb)	2.35E-02
Total Water Emissions (lb)	8.67E-02
VOCs (lb)	6.50E-08
Total Soil Emissions (lb)	1.27E-05
Total Emissions (lb)	**5.78E+00**
CED (MJ)	5.66E+01

Hydrochloric acid. There are many different routes for HCl production that are modeled in the SimaPro® databases. It is assumed that the HCl used in the DuPont process is produced using the most common processing route for pure HCl. This process is the generation of HCl from the exothermic reaction of chlorine and hydrogen, as seen in Equation 5 [112]. This process involves burning hydrogen gas and chlorine gas within a combustion chamber, to produce hydrogen chloride. The HCl gas passes through a cooler and then an absorber. In this absorption process water is introduced, which produces aqueous hydrochloric acid [113]. Technical grade was assumed for this process, which is 31% - 33% HCl. Information from manufacturing sites in Europe was used to create the LCI for HCl production through synthesis of hydrogen and chlorine [114].

$$H_2 + Cl_2 \rightarrow 2HCl \tag{5}$$

The LCI data for the manufacture of 1 lb of HCl are shown in Table 18. The manufacture of 1 lb of HCl requires 9,290 lb of water. The total emissions (1.50 lb) and the CED (13 MJ) associated with the manufacture of HCl are much lower compared to NMP, generic solvent, TFA and HEMA. The LCI of the manufacture of HCl follows trends similar to the LCIs of other chemicals used in the DuPont process. The emissions generated in by the manufacture HCl consist mostly of emissions to air, which total 1.28 lb or 83% of the total emissions. CO_2 contributes to 99% of the air emissions released from HCl manufacture. Emissions to water contribute to 17% of the total emissions, while emissions to soil are trace.

Table 18

LCI for the manufacture of 1 lb of HCl

Water Used (lb)	9.29E+03
Total Air Emissions (lb)	1.28E+00
CO_2 (lb)	1.27E+00
CO (lb)	9.20E-04
CH_4 (lb)	2.58E-03
NO_X (lb)	2.37E-03
NMVOC (lb)	2.78E-04
Particulate (lb)	1.33E-03
SO_2 (lb)	4.25E-03
Total Water Emissions (lb)	2.18E-01
VOCs (lb)	1.26E-06
Total Soil Emissions (lb)	4.13E-04
Total Emissions (lb)	**1.50E+00**
CED (MJ)	1.28E+01

Ultrapure water. The water used in the DuPont process is classified as ultrapure. The LCI of ultrapure water was analyzed using SimaPro®. The SimaPro® databases model the manufacture of ultra-pure water as the process of electrodeionization [115]. However, the water purification process at the DuPont Parlin Plant uses reverse osmosis (RO) followed by ion exchange to purify ground water from an aquifer. LCI data for ultrapure water produced using electrodeionization, deionized water produced from ground water using RO, and deionized water produced from drinking water using ion exchange were determined using SimaPro®, shown in Table 19. The LCI data for ultrapure water produced at the DuPont Parlin Plant was calculated using the LCI data for deionized water produced by RO and ion exchange. The LCI data for the production of 1 lb of deionized water from ground water using RO was added to the LCI data for the production of 1 lb of deionized water from drinking water using ion exchange. This was done because to produce 1 lb of ultrapure water using the DuPont ultrapure water production system, 1 lb of water treated through RO is sent through the ion exchange unit to produce 1 lb of ultrapure water. The LCI for the production of 1 lb of ultrapure water using both RO and ion exchange is shown in Table 20.

Table 19

LCIs for the manufacture of 1 lb of ultrapure water, RO DI water, and ion exchange DI water

	Ultrapure Water	**RO DI Water**	**Ion Exchange DI Water**
Water Used (lb)	5.08E+00	1.02E+00	9.43E+00
Total Air Emissions (lb)	6.83E-04	8.17E-03	1.03E-03
CO_2 (lb)	6.77E-04	8.12E-03	1.02E-03
CO (lb)	1.30E-06	3.30E-06	1.72E-06
CH_4 (lb)	1.17E-06	1.27E-05	1.55E-06
NO_X (lb)	1.07E-06	1.57E-05	1.62E-06
NMVOC (lb)	1.04E-07	5.52E-07	1.86E-07
Particulate (lb)	6.81E-07	9.49E-07	9.45E-07
SO_2 (lb)	1.77E-06	1.46E-05	2.40E-06
Total Water Emissions (lb)	5.45E-04	1.89E-03	4.56E-04
VOCs (lb)	5.22E-10	6.14E-11	9.77E-10
Total Soil Emissions (lb)	1.19E-07	1.86E-07	3.13E-07
Total Emissions (lb)	**1.23E-03**	**1.01E-02**	**1.48E-03**
CED (MJ)	5.48E-03	4.73E-02	8.69E-03

Table 20

LCI for the manufacture of 1 lb of ultrapure water using RO and ion exchange

Water Used (lb)	1.05E+01
Total Air Emissions (lb)	9.19E-03
CO_2 (lb)	9.13E-03
CO (lb)	5.02E-06
CH_4 (lb)	1.42E-05
NO_X (lb)	1.73E-05
NMVOC (lb)	7.38E-07
Particulate (lb)	1.89E-06
SO_2 (lb)	1.70E-05
Total Water Emissions (lb)	2.35E-03
VOCs (lb)	1.04E-09
Total Soil Emissions (lb)	4.99E-07
Total Emissions (lb)	1.15E-02
CED (MJ)	4.81E-02

A comparison of the LCI data for ultrapure water produced through electrodeionization and ultrapure water produced using the system at the DuPont Parlin Plant showed that the process used to purify water significantly impacts the LCI. The DuPont ultrapure water system (RO and ion exchange) releases 13 times more CO_2 into the air than the electrodeionization process. In addition, the energy requirement for the DuPont ultrapure water system is 9 times greater than that for the electrodeionization process. The DuPont system also uses two times more water than the electrodeionization process. The LCI data for deionized water produced by RO and ion exchange was used because it more accurately represents ultrapure water production at the DuPont Parlin Plant.

In Table 20, it is shown that 0.0115 lb of total emissions is generated from the manufacture of 1 lb of ultrapure water. These emissions consist mostly of emissions to air, which total 0.00919 lb or 80% of the total emissions. CO_2 contributes to 99% of the air emissions released from the DuPont ultrapure water process. The remaining 1% of air emissions is mainly CH_4, NO_X, and SO_2. Emissions to water contribute to 20% of the total emissions, while emissions to soil are trace. The CED to produce 1 lb of ultrapure water using DuPont’s system is relatively low, at 0.048 MJ.

Electricity. The electricity used at the DuPont Parlin, NJ Plant comes from the local electrical grid. However, SimaPro$^{®}$ does not have a process to model electricity generation in central New Jersey. The processes in SimaPro$^{®}$ for electricity generation may not be accurate for New Jersey because these processes may not use the fuels typically used in New Jersey. In order to accurately model electricity generation in New Jersey, a custom model was created in SimaPro$^{®}$. The custom model was created using data from the U.S. Energy Administration. In New Jersey, electricity is generated from coal, natural gas, nuclear power, and renewable resources. The fraction of electricity generated by each energy source in 2014 is shown in Table 21 [116]. Table 21 shows that the most common fuels used to produce electricity in New Jersey are natural gas and nuclear power, accounting for 94% of electricity generation. The remaining 6% of electricity is generated from coal and renewable resources.

Table 21

Net electricity generation by source in New Jersey for 2014 [116]

	Coal	**Natural Gas**	**Nuclear**	**Other Renewables**	**Total**
Electricity by Source (GWh)	2,551	30,667	31,507	1,449	66,174
Percentage of Total Electricity (%)	3.9	46.3	47.6	2.2	

The model created in SimaPro® consisted of a combination of all resources used to generated electricity in New Jersey. The percentages associated with each fuel type, shown in Table 21, were used to create the model. In SimaPro®, the inputs used to create 1 MJ of electricity in New Jersey were 0.039 MJ of electricity from coal, 0.463 MJ of electricity from natural gas, 0.476 MJ of electricity from nuclear power, and 0.022 MJ of electricity from biomass. The LCI data for each source of electricity was based off of averaged data from power plants in the United States, which produce electricity from the specified resource. Biomass was chosen to represent renewable resources because the renewable resources used in New Jersey to generate electricity consisted mostly of biomass [116].

The LCI data for the production of 1 MJ of electricity in New Jersey is provided in Table 22. The total emissions released to the environment for the production of 1 MJ of electricity are 0.245 lb. These emissions consist mostly of emissions to air, which total 0.215 lb or 88% of the total emissions. CO_2 contributes to 98% of the air emissions released from electricity generation. The remaining 2% of air emissions is mainly CH_4 and SO_2. Emissions to water contribute to 12% of the total emissions, while emissions to soil are trace. The CED to produce 1 MJ of electricity is 3.88 MJ.

Table 22

LCI of the manufacture of 1 MJ of electricity in New Jersey

Water Used (lb)	3.54E+01
Total Air Emissions (lb)	2.15E-01
CO_2 (lb)	2.11E-01
CO (lb)	1.43E-04
CH_4 (lb)	1.01E-03
NO_X (lb)	1.89E-04
NMVOC (lb)	6.53E-05
Particulate (lb)	7.17E-05
SO_2 (lb)	1.78E-03
Total Water Emissions (lb)	2.98E-02
VOCs (lb)	1.07E-07
Total Soil Emissions (lb)	3.85E-06
Total Emissions (lb)	**2.45E-01**
CED (MJ)	3.88E+00

Steam. The DuPont Parlin Plant produces steam using natural gas. In this process, natural gas is combusted to provide heat energy to boil water, thus generating steam. In SimaPro®, the LCI data for process steam generated from natural gas were used to model the steam generation process at the DuPont Parlin Plant. The LCI for the generation of process was calculated on a 1 MJ basis, using SimaPro®. In Table 23, it is shown that 0.148 lb of total emissions is generated from the manufacture of 1 MJ of process steam. These emissions consist mostly of emissions to air, which total 0.148 lb or almost 100% of the total emissions. CO_2 contributes to 99% of the air emissions released from electricity generation. The remaining 1% of air emissions is mainly CH_4, NO_X, CO, and SO_2. Emissions to water and soil are trace. The amount of water and energy used to manufacture 1 MJ of process steam is 0.00265 lb and 1.19 MJ, respectively.

Table 23

LCI of the manufacture of steam produced by natural gas

Water Used (lb)	2.65E-03
Total Air Emissions (lb)	1.48E-01
CO_2 (lb)	1.47E-01
CO (lb)	5.27E-05
CH_4 (lb)	2.34E-04
NO_X (lb)	9.87E-05
NMVOC (lb)	1.25E-06
Particulate (lb)	1.77E-06
SO_2 (lb)	5.09E-05
Total Water Emissions (lb)	7.12E-04
VOCs (lb)	7.99E-09
Total Soil Emissions (lb)	6.12E-06
Total Emissions (lb)	**1.48E-01**
CED (MJ)	1.19E+00

Hazardous waste incineration. The DuPont process generates hazardous waste from the washing process. This waste contains water and 17% NMP, with a small composition of HCl, TFA, and HEMA. The case study treats the hazardous waste as being sent off site for incineration. The HCl, TFA, and HEMA in the hazardous waste are ignored since their incineration will have a negligible impact on the environment, due to their low composition. So, the incineration of DuPont's hazardous waste is modeled as the incineration of NMP and water. In previous Rowan studies, the environmental impact of solvent incineration was modeled using EcoSolvent. EcoSolvent provides raw material use and the emissions released for the incineration of a specified solvent mixture. It was decided that it would be better to use SimaPro® to model the environmental impact of solvent incineration because it would provide a more detailed LCI and impact assessment methods not available in EcoSolvent. Also, NMP is not in the EcoSolvent database, so a replacement such as DMF would have to be used. The SimaPro® database has a process that models the incineration of aqueous solvent, containing 16.5 wt.% water. The incineration process used in SimaPro® models the incineration of generic solvent, with designated upper and lower heating values of 41.8 MJ/kg and 34.7 MJ/kg, respectively. The SimaPro® data is based off of a German plant using a thermal incinerator that is common throughout Europe, North America, and Japan [117]. It is reasonable to assume that the life cycle emission data would be similar to solvent incineration in North America as solvent combustion requires the same energy input and releases the same combustion products in all parts of the world.

In order to ensure that the SimaPro® incineration process is accurate, the EcoSolvent LCI data were compared to the SimaPro® LCI data. The EcoSolvent LCI was found for waste containing 16.5 wt.% water and 83.5 wt.% DMF, since NMP is not in EcoSolvent. This composition was chosen because it allows for direct comparison with the SimaPro® LCI, which models the incineration of waste containing 16.5 wt.% water and 83.5 wt.% generic solvent. The LCIs, listed in Table 24, provide the emissions generated and water used in the incineration of solvent waste. The SimaPro® LCI is more detailed, as it includes emissions to water and soil. However, the air and CO_2 emissions are very similar for the SimaPro® and EcoSolvent LCIs. The air and CO_2 emissions for the SimaPro® and EcoSolvent LCIs have percent differences of 3.1% and 3.6%, respectively. These LCIs are also similar to the incineration of 1 lb of generic solvent, which generates about 2 lb of air emissions [32]. This comparison shows that SimaPro® also accurately models the incineration of solvent waste containing 16.5 wt.% water.

Table 24

LCI for incineration of 1 lb of DMF/H_2O solvent waste (16.5 wt.% water and 83.5 wt.% solvent)

	Incineration (SimaPro®)	**Incineration (EcoSolvent)**
Water Used (lb)	5.43E+02	8.73E+01
Total air emissions (lb)	1.97E+00	1.91E+00
CO_2 (lb)	1.97E+00	1.90E+00
CO (lb)	2.06E-04	2.26E-05
CH_4 (lb)	3.15E-04	0.00E+00
NO_X (lb)	7.79E-04	4.54E-03
NMVOC (lb)	9.08E-05	3.09E-06
Particulate (lb)	1.53E-04	3.78E-05
SO_2 (lb)	4.04E-04	0.00E+00
Total Water Emissions (lb)	1.24E-01	0.00E+00
VOCs (lb)	8.16E-07	0.00E+00
Total Soil Emissions (lb)	1.69E-04	0.00E+00
Total Emissions (lb)	**2.09E+00**	**1.91E+00**
CED (MJ)	1.71E+00	0.00E+00

Prior to calculating the LCI for the incineration of DuPont’s solvent waste, the SimaPro® solvent waste incineration model was modified to account for the energy recovered from incineration. Typically, the energy released from the incineration of solvent waste, is used to generate steam. This means that steam is a usable byproduct created from the incineration process. To accurately determine the LCI of the incineration of solvent waste, the byproduct steam should be taken into account natural gas combustion is avoided for the steam produced from solvent incineration. The SimaPro® model for solvent waste incineration shows about 9 MJ of heat is released to air and water per lb of waste incinerated, indicating that the SimaPro® model does not account for energy recovery. To account for energy recovery, process steam from natural gas was added as a byproduct credit. For this case, byproduct credits refer to the emissions saved from not having to combust natural gas to produce steam. Typically, incinerators have an efficiency of about 75%, so it was assumed that 75% of the heat released to air and water would be converted into steam [118]. This means that the emissions associated with the production of 6.75 MJ of steam, using natural gas, are avoided. SimaPro® modeled the modified solvent incineration process by subtracting the life cycle emissions of the production of 6.75 MJ of steam from the life cycle emissions of the incineration of 1 lb of solvent waste.

The resulting LCI was modified because the solvent waste in the SimaPro® incineration process contains 16.5 wt.% water. This is similar to DuPont's solvent waste, which also contains water. However, DuPont's solvent waste contains much more than 16.5 wt.% water. But, the water in the solvent waste does not lead to pollutant emissions because it forms water vapor during incineration. Water vapor is not a pollutant, so it is not included in the LCI. The LCI emissions are only associated with the incineration of solvent, which does create pollutants. This means that the solvent in the waste affects the LCI, not the water. The LCI data from SimaPro® for the incineration of 1 lb of solvent waste (16.5 wt.% water) was divided by the mass fraction of solvent in the waste (0.835), to calculate the LCI data for the incineration of 1 lb of solvent (0 wt.% water). This was then multiplied by the mass fraction of solvent in DuPont's waste, 0.17, to calculate the LCI for the incineration of 1 lb of DuPont's solvent waste. Equation 6, was used to calculate the LCI for incineration of DuPont's waste, which contains 17 wt.% solvent.

$$LCI_{1\ lb\ DuPont\ waste} = LCI_{1\ lb\ SimaPro\ waste} \cdot \frac{0.17}{0.835} \tag{6}$$

The LCI for the incineration of 1 lb of solvent waste, containing 17 wt.% solvent, is shown in Table 25. As mentioned previously, byproduct credit was given for the steam generated from the heat released from incineration. Byproduct credits are shown in Table 25, along with the life cycle emissions before and after inclusion of credits. The emissions released from incineration are low due to byproduct credit. Some emissions even have a negative value because byproduct credits are larger than the emissions released from incineration. With incorporation of byproduct credits, the incineration of 1 lb of DuPont's waste generates 0.217 lb of total emissions. These emissions consist mostly of emissions to air, which total 0.192 lb or 88% of the total emissions. These air emissions consist largely of CO_2. The CO and CH_4 emissions to air are negative, indicating that steam production through solvent incineration generates less CO and CH_4 emissions than steam production through combustion of natural gas. However, overall solvent incineration is an inferior method of generating steam, as all other emissions and water use are greater for steam production through solvent incineration.

Table 25

LCI for the incineration of 1 lb of DuPont's hazardous waste (17 wt.% NMP and 83 wt.% water)

	Incineration	**Byproduct credit**	**Overall**
Water Used (lb)	1.11E+02	-7.34E-03	1.11E+02
Total Air emissions (lb)	4.01E-01	-2.09E-01	1.92E-01
CO_2 (lb)	4.00E-01	-2.07E-01	1.93E-01
CO (lb)	4.20E-05	-7.45E-05	-3.25E-05
CH_4 (lb)	6.41E-05	-3.31E-04	-2.67E-04
NO_X (lb)	1.59E-04	-1.40E-04	1.89E-05
NMVOC (lb)	1.85E-05	-1.77E-06	1.67E-05
Particulate (lb)	3.12E-05	-2.50E-06	2.87E-05
SO_2 (lb)	8.23E-05	-7.21E-05	1.02E-05
Total Water Emissions (lb)	2.52E-02	-1.01E-03	2.42E-02
VOCs (lb)	1.66E-07	-1.13E-08	1.55E-07
Total Soil Emissions (lb)	3.44E-05	-8.66E-06	2.57E-05
Total Emissions (lb)	4.26E-01	-2.09E-01	**2.17E-01**
CED (MJ)	3.49E-01	-1.69E+00	-1.34E+00

Non-hazardous wastewater disposal. In addition to hazardous waste, the DuPont process also generates non-hazardous wastewater from the washing process. This waste contains water with trace quantities of NMP (0.15%), HCl, TFA, and HEMA. This wastewater is non-hazardous, so it is not required to be sent to an off-site facility for incineration. Instead, it is pooled with other aqueous plant waste and modeled as being sent to a public wastewater treatment facility. The LCI data of the treatment of this wastewater was found using a SimaPro® model for treatment at a public wastewater treatment facility. Treatment includes mechanical, biological, and chemical treatment steps.

The LCI for the treatment of 1 lb of wastewater was found using SimaPro®. In Table 26, it is shown that 0.0280 lb of total emissions is generated from the treatment of

1 lb of wastewater. These emissions consist mostly of emissions to air, which total 0.0277 lb or 99% of the total emissions. CO_2 contributes to 99% of the air emissions released from NMP manufacture. The remaining 1% of air emissions is mainly CH_4, NO_X, and SO_2. Emissions to water contribute to 1% of the total emissions, while emissions to soil are trace. The amount of energy used to manufacture 1 lb of wastewater is 0.0780 MJ. The value for water used is negative because water is the product of this process. The treated water is released back into the environment.

Table 26

LCI for the treatment of 1 lb of wastewater

	Wastewater Treatment
Water Used (lb)	-8.96E-01
Total Air Emissions (lb)	2.77E-02
CO_2 (lb)	2.75E-02
CO (lb)	2.27E-06
CH_4 (lb)	2.43E-05
NO_X (lb)	5.74E-05
NMVOC (lb)	7.64E-07
Particulate (lb)	7.55E-07
SO_2 (lb)	2.76E-05
Total Water Emissions (lb)	3.59E-04
VOCs (lb)	8.88E-11
Total Soil Emissions (lb)	3.04E-07
Total Emissions (lb)	**2.80E-02**
CED (MJ)	7.80E-02

Life Cycle Emissions of the DuPont Process

The total life cycle emissions and life cycle CO_2 emissions, for each raw material used and waste disposed of in the DuPont resin precursor process, was determined using the annualized quantities shown previously in Table 12. The annualized quantities of each raw material and waste were multiplied by their corresponding LCI on a 1 lb basis. The total life cycle emissions and life cycle CO_2 emissions associated with each raw material used and waste disposed of within the LCA boundaries of the current DuPont resin precursor process are shown in Table 27. As mentioned previously, the impact of utility use during the resin precursor washing process is not included in the LCA because these utilities are also used in alternative green process options. The impacts from resin precursor synthesis and filter press operation are also not included because they are outside the boundaries of the LCA.

Table 27

Total and CO_2 life cycle emissions for the current DuPont process

Material	**Total Life Cycle Emissions (lb/yr)**	**Life Cycle CO_2 Emissions (lb/yr)**
NMP Manufacture	1.70E+06	1.50E+06
Minor Reagents	1.43E+05	1.31E+05
HEMA Manufacture	6.86E+04	6.64E+04
TFA Manufacture	5.70E+04	4.94E+04
HCl Manufacture	1.78E+04	1.51E+04
Ultrapure Water Manufacture	1.05E+05	8.28E+04
Hazardous Waste Disposal	5.15E+05	4.58E+05
Non-hazardous Wastewater Disposal	2.00E+05	1.96E+05
Total	2.67E+06	2.37E+06

The emissions associated with the manufacture of NMP contribute the most to the total life cycle emissions, accounting for 64% of the total life cycle emissions of the DuPont process. The emissions from hazardous waste disposal account for 19% of the total life cycle emissions of the DuPont process. Non-hazardous wastewater disposal, manufacture of minor reagents, and ultrapure water production account for 7%, 5%, and 4% of the total life cycle emissions of the DuPont process, respectively. The CO_2 emissions associated with the manufacture of NMP contribute the most to the life cycle CO_2 emissions, accounting for 63% of the life cycle CO_2 emissions of the DuPont process. Hazardous waste disposal, non-hazardous waste disposal, manufacture of minor reagents, and ultrapure water production account for 19%, 8%, 6%, and 4% of the life cycle CO_2 emissions of the DuPont process, respectively.

Equation 7 was used to calculate life cycle emissions of the DuPont process to air, water, and soil; along with water and energy use. The life cycle emissions for the current DuPont process, within the LCA boundaries, were determined using the annualized values shown previously in Table 12. The impact of utility use during the resin precursor washing process, resin precursor synthesis, and filter press operation are not included in the LCA. Life cycle emissions and water and energy use for the current DuPont resin precursor process are shown in Table 28. The current DuPont resin precursor process generates 2,670,000 lb/yr of total life cycle emissions. Of these life cycle emissions, 90% are emissions to air. Of the emissions to air, 99% are CO_2 emissions. The remaining 10% of emissions are to water, while emissions to soil are trace.

$$\begin{aligned} LCE_{base\ case} = {} & m_{NMP} \cdot LCI_{NMP} + m_{TFA} \cdot LCI_{TFA} + m_{HEMA} \cdot LCI_{HEMA} + m_{HCl} \\ & \cdot LCI_{HCl} + m_{UPW} \cdot LCI_{UPW} + m_{HW,BC} \cdot LCI_{HW} + m_{NHWW,BC} \\ & \cdot LCI_{NHWW} \end{aligned} \tag{7}$$

In Equation 7, m_{NMP}, m_{TFA}, m_{HEMA}, m_{HCl}, and m_{UPW} are the masses of NMP, TFA, HEMA, HCl, and ultrapure water entering the wash tanks in lb/yr, respectively. $m_{HW,BC}$ and $m_{NHWW,BC}$ are the mass of hazardous and non-hazardous wastewater generated by the base case (current DuPont process) in lb/yr. LCI_{NMP}, LCI_{TFA}, LCI_{HEMA}, LCI_{HCl}, and LCI_{UPW} are the LCIs for the manufacture of NMP, TFA, HEMA, HCl and ultrapure water on a 1 lb basis. LCI_{HW} and LCI_{NHWW} are the LCIs for the disposal of hazardous and non-hazardous wastewater on a 1 lb basis.

Table 28

Life cycle emissions for the current DuPont process

Water Used (lb/yr)	5.24E+09
Total Air Emissions (lb/yr)	2.39E+06
CO_2 (lb/yr)	2.37E+06
CO (lb/yr)	1.14E+03
CH_4 (lb/yr)	4.26E+03
NO_X (lb/yr)	3.22E+03
NMVOC (lb/yr)	9.65E+02
Particulate (lb/yr)	1.01E+03
SO_2 (lb/yr)	4.56E+03
Total Water Emissions (lb/yr)	2.73E+05
VOCs (lb/yr)	2.41E+00
Total Soil Emissions (lb/yr)	6.88E+02
Total Emissions (lb/yr)	2.67E+06
CED (MJ/yr)	1.56E+07

Life Cycle Emission Reduction Calculations

Alternative processes (green engineering options) to the current DuPont resin precursor process were designed to reduce environmental impact. These designs are described in subsequent sections in this report. Reduction in environmental impact is achieved through a combination of NMP recovery, substitution to a more benign solvent, and ultrapure water recovery. The life cycle emissions of recovery processes were calculated using Equation 8. Equation 8 is similar to Equation 7 except the emissions associated with recovered solvent and ultrapure water are not included in the life cycle emissions. Also, Equation 8 accounts for additional utility use from recovery equipment. The mass of hazardous waste and/or non-hazardous wastewater generated in the alternative processes will be lower than for the base case, due to recovery of solvent and/or ultrapure water. The avoided life cycle emissions from using an alternative process were calculated using Equation 9. The avoided emissions will be used to determine if an alternative process has a lesser environmental impact than the current DuPont process.

$$\begin{aligned} LCE_{alternative\ process} &= (m_{Solv} - r_{Solv}) \cdot LCI_{Solv} + m_{TFA} \cdot LCI_{TFA} + m_{HEMA} \cdot LCI_{HEMA} \\ &+ m_{HCl} \cdot LCI_{HCl} + (m_{UPW} - r_{UPW}) \cdot LCI_{UPW} + m_{HW,AP} \cdot LCI_{HW} \\ &+ m_{NHWW,AP} \cdot LCI_{NHWW} + S \cdot LCI_s + E \cdot LCI_E \end{aligned} \tag{8}$$

In Equation 8, m_{Solv} is the mass of solvent (NMP or solvent substitute) entering the wash tanks in lb/yr. LCI_{Solv} is the LCI for the manufacture of solvent on a 1 lb basis. r_{Solv} and r_{UPW} are the masses of solvent and ultrapure water recovered in lb/yr. $m_{HW,AP}$ and $m_{NHWW,AP}$ are the mass of hazardous waste and non-hazardous wastewater generated by the alternative process in lb/yr. S and E are the amount of steam and electricity used in the alternative process in MJ/yr, not including steam electricity used in the base case. LCI_S and LCI_E are the LCIs for the production of steam and electricity on a 1 MJ basis.

$$LCE_{avoided} = LCE_{base\ case} - LCE_{alternative\ process} \tag{9}$$

ReCiPe Damage Assessment

Another method that can be used to assess the environmental impact of a process is damage assessment. Damage assessment is different than life cycle emissions because the relative contribution of each substance is taken into consideration. For example, the release of 1 lb of methane does not cause the same harm as the release of 1 lb of CO_2 because methane has a higher global warming potential. The release of 1 lb of methane causes the same amount of climate change as the release of 25 lb of CO_2. Damage assessment methods take into account the relative damage of all emissions [119]. There are different damage assessment methods that can be used in SimaPro®, which calculate damage differently. The ReCiPe assessment method was used for this project to assess potential damage to human health, ecosystems, and resources [120]. This method is useful for presenting results at conferences on life cycle assessment since it represents different impact categories.

A literature review of the use of the ReCiPe method in similar applications was conducted. Luis *et al.* used the ReCiPe method to analyze the LCAs of solvent separation/recovery processes [121]. They compared the use of distillation and pervaporation to separate a methanol and tetrahydrofuran mixture. They also compared the solvent recovery processes to disposal of the solvent mixture using incineration. The

ReCiPe method has been used to compare pharmaceutical synthesis routes, bio-based and fossil fuel-based resin synthesis, pharmaceutical wastewater treatment plants, and paper manufacturing using different types of pulp [122, 123, 124, 125].

ReCiPe is available for analysis via three different perspectives. They are ReCiPe (I), ReCiPe (H), and ReCiPe (E) [120]. Perspective (I) represents the individualist approach. This is primarily based on short-term interest and uses impacts that are undisputed. Perspective (H) represents the hierarchist approach. It is based on the most commonly used principles with regard to time and other issues. Finally, Perspective (E) represents the egalitarian approach, which is the most precautionary method and accounts for the longest timeframe. Perspective (E) may also take into account impacts that are not fully established, but for which some information is available [120]. ReCiPe (H) was chosen because it is based on the most common policies.

The ReCiPe (H) method assesses the impact of a process using 18 impact categories. Each impact category or midpoint is based on a different problem associated with the environment, human health, or natural resource use. Examples of midpoints include climate change, human toxicity, agricultural land occupation, and fossil fuel depletion [120]. SimaPro® is used to calculate values for each midpoint (impact category indicators) based on the chosen process. Impact category indicators are calculated based off of substances that contribute to the midpoint. For example, the impact category indicator for climate change is based off of greenhouse gas emissions which include CO_2, methane, and many halogenated hydrocarbons. The substances that contribute to the midpoint are multiplied by a characterization factor that expresses the relative contribution of the substance. These values are then summed to calculate the impact category indicator [119]. For the climate change midpoint, impact is reported in the unit of kg of CO_2 equivalent. This means all emissions are multiplied by a characterization factor based on their global warming potential and the global warming potential of CO_2. So, methane emissions are multiplied by 25, since the global warming potential of methane is 25 times greater than that of CO_2.

The midpoints can be combined into three separate damage categories called endpoints [120]. The ReCiPe (H) endpoints are human health, ecosystems, and resources. These endpoints use data from their respective midpoints to determine potential damage. The midpoints associated with each endpoint can be seen in Table 29, along with examples of substances that contribute to each midpoint. To calculate damage, midpoints must be converted to common units. This is done by multiplying each substance that contributes to a midpoint by the characterization factor and damage factor, and then the values for each substance are summed [119]. The damage factor converts all midpoints associated with human health into units of DALY. DALY stands for disability-adjusted life years, which is the sum of years of life lost and years of life disabled. All midpoints associated with ecosystems are converted into units of species·yr, which measures extinction rate. Finally, all midpoints associated with resources are converted into units of $, which describes resource surplus costs. After the midpoints are converted into common units, all midpoints with the same units are summed to calculate values for the endpoints (damage category indicators) [119].

Table 29

Endpoints with respective midpoints and examples of contributing substances

Endpoint	Associated Midpoints	Examples of Emissions/Resources Used
Human Health	Climate Change (Human Health) Ozone Depletion Human Toxicity Photochemical Oxidant Formation Particulate Matter Formation Ionizing Radiation	CO_2 (air) Methane compounds (air) Mercury (air) Benzene compounds (air) Sulfur Dioxide (air) Iodine (air)
Ecosystems	Climate Change (Ecosystems) Terrestrial Acidification Freshwater Eutrophication Terrestrial Ecotoxicity Freshwater Ecotoxicity Marine Ecotoxicity Agricultural Land Occupation Urban Land Occupation Natural Land Transformation	Sulfur Hexafluoride (air) Ammonia (air) Phosphorous (soil) Silver (soil) Tributylin compounds (water) Mercury (water) Occupation, permanent crop Occupation, traffic areas Transformation, from tropical rain forest
Resources	Metal Depletion Fossil Fuel Depletion	Platinum, in ground Oil, crude, in ground

The damage category indicators are normalized and weighted to produce a single score for the process modeled in SimaPro®. The endpoints are normalized using yearly environmental load in Europe, divided by the European population. A European basis is used because PRé, the developer of SimaPro®, is a European company. It is appropriate to use a European basis for normalization because life cycle emissions have the same potential damage in Europe, North America, and the rest of the world. Also, in this case study the ReCiPe methodology is used to compare LCAs of various processes. This can be done properly if all endpoints are normalized in the same manner.

After normalization, the damage category indicators are weighted to create a single score [119]. The average weighting set was chosen because it is recommended. The damage category indicators for human health, ecosystems, and resources are multiplied by 400 Pt, 400 Pt, and 200 Pt, respectively. This provides a score in Pt for potential damage to human health, ecosystems, and resources by the process modeled in SimaPro®. A single score for the process can be calculated by adding up the potential damage to human health, ecosystems, and resources. In order to provide some perspective on ReCiPe results, the potential damage caused by the production of common goods was determined using SimaPro®. Figure 10 shows the damage caused by the production of 1 lb of corn, sugar, and ethanol. The production of 1 lb of corn causes 8 mPt of damage to human health, 19 mPt of damage to ecosystems, and 4 mPt of damage to resources. The production of 1 lb of sugar causes 8 mPt of damage to human health, 22 mPt of damage to ecosystems, and 6 mPt of damage to resources. The production of 1 lb of ethanol causes 19 mPt of damage to human health, 11 mPt of damage to ecosystems, and 60 mPt of damage to resources.

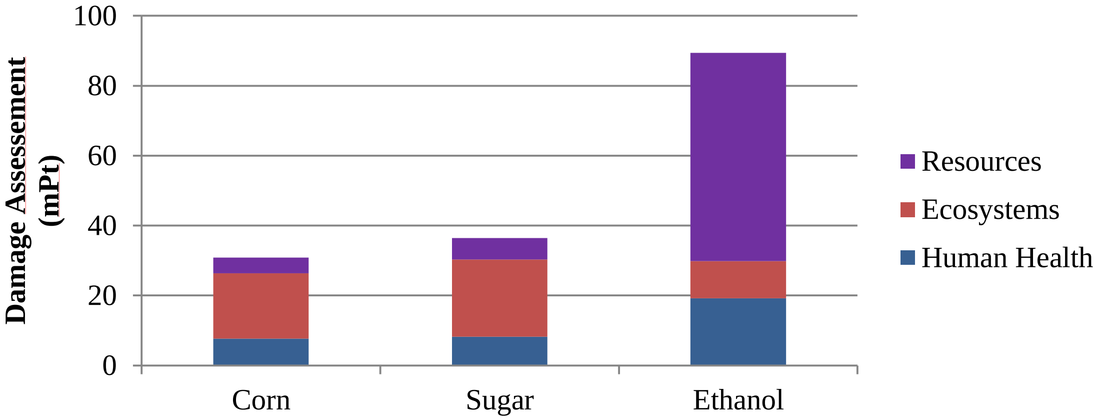


Figure 10. ReCiPe damage assessment for the production of 1 lb of common goods

ReCiPe Damage Assessment of DuPont Process

In this project, the ReCiPe damage assessment methodology was used as another environmental metric, in addition to life cycle emissions mass amounts, to quantify the sustainability of the current DuPont process and suggest green alternative processes. This additional metric provides further insight on the environmental impact of the current DuPont process and proposed alternative processes.

The potential damage caused by the raw materials used and waste disposed of in the DuPont process, along with utilities for solvent recovery equipment, were modeled in SimaPro®. The processes used to model raw material manufacture, waste disposal, and utility generation are the same as those used to create the LCIs. The ReCiPe damage scores for each raw material manufacture, waste disposal, and utility generation process were found using SimaPro® on a 1 lb or 1 MJ basis. SimaPro® directly calculates the potential damage to human health, ecosystems, and resources in mPt; along with the total potential damage. The ReCiPe damage scores for raw material manufacture and waste disposal, on a 1 lb basis, are shown in Table 30 and Table 31, respectively. The damage caused by disposal of 1 lb of DuPont's hazardous waste (17% NMP) was calculated using Equation 6. The ReCiPe damage scores for utility generation, on a 1 MJ basis, are shown in Table 32.

Table 30

ReCiPe damage assessment for the manufacture of 1 lb of raw materials

	NMP	**TFA**	**HEMA**	**HCl**	**Ultrapure water**
Human Health (mPt)	6.62E+01	1.12E+02	1.05E+02	3.19E+01	1.43E-01
Ecosystems (mPt)	3.49E+01	4.00E+01	5.54E+01	1.19E+01	7.81E-02
Resources (mPt)	9.77E+01	9.26E+01	1.48E+02	2.22E+01	1.04E-01
Total (mPt/yr)	1.99E+02	2.45E+02	3.08E+02	6.60E+01	3.25E-01

Table 31

ReCiPe damage assessment for the disposal of 1 lb of waste

	Hazardous Waste	**Non-hazardous Wastewater**
Human Health (mPt)	2.52E+00	4.04E-01
Ecosystems (mPt)	1.62E+00	2.35E-01
Resources (mPt)	-3.95E+00	1.03E-01
Total (mPt/yr)	1.97E-01	7.42E-01

Table 32

ReCiPe damage assessment for the generation of 1 MJ of utilities

	Electricity	**Steam**
Human Health (mPt)	4.26E+00	2.01E+00
Ecosystems (mPt)	1.91E+00	1.26E+00
Resources (mPt)	4.78E+00	3.38E+00
Total (mPt/yr)	1.09E+01	6.65E+00

The ReCiPe damage scores for raw material manufacture, waste disposal, and utility generation on a 1 lb or 1 MJ basis show similar trends to the LCIs. For raw material manufacture, HEMA was shown to have the most potential damage per lb, followed by TFA, NMP, HCl, and ultrapure water. HEMA manufacture was also shown to have the most life cycle emissions per lb, followed by TFA, NMP, HCl, and ultrapure water. The potential damage to resources is negative for hazardous waste disposal because energy is recovered from the incineration process. This is also shown in the LCI for hazardous waste disposal, which has a negative CED. However, the damage to human health and ecosystems is greater for hazardous waste disposal than wastewater disposal because hazardous waste disposal generates more life cycle emissions. The ReCiPe damage scores for utility generation show that electricity generation has more potential damage than steam generation per MJ. The LCIs also show that electricity generation causes more harm to the environment, as it generates more life cycle emissions.

The ReCiPe damage score for each raw material used and waste disposed of in the current DuPont process was determined based on the annualized quantities shown previously in Table 12. The annualized quantities of each raw material and waste were multiplied by their corresponding damage score on a 1 lb basis to calculate annual damage scores, shown in Table 33. As mentioned previously, the impact of utility use during the resin precursor washing process is not included in the LCA because these utilities are also used in alternative green process options. The impacts from resin precursor synthesis and filter press operation are also not included because they are outside the boundaries of the LCA.

Table 33

ReCiPe damage assessment for DuPont process

Material	Human Health (mPt/yr)	Ecosystems (mPt/yr)	Resources (mPt/yr)	Total (mPt/yr)
NMP Manufacture	2.67E+07	1.41E+07	3.95E+07	8.03E+07
Minor Reagents	2.96E+06	1.27E+06	3.12E+06	7.35E+06
HEMA Manufacture	1.25E+06	6.58E+05	1.76E+06	3.66E+06
TFA Manufacture	1.33E+06	4.75E+05	1.10E+06	2.90E+06
HCl Manufacture	3.79E+05	1.41E+05	2.64E+05	7.84E+05
Ultrapure Water Manufacture	1.30E+06	7.08E+05	9.42E+05	2.95E+06
Hazardous Waste Disposal	6.00E+06	3.85E+06	-9.38E+06	4.69E+05
Non-hazardous Wastewater Disposal	2.88E+06	1.67E+06	7.34E+05	5.29E+06
Total	3.99E+07	2.16E+07	3.49E+07	9.63E+07

The manufacture of NMP contributes the most to the potential damage caused by the current DuPont resin precursor process, accounting for 83% of the total damage score. The damage from minor reagent manufacture accounts for 8% of the total score of the DuPont process. Non-hazardous waste disposal, ultrapure water production, and hazardous waste disposal account for 6%, 3%, and <1% of the total damage score of the DuPont process, respectively. The analysis of life cycle emissions also shows that NMP manufacture causes the most harm to the environment. However, the life cycle emission analysis showed that hazardous waste disposal causes the second most harm to the environment. This is not true for the analysis of total damage scores because hazardous waste disposal has a large negative value for damage to resources, resulting in a low total damage score. But, hazardous waste disposal does have the second highest damage score for human health and ecosystems. Hazardous waste disposal accounts for 15% and 18% of the total human health and total ecosystems damage scores, respectively.

Equation 10 was used to calculate the damage scores for human health, ecosystems, and resources and the total damage score for the current DuPont resin precursor process. The damage scores for the current DuPont process, within the LCA boundaries, were determined using the annualized values shown in Table 12. Damage scores for the current DuPont resin precursor process are shown in Table 34. The current DuPont resin precursor process has potential damages of 39,900,000 mPt/yr, 21,600,000 mPt/yr, and 34,900,000 mPt/yr to human health, ecosystems, and resources; respectively.

$$\begin{aligned} DS_{base\ case} = {} & m_{NMP} \cdot DS_{NMP} + m_{TFA} \cdot DS_{TFA} + m_{HEMA} \cdot DS_{HEMA} + m_{HCl} \cdot DS_{HCl} \\ & + m_{UPW} \cdot DS_{UPW} + m_{HW,BC} \cdot DS_{HW} + m_{NHWW,BC} \cdot DS_{NHWW} \end{aligned} \tag{10}$$

In Equation 10, DS_{NMP}, DS_{TFA}, DS_{HEMA}, DS_{HCl}, and DS_{UPW} are the damage scores for the manufacture of NMP, TFA, HEMA, HCl and ultrapure water on a 1 lb basis. DS_{HW} and DS_{NHWW} are the damage scores for the disposal of hazardous waste and non-hazardous wastewater on a 1 lb basis.

Table 34

ReCiPe damage assessment for the current DuPont process

Human Health (mPt/yr)	3.99E+07
Ecosystems (mPt/yr)	2.16E+07
Resources (mPt/yr)	3.49E+07
Total (mPt/yr)	9.63E+07

Damage Reduction Calculations

Alternative greener processes to the current DuPont process will be designed to reduce environmental impact, through a combination of NMP recovery, solvent substitution, and ultrapure water recovery. These designs are described in subsequent sections in this report. The damage scores of recovery processes were calculated using Equation 11. Equation 11 is similar to Equation 10 except the emissions associated with recovered solvent and ultrapure water are not included in the damage score. Also, Equation 11 accounts for additional utility use from recovery equipment. The mass of hazardous waste and/or non-hazardous wastewater generated in the alternative processes will be lower than for the base case, due to recovery of solvent and/or ultrapure water. The avoided damage from using an alternative process was calculated using Equation 12. The avoided emissions will be used to determine if an alternative process has a lesser environmental impact than the current DuPont process.

$$\begin{aligned} DS_{alternative\ process} \\ &= (m_{Solv} - r_{Solv}) \cdot DS_{Solv} + m_{TFA} \cdot DS_{TFA} + m_{HEMA} \cdot DS_{HEMA} \\ &+ m_{HCl} \cdot DS_{HCl} + (m_{UPW} - r_{UPW}) \cdot DS_{UPW} + m_{HW,AP} \cdot DS_{HW} \\ &+ m_{NHWW,AP} \cdot DS_{NHWW} + S \cdot DS_s + E \cdot DS_E \end{aligned} \tag{11}$$

In Equation 11, DS_{Solv} is the damage score for the manufacture of solvent (NMP or solvent substitute) on a 1 lb basis. DS_S and DS_E are the damage scores for the production of steam and electricity on a 1 MJ basis.

$$Damage_{avoided} = DS_{base\ case} - DS_{alternative\ process} \tag{12}$$

Operating Cost of the DuPont Process

The current DuPont resin precursor process and alternative processes were evaluated using economic metrics, in addition to the environmental metrics mentioned previously. The life cycle operating cost of the current process and alternative processes were calculated to determine if operating costs were saved. The cost of raw materials used and waste disposed of in the DuPont process, along with utilities for solvent recovery equipment, were provided by DuPont or estimated. DuPont provided the cost of NMP, ultrapure water, hazardous waste disposal, and non-hazardous wastewater disposal; shown in Table 35. It costs the DuPont Parlin Plant 1.95 \$/lb to purchase electronics grade virgin NMP. It also costs DuPont 0.00613 \$/lb to produce ultrapure water. This includes the cost to operate the ultrapure water production system and dispose of wastewater generated by the reverse osmosis unit. It costs the DuPont Parlin Plant 0.241 \$/lb and 0.00475 \$/lb to dispose of the hazardous waste and non-hazardous wastewater, respectively. The hazardous waste, containing mainly NMP and water, is sent off-site for incineration. The non-hazardous waste is sent to a public wastewater treatment plant.

Table 35

Raw material, utility, and waste disposal costs

NMP	1.95 \$/lb
HEMA	1.06 \$/lb
TFA	0.126 \$/lb
HCl	0.126 \$/lb
Ultrapure Water	0.00613 \$/lb
Hazardous Waste Disposal	0.241 \$/lb
Non-hazardous Wastewater Disposal	0.00475 \$/lb
Electricity	0.0314 \$/MJ
High Pressure Steam	0.00682 \$/lb

The industrial cost of HEMA and HCl were found from ICIS. The cost for HEMA was estimated to be the same as the cost of methyl methacrylate. As mentioned previously, the manufacturing process to produce HEMA is similar to that of methyl methacrylate. The 2008 cost for methyl methacrylate was 1.06 \$/lb [126]. It was estimated that the cost of HEMA was 1.06 \$/lb in 2008. The fourth quarter 2014 cost of HEMA was estimated to be 1.06 \$/lb, using Equation 13. The 2007 cost for HCl is 0.115 \$/lb [126]. The fourth quarter 2014 cost of HCl was estimated to be 0.126 \$/lb using Equation 13. It was assumed the cost of TFA is the same as HCl because ICIS does not list the industrial cost of TFA. The cost of industrial electricity in New Jersey in 2015 is 0.0314 \$/MJ [116]. The cost of high pressure steam (240ºC and 40 bar) was estimated using Equation 14 [127]. In Equation 14, the cost of fuel is 7.87 \$/MMBtu, which is the average cost of natural gas in New Jersey for 2015 [128]. The boiler efficiency is 85% and the heating rate is 0.736 MMBtu/Mlb, calculated using Equation 15.

$$Cost_{2014} = Cost_{year\ a} \times \frac{Cost\ Index_{2014}}{Cost\ Index_{year\ a}} \tag{13}$$

In Equation 13, $Cost_{2014}$ is the fourth quarter 2014 cost, $Cost_{year\ a}$ is the cost in a previous year, $Cost\ Index_{year\ a}$ is the cost index for the previous year, and $Cost\ Index_{2014}$ is the cost index for the fourth quarter 2014. The fourth quarter 2014 cost index is 576.1, the 2008 cost index is 575.4, and the 2007 cost index is 525.4 [129].

$$Cost_{HP\ Steam} = Cost_{Fuel} \times \frac{dH_b}{\eta_b} \tag{14}$$

In Equation 14, $Cost_{HP\ Steam}$ is the cost of high pressure steam in \$/Mlb, $Cost_{Fuel}$ is the cost of natural gas in \$/MMBtu, dH_b is the heating rate in MMBtu/Mlb, and η_b is the boiler efficiency.

$$dH_b = (h_s - h_e) \times \frac{1\ kg}{2.20462\ lb} \times \frac{1\ Btu}{1.055\ kJ} \times \frac{MMBtu}{1{,}000{,}000\ Btu} \times \frac{1{,}000\ lb}{Mlb} \tag{15}$$

In Equation 15, h_s and h_e are the enthalpies of saturated steam and water, respectively, in kJ/kg. High pressure steam is 240°C so h_s and h_e are 2,800 kJ/kg and 1,087 kJ/kg, respectively.

The cost of each raw material used and waste disposed of in the DuPont resin precursor process was determined using the annualized quantities shown previously in Table 12. The annualized quantities of each raw material and waste were multiplied by their corresponding costs in $/lb. The operating costs for each raw material used and waste disposed of within the LCA boundaries of the current DuPont resin precursor process are shown in Table 36. As mentioned previously, the utility use during the resin precursor washing process is not included in the analysis because these utilities are also used in alternative green process options. The resin precursor synthesis and filter press operation are not included because they are outside the boundaries of the analysis. The total operating cost of the current DuPont resin precursor process was calculated using Equation 16. Table 36 shows that virgin NMP purchase and hazardous waste disposal have the highest costs, accounting for 54% and 39% of the total operating cost, respectively. Ultrapure water production, non-hazardous wastewater disposal, and minor reagents purchase account for 4%, 2% and 1% of the total operating cost, respectively.

Table 36

Operating cost of the DuPont process

Material	Cost ($/yr)
Purchased Virgin NMP	7.87E+05
Purchased Minor Reagents	1.56E+04
Purchased HEMA	1.26E+04
Purchased TFA	1.50E+03
Purchased HCl	1.50E+03
Ultrapure Water Production	5.55E+04
Hazardous Waste Disposal	5.73E+05
Non-hazardous Wastewater Disposal	3.38E+04
Total	1.47E+06

$$Cost_{base\ case} = m_{NMP} \cdot Cost_{NMP} + m_{TFA} \cdot Cost_{TFA} + m_{HEMA} \cdot Cost_{HEMA} + m_{HCl} \cdot Cost_{HCl} + m_{UPW} \cdot Cost_{UPW} + m_{HW,BC} \cdot Cost_{HW} + m_{NHWW,BC} \cdot Cost_{NHWW} \tag{16}$$

In Equation 16, $Cost_{NMP}$, $Cost_{TFA}$, $Cost_{HEMA}$, $Cost_{HCl}$, and $Cost_{UPW}$ are the costs for NMP, TFA, HEMA, HCl and ultrapure water on a 1 lb basis. $Cost_{HW}$ and $Cost_{NHWW}$ are the costs for the disposal of hazardous and non-hazardous wastewater on a 1 lb basis.

Operating Cost Savings Calculations

Alternative processes to the current DuPont resin precursor process were designed to reduce cost, in addition to environmental impact. Reduction in environmental impact and cost is achieved through a combination of NMP recovery, substitution to a more benign solvent, and ultrapure water recovery. The operating costs of recovery processes were calculated using Equation 17. Equation 17 is similar to Equation 16 except the costs associated with recovered solvent and ultrapure water are not included and the cost for additional utility use from recovery equipment is included. The mass of hazardous waste and/or non-hazardous wastewater generated in the alternative processes will be lower than for the base case, due to recovery of solvent and/or ultrapure water. The avoided operating cost from using an alternative process was calculated using Equation 18. The avoided cost will be used to determine if an alternative process has a lesser economic impact than the current DuPont process.

$$
\begin{aligned}
Cost_{alternative\ process} \\
&= (m_{Solv} - r_{Solv}) \cdot Cost_{Solv} + m_{TFA} \cdot Cost_{TFA} + m_{HEMA} \\
&\cdot Cost_{HEMA} + m_{HCl} \cdot Cost_{HCl} + (m_{UPW} - r_{UPW}) \cdot Cost_{UPW} \\
&+ m_{HW,AP} \cdot Cost_{HW} + m_{NHWW,AP} \cdot Cost_{NHWW} + S \cdot Cost_s + E \\
&\cdot Cost_E + Cost_M
\end{aligned}
\tag{17}
$$

In Equation 17, $Cost_{Solv}$ is the cost of the solvent on a 1 lb basis. $Cost_S$ and $Cost_E$ are the costs of steam and electricity on a 1 MJ basis. $Cost_M$ is the maintenance cost for solvent recovery equipment in $/yr.

$$
Cost_{avoided} = Cost_{base\ case} - Cost_{alternative\ process} \tag{18}
$$

Economic Analysis Method for Alternative Processes

Economic analyses were conducted to compare the current DuPont resin precursor process to the alternative processes based on both operating cost savings and recovery equipment capital costs. This was done to determine if alternative processes would save DuPont money. Operating cost savings alone may not result in savings because capital equipment may also need to be purchased. To determine if alternative processes are profitable, internal rate of return (IRR), return on investment (ROI), payback time after tax, net present value after 5 yr, and net present value after 10 yr were calculated. These calculations were performed using the 7 yr modified accelerated cost recovery system (MACRS) depreciation method, a 35% tax rate, and a 15% interest rate [127]. In these analyses, the capital cost of the recovery equipment was invested and pretax cash flow was set equal to the negative of the capital cost in Year 0 and set equal to the operating cost savings in Years 1-10. Equations 19 -27 were used to calculate the IRR, ROI, payback time after tax, and net present values at 5 and 10 yr for alternative processes. All economic metrics are zero for the current DuPont process because it does not have an investment for recovery equipment or operating savings from recovery.

$$D_n = \frac{investment \times DF_n}{100} \tag{19}$$

In Equation 19, DF_n is the depreciation charge in year n, $investment$ is the total capital cost, and DF_n is the depreciation factor in year n specified by the MACRS depreciation method. D_n is zero for Year 0 and was calculated for Years 1-10 using Equation 19.

$$book\ value = investment - \sum_{n=1}^{n=t} D_n \tag{20}$$

In Equation 20, the $book\ value$ is zero for Year 0 and t is the number of years of depreciation. The $book\ value$ was calculated for Years 1-10 using Equation 20.

$$income = pretax\ cash\ flow - D_n \tag{21}$$

In Equation 21, the $income$ is zero for Year 0 and the $pretax\ cash\ flow$ is equal to the operating cost savings for Years 1-10. $Income$ was calculated for Years 1-10 using Equation 21.

$$tax = tax\ rate \times income_{n-1} \tag{22}$$

In Equation 22, the tax is zero for Year 0, the $tax\ rate$ is 0.35, and $income_{n-1}$ is the income in year n−1. The tax was calculated for Years 1-10 using Equation 22.

$$cash\ flow = pretax\ cash\ flow - tax \tag{23}$$

In Equation 23, $pretax\ cash\ flow$ is the negative of the capital invest for Year 0 and the operating savings for Years 1-10. The $cash\ flow$ was calculated using Equation 23 for Years 0-10.

$$payback\ time\ after\ tax = \frac{investment}{average\ cash\ flow} \tag{24}$$

In Equation 24, the $average\ cash\ flow$ is the average cash flow from Years 0-10.

$$ROI = \frac{average\ cash\ flow}{investment} \tag{25}$$

In Equation 25, ROI is the return on investment.

$$NPV = \sum_{n=1}^{n=t} cash\ flow \times (1+i)^{-n} \tag{26}$$

In Equation 26, NPV is the net present value, i is the interest rate (0.15), and n is the number of years (5 or 10).

$$0 = \sum_{n=1}^{n=10} cash\,flow \times (1+i)^{-n} \tag{27}$$

In Equation 27, i is the internal rate of return (IRR).

Chapter 5

Case Studies Investigated

The green engineering design followed a hierarchal approach. This started with a basic representation of the waste stream as a binary system containing NMP and water. This preliminary analysis (Case 1) was conducted to understand any limitations to the separation of NMP and water and to determine feasible separation techniques. In Case 1, NMP recovery from water using distillation (Case 1B-NMP) and pervaporation (Case 1C-NMP) was evaluated. Use of solvent substitutes was also analyzed. Case 2 is a representation of the multi-component compositions (NMP, water, HEMA, TFA, HCl) at the DuPont facility. Only the separation process shown feasible and solvent substitutes shown feasible in Case 1 are analyzed in this study. This case only analyzed the solvent waste stream. Variations of Case 2 were explored, where NMP is recovered at the Parlin Plant (Case 2A-NMP) and where NMP reprocessing occurs at another facility (Case 2B-NMP). Solvent substitution was also investigated for Case 2. This evaluation included the use of solvent substitutes in Case 2 without recovery (Base Case 2-DMSO and Base Case 2-Sulfolane) and use of solvent substitutes in Case 2 with recovery (Case 2A-DMSO and Case 2A-Sulfolane). Cases 3A and 3B explore solvent waste and wash water waste recovery for the DuPont process. A short description of all case studies investigated, in order of appearance in this report, is included in Table 37.

Table 37

Description of case studies investigated

Case 1A-NMP	NMP is not recovered from binary waste stream consisting of NMP and water
Case 1B-NMP	NMP is recovered from binary waste stream consisting of NMP and water using distillation
Case 1C-NMP	NMP is recovered from binary waste stream consisting of NMP and water using pervaporation
Case 1A-DMSO	NMP is substituted with DMSO; DMSO is not recovered from binary waste stream consisting of DMSO and water
Case 1A-Sulfolane	NMP is substituted with sulfolane; sulfolane is not recovered from binary waste stream consisting of sulfolane and water
Case 1B-DMSO	NMP is substituted with DMSO; DMSO is recovered from binary waste stream consisting of DMSO and water using distillation
Case 1B-Sulfolane	NMP is substituted with sulfolane; sulfolane is recovered from binary waste stream consisting of sulfolane and water using distillation
Case 2A-NMP	NMP is recovered from the resin precursor process solvent waste stream at the Parlin Plant
Case 2B-NMP	NMP is recovered from the resin precursor process solvent waste stream at an off-site facility
Base Case 2 -DMSO	NMP is substituted with DMSO in the resin precursor process; DMSO is not recovered from the solvent waste stream
Base Case 2 -Sulfolane	NMP is substituted with sulfolane in the resin precursor process; sulfolane is not recovered from the solvent waste stream
Case 2A-DMSO	NMP is substituted with DMSO in the resin precursor process; DMSO is recovered from the solvent waste stream on-site
Case 2A-Sulfolane	NMP is substituted with sulfolane in the resin precursor process; sulfolane is recovered from the solvent waste stream on-site
Case 3A	NMP is recovered from the resin precursor process solvent waste stream and water is recovered from the wastewater from resin precursor washing
Case 3B	NMP is recovered from the resin precursor process solvent waste stream and water is recovered from the combined wastewater from resin precursor washing and NMP recovery (neutralized distillate of Step 1)

Chapter 6

Case 1: Preliminary Analysis of NMP and Water System

Preliminary designs for solvent recovery were investigated in Case 1, which consists of an aqueous NMP waste stream. Recovery of NMP from an aqueous stream was investigated because water is the main contaminant in the hazardous solvent waste generated by DuPont's resin precursor process. The analysis of Case 1 provided techniques for removing water from DuPont's hazardous solvent waste and provided an initial evaluation of the environmental and economic impact of NMP recovery. Also, the work-ups for reactions using NMP and other dipolar aprotic solvents usually require large quantities of water [19]. Therefore, aqueous NMP waste streams are common throughout the pharmaceutical and specialty chemical sectors. The Case 1 analysis of NMP recovery from an aqueous waste stream is applicable to the entire specialty chemical sector, as well as the DuPont Parlin plant.

NMP recovery from an aqueous waste stream was designed and evaluated for various compositions of NMP. The NMP composition in the waste stream was varied from 10 wt.% to 90 wt.%, in 10 wt.% increments. Waste streams with NMP compositions of 5 wt.% and 95 wt.% were also analyzed to evaluate solvent recovery at low and high compositions of NMP. The NMP composition in the aqueous waste stream was varied to determine the effect of NMP composition in the waste stream on the environmental and economic impact of NMP recovery. It may be found the NMP recovery is only environmentally and/or economically beneficial when the NMP in the waste stream is at certain compositions. Also, the best separation technique for NMP recovery, based on environmental impact and cost, may vary depending on the NMP composition in the waste stream. The annualized flow rate of the aqueous NMP waste stream was set to 2,500,000 lb/yr, which is similar to the flow rate of hazardous solvent waste generated by the DuPont resin precursor process.

Case 1A-NMP: No NMP Recovery

Case 1A-NMP evaluated the Case 1 scenarios without NMP recovery. An analysis of Case 1A-NMP is necessary for evaluation of Cases 1B-NMP and 1C-NMP. Cases 1B-NMP and 1C-NMP will be compared to Case 1A-NMP to determine the environmental and economic impact of solvent recovery. The raw material use and waste generation associated with each Case 1A-NMP scenario is shown in Table 38. The hazardous waste generated for Case 1A-NMP is 2,500,000 lb/yr, which is the same for all Case 1A-NMP scenarios. The hazardous waste consists of NMP and water. It is assumed that the NMP present in the hazardous waste is the amount of virgin NMP inputted to the process, while the amount of water present in the hazardous waste is the amount of ultrapure water inputted to the process. The virgin NMP use associated with each Case 1A-NMP scenario was calculated using the NMP composition in the waste stream and the quantity of hazardous waste generated. The ultrapure water use associated with each waste stream was calculated using the water composition in the waste stream and the quantity of hazardous waste generated. Table 38 shows that virgin NMP use increases and ultrapure water use decreases as the NMP composition in the hazardous waste increases.

Table 38

Raw material use and waste generation for each Case 1A-NMP scenario

Hazardous Waste NMP Composition	**NMP Used (lb/yr)**	**Ultrapure Water Used (lb/yr)**	**Hazardous Waste Generated (lb/yr)**
5 wt.%	125,000	2,375,000	2,500,000
10 wt.%	250,000	2,250,000	2,500,000
20 wt.%	500,000	2,000,000	2,500,000
30 wt.%	750,000	1,750,000	2,500,000
40 wt.%	1,000,000	1,500,000	2,500,000
50 wt.%	1,250,000	1,250,000	2,500,000
60 wt.%	1,500,000	1,000,000	2,500,000
70 wt.%	1,750,000	750,000	2,500,000
80 wt.%	2,000,000	500,000	2,500,000
90 wt.%	2,250,000	250,000	2,500,000
95 wt.%	2,375,000	125,000	2,500,000

The life cycle emissions associated with each Case 1A-NMP scenario are shown in Table 39 and Table 40. The life cycle emissions for each scenario are a sum of the life cycle emissions from NMP manufacture, ultrapure water production, and hazardous waste disposal; as shown in Equation 28. The scenario with a waste stream of 95 wt.% NMP has the most total life cycle emissions, 13,100,000 lb/yr, and the most life cycle CO_2 emissions, 11,500,000 lb/yr. The scenario with a waste stream of 5 wt.% NMP has the least total and CO_2 life cycle emissions, at 714,000 lb/yr and 628,000 lb/yr, respectively. NMP manufacture contributes the most to life cycle emissions, accounting for about 75% of the total life cycle emissions. Hazardous waste disposal contributed the second most to life cycle emissions, accounting for almost 25% of the total life cycle emissions. Ultrapure water production had the least life cycles emissions, at less than 5%.

Table 39

Life cycle emissions for Case 1A-NMP scenarios with 5 wt.% to 50 wt.% NMP

	5 wt.%	**10 wt.%**	**20 wt.%**	**30 wt.%**	**40 wt.%**	**50 wt.%**
Water Used (lb/yr)	1.52E+09	3.01E+09	6.00E+09	8.98E+09	1.20E+10	1.50E+10
Total Air Emissions (lb/yr)	6.35E+05	1.25E+06	2.47E+06	2.84E+06	4.92E+06	6.14E+06
CO_2 (lb/yr)	6.28E+05	1.23E+06	2.44E+06	2.81E+06	4.87E+06	6.08E+06
CO (lb/yr)	2.86E+02	5.59E+02	1.10E+03	1.79E+03	2.20E+03	2.74E+03
CH_4 (lb/yr)	1.05E+03	2.06E+03	4.08E+03	7.28E+03	8.13E+03	1.02E+04
NO_X (lb/yr)	7.71E+02	1.50E+03	2.96E+03	4.33E+03	5.87E+03	7.32E+03
NMVOC (lb/yr)	2.49E+02	4.96E+02	9.91E+02	1.41E+03	1.98E+03	2.47E+03
Particulate (lb/yr)	2.86E+02	5.67E+02	1.13E+03	1.56E+03	2.25E+03	2.81E+03
SO_2 (lb/yr)	9.79E+02	1.92E+03	3.79E+03	5.62E+03	7.54E+03	9.41E+03
Total Water Emissions (lb/yr)	7.97E+04	1.54E+05	3.01E+05	3.42E+05	5.97E+05	7.45E+05
VOCs (lb/yr)	7.03E-01	1.40E+00	2.80E+00	3.52E+00	5.60E+00	7.00E+00
Total Soil Emissions (lb/yr)	2.00E+02	3.99E+02	7.97E+02	1.08E+03	1.59E+03	1.99E+03
Total Emissions (lb/yr)	**7.14E+05**	**1.40E+06**	**2.77E+06**	**3.19E+06**	**5.51E+06**	**6.88E+06**
CED (MJ/yr)	4.22E+06	8.31E+06	1.65E+07	3.06E+07	3.29E+07	4.11E+07

Table 40

Life cycle emissions for Case 1A-NMP scenarios with 60 wt.% to 95 wt.% NMP

	60 wt.%	**70 wt.%**	**80 wt.%**	**90 wt.%**	**95 wt.%**
Water Used (lb/yr)	1.79E+10	2.09E+10	2.39E+10	2.69E+10	2.84E+10
Total Air Emissions (lb/yr)	7.36E+06	8.59E+06	9.81E+06	1.10E+07	1.16E+07
CO_2 (lb/yr)	7.29E+06	8.50E+06	9.71E+06	1.09E+07	1.15E+07
CO (lb/yr)	3.29E+03	3.83E+03	4.38E+03	4.93E+03	5.20E+03
CH_4 (lb/yr)	1.22E+04	1.42E+04	1.62E+04	1.83E+04	1.93E+04
NO_X (lb/yr)	8.78E+03	1.02E+04	1.17E+04	1.31E+04	1.39E+04
NMVOC (lb/yr)	2.97E+03	3.46E+03	3.96E+03	4.45E+03	4.70E+03
Particulate (lb/yr)	3.38E+03	3.94E+03	4.50E+03	5.06E+03	5.34E+03
SO_2 (lb/yr)	1.13E+04	1.32E+04	1.50E+04	1.69E+04	1.78E+04
Total Water Emissions (lb/yr)	8.92E+05	1.04E+06	1.19E+06	1.34E+06	1.41E+06
VOCs (lb/yr)	8.40E+00	9.80E+00	1.12E+01	1.26E+01	1.33E+01
Total Soil Emissions (lb/yr)	2.39E+03	2.79E+03	3.18E+03	3.58E+03	3.78E+03
Total Emissions (lb/yr)	**8.25E+06**	**9.62E+06**	**1.10E+07**	**1.24E+07**	**1.31E+07**
CED (MJ/yr)	4.93E+07	5.75E+07	6.56E+07	7.38E+07	7.79E+07

$$LCE_{C1A} = m_{NMP} \cdot LCI_{NMP} + m_{UPW} \cdot LCI_{UPW} + m_{HW,C1A} \cdot LCI_{HW} \cdot \frac{x_{NMP,HW}}{0.17} \qquad (28)$$

In Equation 28, LCE_{C1A} is the life cycle emissions associated with Case 1A-NMP in lb/yr, $m_{HW,C1A}$ is the mass of hazardous waste generated by Case 1A-NMP in lb/yr, and $x_{NMP,HW}$ is the mass fraction of NMP in the hazardous waste.

ReCiPe methodology was used to calculate the damage associated with each Case 1A-NMP scenario, shown in Table 41. The damage for each scenario is the sum of the damage from NMP manufacture, ultrapure water production, and hazardous waste disposal; as shown in Equation 29. The scenario with a waste stream of 95 wt.% NMP has the most damage to human health (193,000,000 mPt/yr), ecosystems (106,000,000 mPt/yr), and resources (177,000,000 mPt/yr). The scenario with a waste stream of 5 wt.% NMP has the least damage to human health, ecosystems, and resources with damage scores of 10,500,000 mPt/yr, 5,740,000 mPt/yr, and 9,560,000 mPt/yr; respectively. NMP manufacture contributes the most to total damage, accounting for over 96% of the total damage. Hazardous waste disposal does not contribute much to the total damage because damage to resources is negative, lowering the total damage score.

Table 41

ReCiPe damage assessment for Case 1A-NMP scenarios

Hazardous Waste NMP Composition	**Human Health (mPt/yr)**	**Ecosystems (mPt/yr)**	**Resources (mPt/yr)**	**Total (mPt/yr)**
5 wt.%	1.05E+07	5.74E+06	9.56E+06	2.58E+07
10 wt.%	2.06E+07	1.13E+07	1.89E+07	5.07E+07
20 wt.%	4.08E+07	2.24E+07	3.74E+07	1.01E+08
30 wt.%	6.10E+07	3.35E+07	5.60E+07	1.51E+08
40 wt.%	8.13E+07	4.46E+07	7.46E+07	2.00E+08
50 wt.%	1.01E+08	5.57E+07	9.32E+07	2.50E+08
60 wt.%	1.22E+08	6.67E+07	1.12E+08	3.00E+08
70 wt.%	1.42E+08	7.78E+07	1.30E+08	3.50E+08
80 wt.%	1.62E+08	8.89E+07	1.49E+08	4.00E+08
90 wt.%	1.82E+08	1.00E+08	1.68E+08	4.50E+08
95 wt.%	1.93E+08	1.06E+08	1.77E+08	4.75E+08

$$DS_{C1A} = m_{NMP} \cdot DS_{NMP} + m_{UPW} \cdot DS_{UPW} + m_{HW,C1A} \cdot DS_{HW} \cdot \frac{x_{NMP,HW}}{0.17} \tag{29}$$

In Equation 29, DS_{C1A} is the damage score for Case 1A-NMP in mPt/yr.

The operating costs associated with each Case 1A-NMP scenario are shown in Table 42. The operating costs for each scenario are a sum of the cost to purchase virgin NMP, produce ultrapure water, and dispose of hazardous waste; as shown in Equation 30. The scenario with a waste stream consisting of 95 wt.% NMP has the highest operating cost, 5,236,000 $/yr. The scenario with a waste stream of 5 wt.% NMP has the lowest operating cost, 862,000 $/yr. The operating cost significantly increases as NMP use increases, due to the high cost to purchase NMP. Table 42 also shows that the cost to produce ultrapure water is low, in comparison to the cost to purchase NMP and dispose of hazardous waste.

Table 42

Operating costs for Case 1A-NMP scenarios

Hazardous Waste NMP Composition	**Purchased NMP ($/yr)**	**Ultrapure Water Production ($/yr)**	**Hazardous Waste Disposal ($/yr)**	**Total Cost ($/yr)**
5 wt.%	243,800	14,550	603,600	861,900
10 wt.%	487,500	13,780	603,600	1,105,000
20 wt.%	975,000	12,250	603,600	1,591,000
30 wt.%	1,463,000	10,720	603,600	2,077,000
40 wt.%	1,950,000	9,187	603,600	2,563,000
50 wt.%	2,438,000	7,656	603,600	3,049,000
60 wt.%	2,925,000	6,125	603,600	3,535,000
70 wt.%	3,413,000	4,594	603,600	4,021,000
80 wt.%	3,900,000	3,062	603,600	4,507,000
90 wt.%	4,388,000	1,531	603,600	4,993,000
95 wt.%	4,631,000	766	603,600	5,236,000

$$Cost_{C1A} = m_{NMP} \cdot Cost_{NMP} + m_{UPW} \cdot Cost_{UPW} + m_{HW,C1A} \cdot Cost_{HW} \tag{30}$$

In Equation 30, $Cost_{C1A}$ is the operating cost for Case 1A-NMP in $/yr.

Case 1B-NMP: NMP Recovery Using Distillation

Various separation techniques were investigated for the separation of NMP and water. Distillation was investigated first since it is the most common method of solvent separation [130]. A T-*x*-*y* equilibrium diagram for NMP and water at 1 atm was generated in Aspen Plus® to determine if distillation is a viable separation technique. The UNIQUAC model was chosen for the NMP and water system because both components are polar [131]. The T-x-y diagram in Figure 11 shows that an azeotrope does not exist for the NMP and water system. The equilibrium data for NMP and water show that distillation is a feasible separation option because a good separation can be achieved at atmospheric pressure.

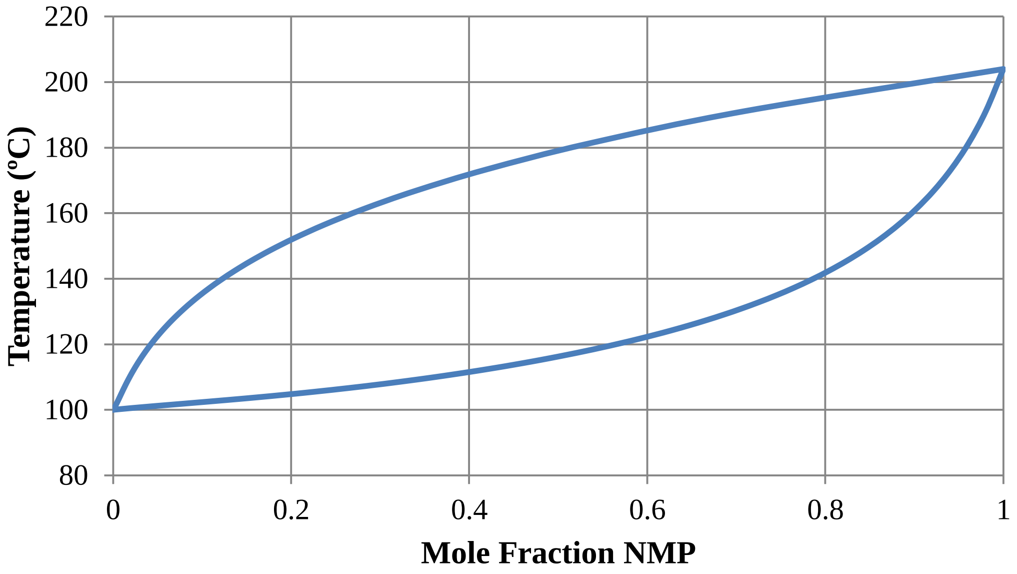


Figure 11. T-*x*-*y* equilibrium diagram for NMP and water system

NMP recovery using distillation was investigated in Case 1B-NMP for all NMP waste stream compositions, to determine if environmental and economic impact could be reduced. This green engineering approach focuses on Green Engineering Principles 3, 4, 10, and 12. Principle 3 relates to this green engineering approach because the solvent recovery system is designed with energy use in mind. This green engineering approach also focuses on Principles 4, 10, and 12 because the purpose of NMP recovery is to reduce the use of virgin NMP, making the process more efficient and sustainable.

Distillation systems were designed and optimized using the R.SWEET software for solvent recovery assessment that was developed in past work at Rowan University supported by EPA [132]. In Case 1B-NMP, NMP is recovered from the bottoms of the distillation column, as shown in Figure 12. The recovered NMP is then reused in the process. It was assumed that the Case 1 process uses electronics grade NMP, like DuPont uses in its resin precursor process. The water composition in the recovered NMP was specified at 300 ppm, to meet the specifications of electronics grade NMP. This resulted in a desired purity of 99.97 wt.%. for the recovered NMP. In R.SWEET the NMP composition in the distillation column bottoms was specified as 99.97 wt.%. The distillate from the distillation column contains water with trace NMP and is sent to a public wastewater treatment plant. The distillate is considered non-hazardous wastewater since it has an NMP composition below 0.15 wt.%. It is known that the wastewater generated from DuPont's resin precursor washing, which has an NMP composition of 0.15 wt.%, can be sent to the public wastewater treatment plant. It is assumed that other wastewater with the same or lower composition of NMP can also be sent to the public wastewater treatment plant.

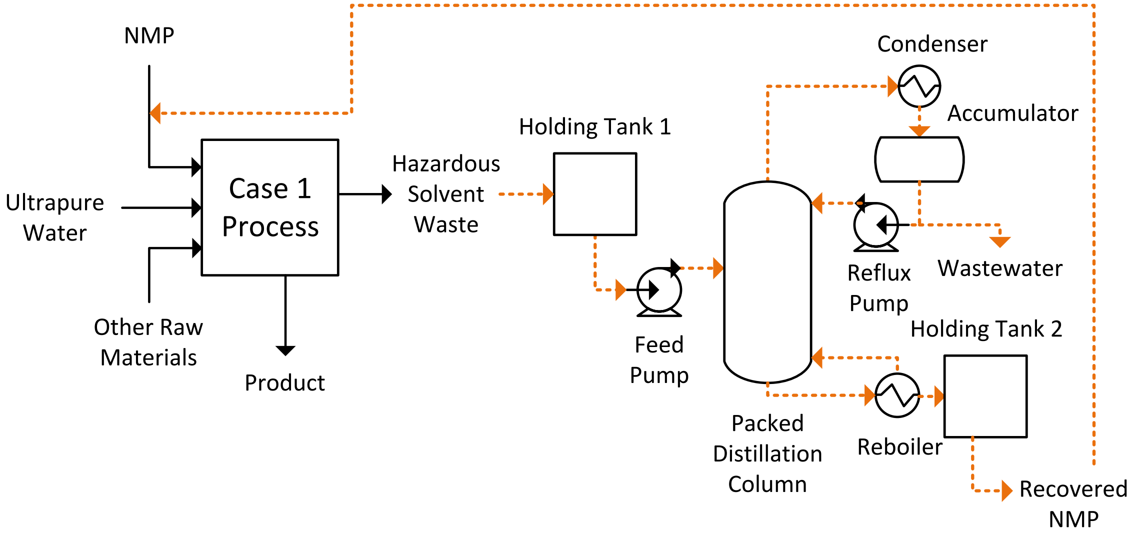


Figure 12. Case 1B-NMP distillation system for NMP recovery

The distillation systems were designed to treat 2,500,000 lb/yr of hazardous waste, as mentioned previously. The feed flow rate to the distillation system was set to

5,000 lb/hr for all Case 1B-NMP scenarios. This results in an operating time of about 500 hr/yr. The distillation columns were designed to operate at atmospheric pressure because the T-*x*-*y* diagram (Figure 11) showed a favorable separation of NMP and water at atmospheric pressure. Distillation systems for all Case 1B-NMP scenarios were designed based on these specifications. However, the distillation systems for Case 1B-NMP scenarios were individually designed and optimized, therefore the environmental impact from operation, capital cost, and operating cost vary for each scenario.

The environmental impact from operation of the distillation systems was based on the steam used by the reboiler; the electricity to pump the feed to the column, pump the reflux to the column, and pump the condenser cooling water; and the disposal of the distillate wastewater. The life cycle emissions of the Case 1B-NMP scenarios were calculated using Equation 31. The damage scores for these scenarios were calculated using Equation 32. Finally, the operating costs for the Case 1B-NMP scenarios were calculated using Equation 33. In Equation 33, the yearly maintenance cost for recovery equipment was estimated as 2.5% of the installed capital cost of all recovery unit operations.

$$\begin{aligned} LCE_{AP1} = {} & (m_{NMP} - r_{NMP}) \cdot LCI_{NMP} + m_{UPW} \cdot LCI_{UPW} + m_{HW,AP1} \cdot LCI_{HW} \cdot \frac{x_{NMP,HW}}{0.17} \\ & + m_{NHWW,AP1} \cdot LCI_{NHWW} + S \cdot LCI_s + E \cdot LCI_E \end{aligned} \tag{31}$$

In Equation 31, LCE_{AP1} is the life cycle emissions from the Case 1 process with solvent recovery in lb/yr and r_{NMP} is the mass of NMP recovered in lb/yr. $m_{HW,AP1}$ and $m_{NHWW,AP1}$ are the mass of hazardous waste and non-hazardous wastewater generated by the Case 1 process with solvent recovery in lb/yr. S and E are the amount of steam and electricity used by the Case 1 recovery equipment in MJ/yr.

$$DS_{AP1} = (m_{NMP} - r_{NMP}) \cdot DS_{NMP} + m_{UPW} \cdot DS_{UPW} + m_{HW,AP1} \cdot DS_{HW} \cdot \frac{x_{NMP,HW}}{0.17} + m_{NHWW,AP1} \cdot DS_{NHWW} + S \cdot DS_s + E \cdot DS_E \tag{32}$$

In Equation 32, DS_{AP1} is the damage score for the Case 1 process with solvent recovery in mPt/yr.

$$Cost_{AP1} = (m_{NMP} - r_{NMP}) \cdot Cost_{NMP} + m_{UPW} \cdot Cost_{UPW} + m_{HW,AP1} \cdot Cost_{HW} + m_{NHWW,AP1} \cdot Cost_{NHWW} + S \cdot Cost_s + E \cdot Cost_E + Cost_M \tag{33}$$

In Equation 33, $Cost_{AP1}$ is the operating cost for the Case 1 process with solvent recovery in \$/yr and $Cost_M$ is the maintenance cost for solvent recovery equipment in \$/yr.

The distillation system shown in Figure 12 was designed for each Case 1B-NMP scenario. Holding Tank 1 is used to store the hazardous solvent waste prior to distillation. The distillation system is designed to run for 9.6 hr/week, resulting in operation for 500 hr/yr. Holding Tank 1 must store 5,900 gal of hazardous solvent waste, so it was designed to hold 5,900 gal of liquid and have a head space of about 20%. The total tank volume is 7,200 gal, with a diameter of 8.5 ft and a height of 17 ft. Holding Tank 1 was designed as a vertical flat bottomed storage tank, with specifications that are listed in Table 43. Holding Tank 1 was designed to be constructed of glass-lined carbon steel to prevent metal ions from leaching into the NMP. The corrosion allowance for

Holding Tank 1 is 0 in because NMP and water are not corrosive chemicals. Once 5,900 gal of hazardous solvent waste is collected in Holding Tank 1, it is fed to the distillation column at a flow rate of 5,000 lb/hr. The hazardous solvent waste is fed using a centrifugal pump, with specifications listed in Table 43. The pump head was specified at 25 ft to ensure it would be able to send the solvent waste stream to the feed stage of the distillation column. Specifications for Holding Tank 1 and the feed pump are the same for all Case 1B-NMP scenarios because the feed flow rate to the distillation column is the same for all scenarios.

Table 43

Case 1B-NMP Holding Tank 1 and distillation feed pump specifications

Holding Tank 1		**Feed Pump**	
Material of Construction	Glass-lined Carbon Steel	Material of Construction	Stainless Steel
Diameter	8.5 ft	Liquid Flow Rate	10 gpm
Height	17 ft	Fluid Head	25 ft
Volume	7,200 gal	Design Pressure	50 psig
Design Pressure	15 psig	Design Temperature	150ºF
Design Temperature	150ºF	Pump Efficiency	70%
Corrosion Allowance	0 in	Power	0.125 hp

Distillation columns were individually designed using R.SWEET for all Case 1B-NMP scenarios. However, there were common design specifications, listed in Table 44. All distillation columns were designed as packed columns, constructed out of glass-lined carbon steel and operated at atmospheric pressure. Using R.SWEET it was found that the distillation columns for all scenarios required seven stages. This resulted in a packing height of 12 ft and a total column height of 18 ft, for all distillation columns. All columns were packed with 1.5 in ceramic Intalox saddles. It was found that the column diameter varied for each scenario. Table 45 shows that column diameter decreased as NMP composition increased. When water composition in the feed stream decreased, column diameter decreased because less vapor is present in the column.

Table 44

Case 1B-NMP distillation column specifications

Distillation Column	
Material of Construction	Glass-lined Carbon Steel
Number of Stages	7
Feed Stage	4
Packing Material	1.5 in ceramic Intalox saddles
Height	18 ft
Packed Height	12 ft
Design Pressure	25 psig
Design Temperature	460ºF

Table 45

Case 1B-NMP distillation system specifications

Hazardous Waste NMP Composition	**Column Diameter (ft)**	**Reboiler Duty (kW)**	**Condenser Duty (kW)**	**Reboiler Area (ft^2)**	**Condenser Area (ft^2)**
5 wt.%	5	2,889	-2,712	850	1,625
10 wt.%	5	2,753	-2,569	810	1,540
20 wt.%	4.75	2,480	-2,283	730	1,365
30 wt.%	4.5	2,206	-1,998	650	1,195
40 wt.%	4.25	1,933	-1,712	570	1,025
50 wt.%	4	1,658	-1,427	485	855
60 wt.%	3.5	1,381	-1,141	405	685
70 wt.%	3.25	1,100	-856	325	515
80 wt.%	2.75	814	-570	240	345
90 wt.%	2.5	589	-356	175	215
95 wt.%	2	435	-231	130	130

R.SWEET was also used to calculate the reboiler and condenser duties. It was found that condenser and reboiler duties varied for the Case 1B-NMP scenarios. Table 45 shows that condenser duty and reboiler duty decreased as NMP composition in the feed stream increased. As water content decreased, duties decreased because less water was boiled for removal from the NMP. Since reboiler and condenser duties varied for each scenario, the heat transfer area of the reboilers and condensers also varied. Reboiler heat transfer area was calculated assuming an overall heat transfer coefficient of 1,000 $W/m^2 \cdot {}^oC$ and use of saturated steam at 30 bar (234ºC) [127]. Condenser heat transfer area was calculated assuming an overall heat transfer coefficient of 1,200 $W/m^2 \cdot {}^oC$ and a cooling water temperature change of 15ºC [127]. The reboilers were designed as kettle reboilers, while the condensers were designed as TEMA heat exchangers. The common specifications for the reboilers and condensers are shown in Table 46.

Table 46

Case 1B-NMP reboiler and condenser specifications

	Reboiler	**Condenser**
Material of Construction	Glass-lined Carbon Steel	Glass-lined Carbon Steel
Design Pressure	500 psig	50 psig
Design Temperature	460ºF	270ºF

The accumulator and reflux pump designs varied for each Case 1B-NMP scenario because distillate and reflux flow rates decreased as NMP composition in the feed stream increased. The specifications that varied were the diameter and length of the accumulator and the liquid flow rate fed through the reflux pump. The accumulator diameter and length were calculated using the flow rate out of the condenser and a residence time of 10 min. The liquid flow rate through the reflux pump was the reflux flow rate. Table 47 shows that accumulator dimensions and reflux flow rate decreased as NMP composition in the feed stream increased. This occurred because less vapor is present in the distillation column, so the flow rate of material out of the top of the column decreases. The accumulator and reflux pump specifications that remained consistent for all scenarios are shown in Table 48.

Table 47

Case 1B-NMP accumulator and reflux pump specifications for all scenarios

Hazardous Waste NMP Composition	**Accumulator Diameter (ft)**	**Accumulator Length (ft)**	**Reflux Pump Flow Rate (gpm)**
5 wt.%	2	8	10
10 wt.%	2	8	9.5
20 wt.%	2	8	8.5
30 wt.%	2	8	7.5
40 wt.%	1.75	7	6.5
50 wt.%	1.75	7	5.5
60 wt.%	1.5	6	4.5
70 wt.%	1.5	6	3.5
80 wt.%	1.25	5	2
90 wt.%	1	4	1.5
95 wt.%	1	4	1

Table 48

Case 1B-NMP accumulator and reflux pump specifications

Accumulator		**Reflux Pump**	
Material of Construction	Glass-lined Carbon Steel	Material of Construction	Stainless Steel
Design Pressure	50 psig	Fluid Head	25 ft
Design Temperature	270ºF	Design Pressure	50 psig
Corrosion Allowance	0 in	Design Temperature	270ºF
		Pump Efficiency	70%
		Power	0.125 hp

Holding Tank 2 was designed to store the recovered NMP, prior to use in the Case 1 process. As mentioned previously, the distillation system is designed to run for 9.6 hr/week. Holding Tank 2 must store the recovered NMP from 9.6 hr of operation of the distillation system. For each scenario, Holding Tank 2 was designed as a vertical flat bottomed storage tank to hold the volume of recovered NMP from 9.6 hr of distillation and have a head space of about 20%. The dimensions of Holding Tank 2 varied for each scenario, as the volume of NMP recovered increased as NMP composition in the feed stream increased. The specifications for Holding Tank 2, for all scenarios, are listed in Table 49. The Holding Tank 2 specifications that remained consistent for all scenarios are shown in Table 50.

Table 49

Case 1B-NMP Holding Tank 2 dimensions for all scenarios

NMP Composition	Diameter (ft)	Height (ft)	Total Volume (gal)
5 wt.%	3.25	6.5	400
10 wt.%	4	8	750
20 wt.%	5	10	1,500
30 wt.%	5.75	11.5	2,200
40 wt.%	6.25	12.5	2,900
50 wt.%	6.75	13.5	3,600
60 wt.%	7.25	14.5	4,500
70 wt.%	7.5	15	5,000
80 wt.%	8	16	6,000
90 wt.%	8.25	16.5	6,600
95 wt.%	8.25	16.5	6,600

Table 50

Case 1B-NMP Holding Tank 2 specifications

Material of Construction	Glass-lined Carbon Steel
Design Pressure	15 psig
Design Temperature	460ºF
Corrosion Allowance	0 in

The installed capital cost for each distillation system, based on fourth quarter 2014 costs, was estimated using Aspen Capital Cost Estimator V8.4. The installed capital cost includes the cost for equipment, piping, support structures, electrical work, insulation, and manpower. The equipment included in the installed capital cost are Holding Tanks 1 and 2, the feed and reflux pumps, the distillation column, the reboiler, the condenser, and the accumulator; shown previously in Figure 12. The installed capital cost for the distillation system for each scenario is shown in Table 51. Table 51 shows that capital cost decreases as NMP composition increases. This is due to the decrease in capital cost for the distillation column, reboiler, condenser, accumulator, and reflux pump as NMP composition increases. As mentioned previously, the sizes of these equipment decrease as NMP composition increases. However, the capital cost for Holding Tank 2 increases as NMP composition increases because more NMP is recovered. The increase in cost for Holding Tank 2 resulted in a slight increase in capital cost when going from 20 wt.% NMP in the feed stream to 30 wt.% NMP.

Table 51

Case 1B-NMP distillation system capital costs

NMP Composition	**Capital Cost ($)**
5 wt.%	1,180,000
10 wt.%	1,178,000
20 wt.%	1,174,000
30 wt.%	1,185,000
40 wt.%	1,157,000
50 wt.%	1,091,000
60 wt.%	1,058,000
70 wt.%	1,043,000
80 wt.%	975,000
90 wt.%	953,000
95 wt.%	897,000

The raw materials used, utilities used, and waste generated by all Case 1B-NMP scenarios are shown in Table 52. Table 52 shows that ultrapure water use, steam use, electricity use, and wastewater generation decrease as NMP composition in the waste stream increases. NMP use slightly increases as NMP composition increases. The mass of recovered NMP and distillate wastewater were found using the R.SWEET program. There was no hazardous waste generated by the Case 1B-NMP scenarios. The utility use of the distillation processes was calculated using the reboiler and condenser duties shown in Table 45. The steam energy use was calculated using the reboiler duty, operating hours of the reboiler, and reboiler efficiency; as shown Equation 34. The electricity used to pump cooling water through the condenser was calculated using heuristic that it takes 2 kWh of electricity to pump 1000 gal of cooling water [127]. The condenser duty, the density and heat capacity of water, the temperature change of the cooling water, and the operating hours of the condenser were also used to calculate the electricity used to pump cooling water; as shown in Equation 35. The electricity used by the feed and reflux pumps were calculated using Equation 36. The power drawn by both pumps is 0.125 hp.

Table 52

Raw material use, utility use, and waste generation for Case 1B-NMP scenarios

Hazardous Waste NMP Composition	**NMP Used (lb/yr)**	**Ultrapure Water Used (lb/yr)**	**Wastewater Generated (lb/yr)**	**Steam Used (MJ/yr)**	**Electricity Used (MJ/yr)**
5 wt.%	675	2,375,000	2,372,000	5,768,000	164,600
10 wt.%	856	2,250,000	2,247,000	5,496,000	155,900
20 wt.%	1,213	2,000,000	1,997,000	4,951,000	138,600
30 wt.%	1,565	1,750,000	1,747,000	4,406,000	121,300
40 wt.%	1,910	1,500,000	1,498,000	3,859,000	104,100
50 wt.%	2,248	1,250,000	1,248,000	3,310,000	86,760
60 wt.%	2,578	1,000,000	998,000	2,757,000	69,470
70 wt.%	2,899	750,000	748,800	2,197,000	52,170
80 wt.%	3,209	500,000	499,100	1,625,000	34,880
90 wt.%	3,311	250,000	249,200	1,176,000	21,890
95 wt.%	3,368	125,000	124,300	869,000	13,230

$$S = \frac{q_{reboiler} \times \frac{3600\ s}{hr} \times t_{operating}}{\frac{1000\ kJ}{MJ} \times 0.9} \tag{34}$$

In Equation 34, S is the steam energy used by the distillation system in MJ/yr, $q_{reboiler}$ is the reboiler duty in kW, and $t_{operating}$ is the operating time in hr/yr.

$$E_{cooling\ water} = \frac{q_{condenser} \times \frac{0.264\ gal}{kg} \times \frac{3600\ s}{hr} \times \frac{2\ kWh}{1000\ gal} \times t_{operating} \times \frac{3.6\ MJ}{kWh}}{C_p \times \Delta T \times 0.9} \tag{35}$$

In Equation 35, $E_{cooling\ water}$ is the electricity used to pump the cooling water in MJ/yr, $q_{condenser}$ is the condenser duty in kW, C_p is the heat capacity of water in $\frac{KJ}{kg \cdot {}^{\circ}C}$, and ΔT is the temperature change of the cooling water (15ºC).

$$E_{pump} = p \times \frac{0.7457\ kW}{hp} \times \frac{3600\ s}{hr} \times t_{operating} \times \frac{MJ}{1000\ kJ} \tag{36}$$

In Equation 36, E_{pump} is the electricity used by the pump in MJ/yr and p is the power drawn by the pump in hp.

The environmental impact of Case 1B-NMP scenarios was calculated using Equations 31 and 32, and the raw material use, utility use, and waste generation values in Table 52. The life cycle emissions for Case 1B-NMP scenarios are shown in Table 53 and Table 54. More than 85% of the total life cycle emissions, for each scenario, are attributed to steam generation for operation of the distillation column reboiler. The total life cycle emissions decrease as NMP composition increases because less steam is needed to operate the distillation column, as shown in Table 52. The recovery scenario with a waste stream of 95 wt.% NMP has the least total life cycle emissions, 151,000 lb/yr, and the least life cycle CO_2 emissions, 148,000 lb/yr. The recovery scenario with a waste stream of 5 wt.% NMP has the most total and CO_2 life cycle emissions, at 991,000 lb/yr and 972,000 lb/yr, respectively.

Table 53

Life cycle emissions for Case 1B-NMP scenarios for 5 wt.% to 50 wt.% NMP

	5 wt.%	**10 wt.%**	**20 wt.%**	**30 wt.%**	**40 wt.%**	**50 wt.%**
Water Used (lb/yr)	3.62E+07	3.67E+07	3.77E+07	3.87E+07	3.96E+07	4.04E+07
Total Air Emissions (lb/yr)	9.79E+05	9.33E+05	8.41E+05	7.49E+05	6.56E+05	5.63E+05
CO_2 (lb/yr)	9.72E+05	9.26E+05	8.35E+05	7.43E+05	6.51E+05	5.59E+05
CO (lb/yr)	3.46E+02	3.30E+02	2.98E+02	2.66E+02	2.34E+02	2.01E+02
CH_4 (lb/yr)	1.61E+03	1.54E+03	1.39E+03	1.24E+03	1.08E+03	9.32E+02
NO_X (lb/yr)	7.82E+02	7.45E+02	6.71E+02	5.97E+02	5.23E+02	4.49E+02
NMVOC (lb/yr)	2.28E+01	2.20E+01	2.05E+01	1.90E+01	1.75E+01	1.59E+01
Particulate (lb/yr)	2.97E+01	2.86E+01	2.65E+01	2.44E+01	2.22E+01	2.01E+01
SO_2 (lb/yr)	6.98E+02	6.64E+02	5.97E+02	5.30E+02	4.63E+02	3.95E+02
Total Water Emissions (lb/yr)	1.57E+04	1.50E+04	1.36E+04	1.22E+04	1.08E+04	9.34E+03
VOCs (lb/yr)	6.95E-02	6.71E-02	6.23E-02	5.75E-02	5.26E-02	4.77E-02
Total Soil Emissions (lb/yr)	3.88E+01	3.73E+01	3.42E+01	3.11E+01	2.80E+01	2.48E+01
Total Emissions (lb/yr)	**9.91E+05**	**9.44E+05**	**8.51E+05**	**7.57E+05**	**6.64E+05**	**5.70E+05**
CED (MJ/yr)	7.83E+06	7.46E+06	6.73E+06	6.00E+06	5.26E+06	4.52E+06

Table 54

Life cycle emissions for Case 1B-NMP scenarios for 60 wt.% to 95 wt.% NMP

	60 wt.%	**70 wt.%**	**80 wt.%**	**90 wt.%**	**95 wt.%**
Water Used (lb/yr)	4.12E+07	4.18E+07	4.23E+07	4.06E+07	3.97E+07
Total Air Emissions (lb/yr)	4.70E+05	3.75E+05	2.79E+05	2.01E+05	1.49E+05
CO_2 (lb/yr)	4.66E+05	3.72E+05	2.77E+05	1.99E+05	1.48E+05
CO (lb/yr)	1.69E+02	1.36E+02	1.02E+02	7.48E+01	5.66E+01
CH_4 (lb/yr)	7.79E+02	6.24E+02	4.66E+02	3.39E+02	2.54E+02
NO_X (lb/yr)	3.75E+02	2.99E+02	2.23E+02	1.58E+02	1.17E+02
NMVOC (lb/yr)	1.43E+01	1.27E+01	1.11E+01	9.50E+00	8.47E+00
Particulate (lb/yr)	1.79E+01	1.56E+01	1.34E+01	1.12E+01	9.82E+00
SO_2 (lb/yr)	3.28E+02	2.60E+02	1.91E+02	1.35E+02	9.84E+01
Total Water Emissions (lb/yr)	7.90E+03	6.46E+03	5.00E+03	3.66E+03	2.87E+03
VOCs (lb/yr)	4.27E-02	3.76E-02	3.23E-02	2.76E-02	2.43E-02
Total Soil Emissions (lb/yr)	2.17E+01	1.84E+01	1.51E+01	1.23E+01	1.03E+01
Total Emissions (lb/yr)	**4.75E+05**	**3.80E+05**	**2.82E+05**	**2.03E+05**	**1.51E+05**
CED (MJ/yr)	3.78E+06	3.03E+06	2.26E+06	1.65E+06	1.24E+06

ReCiPe methodology was also used to calculate the environmental impact of the Case 1B-NMP scenarios. The damage for each scenario is shown in Table 55. The damage assessment also shows that for distillation scenarios, environmental impact decreases as NMP composition in the hazardous waste stream increases. This is due to reduction in steam use as NMP composition increases. Steam generation is the biggest source of damage for the recovery scenarios, accounting for more than 85% of the total damage, for each scenario. As seen with the life cycle emissions analysis, the recovery scenario with a waste stream of 5 wt.% NMP has the greatest environmental impact. The damage to human health, ecosystems, and resources for this scenario are 13,600,000 mPt/yr, 8,340,000 mPt/yr, and 20,900,000 mPt/yr; respectively. The scenario with a waste stream of 95 wt.% NMP has the least environmental impact based on life cycle emissions and damage. The damage to human health, ecosystems, and resources for this scenario are 2,090,000 mPt/yr, 1,270,000 mPt/yr, and 3,360,000 mPt/yr; respectively.

Table 55

ReCiPe damage assessment for Case 1B-NMP scenarios

Hazardous Waste NMP Composition	Human Health (mPt/yr)	Ecosystems (mPt/yr)	Resources (mPt/yr)	Total (mPt/yr)
5 wt. %	1.36E+07	8.34E+06	2.09E+07	4.28E+07
10 wt. %	1.30E+07	7.95E+06	1.99E+07	4.08E+07
20 wt. %	1.17E+07	7.16E+06	1.79E+07	3.68E+07
30 wt. %	1.04E+07	6.38E+06	1.60E+07	3.28E+07
40 wt. %	9.13E+06	5.59E+06	1.40E+07	2.88E+07
50 wt. %	7.84E+06	4.80E+06	1.21E+07	2.47E+07
60 wt. %	6.54E+06	4.01E+06	1.01E+07	2.07E+07
70 wt. %	5.23E+06	3.20E+06	8.12E+06	1.65E+07
80 wt. %	3.90E+06	2.38E+06	6.08E+06	1.24E+07
90 wt. %	2.81E+06	1.72E+06	4.46E+06	8.98E+06
95 wt. %	2.09E+06	1.28E+06	3.36E+06	6.72E+06

The reduction in environmental impact from solvent recovery, using distillation, is shown in Table 56. Table 56 shows the percent reduction in life cycle CO_2 emissions, total life cycle emissions, damage to human health, damage to ecosystems, and damage to resources. It is environmentally beneficial to recover NMP from the solvent waste for all Case 1 scenarios, except when the waste contains 5 wt.% NMP. This due to the fact that the scenario with waste containing 5 wt.% NMP has a low environmental impact without solvent recovery. For this scenario, the environmental impact from NMP manufacture and hazardous solvent waste disposal is relatively low, while the recovery of NMP requires large quantities of steam. The impact from steam generation is greater than the emissions from NMP manufacture and hazardous waste disposal for the scenario without solvent recovery. It is also observed, that the reduction in environmental impact increases as NMP composition in the waste stream increases. This occurs because the environmental impact of scenarios without solvent recovery increases as NMP composition increases, while environmental impact of scenarios with solvent recovery decreases as NMP composition increases.

Table 56

Percent reduction in environmental metrics from distillation NMP recovery

Hazardous Waste NMP Composition	CO_2 Emissions (%)	Total Emissions (%)	Human Health (%)	Ecosystems (%)	Resources (%)
5 wt. %	-54.7	-38.7	-30.0	-45.3	-118.2
10 wt. %	24.9	32.5	37.0	29.6	-5.5
20 wt. %	65.9	69.3	71.3	68.0	52.1
30 wt. %	79.7	81.7	82.9	80.9	71.5
40 wt. %	86.6	88.0	88.8	87.5	81.2
50 wt. %	90.8	91.7	92.3	91.4	87.0
60 wt. %	93.6	94.2	94.6	94.0	91.0
70 wt. %	95.6	96.1	96.3	95.9	93.8
80 wt. %	97.2	97.4	97.6	97.3	95.9
90 wt. %	98.2	98.4	98.5	98.3	97.3
95 wt. %	98.7	98.8	98.9	98.8	98.1

The operating costs associated with Case 1A-NMP and Case 1B-NMP scenarios are shown in Table 57. The operating cost for each Case 1B-NMP scenario was calculated using Equation 33. Table 57 shows that the operating cost of Case 1B-NMP scenarios decreases as NMP composition increases. The percent saved from solvent recovery was also calculated for each scenario, shown in Table 57. It was found that operating costs were saved for all scenarios by recovering solvent.

Table 57

Operating costs for Cases 1A-NMP and 1B-NMP

Hazardous Waste NMP Composition	**Case 1A-NMP ($/yr)**	**Case 1B-NMP($/yr)**	**Percent Saved (%)**
5 wt.%	862,000	104,000	87.9
10 wt.%	1,105,000	101,000	90.9
20 wt.%	1,591,000	93,000	94.1
30 wt.%	2,077,000	85,000	95.9
40 wt.%	2,563,000	77,000	97.0
50 wt.%	3,049,000	68,000	97.8
60 wt.%	3,535,000	60,000	98.3
70 wt.%	4,021,000	52,000	98.7
80 wt.%	4,507,000	42,000	99.1
90 wt.%	4,993,000	35,000	99.3
95 wt.%	5,236,000	30,000	99.4

Economic analyses were conducted to evaluate the Case 1B-NMP scenarios based on both operating cost savings and recovery equipment capital costs. This was done to determine if distillation solvent recovery would save money for Case 1 scenarios. Operating cost savings alone may not result in savings because capital equipment is also needed. To determine if distillation solvent recovery is profitable for Case 1, internal rate of return (IRR), return on investment (ROI), payback time after tax, net present value after 5 yr, and net present value after 10 yr were calculated for Case 1B-NMP scenarios. These calculations were performed using Equations 19 -27, shown previously. Table 58 shows that solvent recovery is profitable for all Case 1B-NMP scenarios. However, it is more profitable as NMP composition in the waste stream increases. This is due to decreased capital costs and increased operating cost savings.

Table 58

Economic analysis of Case 1B-NMP scenarios

Hazardous Waste NMP Composition	**IRR (%)**	**ROI (%)**	**Payback time after tax (yr)**	**5 yr NPV ($)**	**10 yr NPV ($)**
5 wt.%	52.4	47.5	2.93	880,000	1,747,000
10 wt.%	70.9	61.9	2.12	1,494,000	2,629,000
20 wt.%	109.0	90.9	1.36	2,723,000	4,392,000
30 wt.%	146.6	118.7	1.01	3,939,000	6,144,000
40 wt.%	190.9	150.6	0.78	5,189,000	7,927,000
50 wt.%	247.4	190.7	0.61	6,475,000	9,747,000
60 wt.%	301.4	228.6	0.50	7,732,000	11,539,000
70 wt.%	352.2	264.1	0.43	8,970,000	13,311,000
80 wt.%	428.6	317.1	0.36	10,258,000	15,133,000
90 wt.%	490.2	359.8	0.31	11,501,000	16,910,000
95 wt.%	550.1	401.1	0.28	12,166,000	17,842,000

The evaluation of Case 1B-NMP showed that it is environmentally and economically favorable to recover NMP from aqueous waste streams containing 10 wt.% NMP or greater. Recovery of NMP from the Case 1 waste stream with 10 wt.% NMP resulted in a 33% reduction in total life cycle emissions and savings of $2,629,000 after 10 yr. However, it was found that environmental impact was not reduced when NMP was recovered from the 5 wt.% NMP waste stream. Recovery of NMP from the 5 wt.% NMP waste stream resulted in a 39% increase in total life cycle emissions. It was found that recovery of NMP from this waste stream did result in savings of $1,747,000 after 10 yr. For the 5 wt.% NMP waste stream, it is not recommended to recover NMP if environmental impact is of primary concern. However, if cost reduction is of primary concern, it is recommended to recover NMP.

Case 1C-NMP: NMP Recovery Using Pervaporation

Although distillation is a widely used method, it can be energy intensive resulting in high operating costs and environmental impact. This is a concern for Case 1 because

NMP has a high boiling point, 202ºC. To recover NMP through distillation, the water present in the waste streams must be boiled. This is energy intensive and may result in high costs and environmental impact from operation of the distillation system. NMP recovery using pervaporation was also evaluated to determine if lower operating costs and environmental impact could be achieved compared to distillation. Past work with solvent recovery in the pharmaceutical industry has shown that use of pervaporation reduces the economic and environmental impact of solvent recovery of azeotropic mixtures [33, 18]. The NMP and water waste streams in Case 1 are not azeotropic; however, pervaporation could still reduce the energy required for NMP recovery. The pervaporation systems were designed to dehydrate NMP, where the resulting permeate contains mostly water and the retentate produced contains purified solvent. This type of pervaporation system is economical when water is the minor component of the feed mixture because water is permeated through the pervaporation system. Recovery of NMP, using pervaporation, was evaluated for Case 1 scenarios with an NMP composition of 70 wt.% and greater.

As mentioned previously, NMP recovery focuses on Green Engineering Principles 3, 4, 10, and 12. Principles 4, 10, and 12 focus on using raw materials and energy efficiently. NMP recovery allows for efficient use of NMP because it can be reused in the process, thus reducing the use of virgin NMP. Principle 3 was also applied by investigating a second recovery technique. NMP recovery using pervaporation was investigated in attempt to minimize the energy used in the recovery process.

Pervaporation systems were designed and optimized using the R.SWEET software for solvent recovery assessment. NMP is recovered from the retentate stream of the pervaporation unit, as shown in Figure 13. The recovered NMP is then reused in the process. As mentioned previously, the purity of the recovered NMP was specified as 99.97 wt.% (electronics grade). The permeate stream from the pervaporation unit contains water with an NMP composition greater than 0.15 wt.%, so it is considered hazardous waste. The permeate stream is sent off site for incineration.

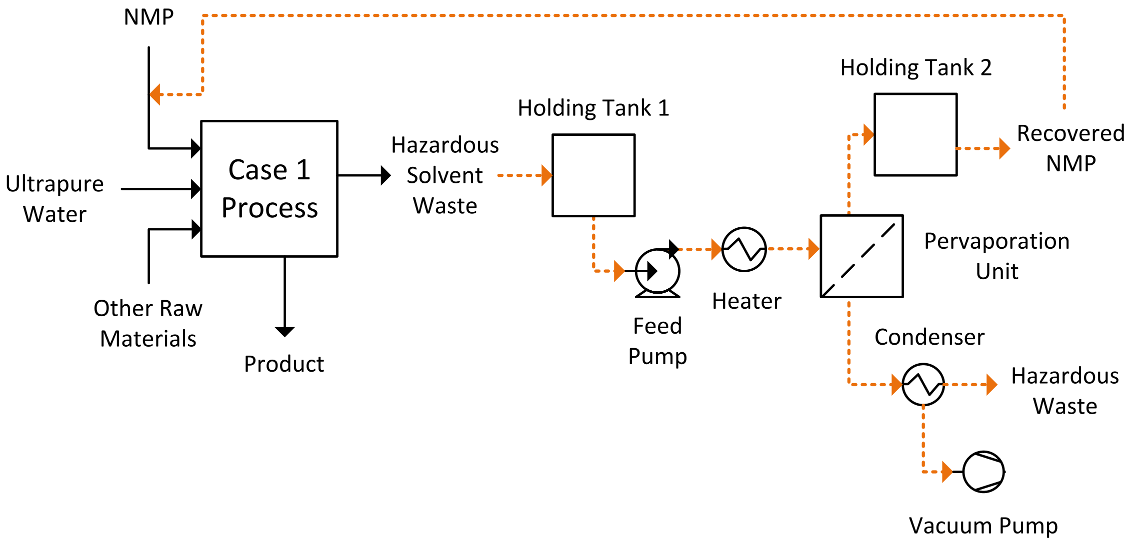


Figure 13. Case 1C-NMP pervaporation recovery system

The pervaporation systems were designed to treat 2,500,000 lb/yr of hazardous waste. The feed flow rate to the pervaporation system was set to 347 lb/hr for all Case 1C-NMP scenarios. This results in an operating time of about 7,200 hr/yr. The NaA type zeolite membrane, sold by Mitsui & Co., was chosen for the pervaporation unit. A ceramic membrane was chosen for its solvent and temperature stability [133]. Polymeric membranes have limited solvent stability and will be ruined by the NMP present in the feed stream. As mentioned previously, NMP is a very strong solvent and can dissolve polymeric membranes. Polymeric membranes cannot be used for the Case 1C-NMP pervaporation recovery scenarios because performance would be very poor. The pervaporation systems for Case 1C-NMP scenarios were individually designed and optimized based on the specifications previously discussed. Therefore the environmental impact from operation, capital cost, and operating cost vary for each scenario.

The pervaporation system shown in Figure 13 was designed for Case 1 scenarios with hazardous waste NMP compositions of 70 wt.% and greater. Similar to the distillation recovery design, Holding Tank 1 is used to store the hazardous solvent waste prior to pervaporation. The pervaporation system is designed to run for about 138 hr/week, resulting in operation for 7,200 hr/yr. Holding Tank 1 must store 5,900 gal of hazardous solvent waste, the same as Holding Tank 1 in the distillation system. Both holding tanks have the same specifications, listed previously in Table 43. Once 5,900 gal of hazardous solvent waste is collected in Holding Tank 1, it is fed to the pervaporation system at a flow rate of 347 lb/hr and a pressure of 45 psia. The hazardous solvent waste is fed using a centrifugal pump, with specifications listed in Table 59. The pump head was calculated to be 75 ft, using Equation 37. Specifications for Holding Tank 1 and the feed pump are the same for all Case 1C-NMP scenarios because the feed flow rate to the pervaporation system is the same for all scenarios.

Table 59

Case 1C-NMP feed pump specifications

Material of Construction	Stainless Steel
Liquid Flow Rate	1 gpm
Fluid Head	75 ft
Design Pressure	80 psig
Design Temperature	150ºF
Pump Efficiency	70%
Power	0.125 hp

$$h = (P_{outlet} - P_{inlet}) \times \frac{144\ in^2}{ft^2} \times \frac{g_c}{\rho g} \qquad (37)$$

In Equation 37, h is the pump head in ft, P_{inlet} and P_{outlet} are the inlet and outlet pressures of the pump in psi, g_c is $\frac{32.2\ lb_m ft}{lb_f s^2}$, ρ is the density of the feed stream in $\frac{lb_m}{ft^3}$, and g is the gravitational acceleration constant $\frac{32.2\ ft}{s^2}$.

The hazardous solvent waste is pumped into a heater to heat the feed stream from 25ºC to the desired temperature, found using R.SWEET. The desired inlet temperature for each scenario, along with the heater duty, is shown in Table 60. After the feed stream is heated, it is sent through the pervaporation unit. The pervaporation unit consists of a series of elements/modules, which each have a membrane area of 10 m^2. The number of modules required to recover NMP to the desired specifications, determined using R.SWEET, is listed in Table 60. Solvent and water flux data for isopropanol dehydration using the Mitsui NaA type zeolite membrane was used to model the dehydration of NMP. This is a reasonable assumption, as water permeates across the membrane. The modules are operated adiabatically, where the feed stream to each module is heated back to the desired inlet temperature. The energy required to heat the feed streams to the modules is shown in Table 60. As shown in Figure 13, a vacuum pump is used to create a vacuum on the permeate side of the membrane and draw water across the membrane. The permeate stream is condensed and disposed of as hazardous waste, as it contains a large composition of NMP. The electricity requirements for the vacuum pumps and condensers are shown in Table 60 as pervaporation electricity requirements.

Table 60

Case 1C-NMP pervaporation system specifications

	70 w.% NMP	**80 wt.% NMP**	**90 wt.% NMP**	**95 wt.% NMP**
Pervaporation Inlet Temperature (ºC)	122	121	118	103
Heater Duty (kW)	14.6	14.0	13.1	10.8
Number of Modules	4	3	2	2
Pervaporation Heat Requirements (kW)	24.0	14.9	6.6	4.5
Pervaporation Electricity Requirements (kW)	111	71.7	36.7	22.5

Holding Tank 2 was designed to store the recovered NMP, prior to reuse in the Case 1 process. As mentioned previously, the pervaporation system is designed to run for 138 hr/week. Holding Tank 2 must store the recovered NMP from 138 hr of operation of the pervaporation system. For each scenario, Holding Tank 2 was designed as a vertical flat bottomed storage tank, with a head space of about 20%. The dimensions of Holding Tank 2 varied for each scenario, as the volume of NMP recovered increased as NMP composition in the feed stream increased. The specifications for Holding Tank

2, for the four scenarios, are listed in Table 61. The Holding Tank 2 specifications that remained consistent for all scenarios are shown previously in Table 50.

Table 61

Case 1C-NMP Holding Tank 2 dimensions for all scenarios

NMP Composition	Diameter (ft)	Height (ft)	Total Volume (gal)
70 wt.%	7.25	14.5	4,500
80 wt.%	7.5	15	5,000
90 wt.%	7.75	15.5	5,500
95 wt.%	8	16	6,000

The installed capital cost for each pervaporation system, based on fourth quarter 2014 costs, was estimated using Aspen Capital Cost Estimator V8.4 and pervaporation cost literature. The costs for Holding Tanks 1 and 2 were using Aspen Capital Cost Estimator, as was done for the distillation system. The cost for the pervaporation unit was found in literature. The cost for the Mitsui NaA type zeolite membrane modules, including the pressure vessel housing, is 5,270 $\$/m^2$ [133]. The total installed capital cost for a pervaporation unit is double the cost of the membrane modules and housing, 10,540 $\$/m^2$ [133]. The installed cost includes the cost of the modules, housing, pumps, heaters, condenser, piping, and installation. The total installed cost of the pervaporation system was calculated by combining the costs of Holding Tanks 1 and 2 with the cost of the pervaporation unit. The installed capital costs are shown in Table 62. The capital cost decreases as NMP composition increases because less membrane modules are needed. However, the capital cost for Holding Tank 2 increases as NMP composition increases because more NMP is recovered. The increase in cost for Holding Tank 2 resulted in a slight increase in capital cost when going from 90 wt.% NMP in the feed stream to 95 wt.% NMP.

Table 62

Case 1C-NMP pervaporation system capital costs

NMP Composition	Capital Cost ($)
70 wt.%	752,000
80 wt.%	650,000
90 wt.%	546,000
95 wt.%	549,000

The raw materials used, utilities used, and waste generated by all Case 1C-NMP scenarios is shown in Table 63. Ultrapure water use, steam use, electricity use, and hazardous waste generation decrease as NMP composition in the waste stream increases. NMP use slightly increases as NMP composition increases. The mass of recovered NMP and permeate hazardous waste was found using the R.SWEET program. The steam energy use was calculated using the heater duty and heat requirements for the pervaporation unit; as shown Equation 34. The electricity used by the vacuum pump and condenser was found using R.SWEET, shown in Table 60. The electricity used by the feed pumps was calculated using Equation 36, where the power drawn by the pump is 0.125 hp.

Table 63

Raw material use, utility use, and waste generation for Case 1C-NMP scenarios

	70 wt.% NMP	**80 wt.% NMP**	**90 wt.% NMP**	**95 wt.% NMP**
NMP Used (lb/yr)	264,961	325,990	352,970	359,556
Ultrapure Water Used (lb/yr)	750,000	500,000	250,000	125,000
Hazardous Waste Generated (lb/yr)	1,015,000	826,029	603,009	484,595
Steam Used (MJ/yr)	1,111,104	831,168	566,216	440,640
Electricity Used (MJ/yr)	2,876,944	1,860,880	953,680	585,616

The environmental impact of Case 1C-NMP scenarios were calculated using Equations 31 and 32, and the raw material use, utility use, and waste generation values in Table 63. The life cycle emissions for Case 1C-NMP scenarios are shown in Table 64. The majority of total life cycle emissions are attributed to NMP manufacture. Depending on the scenario, NMP manufacture accounts for 50% to 70% of the total life cycle emissions. There are also significant life cycle emissions from hazardous waste disposal and electricity generation. The total life cycle emissions slightly decrease as NMP composition increases because less electricity, steam, and ultrapure water are needed. However, more NMP is needed and more hazardous waste is generated, as NMP composition increases. The pervaporation scenario with a waste stream of 95 wt.% NMP has the least total life cycle emissions, 2,190,000 lb/yr, and the least life cycle CO_2 emissions, 1,940,000 lb/yr. The pervaporation scenario with a waste stream of 80 wt.% NMP has the most total and CO_2 life cycle emissions at 2,260,000 lb/yr and 2,000,000 lb/yr, respectively.

Table 64

Life cycle emissions for Case 1C-NMP scenarios

	70 wt.% NMP	**80 wt.% NMP**	**90 wt.% NMP**	**95 wt.% NMP**
Water Used (lb/yr)	3.28E+09	3.97E+09	4.25E+09	4.32E+09
Total Air Emissions (lb/yr)	2.09E+06	2.12E+06	2.02E+06	1.96E+06
CO_2 (lb/yr)	2.06E+06	2.10E+06	2.00E+06	1.94E+06
CO (lb/yr)	1.05E+03	1.03E+03	9.40E+02	8.95E+02
CH_4 (lb/yr)	5.33E+03	4.73E+03	3.96E+03	3.61E+03
NO_X (lb/yr)	2.21E+03	2.35E+03	2.30E+03	2.26E+03
NMVOC (lb/yr)	7.14E+02	7.68E+02	7.61E+02	7.50E+02
Particulate (lb/yr)	8.06E+02	8.69E+02	8.64E+02	8.52E+02
SO_2 (lb/yr)	7.18E+03	5.81E+03	4.38E+03	3.77E+03
Total Water Emissions (lb/yr)	2.45E+05	2.50E+05	2.39E+05	2.31E+05
VOCs (lb/yr)	1.80E+00	2.03E+00	2.08E+00	2.08E+00
Total Soil Emissions (lb/yr)	4.40E+02	5.31E+02	5.69E+02	5.77E+02
Total Emissions (lb/yr)	**2.33E+06**	**2.37E+06**	**2.26E+06**	**2.19E+06**
CED (MJ/yr)	2.12E+07	1.89E+07	1.60E+07	1.46E+07

ReCiPe methodology was also used to calculate the environmental impact of the Case 1C-NMP scenarios. The damage for each scenario is shown in Table 65. The damage assessment also shows that for pervaporation scenarios, environmental impact decreases slightly as NMP composition in the hazardous waste stream increases. This is due to reduction in electricity, steam, and ultrapure water use as NMP composition increases. NMP manufacture is the biggest source of damage for the recovery scenarios, accounting for more than 50% of the total damage, for each scenario. The pervaporation scenarios with waste streams of 70 wt.% NMP and 80 wt.% NMP have the greatest damage to human health, 36,100,000 mPt/yr. The scenario with 80 wt.% NMP has the greatest damage to ecosystems, 19,100,000 mPt/yr; while the scenario with 70 wt.% has the greatest damage to resources; 37,300,000 mPt/yr. The scenario with a waste stream of 95 wt.% NMP has the least environmental impact based on life cycle emissions and damage. The damage to human health, ecosystems, and resources for this scenario is 2,090,000 mPt/yr, 1,270,000 mPt/yr, and 3,360,000 mPt/yr; respectively.

Table 65

ReCiPe damage assessment for Case 1C-NMP scenarios

Hazardous Waste NMP Composition	Human Health (mPt/yr)	Ecosystems (mPt/yr)	Resources (mPt/yr)	Total (mPt/yr)
70 wt. %	3.61E+07	1.87E+07	3.73E+07	9.21E+07
80 wt. %	3.61E+07	1.91E+07	3.61E+07	9.12E+07
90 wt. %	3.38E+07	1.82E+07	3.28E+07	8.49E+07
95 wt. %	3.25E+07	1.77E+07	3.11E+07	8.13E+07

The reduction in environmental impact from solvent recovery using pervaporation is shown in Table 66. Table 66 shows the percent reduction in life cycle CO_2 emissions, total life cycle emissions, damage to human health, damage to ecosystems, and damage to resources. It is environmentally beneficial to recover NMP from the solvent waste for all Case 1C-NMP scenarios. However, the reduction in environmental impact increases as NMP composition in the waste stream increases. This occurs because the environmental impact of scenarios without solvent recovery increases as NMP composition increases, while environmental impact of scenarios with solvent recovery decreases as NMP composition increases.

Table 66

Percent reduction in environmental metrics from pervaporation solvent recovery

Hazardous Waste NMP Composition	**CO_2 Emissions (%)**	**Total Emissions (%)**	**Human Health (%)**	**Ecosystems (%)**	**Resources (%)**
70 wt. %	75.7	75.8	74.6	76.0	71.4
80 wt. %	78.4	78.4	77.8	78.5	75.8
90 wt. %	81.7	81.7	81.4	81.8	80.4
95 wt. %	83.2	83.2	83.1	83.3	82.4

The operating costs associated with Case 1A-NMP and Case 1C-NMP scenarios are shown in Table 67. The operating cost for each Case 1C-NMP scenario was calculated using Equation 33. In Equation 33, the maintenance cost is 2.5% of the capital cost of the unit operations in the pervaporation system and the cost for membrane module replacement. It costs 4,480 $\$/m^2$ for the membrane modules to be replacement, and they must be replaced every 3.3 yr. Table 67 shows that the operating cost of solvent recovery scenarios tends to decrease as NMP composition increases. The percent saved from solvent recovery was also calculated for each scenario, shown in Table 67. It was found that operating costs were saved for all scenarios by recovering solvent.

Table 67

Operating costs for Case 1A-NMP and Case 1C-NMP scenarios

Hazardous Waste NMP Composition	**Case 1A-NMP ($/yr)**	**Case 1C-NMP ($/yr)**	**Percent Saved (%)**
70 wt.%	4,021,000	932,000	76.8
80 wt.%	4,507,000	953,000	78.9
90 wt.%	4,993,000	903,000	81.9
95 wt.%	5,236,000	874,000	83.3

Economic analyses were conducted to evaluate the Case 1C-NMP scenarios based on both operating cost savings and recovery equipment capital costs. This was done to determine if solvent recovery using pervaporation would save money for the Case 1 scenarios. To determine if solvent recovery using pervaporation is profitable for Case 1, internal rate of return (IRR), return on investment (ROI), payback time after tax, net present value after 5 yr, and net present value after 10 yr were calculated for the Case 1C-NMP scenarios. These calculations were performed using Equations 19 -27, shown previously. Table 68 shows that solvent recovery is profitable for all Case 1C-NMP scenarios. However, it is more profitable as NMP composition in the waste stream increases. This is due to decreased capital costs and increased operating cost savings.

Table 68

Economic analysis of Case 1C-NMP

Hazardous Waste NMP Composition	**IRR (%)**	**ROI (%)**	**Payback time after tax (yr)**	**5 yr NPV ($)**	**10 yr NPV ($)**
70 wt.%	382.2	284.9	0.40	7,032,000	10,408,000
80 wt.%	516.7	378.1	0.30	8,273,000	12,149,000
90 wt.%	717.7	516.6	0.22	9,692,000	14,144,000
95 wt.%	762.8	547.6	0.20	10,365,000	15,112,000

Case 1 Conclusion

The evaluation of NMP recovery for Case 1 showed that it is environmentally and economically favorable to use distillation to recover NMP from aqueous waste streams containing 10 wt.% NMP or greater. However, it was found that it was only economically favorable to use distillation to recover NMP from the 5 wt.% NMP waste stream. It was also found that it was environmentally and economically beneficial to use pervaporation to recover NMP from aqueous waste streams containing 70 wt.% NMP or greater. For scenarios where distillation and pervaporation were both evaluated, it was found that distillation provided a greater reduction in environmental impact. The reduction in environmental impact from using distillation for recovery was 15% to 20% greater than for using pervaporation, shown in Table 56 and Table 66. Operating cost savings from recovery are also greater when using distillation, compared to pervaporation. Cost savings from using distillation are about 15% to 20% greater than for using pervaporation, shown in Table 57 and Table 67. However, capital costs were significantly less for the pervaporation systems, compared to the distillation systems. This resulted in a higher IRR and ROI and a shorter payback time for the scenarios using pervaporation. The scenarios using distillation did save more money, as these scenarios had higher net present values after 5 and 10 yr.

It is recommended to use distillation to recover NMP from an aqueous waste stream. Although distillation systems have a higher capital cost, more money is saved after 5 and 10 yr compared to pervaporation. Distillation also provides a greater reduction in environmental impact. For Case 1, distillation is favorable because it provides a better separation. Distillation provides a much higher recovery, which reduces the use of virgin NMP. Each separation still produces an unwanted process stream that must be treated. Distillation produces a dilute non-hazardous waste, while pervaporation produces a higher NMP concentration hazardous waste. Although distillation requires much more steam, it provides the lowest impact option because it provides a very high NMP recovery and does not generate hazardous waste. Distillation was chosen for the separation of NMP and water from the actual hazardous solvent waste from the DuPont resin precursor process.

Chapter 7

Case 1: Solvent Substitutes

Solvent Substitute Selection

As mentioned previously, NMP is currently used in the DuPont resin precursor process and other specialty chemical processes due to its dipolar aprotic solvent properties and strong solvating power. Another important property of NMP is its thermal stability. NMP boils at 202ºC and degrades at 365ºC. This allows NMP to remain stable throughout the resin precursor synthesis. Although NMP has many beneficial properties, it has become a target for replacement and disuse due to its harmful health effects, which were discussed previously. Also, the LCI for NMP showed that NMP manufacture generates more life cycle emissions than the average solvent. This is an issue because NMP manufacture has a high contribution to the total life cycle emissions of the DuPont resin precursor process, accounting for over 60% of the total life cycle emissions. Potential solvent substitutes for NMP were investigated, due to the health and environmental concerns of NMP.

Solvent selection guides were consulted as the first step in finding potential substitutes for NMP in the DuPont resin precursor process. Most solvent selection guides group solvents by their families and provides ratings for each solvent in terms of health, safety, and environmental impact. Other dipolar aprotic solvents were investigated because the dipolar aprotic properties are important in the DuPont resin precursor process. The other dipolar aprotic solvents listed in the solvent selection guides are acetonitrile, dimethylformamide (DMF), dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), sulfolane, and n, n′-dimethylpropylene urea (DMPU) [134]. Acetonitrile was not considered as a potential substitute for NMP as Alfonsi *et al.* found that it is a poor substitute for dipolar aprotic solvents [135]. DMPU was also not considered as a potential substitute because it is a poor solvent for synthesis of PI resin precursor [57]. However; DMF, DMAc, and DMSO have been found to be good solvents for PI resin precursor synthesis [57]. Sulfolane was considered as a potential substitute for NMP because it has comparable properties to NMP, DMSO, DMF, and DMAc [136]. It has also been found to be a good replacement for dipolar aprotic solvents in other applications [136].

The main concern associated with NMP is its suspected developmental and reproductive toxicity. The health risks associated with all potential substitutes (DMF, DMAc, DMSO, and sulfolane) were investigated, to determine if any would be a safer alternative. However, DMF and DMAc are also suspected developmental and reproductive toxins [134]. Other health metrics were also investigated to compare the potential substitutes. The LC50, TLV, PEL, and Skin Permeability for NMP and potential substitutes are listed in Table 69.

Table 69

Health data for NMP and potential solvent substitutes

	LC50	**TLV**	**PEL**	**Skin Permeability**
NMP	5,100 mg/m^3 4 hr [137]	10 ppm (skin) AIHA [138]	No Data	171 mg/m^2/hr [136]
DMF	4,700 mg/m^3 4 hr [139]	10 ppm (skin) ACGIH [140]	10 ppm (skin) OSHA [140]	98 mg/m^2/hr [136]
DMAc	4,410 mg/m^3 4 hr [141]	10 ppm (skin) ACGIH [142]	10 ppm (skin) OSHA [142]	107 mg/m^2/hr [136]
DMSO	40,250,000 mg/m^3 4 hr [143]	No Data	No Data	176 mg/m^2/hr [136]
Sulfolane	12,000 mg/m^3 4 hr [144]	No Data	No Data	0.2 mg/m^2/hr [136]

LC50 refers to the lethal concentration of a chemical that is needed to kill 50% of a population of test animals. The LC50s in Table 69 refer to the concentration of chemical in the air. Therefore, they represent the inhalation toxicity of each chemical. DMSO is the least toxic of the solvents listed in Table 69 because it has a significantly larger LC50 then the other solvents. Sulfolane has the second highest LC50, so it is second least toxic solvent. DMAc is most toxic solvent in Table 69, followed DMF and NMP, respectively.

Threshold limit value (TLV) is the concentration of an airborne substance that an average person can be repeatedly exposed to without adverse effects. The TLVs in Table 69 are calculated using a time weighted average, for an 8 hour day, 40 hour week. There is no TLV data from DMSO and sulfolane. The TLV data for NMP, DMF, and DMAc show that the three solvents are equally toxic. Permissible exposure limit (PEL) is the same as TLV, except it is set and enforced by OSHA. OSHA does not have PEL regulations for NMP, DMSO, and sulfolane. DMF and DMAc have the same PELs.

The final health metric investigated is skin permeability. This shows how easily the solvent can go from the surface of the skin into the body. Its units represent the mass of solvent absorbed per unit area of skin, per unit time. Sulfolane has a much lower skin permeability than the other solvents in Table 69. Sulfolane has a skin permeability of 0.2 $mg/m^2/hr$. DMSO has the highest skin permeability, at 176 $mg/m^2/hr$. NMP, DMAc, and DMF have skin permeabilities of 171, 107, and 98 $mg/m^2/hr$; respectively.

Based on health, DMSO and sulfolane are the best substitutes for NMP. Sulfolane is less toxic than NMP and has significantly lower skin permeability. Although DMSO has a slightly higher skin permeability than NMP, it is significantly less toxic.

This makes DMSO more favorable than NMP. Also, DMSO and sulfolane are not suspected reproductive and developmental toxins like NMP, DMF, and DMAc. DMF and DMAc are not good substitutes for NMP, based on health. They do have lower skin permeability; however, they have higher toxicities than NMP. These conclusions are consistent with the solvent selection guides, which show that DMF and DMAc are at least as hazardous to health as NMP [134]. The solvent selection guides also show the DMSO and sulfolane are less hazardous to health than NMP, DMF, and DMAc [134].

Physical properties related to health and safety were also considered when investigating potential substitutes for NMP. The vapor pressures of the solvents were researched and are listed in Table 70. Vapor pressure indicates the volatility of a chemical. It is important to consider vapor pressure because NMP and the potential solvent substitutes can cause harm when inhaled, as discussed previously. The solvent with the highest vapor pressure is DMF with a value of 0.37 kPa. The solvents with the next highest vapor pressures are DMAc, DMSO, and NMP with values of 0.13 kPa, 0.06 kPa, and 0.05 kPa, respectively. The solvent that has the lowest vapor pressure is sulfolane with a value much lower than the rest at 0.0091 kPa. Substitution to DMF or DMAc could cause potential health issues as they have higher vapor pressures than NMP. The vapor pressures of DMSO and sulfolane do not pose any concerns.

Table 70

Physical properties of NMP and solvent substitutes

	NMP	**DMF**	**DMAc**	**DMSO**	**Sulfolane**
Vapor Pressure at 25°C (kPa)	0.050 [136]	0.37 [136]	0.13 [136]	0.06 [136]	0.0091 [136] [2]
Flash Point (°C)[1]	96 [145]	67 [139]	70 [146]	95 [147]	166 [144]
Ignition Point (°C)[1]	346 [145]	445 [139]	490 [146]	215 [147]	528 [148]
Boiling Pt. (°C)[1]	202 [145]	153 [139]	164 [146]	189 [136]	287 [144]
Decomposition Temperature (°C)	365 [137]	350 [149]	350 [150]	>189 [151]	220 [148]
Azeotrope with Water	No	No	No	No	No

[1] At 1 atm
[2] At 30°C

Another property that was considered is the potential for solvent ignition, leading to fire and/or explosion. Flash point is the lowest temperature at which a chemical can form an ignitable vapor in air. DMF and DMAc have the lowest flash points, at 67ºC and 70ºC, respectively. DMSO and NMP have the next lowest flash points; 95ºC and 96ºC, respectively. The flash points of these four solvents pose a concern, as the maximum temperature reached by DuPont's resin precursor process is about 100ºC. However, use of DMSO would not change DuPont's safety concerns because it has a similar flash point to NMP. Use of sulfolane would reduce the safety risk because the flash point of sulfolane (166ºC) is well above the operating temperature of the resin precursor process. The ignition points of the solvents do not pose concerns because they are well above the operating temperature of DuPont's resin precursor process.

The boiling points of the potential solvent substitutes were also considered. The solvent used in the resin precursor process must have a boiling point above the maximum operating temperature (about 100ºC). All potential substitutes have boiling points well above 100ºC. The decomposition temperatures of the potential substitutes were also investigated to determine if they would be stable during operating conditions. All potential substitutes have decomposition temperatures well above 100ºC. The final properties that were investigated related to the potential solvents' abilities to be recovered from an aqueous solution. All potential substitutes are miscible with water, but do not form azeotropes. This shows that distillation could potentially be used to recover these solvents, if used in DuPont's resin precursor process. However, Table 70 shows that all potential substitutes have high boiling points, so a distillation recovery process would be energy intensive. Also, DMSO degrades at its boiling point and sulfolane degrades below its boiling point. This means that vacuum distillation could be required to separate DMSO and sulfolane from water.

The LCIs and ReCiPe damage scores for the manufacture of potential solvent substitutes were found, using SimaPro®, so environmental impacts could be compared. The LCI and damage score for the manufacture of DMF was estimated using SimaPro®, which models DMF manufacture using the most common synthesis route [101]. The process consists of the reaction of carbon monoxide with dimethylamine, as shown in Equation 38. The process in SimaPro® assumes a 95% yield for this reaction. In this process, factors such as energy use, infrastructure, and emissions to the environment are included. The LCI for the manufacture of 1 lb of DMF is listed in Table 71. The manufacture of 1 lb of DMF generates 2.28 lb of total emissions. These emissions consist mostly of emissions to air, which total 1.80 lb or 80% of the total emissions. CO_2 contributes to 99% of the air emissions released from DMF manufacture. Emissions to water contribute to 20% of the total emissions, while emissions to soil are trace. The amount of water and energy used to manufacture 1 lb of DMF is 6,920 lb and 27 MJ, respectively. The ReCiPe damage score for the manufacture of 1 lb of DMF is listed in Table 72. The damage to human health, ecosystems, and resources from the manufacture of 1 lb of DMF is 34.5 mPt, 17.6 mPt, and 64.6 mPt; respectively.

$$CO + (CH_3)_2 \rightarrow C_3H_7NO \quad (38)$$

Table 71

LCI of the manufacture of 1 lb of NMP and solvent substitutes

	NMP	**DMF**	**DMAc**	**DMSO**	**Sulfolane**
Water Used (lb)	1.13E+04	6.92E+03	8.01E+03	3.38E+03	1.04E+03
Total Air Emissions (lb)	3.77E+00	1.80E+00	2.14E+00	1.19E+00	7.91E-01
CO_2 (lb)	3.72E+00	1.78E+00	2.10E+00	1.18E+00	7.49E-01
CO (lb)	2.38E-03	2.09E-03	6.14E-03	1.00E-03	9.83E-04
CH_4 (lb)	9.68E-03	4.84E-03	9.86E-03	5.31E-03	3.13E-03
NO_X (lb)	5.73E-03	3.07E-03	3.59E-03	1.98E-03	1.36E-03
NMVOC (lb)	1.88E-03	7.62E-04	8.54E-04	5.03E-04	1.09E-03
Particulate (lb)	2.08E-03	1.24E-03	1.40E-03	6.25E-04	3.73E-04
SO_2 (lb)	7.45E-03	4.84E-03	5.11E-03	1.92E-03	3.59E-02
Total Water Emissions (lb)	4.51E-01	4.72E-01	4.56E-01	1.23E-01	2.82E-02
VOCs (lb)	4.69E-06	8.51E-06	7.59E-06	7.18E-07	7.33E-07
Total Soil Emissions (lb)	1.44E-03	2.10E-03	1.96E-03	3.54E-04	1.71E-04
Total Emissions (lb)	**4.22E+00**	**2.28E+00**	**2.60E+00**	**1.31E+00**	**8.20E-01**
CED (MJ)	4.07E+01	2.67E+01	3.22E+01	2.18E+01	1.69E+01

Table 72

ReCiPe damage assessment for the manufacture of 1 lb of NMP and solvent substitutes

	NMP	**DMF**	**DMAc**	**DMSO**	**Sulfolane**
Human Health (mPt)	6.62E+01	3.45E+01	4.15E+01	2.18E+01	2.93E+01
Ecosystems (mPt)	3.49E+01	1.76E+01	2.15E+01	1.18E+01	7.22E+00
Resources (mPt)	9.77E+01	6.46E+01	7.82E+01	5.49E+01	4.43E+01
Total (mPt)	1.99E+02	1.17E+02	1.41E+02	8.85E+01	8.08E+01

The SimaPro® database models the production of DMAc through the reaction of dimethylamine and acetic acid, shown in Equation 39 [115]. In the SimaPro® model, the yield of DMAc through this synthesis route was 95%. Factors such as energy use, land use, and emissions to the environmental are considered for this process. The LCI for the manufacture of 1 lb of DMAc is shown in Table 71. The manufacture of 1 lb of DMAc generates 2.60 lb of total emissions. These emissions consist mostly of emissions to air, which total 2.14 lb or 82% of the total emissions. CO_2 contributes to 98% of the air emissions released from DMAc manufacture. Emissions to water contribute to 18% of the total emissions, while emissions to soil are trace. The amount of water and energy used to manufacture 1 lb of DMAc is 8,010 lb and 32 MJ, respectively. The ReCiPe damage score for the manufacture of 1 lb of DMAc is listed in Table 72. The damage to human health, ecosystems, and resources from the manufacture of 1 lb of DMAc is 41.5 mPt, 21.5 mPt, and 78.2 mPt; respectively.

$$(CH_3)_2NH + CH_3COOH \rightarrow C_4H_9NO + H_2O \tag{39}$$

The SimaPro® database models the production of DMSO through the oxidation of methanol with hydrogen sulfide, shown in Equation 40 [101]. The SimaPro® model assumes a 95% yield percent for this synthesis. Energy use, infrastructure, and land use were taken into account in the LCI data for the manufacture of DMSO. The LCI for the manufacture of 1 lb of DMSO is shown in Table 71. The manufacture of 1 lb of DMSO generates 1.31 lb of total emissions. These emissions consist mostly of emissions to air, which total 1.19 lb or 91% of the total emissions. CO_2 contributes to 98% of the air emissions released from DMSO manufacture. Emissions to water contribute to 9% of the total emissions, while emissions to soil are trace. The amount of water and energy used to manufacture 1 lb of DMSO is 3,380 lb and 22 MJ, respectively. The ReCiPe damage score for the manufacture of 1 lb of DMSO is listed in Table 72. The damage to human health, ecosystems, and resources from the manufacture of 1 lb of DMSO is 21.8 mPt, 11.8 mPt, and 54.9 mPt; respectively.

$$2CH_3OH + H_2S + O_2 \rightarrow (CH_3)_2SO + H_2O \tag{40}$$

The LCI for the manufacture of sulfolane is not in the SimaPro® databases, so sulfolane was entered as a new material in SimaPro®. The LCI for the manufacture of sulfolane was estimated in SimaPro®, through research of sulfolane's chemical tree. Sulfolane is a product of two reactions. First, sulfur dioxide and butadiene are reacted in a 1:1 molar ratio to produce sulfolene. Sulfolene is then hydrogenated to produce the final product sulfolane, as seen in Figure 14 [148]. The LCI of the manufacture of sulfolane was modeled in SimaPro® using the reaction shown in Figure 14. First, the manufacture of sulfolene was modeled in SimaPro® based on the reaction of sulfur dioxide and butadiene in a 1:1 molar ratio. The LCIs for sulfur dioxide and butadiene are in the SimaPro® databases. In order to model the manufacture of 1 lb of sulfolene, the molar mass of sulfolene was used to convert 1 lb of sulfolene into moles. The moles of sulfolene produced, was equal to the moles of each reactant. The mass of each reactant, in lb, was calculated using the molar mass of each reactant. The activation energy for the reaction to produce sulfolene was added by inputting energy produced by steam to the process [152].

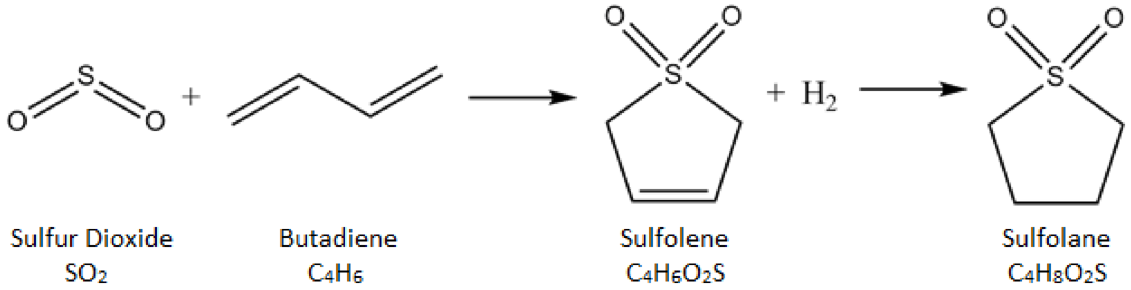


Figure 14. Sulfolane synthesis process

The model for the manufacture of sulfolene was used to determine the LCI for the manufacture of sulfolane. Sulfolane was modeled using the reaction of sulfolene and hydrogen in a 1:1 mole ratio. In order to determine the LCI of the manufacture of 1 lb of sulfolane, the molar mass of sulfolane was used to convert 1 lb of sulfolane into moles. The moles of sulfolane produced, was equal to the moles of each reactant. The mass of each reactant, in lb, was calculated using the molar mass of each reactant. These masses were inputted into SimaPro® to estimate the LCI for the manufacture of 1 lb of sulfolane.

The LCI for the manufacture of 1 lb of sulfolane is shown in Table 71. The manufacture of 1 lb of sulfolane generates 0.82 lb of total emissions. These emissions consist mostly of emissions to air, which total 0.79 lb or 96% of the total emissions. CO_2 contributes to 95% of the air emissions released from sulfolane manufacture. Emissions to water contribute to 4% of the total emissions, while emissions to soil are trace. The amount of water and energy used to manufacture 1 lb of sulfolane is 1,040 lb and 17 MJ, respectively. The ReCiPe damage score for the manufacture of 1 lb of sulfolane is listed in Table 72. The damage to human health, ecosystems, and resources from the manufacture of 1 lb of sulfolane is 29.3 mPt, 7.22 mPt, and 44.3 mPt; respectively.

Table 71 shows that NMP manufacture creates the most life cycles emissions and uses the most energy, when compared to the manufacture of the potential solvent substitutes. The manufacture of DMAc had the second greatest life cycle emissions and energy use, followed by DMF, DMSO and sulfolane. However, the manufacture of DMAc generates 38% less life cycle emissions than NMP manufacture. The manufacture of DMF, DMSO, and sulfolane generate 46%, 69%, and 81% less life cycle emissions than NMP manufacture. Table 72 shows that NMP manufacture causes the most damage to human health, ecosystems, and resources. DMAc manufacture causes the second most damage to these endpoints, followed by DMF manufacture. Sulfolane manufacture causes the least damage to ecosystems and resources, while DMSO manufacture causes the least damage to human health. Sulfolane manufacture causes more damage to human health than DMSO manufacture because more SO_2 emissions are generated from sulfolane manufacture, shown in Table 71.

The analysis of the health, safety, environmental impacts, and physical properties of NMP and potential substitutes showed that DMSO and sulfolane are the best substitute options. DMSO and sulfolane are less toxic than NMP, and are not suspected developmental and reproductive toxins. DMSO and sulfolane both have physical properties that show they would remain stable in the resin precursor process. Use of sulfolane would reduce the safety risk of the DuPont resin precursor process because it has a higher flash point than NMP and DMSO. The manufacturing of DMSO and sulfolane has a much lower impact on the environment, based on life cycle emissions and ReCiPe damage scores.

The cost to purchase DMSO and sulfolane was researched, for comparison to the cost of NMP. As mentioned previously, the cost to purchase NMP is 1.95 \$/lb. Industrial-scale costs for DMSO and sulfolane could not be found, so they were estimated. Spectrum Chemicals lists the cost of NMP, DMSO, and sulfolane as 10.35 \$/lb, 11.13 \$/lb, and 15.24 \$/lb; respectively [153]. This shows that the industrial-scale, "bulk" quantity, cost of NMP is about 19% of the cost of NMP from Spectrum Chemicals. The cost from Spectrum Chemicals is much higher than the industrial scale cost because it is the cost to purchase a small quantity, rather than a large bulk quantity. It was assumed that the industrial-scale costs of DMSO and sulfolane were also 19% of the cost listed by Spectrum Chemicals. The costs for DMSO and sulfolane used in this case study were 2.10 \$/lb and 3.09 \$/lb. DMSO and sulfolane are both more expensive than NMP.

Case 1A-DMSO and Case 1A-Sulfolane: Solvent Substitution

NMP substitution with DMSO and sulfolane, without solvent recovery, were investigated in Case 1A-DMSO and Case 1A-Sulfolane. This green engineering approach focuses on Green Engineering Principle 1 and Green Chemistry Principles 3 and 5. These principles focus on use of less hazardous raw materials. The green engineering approach in this section focuses on replacing NMP with less hazardous solvents. As mentioned previously, DMSO and sulfolane are less hazardous solvents. Use of DMSO and sulfolane was investigated to see if environmental and economic impacts are reduced.

It was assumed that DMSO and sulfolane could be substituted for NMP at a 1:1 mass ratio. Therefore, the annualized flow rate of aqueous solvent waste remains 2,500,000 lb/yr. The raw material use and waste generation associated with Case 1A-DMSO and Case 1A-Sulfolane scenarios is shown in Table 73. The raw material use and waste generated by Case 1A-DMSO and Case 1A-Sulfolane scenarios are the same because both solvents are substituted at a 1:1 ratio. As mentioned previously, it is assumed that the amount of solvent present in the hazardous waste is amount of virgin solvent fed to the process, while the amount of water present in the hazardous waste is the amount of ultrapure water fed to the process.

Table 73

Raw material use and waste generation for Case 1A-DMSO and Case 1A-Sulfolane scenarios

Hazardous Waste Solvent Composition	**Solvent Used (lb/yr)**	**Ultrapure Water Used (lb/yr)**	**Hazardous Waste Generated (lb/yr)**
5 wt.%	125,000	2,375,000	2,500,000
10 wt.%	250,000	2,250,000	2,500,000
20 wt.%	500,000	2,000,000	2,500,000
30 wt.%	750,000	1,750,000	2,500,000
40 wt.%	1,000,000	1,500,000	2,500,000
50 wt.%	1,250,000	1,250,000	2,500,000
60 wt.%	1,500,000	1,000,000	2,500,000
70 wt.%	1,750,000	750,000	2,500,000
80 wt.%	2,000,000	500,000	2,500,000
90 wt.%	2,250,000	250,000	2,500,000
95 wt.%	2,375,000	125,000	2,500,000

The total life cycle emissions and life cycle CO_2 emissions associated with Case 1A-DMSO and Case 1A-Sulfolane scenarios are shown in Table 74. The life cycle emissions for each scenario are a sum of the life cycle emissions from solvent manufacture, ultrapure water production, and hazardous waste disposal; as shown previously in Equation 28. The LCI for hazardous solvent waste disposal is the same for all solvents. For the Case 1A-DMSO, the scenario with a waste stream of 95 wt.% DMSO has the most total life cycle emissions, 6,140,000 lb/yr, and the most life cycle CO_2 emissions, 5,500,000 lb/yr. The scenario with a waste stream of 5 wt.% DMSO has the least total and CO_2 life cycle emissions of the DMSO scenarios, at 350,000 lb/yr and 311,000 lb/yr, respectively. For Case 1A-Sulfolane, the scenario with a waste stream of 95 wt.% sulfolane has the most total life cycle emissions, 4,980,000 lb/yr, and the most life cycle CO_2 emissions, 4,470,000 lb/yr. The scenario with a waste stream of 5 wt.% sulfolane has the least total and CO_2 life cycle emissions of the sulfolane scenarios, at 289,000 lb/yr and 257,000 lb/yr, respectively.

Table 74

Total and CO_2 life cycle emissions for Case 1A-DMSO and Case 1A-Sulfolane

	Case 1A-DMSO		**Case 1A-Sulfolane**	
Hazardous Waste Solvent Composition	**Total Emissions (lb/yr)**	**CO_2 Emissions (lb/yr)**	**Total Emissions (lb/yr)**	**CO_2 Emissions (lb/yr)**
5 wt.%	3.50E+05	3.11E+05	2.89E+05	2.57E+05
10 wt.%	6.72E+05	5.99E+05	5.50E+05	4.91E+05
20 wt.%	1.32E+06	1.17E+06	1.07E+06	9.59E+05
30 wt.%	1.96E+06	1.75E+06	1.59E+06	1.43E+06
40 wt.%	2.60E+06	2.33E+06	2.11E+06	1.90E+06
50 wt.%	3.25E+06	2.90E+06	2.63E+06	2.36E+06
60 wt.%	3.89E+06	3.48E+06	3.15E+06	2.83E+06
70 wt.%	4.53E+06	4.06E+06	3.67E+06	3.30E+06
80 wt.%	5.17E+06	4.63E+06	4.19E+06	3.77E+06
90 wt.%	5.82E+06	5.21E+06	4.72E+06	4.24E+06
95 wt.%	6.14E+06	5.50E+06	4.98E+06	4.47E+06

The reduction in total life cycle emissions and life cycle CO_2 emissions for Case 1A-DMSO and Case 1A-Sulfolane compared to Case 1A-NMP was calculated. Table 75 shows that use of DMSO and sulfolane significantly reduces total life cycle emissions and life cycle CO_2 emissions for the Case 1 scenarios. Use of DMSO reduces life cycle emissions by 51% to 53%, depending on the scenario. However, use of sulfolane further reduces life cycle emissions. The Case 1A-Sulfolane scenarios reduce life cycle emissions by 60% to 62% depending on the scenario.

Table 75

Percent reduction in total and CO_2 life cycle emissions for Case 1A-DMSO and Case 1A-Sulfolane

	Case 1A-DMSO		**Case 1A-Sulfolane**	
Hazardous Waste Solvent Composition	**Total Life Cycle Emissions**	**Life Cycle CO_2 Emissions**	**Total Life Cycle Emissions**	**Life Cycle CO_2 Emissions**
5 wt.%	50.9	50.5	59.5	59.1
10 wt.%	52.0	51.5	60.7	60.2
20 wt.%	52.5	51.9	61.4	60.8
30 wt.%	52.7	52.1	61.6	60.9
40 wt.%	52.8	52.2	61.7	61.0
50 wt.%	52.8	52.2	61.7	61.1
60 wt.%	52.9	52.3	61.8	61.1
70 wt.%	52.9	52.3	61.8	61.2
80 wt.%	53.0	52.3	61.9	61.2
90 wt.%	53.1	52.3	62.0	61.2
95 wt.%	53.1	52.3	62.0	61.2

ReCiPe methodology was used to calculate the damage associated with Case 1 scenarios using DMSO and sulfolane, shown in Table 76. The damage for each scenario is the sum of the damage from solvent manufacture, ultrapure water production, and hazardous waste disposal; as shown in Equation 29. The damage score for hazardous solvent waste disposal is the same for all solvents. For the Case 1A-DMSO, the scenario with a waste stream of 95 wt.% DMSO has the most damage to human health (87,100,000 mPt/yr), ecosystems (50,700,000 mPt/yr), and resources (75,200,000 mPt/yr). The scenario with a waste stream of 5 wt.% DMSO has the least damage of the DMSO scenarios, with damage scores of 4,920,000 mPt/yr, 2,850,000 mPt/yr, and 4,210,000 mPt/yr to human health, ecosystems, and resources; respectively. For Case 1A-Sulfolane, the scenario with a waste stream of 95 wt.% sulfolane has the most damage to human health, ecosystems, and resources; with damage scores of 105,000,000 mPt/yr, 39,800,000 mPt/yr, and 50,000,000 mPt/yr; respectively. The scenario with a waste stream of 5 wt.% sulfolane has the least damage of the sulfolane scenarios, with damage scores of 5,860,000 mPt/yr, 2,280,000 mPt/yr, and 2,880,000 mPt/yr to human health, ecosystems, and resources; respectively.

Table 76

ReCiPe damage assessment for Case 1A-DMSO and Case 1A-Sulfolane

	Case 1A-DMSO			**Case 1A-Sulfolane**		
Hazardous Waste Solvent Composition	**Human Health**	**Ecosystems**	**Resources**	**Human Health**	**Ecosystems**	**Resources**
5 wt.%	4.92E+06	2.85E+06	4.21E+06	5.86E+06	2.28E+06	2.88E+06
10 wt.%	9.48E+06	5.51E+06	8.15E+06	1.14E+07	4.37E+06	5.50E+06
20 wt.%	1.86E+07	1.08E+07	1.60E+07	2.24E+07	8.54E+06	1.07E+07
30 wt.%	2.77E+07	1.61E+07	2.39E+07	3.34E+07	1.27E+07	1.60E+07
40 wt.%	3.69E+07	2.15E+07	3.18E+07	4.44E+07	1.69E+07	2.12E+07
50 wt.%	4.60E+07	2.68E+07	3.97E+07	5.54E+07	2.11E+07	2.65E+07
60 wt.%	5.51E+07	3.21E+07	4.76E+07	6.64E+07	2.52E+07	3.17E+07
70 wt.%	6.42E+07	3.74E+07	5.55E+07	7.74E+07	2.94E+07	3.69E+07
80 wt.%	7.34E+07	4.27E+07	6.34E+07	8.84E+07	3.36E+07	4.22E+07
90 wt.%	8.25E+07	4.80E+07	7.13E+07	9.94E+07	3.77E+07	4.74E+07
95 wt.%	8.71E+07	5.07E+07	7.52E+07	1.05E+08	3.98E+07	5.00E+07

The reduction in damage to human health, ecosystems, and resources from substituting NMP with DMSO and sulfolane in the Case 1 scenarios was calculated. Table 77 shows that use of DMSO and sulfolane significantly reduces the damage caused by the Case 1 scenarios. Use of DMSO provides the greatest reduction in damage to human health, while the use of sulfolane provides the greatest reduction in damage to ecosystems and resources. However, use of sulfolane results in the greatest reduction in total damage, reducing total damage by 57% to 59% depending on the scenario. Use of DMSO reduces total damage by 54% to 55% depending on the scenario. The damage results are consistent with the life cycle emission results, showing that substitution to DMSO and sulfolane is environmentally favorable for all scenarios. However, scenarios using sulfolane have less impact on the environment than those using DMSO.

Table 77

Percent reduction in damage for Case 1A-DMSO and Case 1A-Sulfolane

	Case 1A-DMSO			**Case 1A-Sulfolane**		
Hazardous Waste Solvent Composition	**Human Health**	**Ecosystems**	**Resources**	**Human Health**	**Ecosystems**	**Resources**
5 wt.%	53.0	50.3	56.0	44.1	60.3	69.9
10 wt.%	53.9	51.2	56.8	44.8	61.3	70.8
20 wt.%	54.4	51.6	57.2	45.2	61.8	71.3
30 wt.%	54.6	51.8	57.3	45.3	62.0	71.5
40 wt.%	54.6	51.8	57.4	45.4	62.1	71.6
50 wt.%	54.7	51.9	57.4	45.4	62.2	71.6
60 wt.%	54.7	51.9	57.4	45.5	62.2	71.6
70 wt.%	54.7	51.9	57.4	45.5	62.2	71.7
80 wt.%	54.8	52.0	57.5	45.5	62.3	71.7
90 wt.%	54.8	52.0	57.5	45.5	62.3	71.7
95 wt.%	54.8	52.0	57.5	45.5	62.3	71.7

The operating costs associated with Case 1A-DMSO and Case 1A-Sulfolane scenarios are shown in Table 78. The operating costs for each scenario are a sum of the cost to purchase virgin solvent, produce ultrapure water, and dispose of hazardous waste; as shown in Equation 30. Table 78 shows that operating costs are not reduced from substituting NMP with DMSO and sulfolane. For Case 1A-DMSO, operating costs are slightly higher than for Case 1A-NMP. Operating costs increase by 2% to 7% depending on the scenario. However, using sulfolane significantly increases the operating costs of Case 1 scenarios. Operating costs increase by 17% to 52% depending on the scenario. Although it is environmentally beneficial to replace NMP with sulfolane, it is not economically beneficial because sulfolane is much more expensive than NMP. It is more practical to replace NMP with DMSO because environmental impact is significantly reduced and operating costs are only slightly increased.

Table 78

Operating costs for Case 1A-DMSO and Case 1A-Sulfolane

Hazardous Waste Solvent Composition	**DMSO Operating Cost ($/yr)**	**Sulfolane Operating Cost ($/yr)**	**DMSO Operating Cost Reduction (%)**	**Sulfolane Operating Cost Reduction (%)**
5 wt.%	881,000	1,004,000	-2.2	-16.5
10 wt.%	1,142,000	1,390,000	-3.4	-25.8
20 wt.%	1,666,000	2,161,000	-4.7	-35.8
30 wt.%	2,189,000	2,932,000	-5.4	-41.2
40 wt.%	2,713,000	3,703,000	-5.9	-44.5
50 wt.%	3,236,000	4,474,000	-6.2	-46.7
60 wt.%	3,760,000	5,245,000	-6.4	-48.4
70 wt.%	4,283,000	6,016,000	-6.5	-49.6
80 wt.%	4,807,000	6,787,000	-6.7	-50.6
90 wt.%	5,330,000	7,558,000	-6.8	-51.4
95 wt.%	5,592,000	7,943,000	-6.8	-51.7

Case 1B-DMSO and Case 1B-Sulfolane: Solvent Substitute Recovery Using Distillation

Solvent recovery for Case 1 scenarios using solvent substitutes were evaluated in Case 1B-DMSO and Case 1B-Sulfolane. This green engineering approach combines Green Chemistry Principles 3 and 5 and Green Engineering Principles 1, 3, 4, 10, and 12. This approach follows these principles by using less hazardous solvent and by using this solvent more efficiently, through recovery and reuse. Analysis of this approach will determine if the combination of these principles results in the greenest approach.

Distillation was investigated because it is the most common method of solvent separation [130]. T-*x*-*y* equilibrium diagrams were generated using Aspen Plus® for the DMSO-water system and sulfolane-water system at 1 atm. These diagrams were plotted to determine if distillation is a viable separation technique for the two systems. The UNIQUAC model was chosen for both systems because DMSO, sulfolane, and water are polar [131]. The T-*x*-*y* diagrams in Figure 15 and Figure 16 show that an azeotrope does not exist for the DMSO-water system and the sulfolane-water system. The equilibrium data for the DMSO-water and the sulfolane-water systems show that distillation is a feasible separation option for both solvents. Recovery of DMSO and sulfolane, using distillation, was evaluated for all Case 1 scenarios.

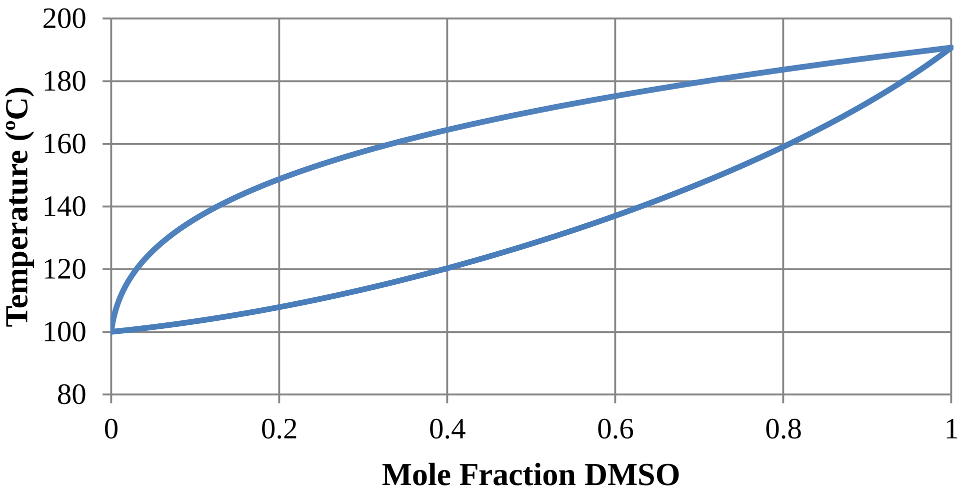


Figure 15. T-*x*-*y* equilibrium diagram for DMSO and water system

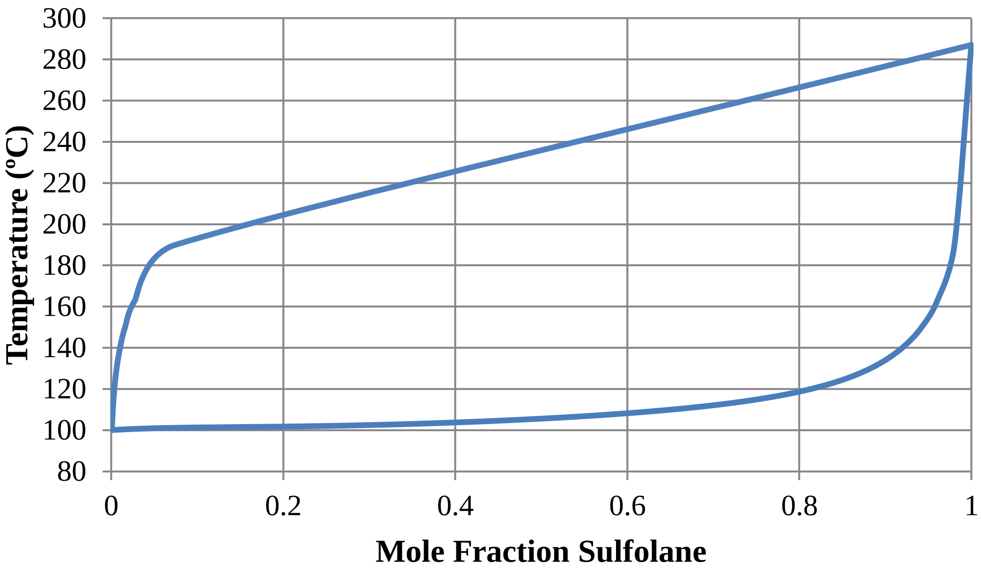


Figure 16. T-*x*-*y* equilibrium diagram for sulfolane and water system

Distillation systems for DMSO and sulfolane recovery were designed and optimized using the R.SWEET software for solvent recovery assessment that was developed at Rowan University [132]. DMSO and sulfolane are recovered using the same approach as NMP, shown previously in Figure 12. Like the Case 1B-NMP scenarios, DMSO and sulfolane are recovered from the bottoms of the distillation column. The recovered solvent is then reused in the process. It was assumed that DMSO and sulfolane are recovered at the same purity as NMP (99.97 wt.%). In R.SWEET, the DMSO and sulfolane composition in the distillation column bottoms was specified as 99.97 wt.%. The distillate from the distillation column contains water with trace solvent (<0.15 wt.% solvent) and is sent to a public wastewater treatment plant.

The distillation systems were designed to treat 2,500,000 lb/yr of hazardous solvent waste. The feed flow rate to the distillation system was again set to 5,000 lb/hr. This results in an operating time of about 500 hr/yr. The distillation columns for DMSO and sulfolane recovery were designed to operate below atmospheric pressure to prevent solvent decomposition. The distillation systems for Case 1B-DMSO and Case 1B-Sulfolane scenarios were individually designed and optimized, using the previously mentioned specifications. Therefore, the environmental impact from operation, capital cost, and operating cost vary for each scenario.

The distillation systems for DMSO and sulfolane recovery scenarios include the equipment shown previously in Figure 12. However, the DMSO and sulfolane distillation systems also include a vacuum pump, so the columns can be operated below atmospheric pressure. Holding Tank 1 is used in each scenario to store the hazardous solvent waste prior to distillation. The distillation systems are designed to run for 9.6 hr/week to reach the operating requirement of 500 hr/yr. Holding Tank 1 must store 5,900 gal of hazardous solvent waste, the same as Holding Tank 1 from the NMP distillation system. This means that Holding Tank 1 has the same specifications for all distillation systems, shown previously in Table 43. Once 5,900 gal of hazardous solvent waste is collected in Holding Tank 1, it is fed to the distillation column at a flow rate of 5,000 lb/hr. The feed pump specifications for the DMSO and sulfolane distillation systems are also the same as the feed pump specifications for the NMP distillation systems, shown previously in Table 43.

Distillation columns were individually designed using R.SWEET for DMSO and sulfolane recovery scenarios. However, there were common design specifications, listed in Table 79. All distillation columns were designed as packed columns, constructed out of glass-lined carbon steel and packed with 1.5 in ceramic Intalox saddles. The DMSO distillation columns were operated at 8.5 psia, to prevent DMSO decomposition. This results in a reboiler operating temperature of 170ºC, which is below the decomposition temperature of 189ºC. The sulfolane distillation columns were operated at 3.5 psia to keep the reboiler temperature at 200ºC. This is below sulfolane’s decomposition temperature, which is 220ºC. R.SWEET was used to determine the number of stages required to recover DMSO and sulfolane from Case 1 scenarios. All sulfolane distillation systems required 6 stages. DMSO distillation systems with feed streams containing less than 90 wt.% DMSO required 7 stages, while distillation systems with feed streams containing 90 wt.% and 95 wt.% DMSO required 8 stages.

Table 79

Case 1B-DMSO and Case 1B-Sulfolane distillation column specifications

	DMSO Recovery	**Sulfolane Recovery**
Material of Construction	Glass-lined Carbon Steel	Glass-lined Carbon Steel
Number of Stages	7 (<90 wt.% DMSO) 8 (90 wt.% and 95 wt.% DMSO)	6
Feed Stage	3 (<90 wt.% DMSO) 4 (90 wt.% and 95 wt.% DMSO)	3
Packing Material	1.5 in ceramic Intalox saddles	1.5 in ceramic Intalox saddles
Height	18 ft (<90 wt.% DMSO) 20 ft (90 wt.% and 95 wt.% DMSO)	10 ft
Packed Height	12 ft (<90 wt.% DMSO) 14 ft (90 wt.% and 95 wt.% DMSO)	16 ft
Design Pressure	25 psig	25 psig
Design Vacuum Pressure	-6.2 psig	-11.2 psig
Design Temperature	390ºF	450ºF

The column diameter, reboiler heat transfer area, and condenser heat transfer area varied for each scenario. Table 80 shows that column diameter decreased as the DMSO composition in the feed increased from 5 wt.% to 50 wt.%. The column diameter increased for DMSO feed compositions of 60 wt.%, 70 wt.%, and 80 wt.% because a higher reflux ratio was needed for the separation. Reboiler heat transfer area was calculated assuming an overall heat transfer coefficient of 1,000 $W/m^2 \cdot {}^\circ C$ and use of saturated steam at 30 bar (234ºC) [127]. Condenser heat transfer area was calculated assuming an overall heat transfer coefficient of 1,200 $W/m^2 \cdot {}^\circ C$ and a cooling water temperature change of 15ºC [127]. The reboilers and condensers for DMSO recovery followed the same trend as column diameter. The duties, and therefore heat transfer areas, decreased as the DMSO feed composition increased from 5 wt.% to 50 wt.%. The duties and heat transfer areas increased for compositions of 60 wt.%, 70 wt.%, and 80 wt.% DMSO. Table 81 shows that for sulfolane recovery column diameter, reboiler heat transfer area, and condenser area decrease as sulfolane composition in the feed stream increases. The common specifications for the reboilers and condensers are shown previously in Table 46.

Table 80

Case 1B-DMSO distillation system specifications

Hazardous Waste DMSO Composition	**Column Diameter (ft)**	**Reboiler Duty (kW)**	**Condenser Duty (kW)**	**Reboiler Area (ft^2)**	**Condenser Area (ft^2)**
5 wt.%	5.5	2,898	-2,757	595	1,650
10 wt.%	5.25	2,764	-2,612	565	1,565
20 wt.%	5	2,492	-2,322	510	1,390
30 wt.%	4.75	2,216	-2,032	455	1,215
40 wt.%	4.5	1,937	-1,742	400	1,045
50 wt.%	4	1,655	-1,452	340	870
60 wt.%	4.5	1,947	-1,741	400	1,045
70 wt.%	4.5	1,946	-1,741	400	1,045
80 wt.%	4.5	1,940	-1,740	400	1,045
90 wt.%	2.5	624	-434	130	260
95 wt.%	2.5	544	-361	115	220

Table 81

Case 1B-Sulfolane distillation system specifications

Hazardous Waste DMSO Composition	**Column Diameter (ft)**	**Reboiler Duty (kW)**	**Condenser Duty (kW)**	**Reboiler Area (ft^2)**	**Condenser Area (ft^2)**
5 wt.%	5	2,895	-2,815	815	1,685
10 wt.%	5	2,752	-2,667	775	1,595
20 wt.%	4.75	2,467	-2,371	695	1,420
30 wt.%	4.5	2,182	-2,074	615	1,240
40 wt.%	4	1,897	-1,778	535	1,065
50 wt.%	3.75	1,611	-1,481	455	890
60 wt.%	3.5	1,325	-1,185	375	710
70 wt.%	3	1,038	-888	295	535
80 wt.%	2.5	749	-592	215	355
90 wt.%	2	459	-296	130	180
95 wt.%	1.5	313	-147	90	90

The accumulator, reflux pump designs, and vacuum pump designs varied for the DMSO and sulfolane distillation systems, as shown in Table 82 and Table 83. The accumulator dimensions were calculated using the flow rate out of the condenser and a residence time of 10 min. The liquid flow rate through the reflux pump was the reflux flow rate. The vacuum pump flow rate was calculated using Equation 41. For the DMSO distillation systems, the accumulator dimensions decreased as the feed composition of DMSO increased. However, the reflux flow rate and vacuum pump flow rate increased as DMSO feed composition increased from 60 wt.% to 80 wt.%. This occurred because a higher reflux ratio was required and distillation equipment was larger. For the sulfolane distillation systems accumulator dimensions, reflux flow rates, and vacuum pump flow rates decreased as the feed sulfolane composition increased. The accumulator and reflux pump specifications that remained consistent for all scenarios are shown previously in Table 48.

Table 82

Case 1B-DMSO accumulator and reflux pump specifications

Hazardous Waste Solvent Composition	**Accumulator Diameter (ft)**	**Accumulator Length (ft)**	**Reflux Pump Flow Rate (gpm)**	**Vacuum Pump Flow Rate (ft^3/min)**
5 wt.%	2	8	10	660
10 wt.%	2	8	9.5	610
20 wt.%	2	8	8.5	550
30 wt.%	2	8	7.5	500
40 wt.%	1.75	7	6.5	440
50 wt.%	1.75	7	5.5	360
60 wt.%	1.75	7	8.5	440
70 wt.%	1.75	7	9.5	440
80 wt.%	1.75	7	10.5	440
90 wt.%	1	4	2	150
95 wt.%	1	4	2	140

Table 83

Case 1B-Sulfolane accumulator and reflux pump specifications

Hazardous Waste Solvent Composition	Accumulator Diameter (ft)	Accumulator Length (ft)	Reflux Pump Flow Rate (gpm)	Vacuum Pump Flow Rate (ft^3/min)
5 wt.%	2	8	10	1,460
10 wt.%	2	8	9.5	1,440
20 wt.%	2	8	8.5	1,280
30 wt.%	2	8	7.5	1,180
40 wt.%	1.75	7	6.5	940
50 wt.%	1.75	7	5.5	840
60 wt.%	1.5	6	4.5	720
70 wt.%	1.5	6	3.5	550
80 wt.%	1.25	5	2	370
90 wt.%	1	4	1	240
95 wt.%	1	4	0.5	160

$$q_{v\,pump} = \frac{V_{system}}{t} \times ln\frac{P_{initial}}{P_{final}} \tag{41}$$

In Equation 41, $q_{v\,pump}$ is the flow rate of the vacuum pump in ft^3/min, V_{system} is the volume of the distillation system (column, accumulator, reboiler, and condenser) in ft^3, t is the time to reach the desired pressure (0.5 min), $P_{initial}$ is the initial pressure (14.7 psi), and P_{final} is the vacuum pressure in psi.

Holding Tank 2 was designed to store the recovered DMSO and sulfolane, prior to use in the Case 1 process. Holding Tank 2 must store the recovered solvent from 9.6 hr of operation of the distillation system. For each scenario, Holding Tank 2 was designed as a vertical flat bottomed storage tank to hold the volume of recovered solvent from 9.6 hr of distillation and have a head space of about 20%. The dimensions of Holding Tank 2 varied for each scenario, as the volume of solvent recovered increased as solvent composition in the feed stream increased. The specifications for Holding Tank 2, for the DMSO and sulfolane distillation systems are listed in Table 84. The Holding Tank 2 specifications that remained consistent for all scenarios are shown previously in Table 50.

Table 84

Case 1B-DMSO and Case 1B-Sulfolane Holding Tank 2 dimensions

	Case 1B-DMSO			**Case 1B-Sulfolane**		
Hazardous Waste Solvent Composition	**Diameter (ft)**	**Height (ft)**	**Total Volume (gal)**	**Diameter (ft)**	**Height (ft)**	**Total Volume (gal)**
5 wt.%	3.25	6.5	400	3.25	6.5	400
10 wt.%	4	8	750	4	8	750
20 wt.%	5	10	1,500	5	10	1,500
30 wt.%	5.75	11.5	2,200	5.75	11.5	2,200
40 wt.%	6.25	12.5	2,900	6.25	12.5	2,900
50 wt.%	6.75	13.5	3,600	6.75	13.5	3,600
60 wt.%	7.25	14.5	4,500	7	14	4,000
70 wt.%	7.5	15	5,000	7.25	14.5	4,500
80 wt.%	8	16	6,000	7.5	15	5,000
90 wt.%	8.25	16.5	6,600	7.75	15.5	5,500
95 wt.%	8.25	16.5	6,600	8	16	6,000

The installed capital cost for each distillation system, based on fourth quarter 2014 costs, was estimated using Aspen Capital Cost Estimator. The installed capital cost includes the cost for equipment, piping, support structures, electrical work, insulation, and manpower. The equipment included in the installed capital cost are Holding Tanks 1 and 2, the feed and reflux pumps, the distillation column, the reboiler, the condenser, and the accumulator; shown previously in Figure 12. The DMSO and sulfolane distillation systems also include a vacuum pump. The installed capital costs for the NMP, DMSO, and sulfolane distillation systems are shown in Table 85. Table 85 shows that capital costs mainly decrease as solvent composition increases. It was also found that the NMP distillation systems have the lowest capital costs for all scenarios. DMSO distillation systems have the second lowest capital costs for scenarios with 10 wt.%, 20 wt.%, 30 wt.%, and 50 wt.% solvent. Sulfolane distillation systems have the second lowest capital costs for the remaining scenarios. The NMP distillation systems have the lowest capital costs because they operate at atmospheric pressure.

Table 85

Case 1 distillation system capital costs

Hazardous Waste Solvent Composition	**NMP Recovery Capital Cost ($)**	**DMSO Recovery Capital Cost ($)**	**Sulfolane Recovery Capital Cost ($)**
5 wt.%	1,180,000	1,262,000	1,255,000
10 wt.%	1,178,000	1,227,000	1,243,000
20 wt.%	1,174,000	1,218,000	1,229,000
30 wt.%	1,185,000	1,219,000	1,246,000
40 wt.%	1,157,000	1,189,000	1,187,000
50 wt.%	1,091,000	1,108,000	1,117,000
60 wt.%	1,058,000	1,229,000	1,090,000
70 wt.%	1,043,000	1,234,000	1,077,000
80 wt.%	975,000	1,242,000	1,006,000
90 wt.%	953,000	982,000	949,000
95 wt.%	897,000	979,000	901,000

The raw materials used, utilities used, and waste generated by the Case 1B-DMSO and Case 1B-Sulfolane scenarios are shown in Table 86 and Table 87. The mass of recovered solvent and distillate wastewater were found using the R.SWEET program. There was no hazardous waste generated by the Case 1 distillation scenarios. The utility use of the distillation processes was calculated using the reboiler and condenser duties shown in Table 80 and Table 81. The steam energy use was calculated using Equation

34, while the electricity used to pump cooling water was calculated using Equation 35. The electricity used by the feed, reflux, and vacuum pumps were calculated using Equation 36. It was found that the sulfolane distillation systems recover the most solvent, followed by the NMP distillation systems and the DMSO distillation systems, respectively. The DMSO distillation systems used the most steam, while the sulfolane distillation systems used the least steam except for in the 5 wt.% scenario. The NMP distillation systems use the least electricity, while the sulfolane distillation scenarios ranging from 5 wt.% to 50 wt.% used the most electricity.

Table 86

Raw material use, utility use, and waste generation for each Case 1B-DMSO scenario

Hazardous Waste DMSO Composition	**DMSO Used (lb/yr)**	**Ultrapure Water Used (lb/yr)**	**Wastewater Generated (lb/yr)**	**Steam Used (MJ/yr)**	**Electricity Used (MJ/yr)**
5 wt.%	871	2,375,000	2,372,000	5,787,000	200,800
10 wt.%	1,093	2,250,000	2,247,000	5,518,000	192,000
20 wt.%	1,562	2,000,000	1,997,000	4,976,000	174,400
30 wt.%	2,084	1,750,000	1,748,000	4,426,000	150,200
40 wt.%	2,700	1,500,000	1,499,000	3,869,000	132,600
50 wt.%	3,501	1,250,000	1,249,000	3,304,000	115,100
60 wt.%	3,063	1,000,000	999,000	3,888,000	132,600
70 wt.%	3,201	750,000	749,100	3,886,000	132,600
80 wt.%	3,302	500,000	499,200	3,874,000	139,200
90 wt.%	3,178	250,000	249,100	1,247,000	36,690
95 wt.%	3,268	125,000	124,200	1,087,000	32,240

Table 87

Raw material use, utility use, and waste generation for each Case 1B-Sulfolane scenario

Hazardous Waste Sulfolane Composition	Sulfolane Used (lb/yr)	Ultrapure Water Used (lb/yr)	Wastewater Generated (lb/yr)	Steam Used (MJ/yr)	Electricity Used (MJ/yr)
5 wt.%	183	2,375,000	2,371,000	5,780,000	251,300
10 wt.%	363	2,250,000	2,246,000	5,496,000	242,300
20 wt.%	717	2,000,000	1,997,000	4,927,000	210,900
30 wt.%	1,063	1,750,000	1,747,000	4,357,000	193,000
40 wt.%	1,401	1,500,000	1,497,000	3,787,000	161,600
50 wt.%	1,734	1,250,000	1,248,000	3,216,000	143,700
60 wt.%	2,062	1,000,000	998,000	2,645,000	112,300
70 wt.%	2,387	750,000	748,300	2,072,000	87,650
80 wt.%	2,710	500,000	498,600	1,496,000	56,290
90 wt.%	3,034	250,000	248,900	916,900	31,640
95 wt.%	3,196	125,000	124,100	625,100	19,310

The environmental impact of Case 1B-DMSO and Case 1B-Sulfolane was calculated using Equations 31 and 32, and the raw material use, utility use, and waste generation values in Table 86 and Table 87. The life cycle emissions for Case 1B-DMSO and Case 1B-Sulfolane are shown in Table 88. More than 85% of the total life cycle emissions, for each scenario, are attributed to steam generation for operation of the distillation column reboiler. The total life cycle emissions mainly decrease as solvent composition increases because less steam is needed to operate the distillation columns. The sulfolane distillation systems generate less total and CO2 emissions than the DMSO distillation systems, except for the scenarios with 5 wt.% and 10 wt.% solvent.

Table 88

Total and CO_2 life cycle emissions for Case 1B-DMSOand Case 1B-Sulfolane

	Case 1B-DMSO		Case 1B-Sulfolane	
Hazardous Waste Solvent Composition	**Total Emissions (lb/yr)**	**CO_2 Emissions (lb/yr)**	**Total Emissions (lb/yr)**	**CO_2 Emissions (lb/yr)**
5 wt.%	1.00E+06	9.81E+05	1.01E+06	9.90E+05
10 wt.%	9.54E+05	9.35E+05	9.62E+05	9.42E+05
20 wt.%	8.60E+05	8.43E+05	8.60E+05	8.42E+05
30 wt.%	7.64E+05	7.49E+05	7.62E+05	7.46E+05
40 wt.%	6.68E+05	6.55E+05	6.60E+05	6.47E+05
50 wt.%	5.71E+05	5.60E+05	5.62E+05	5.50E+05
60 wt.%	6.51E+05	6.40E+05	4.60E+05	4.51E+05
70 wt.%	6.41E+05	6.30E+05	3.60E+05	3.52E+05
80 wt.%	6.32E+05	6.21E+05	2.57E+05	2.52E+05
90 wt.%	2.08E+05	2.04E+05	1.56E+05	1.53E+05
95 wt.%	1.78E+05	1.75E+05	1.05E+05	1.03E+05

Table 89 shows the percent reduction in total life cycle emissions from solvent substitution and/or recovery. These calculations show the reduction in total life cycle emissions compared to Case 1A-NMP scenarios. As mentioned previously, it is environmentally beneficial to recover NMP from the solvent waste for all Case 1 scenarios, except when the waste contains 5 wt.% NMP. It is also environmentally beneficial to use and recover DMSO and sulfolane, except when the waste contains 5 wt.% solvent. Based on life cycle emissions, solvent should not be recovered from the 5 wt.% waste streams. For the Case 1 scenario with a waste stream containing 5 wt.% NMP, the best option in terms of life cycle emissions is to substitute NMP with sulfolane and not recover it. Substitution of NMP with sulfolane, without recovery, is also the best option for the scenario with 10 wt.% NMP. For the scenarios with waste streams containing 20 wt.% and 30 wt.% NMP, the best option is to recover and reuse the NMP. For scenarios with waste streams containing more than 30 wt.% NMP, the best option is to use sulfolane and recover it for reuse. However, the reduction in life cycle emissions from sulfolane recovery scenarios is not much greater than the reduction from DMSO or NMP recovery scenarios.

Table 89

Percent reduction in total life cycle emissions for Case 1 scenarios

Hazardous Waste Solvent Composition	**Case 1B-NMP**	**Case 1A-DMSO**	**Case 1B-DMSO**	**Case 1A-Sulfolane**	**Case 1B-Sulfolane**
5 wt.%	-38.7	50.9	-40.1	59.5	-41.6
10 wt.%	32.5	52.0	31.8	60.7	31.3
20 wt.%	69.3	52.5	69.0	61.4	68.9
30 wt.%	81.7	52.7	81.6	61.6	81.6
40 wt.%	88.0	52.8	87.9	61.7	88.0
50 wt.%	91.7	52.8	91.7	61.7	91.8
60 wt.%	94.2	52.9	92.1	61.8	94.4
70 wt.%	96.1	52.9	93.3	61.8	96.3
80 wt.%	97.4	53.0	94.3	61.9	97.7
90 wt.%	98.4	53.1	98.3	62.0	98.7
95 wt.%	98.8	53.1	98.6	62.0	99.2

ReCiPe methodology was also used to calculate the environmental impact of Case 1B-DMSO and Case 1B-Sulfolane. The damage for each scenario is shown in Table 90. The damage assessment shows that for distillation scenarios, environmental impact mostly decreases as solvent composition in the hazardous waste stream increases. This is due to reduction in steam use as solvent composition increases. Steam generation is the biggest source of damage for the recovery scenarios, accounting for more than 85% of the total damage, for each scenario. As seen with the life cycle emissions analysis, the sulfolane distillation scenarios cause less damage than the DMSO distillation scenarios, except when the solvent composition is 5 wt.% or 10 wt.%.

Table 90

ReCiPe damage assessment for Case 1B-DMSO and Case 1B-Sulfolane

	Case 1B-DMSO			**Case 1B-Sulfolane**		
Hazardous Waste Solvent Composition	**Human Health**	**Ecosystems**	**Resources**	**Human Health**	**Ecosystems**	**Resources**
5 wt.%	1.38E+07	8.42E+06	2.11E+07	1.40E+07	8.50E+06	2.13E+07
10 wt.%	1.31E+07	8.03E+06	2.01E+07	1.33E+07	8.09E+06	2.02E+07
20 wt.%	1.19E+07	7.24E+06	1.82E+07	1.19E+07	7.23E+06	1.81E+07
30 wt.%	1.05E+07	6.43E+06	1.62E+07	1.06E+07	6.41E+06	1.61E+07
40 wt.%	9.21E+06	5.62E+06	1.42E+07	9.15E+06	5.55E+06	1.40E+07
50 wt.%	7.88E+06	4.81E+06	1.22E+07	7.80E+06	4.73E+06	1.19E+07
60 wt.%	8.98E+06	5.50E+06	1.42E+07	6.39E+06	3.87E+06	9.78E+06
70 wt.%	8.84E+06	5.42E+06	1.41E+07	5.01E+06	3.03E+06	7.69E+06
80 wt.%	8.71E+06	5.34E+06	1.41E+07	3.59E+06	2.17E+06	5.55E+06
90 wt.%	2.86E+06	1.75E+06	4.62E+06	2.20E+06	1.31E+06	3.44E+06
95 wt.%	2.46E+06	1.51E+06	4.03E+06	1.50E+06	8.86E+05	2.37E+06

Table 91 shows the percent reduction in total damage from solvent substitution and/or recovery. These calculations show the reduction in damage compared to Case 1A-NMP. The damage reduction calculations show similar results to the life cycle emissions reduction calculations. Both show that it is environmentally beneficial to recover all solvents, except when the waste contains 5 wt.% solvent. Both environmental metrics show that the best option for waste streams containing 5 wt.% and 10 wt.% NMP, is to substitute NMP with sulfolane and not recover it. For waste streams containing 20 wt.% and 30 wt.% NMP, both metrics show it is best to use NMP and recover it for reuse. For scenarios with NMP compositions greater than 30 wt.%, both metrics show that it is best to use sulfolane and recover it. However, the reduction in environmental impact from sulfolane recovery scenarios is not much greater than the reduction from DMSO or NMP recovery scenarios.

Table 91

Percent reduction in total damage for Case 1 scenarios

Hazardous Waste Solvent Composition	**Case 1B-NMP**	**Case 1A-DMSO**	**Case 1B-DMSO**	**Case 1A-Sulfolane**	**Case 1B-Sulfolane**
5 wt.%	-66.1	53.5	-67.9	57.2	-69.7
10 wt.%	19.5	54.4	18.6	58.2	18.0
20 wt.%	63.4	54.8	63.0	58.6	63.0
30 wt.%	78.2	55.0	78.0	58.8	78.1
40 wt.%	85.6	55.0	85.5	58.9	85.7
50 wt.%	90.1	55.1	90.1	58.9	90.2
60 wt.%	93.1	55.1	90.5	58.9	93.3
70 wt.%	95.3	55.1	91.9	59.0	95.5
80 wt.%	96.9	55.1	93.0	59.0	97.2
90 wt.%	98.0	55.2	97.9	59.0	98.5
95 wt.%	98.6	55.2	98.3	59.0	99.0

The operating costs associated with each Case 1 distillation scenario are shown in Table 92. The operating costs for each recovery scenario were calculated using Equation 33. Table 92 shows that the operating cost are lower for the NMP distillation systems. Sulfolane and DMSO distillation systems have the same operating costs for scenarios with 5 wt.% to 30 wt.% solvent. For scenarios with greater than 30 wt.% solvent, the sulfolane distillation systems have the second lowest operating costs.

Table 92

Operating costs for Case 1 distillation scenarios

Hazardous Waste NMP Composition	**NMP Recovery Operating Cost ($/yr)**	**DMSO Recovery Operating Cost ($/yr)**	**Sulfolane Recovery Operating Cost ($/yr)**
5 wt.%	104,000	108,000	108,000
10 wt.%	101,000	104,000	104,000
20 wt.%	93,000	96,000	96,000
30 wt.%	85,000	89,000	89,000
40 wt.%	77,000	81,000	80,000
50 wt.%	68,000	73,000	71,000
60 wt.%	60,000	77,000	63,000
70 wt.%	52,000	74,000	54,000
80 wt.%	42,000	72,000	45,000
90 wt.%	35,000	37,000	36,000
95 wt.%	30,000	34,000	31,000

Economic analyses were conducted to evaluate Case 1B-DMSO and Case 1B-Sulfolane based on both operating cost savings and recovery equipment capital costs. This was done to determine if recovery of an alternative solvent would save money for Case 1 scenarios. Operating cost savings alone may not result in savings because capital equipment is also needed. To determine if recovery of DMSO and sulfolane is profitable for Case 1, internal rate of return (IRR), return on investment (ROI), payback time after tax, net present value after 5 yr, and net present value after 10 yr were calculated for Case 1B-DMSO and Case 1B-Sulfolane. These calculations were performed using Equations 19 -27, shown previously. Table 93 and Table 94 show that DMSO and sulfolane recovery is profitable for all Case 1 scenarios. However, substitution to DMSO and recovery of DMSO for reuse is more profitable for scenarios with 10 wt.%, 20 wt%, 30 wt.%, and 50 wt.% solvent. For the other scenarios, it is more profitable to use sulfolane and recover it for reuse.

Table 93

Economic analysis of Case 1B-DMSO

Hazardous Waste DMSO Composition	IRR (%)	ROI (%)	Payback time after tax (yr)	5 yr NPV ($)	10 yr NPV ($)
5 wt.%	48.5	44.4	3.20	800,000	1,667,000
10 wt.%	67.6	59.4	2.23	1,444,000	2,578,000
20 wt.%	104.5	87.6	1.42	2,677,000	4,344,000
30 wt.%	142.0	115.3	1.05	3,902,000	6,104,000
40 wt.%	185.1	146.5	0.81	5,153,000	7,888,000
50 wt.%	242.9	187.5	0.62	6,449,000	9,717,000
60 wt.%	255.3	196.2	0.59	7,544,000	11,339,000
70 wt.%	292.7	222.6	0.52	8,752,000	13,076,000
80 wt.%	329.3	248.1	0.46	9,958,000	14,812,000
90 wt.%	474.9	349.2	0.32	11,472,000	16,879,000
95 wt.%	501.2	367.4	0.31	12,085,000	17,758,000

Table 94

Economic analysis of Case 1B-Sulfolane

Hazardous Waste Sulfolane Composition	IRR (%)	ROI (%)	Payback time after tax (yr)	5 yr NPV ($)	10 yr NPV ($)
5 wt.%	48.8	44.6	3.18	806,000	1,672,000
10 wt.%	66.7	58.6	2.26	1,429,000	2,562,000
20 wt.%	103.5	86.8	1.43	2,667,000	4,335,000
30 wt.%	138.6	112.8	1.07	3,878,000	6,081,000
40 wt.%	185.6	146.8	0.80	5,157,000	7,894,000
50 wt.%	241.0	186.1	0.62	6,446,000	9,716,000
60 wt.%	291.6	221.8	0.52	7,696,000	11,501,000
70 wt.%	340.3	255.8	0.45	8,935,000	13,274,000
80 wt.%	414.4	307.3	0.37	10,225,000	15,098,000
90 wt.%	492.1	361.1	0.31	11,502,000	16,909,000
95 wt.%	547.0	399.0	0.28	12,158,000	17,832,000

Table 95 shows the 10 yr net present value from solvent substitution and/or recovery. These calculations show the money saved after 10 yr from solvent substitution and/or recovery. Money is lost after 10 yr for the scenarios where NMP is substituted with DMSO and sulfolane, and DMSO and sulfolane are not recovered. Money is saved from recovering NMP, sulfolane, and DMSO. However, the most money is saved from using NMP and recovering it through distillation for reuse.

Table 95

10 yr NPV for Case 1 scenarios

Hazardous Waste Solvent Composition	**Case 1B-NMP**	**Case 1A-DMSO**	**Case 1B-DMSO**	**Case 1A-Sulfolane**	**Case 1B-Sulfolane**
5 wt.%	1,747,000	-94,000	1,667,000	-715,000	1,672,000
10 wt.%	2,629,000	-172,000	2,578,000	-1,430,000	2,562,000
20 wt.%	4,392,000	-376,000	4,344,000	-2,861,000	4,335,000
30 wt.%	6,144,000	-565,000	6,104,000	-4,291,000	6,081,000
40 wt.%	7,927,000	-753,000	7,888,000	-5,721,000	7,894,000
50 wt.%	9,747,000	-941,000	9,717,000	-7,152,000	9,716,000
60 wt.%	11,539,000	-1,129,000	11,339,000	-8,582,000	11,501,000
70 wt.%	13,311,000	-1,317,000	13,076,000	-10,012,000	13,274,000
80 wt.%	15,133,000	-1,506,000	14,812,000	-11,443,000	15,098,000
90 wt.%	16,910,000	-1,694,000	16,879,000	-12,873,000	16,909,000
95 wt.%	17,842,000	-1,788,000	17,758,000	-13,588,000	17,832,000

Analysis of these green engineering approaches to the Case 1 scenarios showed that following more Green Chemistry and Green Engineering Principles will not necessarily result in a more green option. Therefore, it is necessary to perform an overall LCA, including the recovery step, when analyzing the sustainability of a process. The evaluation of all alternative processes to the Case 1 process, showed that for scenarios with a solvent composition greater than 5 wt.% it is recommended to use NMP and recover it through distillation for reuse. This is the best option because it saves the most money and results in a significant reduction in environmental impact. Sulfolane recovery scenarios were found to have a greater reduction in environmental impact. However, the extra costs associated with the sulfolane recovery scenarios are not worth the slight reduction in environmental impact. Sulfolane recovery is more costly than NMP recovery because the distillation column must be operated under vacuum. For the scenario with 5 wt.% solvent, it is recommended to use sulfolane and not recover it if environmental impact is of primary concern. However, if cost reduction is of primary concern, it is recommended to use NMP and recover it through distillation for reuse.

As previously mentioned in the *Case 1 Conclusion*, the preliminary analysis found that NMP recovery using distillation is more environmentally and economically favorable than using pervaporation. Although distillation systems have a higher capital cost, more money is saved after 5 and 10 yr compared to pervaporation. Distillation provides a much higher recovery, which reduces the use of virgin NMP. Each separation still produces an unwanted process stream that must be treated, as will be discussed in the following analysis of the DuPont resin process. Although distillation requires much more steam, it provides the lowest impact option because it provides a very high NMP recovery and minimal waste. Therefore, distillation was chosen for the separation of NMP and water from the actual hazardous solvent waste from the DuPont resin precursor process. The preliminary analysis also showed that use of DMSO and sulfolane, with recovery, provided significant environmental and economic benefits. Therefore, the use of DMSO and sulfolane in the resin precursor process was investigated in Case 2.

Chapter 8

Case 2: NMP Recovery from DuPont's Resin Precursor Process

Case 2A-NMP: On-Site Recovery of NMP

After the preliminary designs for the simplified solvent recovery scenarios were completed, a solvent recovery system was designed and evaluated for DuPont's resin precursor process which consists of a multi-component waste stream. This system was designed to recover NMP from the hazardous solvent waste generated by the resin precursor process. The composition of this waste stream is shown previously in Table 13. Distillation was the first separation process investigated because Case 1 showed that distillation is an environmentally and economically favorable method to separate NMP and water. However, the hazardous solvent waste from the DuPont resin precursor process also contains HEMA, HCl, and TFA. A distillation simulation was created in Aspen Plus® to determine what separation would occur if the hazardous solvent waste was sent to a distillation column. It was found that the distillate stream contains mostly water, HCl, and TFA; with trace amounts of NMP. The bottoms stream contains mostly NMP and HEMA, with trace amounts of water. This simulation showed that distillation could be used to remove the water and acids from the hazardous solvent waste.

Separation techniques were investigated for removal of HEMA from NMP. A T-*x*-*y* equilibrium diagram for NMP and HEMA at 1 atm was generated in Aspen Plus® to determine if distillation is a viable separation technique. The UNIQUAC model was chosen for this system; however, no binary interaction parameters are available for an NMP-HEMA system. The binary interaction parameters for the NMP-HEMA system were estimated using UNIFAC. The T-*x*-*y* diagram in Figure 17 shows that an azeotrope exists for the NMP and HEMA system around 40 mol% NMP. However, the NMP composition in the bottoms steam of the distillation column is above 40 mol%, so the azeotrope is not a concern. The T-*x*-*y* diagram shows that atmospheric distillation is a feasible separation option for NMP and HEMA, as long as the NMP composition is above the azeotrope.

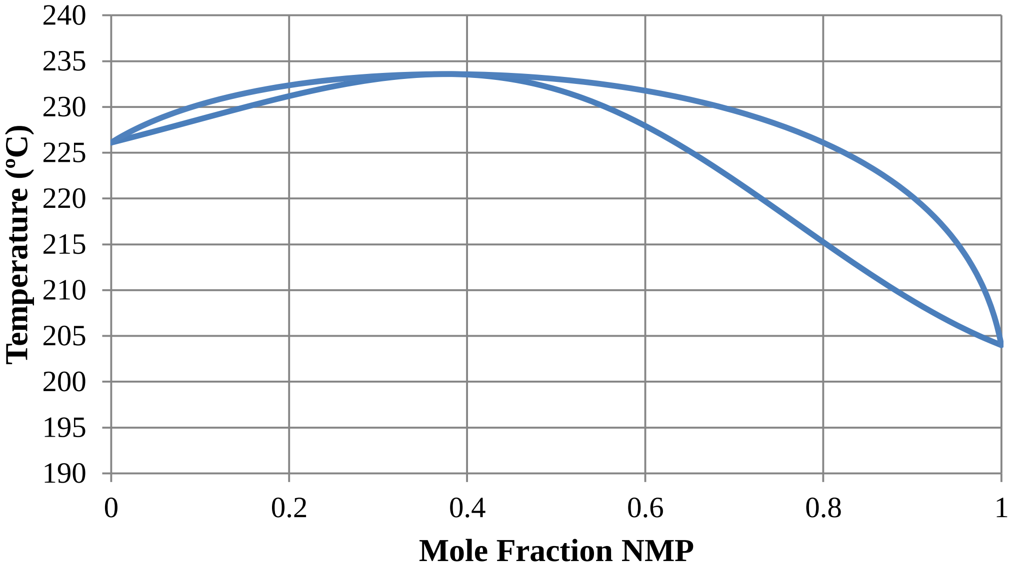


Figure 17. T-*x*-*y* equilibrium diagram for NMP and HEMA system

Distillation processes were chosen for recovery of NMP from DuPont's hazardous solvent waste. Distillation is used to first remove the water and acids from the solvent waste, producing a stream containing mainly NMP and HEMA. Distillation is used a second time to remove the HEMA, producing electronics grade NMP. It is beneficial to use distillation for both steps because the same column can be used, reducing capital costs. Although distillation is energy intensive, the evaluation of Case 1 scenarios showed that pervaporation is less efficient for this system.

The system to recover NMP from DuPont' hazardous solvent waste is shown in Figure 18. The hazardous solvent waste from the DuPont resin precursor process is sent to Holding Tank 1, prior to treatment. This allows the solvent waste to accumulate until there is enough for treatment. The solvent waste is then fed to the packed distillation column. The distillate stream contains water with HCl, TFA, and trace amounts of NMP. The distillate stream is neutralized and sent to a public wastewater treatment plant. The bottoms stream contains NMP and HEMA, with trace amounts of water. This stream is sent to Holding Tank 2. After the first distillation step is complete, the concentrated NMP in Holding Tank 2 is sent to the distillation column. In the second distillation step, electronics grade NMP is produced in the distillate stream, while hazardous waste is produced in the bottoms stream. The specifications for electronics grade NMP require a purity of 99.85 wt.% and a maximum water composition of 300 ppm. The recovered NMP is sent to Holding Tank 3 for storage until it is used in the resin precursor process. The bottoms stream is disposed of as hazardous waste.

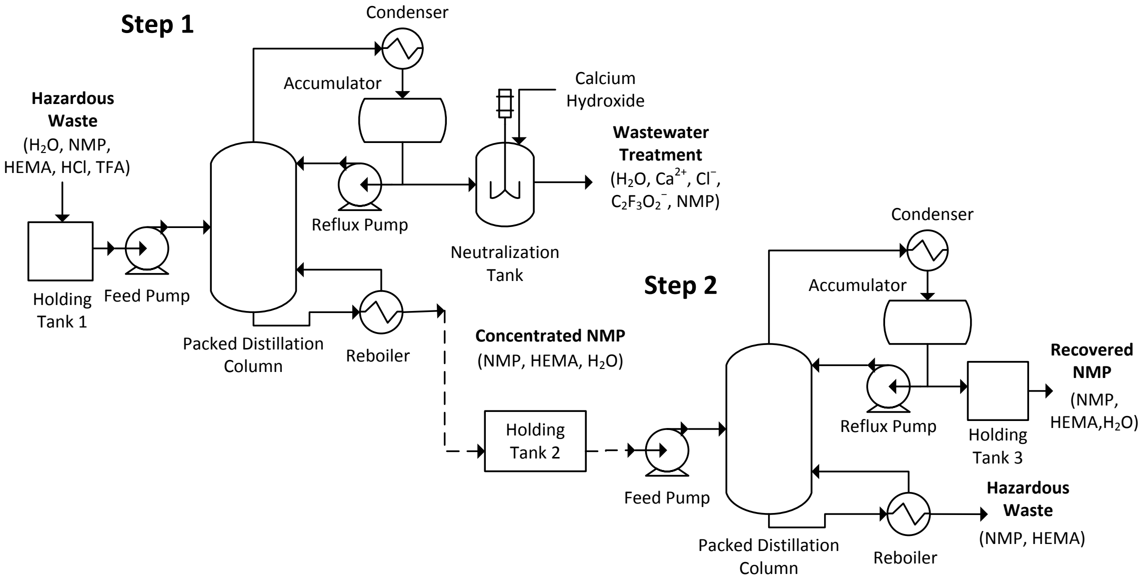


Figure 18. NMP recovery system for DuPont's hazardous solvent waste

The distillation system shown in Figure 18 was designed to treat 2,375,000 lb/yr of hazardous solvent waste. The feed flow rate for the first distillation step was set to 2,855 lb/hr. The annual operating time for the first distillation step is 832 hr, while the weekly operating time is 16 hr. The first distillation step is designed to run in weekly cycles that last for 16 hr. Holding Tank 1 is used to store the hazardous solvent waste required for 16 hr of operation of the first distillation step. Holding Tank 1 must store 5,500 gal of hazardous solvent waste, so it was designed to hold 5,500 gal of liquid and have a head space of about 20%. The total tank volume is 7,100 gal, with a diameter of 8.5 ft and a height of 16.75 ft. Holding Tank 1 was designed as a vertical flat bottomed storage tank, with specifications that are listed in Table 96. Holding Tank 1 was designed to be constructed of glass-lined carbon steel to prevent metal ions from leaching into the NMP. The corrosion allowance for Holding Tank 1 is 0.35 in because HCl and TFA are corrosive chemicals. Once 5,500 gal of hazardous solvent waste is collected in

Holding Tank 1, it is fed to the distillation column at a flow rate of 2,855 lb/hr for 16 hr. The hazardous solvent waste is fed using a centrifugal pump, with specifications listed in Table 96. The pump head was specified at 25 ft to ensure it would be able to send the solvent waste stream to the feed stage of the distillation column.

Table 96

Case 2A-NMP Holding Tank 1 and feed pump specifications

Holding Tank 1		**Feed Pump**	
Material of Construction	Glass-lined Carbon Steel	Material of Construction	Stainless Steel
Diameter	8.5 ft	Liquid Flow Rate	7 gpm
Height	16.75 ft	Fluid Head	25 ft
Volume	7,100 gal	Power	0.125 hp
Corrosion Allowance	0.35 in	Pump Efficiency	70%
Design Pressure	15 psig	Design Pressure	50 psig
Design Temperature	150ºF	Design Temperature	150ºF

A distillation column was designed using Aspen Plus® for use in the step 1 and step 2 distillation processes. The distillation column design specifications are listed in Table 97. The distillation column was designed as a packed column, packed 1.5 in ceramic Intalox saddles. The column was designed to be constructed out of glass-lined carbon steel and operated at atmospheric pressure. The column has a packing height of 14 ft, a total column height of 20 ft, and a diameter of 3.25 ft. Table 98 shows the specifications for the reboiler and condenser. The reboiler heat transfer area was calculated assuming an overall heat transfer coefficient of 1,000 $W/m^2 \cdot {}^\circ C$ and use of saturated steam at 40 bar (250.3ºC) for the first and second distillation steps [127]. Higher temperature steam is used for the second distillation step, to allow for use of the same size reboiler. Condenser heat transfer area was calculated assuming an overall heat transfer coefficient of 1,200 $W/m^2 \cdot °C$ and a cooling water temperature change of 15ºC [127]. The reboiler was designed as a kettle reboiler, while the condenser was designed as a TEMA heat exchanger.

Table 97

Case 2A-NMP distillation column specifications

Distillation Column	
Material of Construction	Glass-lined Carbon Steel
Number of Stages	8
Feed Stage	3
Packing Material	1.5 in ceramic Intalox saddles
Height	20 ft
Packed Height	14 ft
Column Diameter	3.25 ft
Step 1 Reflux Ratio	1
Step 2 Reflux Ratio	7
Design Pressure	25 psig
Design Temperature	520ºF

Table 98

Case 2A-NMP reboiler and condenser specifications

	Reboiler	**Condenser**
Material of Construction	Glass-lined Carbon Steel	Glass-lined Carbon Steel
Step 1 Duty	1,415 kW	-1,394 kW
Step 2 Duty	1,232 kW	-1,228 kW
Heat Transfer Area	1,055 ft^2	835 ft^2
Design Pressure	500 psig	50 psig
Design Temperature	520ºF	450ºF

The accumulator dimensions were calculated using the flow rate out of the condenser and a residence time of 10 min. The liquid flow rate through the reflux pump was the reflux flow rate. Table 99 shows the accumulator and reflux pump specifications. The accumulator has a diameter of 2.75 ft and a length of 11 ft, while the reflux pump has a liquid flow rate of 43 gpm. The distillate stream from the first distillation step is neutralized so it can be sent to a wastewater treatment plant. The distillate stream is neutralized with calcium hydroxide because this is a common and inexpensive method of wastewater neutralization [154]. In the neutralization process, calcium hydroxide slurry (15 wt.% calcium hydroxide) is pumped from the slurry holding tank to the neutralization tank. The slurry holding tank is designed to hold the quantity of slurry needed for 16 hr of operation of the first distillation step. This means that the slurry holding tank must be refilled every week. The slurry holding tank was designed to hold 230 gal of slurry and have a head space of 20%. The slurry holding tank has a diameter of 3 ft and a height of 8 ft. The slurry is pumped into the neutralization tank, to neutralize the acidic distillate stream. The neutralization tank was designed as an agitated vessel, with a residence time of 20 min [154]. The neutralization tank has a diameter of 2 ft and height of 6 ft. The specifications for the slurry holding tank, neutralization tank, and the slurry pump are listed in Table 100.

Table 99

Case 2A-NMP accumulator and reflux pump specifications

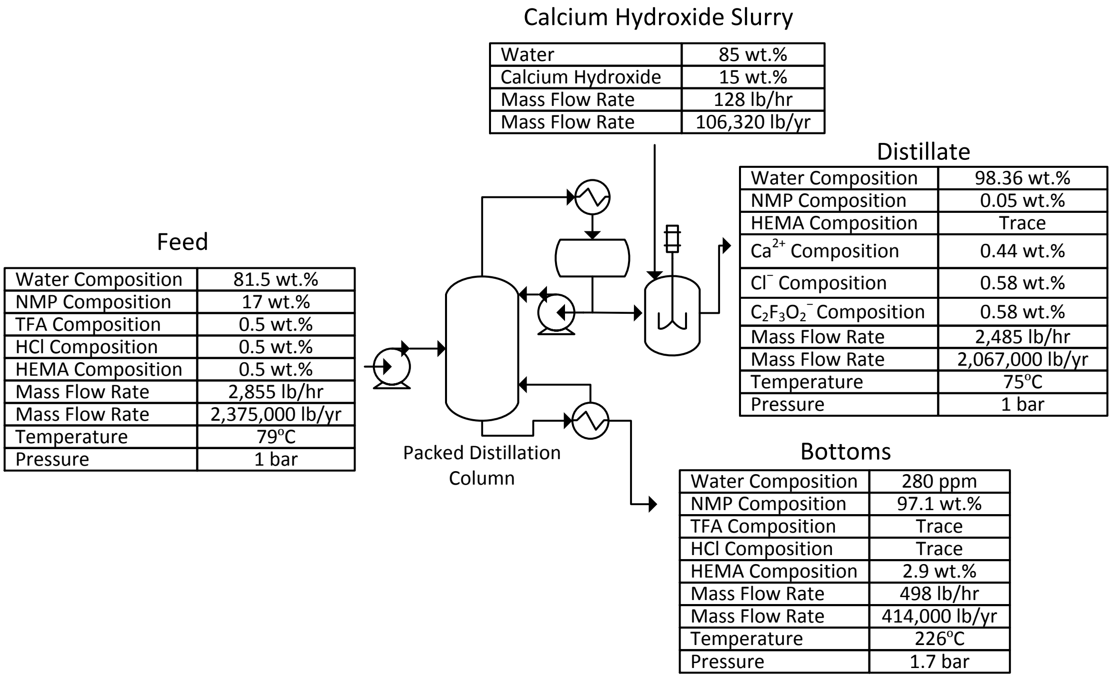
Accumulator		**Reflux Pump**	
Material of Construction	Glass-lined Carbon Steel	Material of Construction	Stainless Steel
Corrosion Allowance	0.35 in	Liquid Flow Rate	43 gpm
Diameter	2.75 ft	Fluid Head	25 ft
Length	11 ft	Pump Efficiency	70%
Volume	490 gal	Power	0.5 hp
Design Pressure	50 psig	Design Pressure	50 psig
Design Temperature	450ºF	Design Temperature	450ºF

Table 100

Case 2A-NMP neutralization equipment specifications

Slurry Holding Tank		**Neutralization Tank**		**Slurry Pump**	
Material of Construction	Stainless Steel	Material of Construction	Stainless Steel	Material of Construction	Stainless Steel
Corrosion Allowance	0.35 in	Corrosion Allowance	0.35 in	Liquid Flow Rate	0.5 gpm
Diameter	3 ft	Diameter	2 ft	Fluid Head	25 ft
Length	8 ft	Length	6 ft	Pump Efficiency	70%
Volume	420 gal	Volume	140 gal	Power	0.125 hp
Design Pressure	15 psig	Design Pressure	50 psig	Design Pressure	50 psig
Design Temperature	150ºF	Design Temperature	220ºF	Design Temperature	150ºF
		Agitator Power	5 hp		

The inlet and outlet streams for the first distillation step are shown in Figure 19. In the first distillation step, the hazardous solvent waste is fed to the distillation column. The bottoms stream contains 97.1 wt% NMP, 2.9 wt.% HEMA, and 280 ppm water. The bottoms stream is sent to Holding Tank 2. The distillate stream contains water, acids, and NMP. This stream neutralized with calcium hydroxide slurry, prior to sending to the wastewater treatment plant. The first distillation step recovers 99.6% of NMP, which shows that a good separation is achieved.



Calcium Hydroxide Slurry

Water	85 wt.%
Calcium Hydroxide	15 wt.%
Mass Flow Rate	128 lb/hr
Mass Flow Rate	106,320 lb/yr

Feed

Water Composition	81.5 wt.%
NMP Composition	17 wt.%
TFA Composition	0.5 wt.%
HCl Composition	0.5 wt.%
HEMA Composition	0.5 wt.%
Mass Flow Rate	2,855 lb/hr
Mass Flow Rate	2,375,000 lb/yr
Temperature	79°C
Pressure	1 bar

Distillate

Water Composition	98.36 wt.%
NMP Composition	0.05 wt.%
HEMA Composition	Trace
Ca^{2+} Composition	0.44 wt.%
Cl^{-} Composition	0.58 wt.%
$C_2F_3O_2^{-}$ Composition	0.58 wt.%
Mass Flow Rate	2,485 lb/hr
Mass Flow Rate	2,067,000 lb/yr
Temperature	75°C
Pressure	1 bar

Bottoms

Water Composition	280 ppm
NMP Composition	97.1 wt.%
TFA Composition	Trace
HCl Composition	Trace
HEMA Composition	2.9 wt.%
Mass Flow Rate	498 lb/hr
Mass Flow Rate	414,000 lb/yr
Temperature	226°C
Pressure	1.7 bar

Figure 19. Distillation step 1 stream flow rates and compositions

Holding Tank 2 was designed to store the bottoms from the first distillation step, prior to treatment in the second distillation step. As mentioned previously, the first distillation step is designed to run in weekly cycles that last for 16 hr. Therefore, Holding Tank 2 must store the concentrated NMP produced from 16 hr of operation of the first distillation step. Holding Tank 2 must store 1,100 gal of concentrated NMP, so it was designed to hold 1,100 gal of liquid and have a head space of about 20%. The total tank volume is 1,500 gal, with a diameter of 5 ft and a height of 10 ft. Holding Tank 2 was designed as a vertical flat bottomed storage tank, with specifications that are listed in

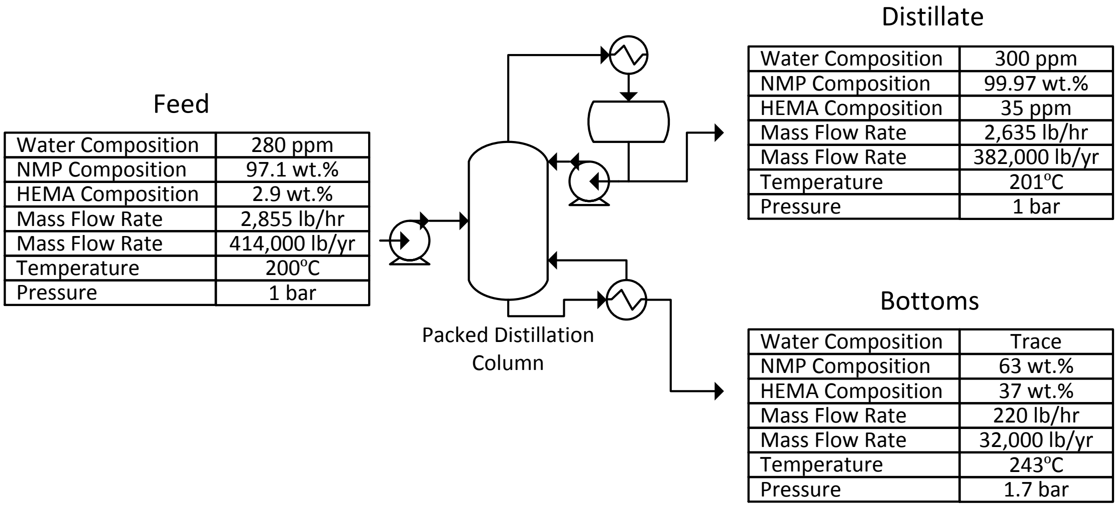
Table 101. Holding Tank 2 was designed to be constructed of glass-lined carbon steel to prevent metal ions from leaching into the NMP. The corrosion allowance for Holding Tank 2 is 0 in because NMP and HEMA are not corrosive chemicals. Once 1,100 gal of concentrated NMP is collected in Holding Tank 2, it is fed to the distillation column at a flow rate of 2,855 lb/hr for 2.8 hr. This flow rate was chosen so that the same size distillation column could be used for the second distillation step. The annual operating time of the second distillation step is 145 hr. The concentrated NMP is fed using the feed pump, with specifications listed previously in Table 96.

Table 101

Case 2A-NMP Holding Tank 2 specifications

Material of Construction	Glass-lined Carbon Steel
Corrosion Allowance	0 in
Diameter	5
Height	10
Total Volume	1,100 gal
Design Pressure	15 psig
Design Temperature	460ºF

The inlet and outlet streams for the first distillation step are shown in Figure 20. In the second distillation step, the concentrated NMP is fed to the distillation column. The distillate stream contains the recovered electronics grade NMP. The recovered NMP has a purity of 99.97 wt.%, with a water composition of 300 ppm and a HEMA composition of 35 ppm. This stream is sent to Holding Tank 3, and is stored there until it is used in the resin precursor process. The bottoms stream contains 63 wt.% NMP and 37 wt.% HEMA. This stream is disposed of as hazardous waste. The distillation system has an NMP recovery of 95%.



Feed

Water Composition	280 ppm
NMP Composition	97.1 wt.%
HEMA Composition	2.9 wt.%
Mass Flow Rate	2,855 lb/hr
Mass Flow Rate	414,000 lb/yr
Temperature	200°C
Pressure	1 bar

Distillate

Water Composition	300 ppm
NMP Composition	99.97 wt.%
HEMA Composition	35 ppm
Mass Flow Rate	2,635 lb/hr
Mass Flow Rate	382,000 lb/yr
Temperature	201°C
Pressure	1 bar

Bottoms

Water Composition	Trace
NMP Composition	63 wt.%
HEMA Composition	37 wt.%
Mass Flow Rate	220 lb/hr
Mass Flow Rate	32,000 lb/yr
Temperature	243°C
Pressure	1.7 bar

Figure 20. Distillation step 2 stream flow rates and compositions

Holding Tank 3 was designed to store the recovered NMP, prior to use in the resin precursor process. As mentioned previously, the second distillation step is designed to run in weekly cycles that last for 2.8 hr. Therefore, Holding Tank 3 must store the recovered NMP from 2.8 hr of operation of the second distillation step. Holding Tank 3 must store 1,000 gal of recovered NMP, so it was designed to hold 1,000 gal of liquid and have a head space of about 20%. The total tank volume is 1,300 gal, with a diameter of 4.75 ft and a height of 9.5 ft. Holding Tank 3 was designed as a vertical flat bottomed storage tank, with specifications that are listed in Table 102.

Table 102

Case 2A-NMP Holding Tank 3 specifications

Material of Construction	Glass-lined Carbon Steel
Corrosion Allowance	0 in
Diameter	4.75 ft
Height	9.5 ft
Total Volume	1,300 gal
Design Pressure	15 psig
Design Temperature	460ºF

The installed capital cost for the equipment in the distillation system, based on fourth quarter 2014 costs, was estimated using Aspen Capital Cost Estimator. The installed capital cost of the equipment includes the cost for equipment, piping, support structures, electrical work, insulation, and manpower. The installed capital cost of the equipment used in the Case 2A-NMP distillation system is shown in Table 103. The total installed capital cost for the Case 2A-NMP distillation system is $1,497,000. Table 103 shows that the packed distillation column has the highest capital cost of all the equipment used in the Case 2A-NMP recovery system, with a capital cost of $307,000. The reboiler has the second highest capital cost ($228,000), followed by the condenser ($186,000), Holding Tank 1 ($170,000), neutralization tank ($164,000), and accumulator ($157,000). The rest of the equipment have capital costs below $100,000.

Table 103

Case 2A-NMP distillation system capital costs

Equipment	Capital Cost ($)
Holding Tank 1	170,000
Feed Pump	20,000
Packed Column	307,000
Reboiler	228,000
Condenser	186,000
Accumulator	157,000
Reflux Pump	27,000
Slurry Holding Tank	51,000
Neutralization Tank	164,000
Slurry Pump	18,000
Holding Tank 2	86,000
Holding Tank 3	83,000
Total	1,497,000

The raw materials used, utilities used, and waste generated by the DuPont resin precursor process with and without NMP recovery is shown in Table 104. The steam energy use was calculated using Equation 34, while the condenser electricity use was calculated using in Equation 35. The electricity used by the feed and reflux pumps and the neutralization tank agitator were calculated using Equation 36. Table 104 shows that NMP recovery reduces virgin NMP use by 382,000 lb/yr and reduces hazardous waste generation by 2,343,000 lb/yr. However, non-hazardous wastewater generation is increased by 2,067,000 lb/yr. Also, 175,400 MJ/yr of electricity, 5,424,000 MJ/yr of steam, and 15,950 lb/yr of calcium hydroxide slurry is required for NMP recovery.

Table 104

Raw material use, utility use, and waste generation for Base Case 2 and Case 2A-NMP

	Base Case 2	**Case 2A-NMP**
NMP (lb/yr)	403,800	21,530
Minor Reagents		
HEMA (lb/yr)	11,880	11,880
TFA (lb/yr)	11,880	11,880
HCl (lb/yr)	11,880	11,880
Ultrapure water (lb/yr)	9,062,000	9,062,000
Hazardous Solvent Waste (lb/yr)	2,375,245	31,960
Non-hazardous Wastewater (lb/yr)	7,125,735	9,193,000
Electricity (MJ/yr)	0	175,400
Steam (MJ/yr)	0	5,424,000
Calcium Hydroxide Slurry (lb/yr)	0	15,950

The life cycle emissions of the DuPont resin precursor process with and without NMP recovery were calculated using Equations 8 and 7, respectively. The life cycle emissions for the process with and without NMP recovery consisted of virgin NMP manufacture, minor reagent manufacture, ultrapure water generation, hazardous solvent waste disposal, and non-hazardous wastewater disposal. The process with NMP recovery also has life cycle emissions from steam generation, electricity generation, and calcium hydroxide manufacture. The LCI for the manufacture of calcium hydroxide slurry was estimated using SimaPro®. Within SimaPro®, calcium hydroxide slurry was modeled as hydrated lime, which is calcium hydroxide. The LCI for the manufacture of 1 lb of calcium hydroxide slurry is listed in Table 105.

Table 105

LCI for the manufacture of 1 lb of calcium hydroxide slurry

Water Used (lb/yr)	2.31E+03
Total Air Emissions (lb/yr)	7.46E-01
CO_2 (lb/yr)	7.40E-01
CO (lb/yr)	3.73E-03
CH_4 (lb/yr)	4.68E-04
NO_X (lb/yr)	4.84E-04
NMVOC (lb/yr)	2.61E-04
Particulate (lb/yr)	3.20E-04
SO_2 (lb/yr)	3.40E-04
Total Water Emissions (lb/yr)	4.73E-03
VOCs (lb/yr)	1.14E-06
Total Soil Emissions (lb/yr)	3.22E-05
Total Emissions (lb/yr)	**7.51E-01**
CED (MJ/yr)	2.01E+00

The life cycle emissions for these processes are shown in Table 106. The emissions due the manufacture of calcium hydroxide slurry were calculated by multiplying the annual use of calcium hydroxide slurry in lb/yr by the LCI for calcium hydroxide slurry manufacture on a 1 lb basis. The reduction in life cycle emissions from NMP recovery were calculated using Equation 9 and are also shown in Table 106. Recovery of NMP reduces the total life cycle emissions by 1,170,000 lb/yr and reduces the life cycle CO_2 emissions by 940,000 lb/yr. This is a 44% reduction in total life cycle emissions and a 40% reduction in life cycle CO_2 emissions.

Table 106

Life cycle emissions for Base Case 2 and Case 2A-NMP

	Base Case 2	**Case 2A-NMP**	**Avoided Emissions**
Water Used (lb/yr)	5.24E+09	7.24E+08	4.52E+09
Total Air Emissions (lb/yr)	2.39E+06	1.44E+06	9.52E+05
CO_2 (lb/yr)	2.37E+06	1.43E+06	9.40E+05
CO (lb/yr)	1.14E+03	6.74E+02	4.64E+02
CH_4 (lb/yr)	4.26E+03	2.64E+03	1.61E+03
NO_X (lb/yr)	3.22E+03	1.68E+03	1.54E+03
NMVOC (lb/yr)	9.65E+02	2.34E+02	7.31E+02
Particulate (lb/yr)	1.01E+03	1.85E+02	8.29E+02
SO_2 (lb/yr)	4.56E+03	2.34E+03	2.22E+03
Total Water Emissions (lb/yr)	2.73E+05	5.76E+04	2.15E+05
VOCs (lb/yr)	2.41E+00	3.56E-01	2.05E+00
Total Soil Emissions (lb/yr)	6.88E+02	1.16E+02	5.72E+02
Total Emissions (lb/yr)	**2.67E+06**	**1.49E+06**	**1.17E+06**
CED (MJ/yr)	1.56E+07	1.03E+07	5.30E+06

Figure 21 shows the total and CO_2 life cycle emissions associated with each raw material, waste disposal, and utility use of the resin precursor process, within the LCA boundaries, with and without NMP recovery. The life cycle emissions due to NMP manufacture, minor reagent manufacture, ultrapure water production, hazardous solvent waste disposal, and wastewater disposal are shown. The life cycle emissions due to steam, electricity, and calcium hydroxide slurry used by the recovery system are also shown. Recovery of NMP reduces the total life cycle emissions and CO_2 life cycle emissions of the current DuPont process because hazardous waste generation and virgin NMP manufacture are significantly reduced. However, Figure 21 also shows that steam generation for use in NMP recovery generates significant total and CO_2 life cycle emissions.

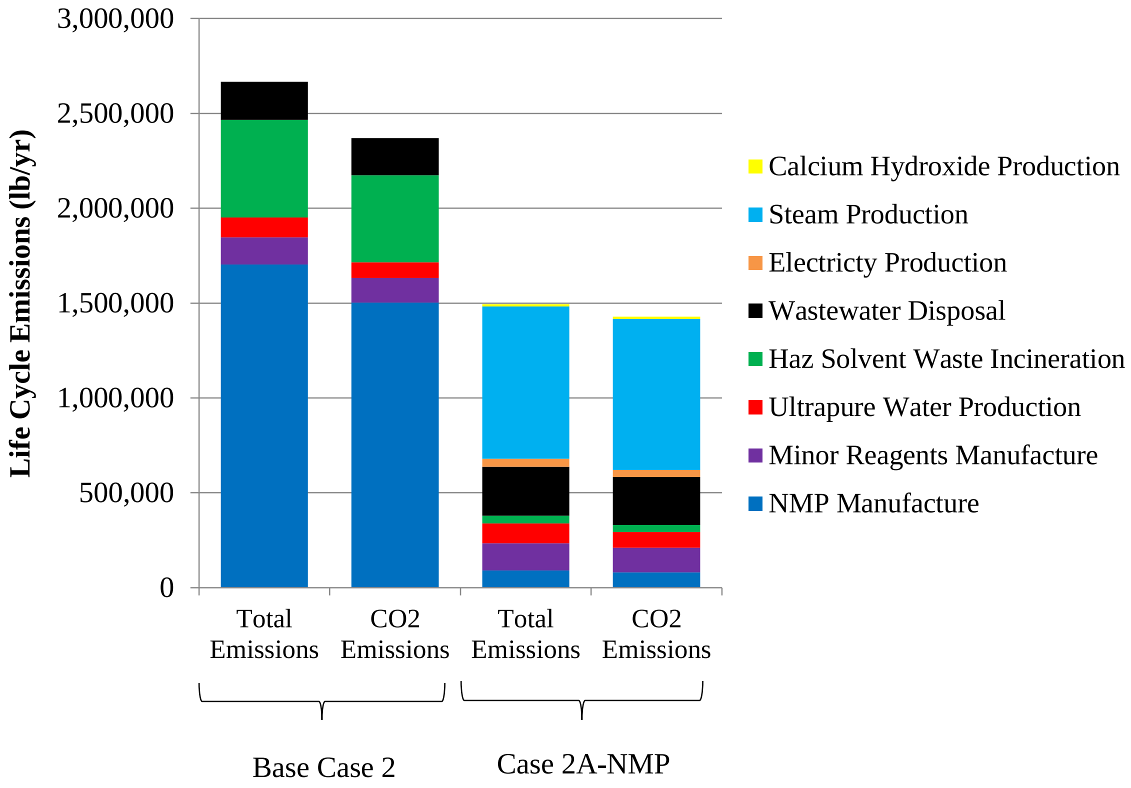


Figure 21. Total and CO_2 life cycle emissions and for Base Case 2 and Case 2A-NMP

The damage caused by the DuPont resin precursor process with and without NMP recovery was calculated using Equations 11 and 10, respectively. The damage caused by the process with and without NMP recovery consisted of virgin NMP manufacture, minor reagent manufacture, ultrapure water generation, hazardous solvent waste disposal, and non-hazardous wastewater disposal. The process with NMP recovery also causes damage through steam generation, electricity generation, and calcium hydroxide manufacture. The damage assessment for the manufacture of calcium hydroxide slurry was estimated using SimaPro®. Within SimaPro®, calcium hydroxide slurry was modeled as hydrated lime, which is calcium hydroxide. The damage assessment for the manufacture of 1 lb of calcium hydroxide slurry is listed in Table 107.

Table 107

ReCiPe damage assessment for the manufacture of 1 lb of calcium hydroxide slurry

Human Health (mPt/yr)	1.03E+01
Ecosystems (mPt/yr)	6.28E+00
Resources (mPt/yr)	4.98E+00
Total (mPt/yr)	2.15E+01

The damage caused by the DuPont resin precursor process with and without NMP recovery is shown in Table 108. The damage due the manufacture of calcium hydroxide slurry was calculated by multiplying the annual use of calcium hydroxide slurry in lb/yr by the damage score for calcium hydroxide slurry manufacture on a 1 lb basis. The reduction in damage from NMP recovery was calculated using Equation 12 and is also shown in Table 108. Recovery of NMP reduces the damage to human health, ecosystems, and resources by 18,200,000 mPt/yr, 9,140,000 mPt/yr, and 9,230,000 mPt/yr; respectively. This is a 46% reduction in damage to human health, a 42% reduction in damage to ecosystems, and a 27% reduction in damage to resources.

Table 108

ReCiPe damage assessment for Base Case 2 and Case 2A-NMP

	Base Case 2	**Case 2A-NMP**	**Avoided Damage**
Human Health (mPt/yr)	3.99E+07	2.17E+07	1.82E+07
Ecosystems (mPt/yr)	2.16E+07	1.25E+07	9.14E+06
Resources (mPt/yr)	3.49E+07	2.56E+07	9.23E+06
Total (mPt/yr)	9.63E+07	5.98E+07	3.66E+07

Figure 22 shows the damage to human health, ecosystems, and resources for each part of the resin precursor process, within the LCA boundaries, with and without NMP recovery. The damage due to NMP manufacture, minor reagent manufacture, ultrapure water production, hazardous solvent waste disposal, and wastewater disposal are shown. The damage due to steam, electricity, calcium hydroxide slurry used by the recovery system are also shown. Recovery of NMP reduces the damage to human health, ecosystems, and resources because hazardous waste generation and virgin NMP manufacture are significantly reduced. Figure 22 shows the same trend as Figure 21, where NMP recovery significantly reduces environmental impact due to reduction in virgin NMP use and hazardous solvent waste disposal. However, both analyses show that the steam used for operation of the distillation column causes significant impact to the environment. A large quantity of steam is required to operate the distillation column, due to the large composition of water present in the solvent waste stream.

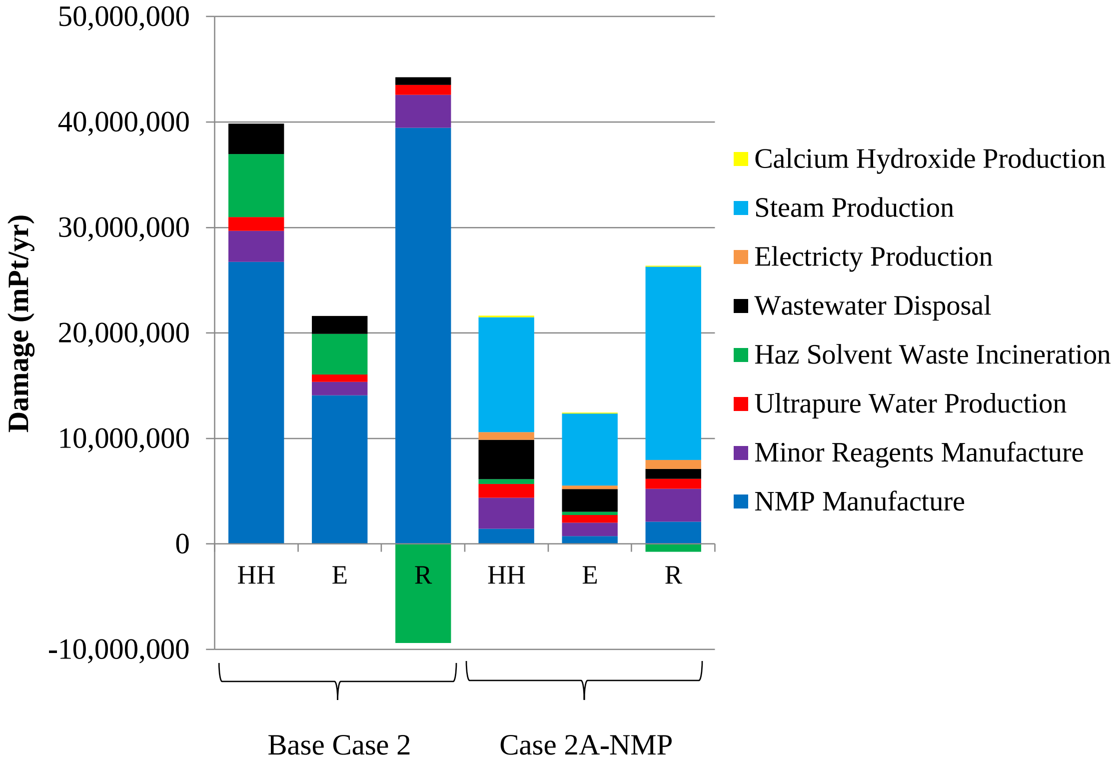


Figure 22. ReCiPe damage assessment for Base Case 2 and Case 2A-NMP, where HH is human health, E is ecosystems, and R is resources

The operating costs associated with the DuPont resin precursor process with and without NMP recovery are shown in Table 109. The operating cost for the current DuPont process was calculated using Equation 16, while the operating cost for the DuPont process with NMP recovery was calculation using Equation 17. The cost to purchase calcium hydroxide slurry is 0.113 $/lb [155]. In Equation 17, the maintenance cost for the NMP recovery system is 27,700 $/yr. The maintenance cost is 2.5% of the capital cost for all unit operations. The operating cost savings from NMP recovery were calculated using Equation 18. Recovery of NMP results in operating cost savings of 1,217,000 $/yr or 83%.

Table 109

Operating costs for Base Case 2 and Case 2A-NMP

	Base Case 2	**Case 2A-NMP**	**Avoided Costs**
Operating Cost ($/yr)	1,466,000	248,900	1,217,000

Figure 23 shows the operating costs for raw material use, waste disposal, and utility use for the resin precursor process, within the LCA boundaries, with and without NMP recovery. The operating costs due to NMP manufacture, minor reagent manufacture, ultrapure water production, hazardous solvent waste disposal, and wastewater disposal are shown. The costs due to steam, electricity, and calcium hydroxide slurry used by the recovery systems are also shown. Operating costs due to equipment maintenance are also included. Recovery of NMP results in significant operating cost savings because hazardous waste generation and virgin NMP manufacture are significantly reduced.

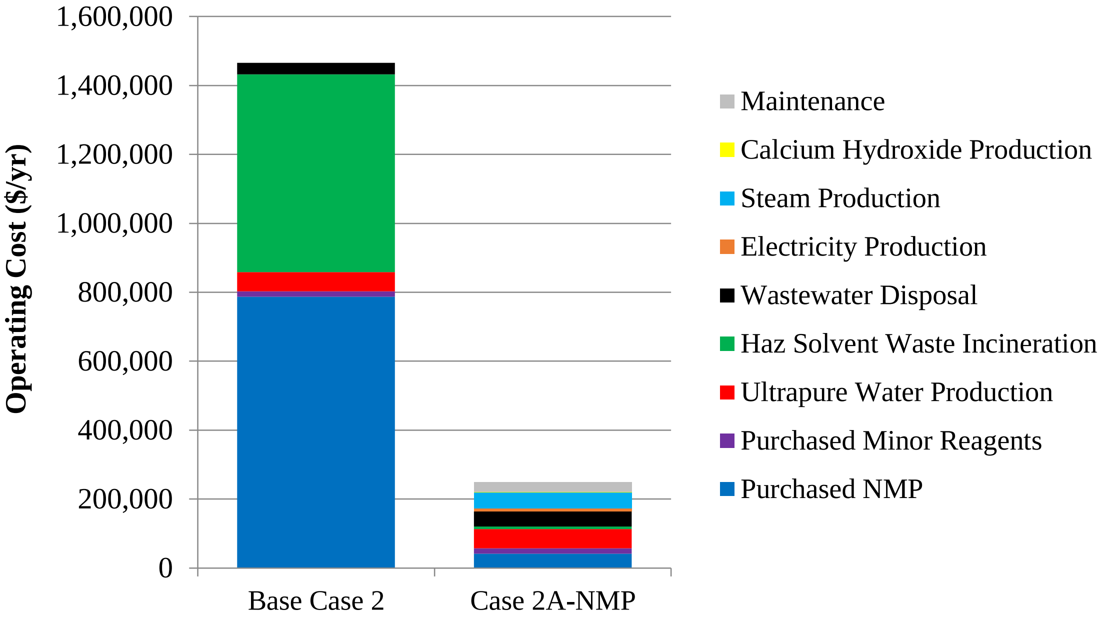


Figure 23. Operating costs for Base Case 2 and Case 2A-NMP

An economic analysis was conducted to evaluate Case 2A-NMP based on both operating cost savings and recovery equipment capital costs. This was done to determine if NMP recovery would save money. Operating cost savings alone may not result in savings because capital equipment is also needed. To determine if NMP recovery is profitable for Case 2, internal rate of return (IRR), return on investment (ROI), payback time after tax, net present value after 5 yr, and net present value after 10 yr were calculated for Case 2A-NMP. These calculations were performed using Equations 19-27, shown previously. Table 110 shows that NMP recovery is profitable for the DuPont resin precursor process. NMP recovery results in cost savings of $1,750,000 after 5 yr and $3,128,000 after 10 yr.

Table 110

Economic analysis of Case 2A-NMP

	IRR (%)	**ROI (%)**	**Payback time after tax (yr)**	**5 yr NPV ($)**	**10 yr NPV ($)**
Case 2A-NMP	67.3	59.2	2.2	1,750,000	3,128,000

The evaluation of NMP recovery for the DuPont resin precursor process showed that it is beneficial to recover NMP because environmental impact is reduced and money is saved. Recovery of NMP reduces total life cycle emissions and life cycle CO_2 emissions by 44% and 40%, respectively. Damage to human health, ecosystems, and resource is reduced by 46%, 42%, and 27%; respectively; from NMP recovery. In addition, $1,750,000 is saved after 5 yr and $3,128,000 is saved after 10 yr. It is recommended to recover and reuse the NMP from the hazardous solvent waste generated by DuPont resin precursor process.

Case 2B-NMP: Off-Site Recovery of NMP

Off-site recovery of NMP from the hazardous waste generated by DuPont's resin precursor process was investigated. This approach was researched in attempt to recover NMP more economically. The previous approach to NMP recovery (Case 2A-NMP) requires the DuPont Parlin Plant to purchase the capital equipment required for NMP recovery. Off-site NMP recovery could be beneficial because the Parlin Plant would not need to invest in solvent recovery equipment. The environmental and economic impact of NMP recovery at a solvent recycling facility (Case 2B-NMP) was evaluated to determine if it is a viable alternative to NMP recovery at the Parlin Plant. Clean Harbors Environmental Services was contacted about NMP recycling opportunities at their facilities. Clean Harbors provides hazardous material management and disposal services including the collection, packaging, transportation, recycling, treatment, and disposal of hazardous and non-hazardous waste. More specifically, they have tolling (outside party processing) programs to recycle spent solvents such as NMP, tetrahydrofuran, ester solvents, ketones, alcohols, aliphatic hydrocarbon solvents, and aromatic hydrocarbon solvents [156]. Clean Harbors New Jersey locations, but they only have the equipment to recover NMP at their Chicago facility.

The NMP recovery approach for Case 2B-NMP involves shipping the hazardous waste generated by the DuPont process to the Clean Harbors Chicago facility. At the Clean Harbors facility, electronics grade NMP will be recovered from the hazardous waste and sent back to the Parlin Plant for reuse in the resin precursor process. In the analysis of this approach, it was assumed that Clean Harbors recovers 95% of the NMP present in the hazardous waste, as was achieved in the Case 2A-NMP simulation. For the environmental analysis, it was assumed that the environmental impact of NMP recovery equipment operation at the Clean Harbors facility is the same as the recovery system designed in Case 2A-NMP. The environmental analysis also includes the environmental impact from shipping the hazardous waste from the Parlin Plant to the Chicago facility and shipping the recovered NMP back to the Parlin Plant. The distance from the Parlin Plant to the Chicago facility is 800 miles. The life cycle emissions and damage associated with the Case 2B-NMP recovery approach were calculated using Equations 42 and 43.

$$\begin{aligned} LCE_{Case\ 2B} = (m_{NMP} - r_{NMP}) \cdot LCI_{NMP} + m_{TFA} \cdot LCI_{TFA} + m_{HEMA} \cdot LCI_{HEMA} \\ + m_{HCl} \cdot LCI_{HCl} + m_{UPW} \cdot LCI_{UPW} + m_{NHWW} \cdot LCI_{NHWW} \\ + x_{shipping} \cdot LCI_{shipping} + LCE_{NMP\ Recovery} \end{aligned} \tag{42}$$

In Equation 42, $LCE_{Case\ 2B}$ is the life cycle emissions associated with Case 2B-NMP in lb/yr, $x_{shipping}$ is the shipping requirement in lb-mile/yr, $LCI_{shipping}$ is the LCI for shipping on a 1 lb-mile basis, and $LCE_{NMP\ Recovery}$ is the life cycle emissions associated with operation of the NMP recovery equipment in lb/yr.

$$\begin{aligned} DS_{Case\ 2B} = (m_{NMP} - r_{NMP}) \cdot DS_{NMP} + m_{TFA} \cdot DS_{TFA} + m_{HEMA} \cdot DS_{HEMA} \\ + m_{HCl} \cdot DS_{HCl} + m_{UPW} \cdot DS_{UPW} + m_{NHWW} \cdot DS_{NHWW} + x_{shipping} \\ \cdot DS_{shipping} + DS_{NMP\ Recovery} \end{aligned} \tag{43}$$

In Equation 43, $DS_{Case\ 2B}$ is the damage associated with Case 2B-NMP in mPt/yr, $DS_{shipping}$ is the damage score for shipping on a 1 lb-mile basis, and $DS_{NMP\ Recovery}$ is the damage associated with operation of the NMP recovery equipment in mPt/yr.

The LCI and damage score for shipping was estimated using SimaPro®. Within SimaPro®, shipping was modeled using a single unit truck with a diesel engine. The transportation of solvent waste and recovered NMP was modeled using a truck because the DuPont Parlin plant currently uses trucks to send solvent waste off-site. Also, the Parlin plant does not have rail infrastructure so it is not feasible to use a rail system for transportation. The LCI and damage score for shipping chemicals on a 1 lb-mile basis is listed in Table 111 and Table 112. The shipping requirement for Case 2B-NMP is 2,203,000,000 lb-mile/yr, calculated using Equation 44.

Table 111

LCI for shipping chemicals 1 lb-mile

Water Used (lb/yr)	0.00E+00
Total Air Emissions (lb/yr)	1.42E-04
CO_2 (lb/yr)	1.40E-04
CO (lb/yr)	7.11E-07
CH_4 (lb/yr)	1.77E-07
NO_X (lb/yr)	1.01E-06
NMVOC (lb/yr)	7.89E-08
Particulate (lb/yr)	3.23E-08
SO_2 (lb/yr)	6.61E-08
Total Water Emissions (lb/yr)	1.49E-05
VOCs (lb/yr)	0.00E+00
Total Soil Emissions (lb/yr)	0.00E+00
Total Emissions (lb/yr)	1.57E-04
CED (MJ/yr)	1.99E-03

Table 112

ReCiPe damage assessment for shipping chemicals 1 lb-mile

Human Health (mPt/yr)	6.52E-03
Ecosystems (mPt/yr)	2.65E-03
Resources (mPt/yr)	5.64E-03
Total (mPt/yr)	1.48E-02

$$x_{shipping} = (m_{HW} + r_{NMP}) \cdot x_{Parlin\ to\ Chicago} \tag{44}$$

In Equation 44, $x_{shipping}$ is the shipping requirement for Case 2B-NMP in lb-mile/yr, m_{HW} is the mass of hazardous waste generated by the DuPont resin precursor process in lb/yr, r_{NMP} is the mass of recovered NMP in lb/yr, $x_{Parlin\ to\ Chicago}$ is the distance between the Parlin Plant and the Clean Harbors Chicago facility in miles.

The life cycle emissions associated with Case 2B-NMP are shown in Table 113, along with the emissions for Base Case 2 and Case 2A-NMP. The avoided life cycle emissions for Cases 2A-NMP and 2B-NMP, compared to Base Case 2, are shown in Table 114. Case 2A-NMP reduces the total life cycle emissions by 44% and reduces the life cycle CO_2 emissions by 40%. Case 2B-NMP reduces the total life cycle emissions and life cycle CO_2 emissions by 31% and 27%, respectively.

Table 113

Life cycle emissions for Base Case 2, Case 2A-NMP, and Case 2B-NMP

	Base Case 2	**Case 2A-NMP**	**Case 2B-NMP**
Water Used (lb/yr)	5.24E+09	7.24E+08	7.24E+08
Total Air Emissions (lb/yr)	2.39E+06	1.44E+06	1.75E+06
CO_2 (lb/yr)	2.37E+06	1.43E+06	1.74E+06
CO (lb/yr)	1.14E+03	6.74E+02	2.24E+03
CH_4 (lb/yr)	4.26E+03	2.64E+03	3.03E+03
NO_X (lb/yr)	3.22E+03	1.68E+03	3.90E+03
NMVOC (lb/yr)	9.65E+02	2.34E+02	4.08E+02
Particulate (lb/yr)	1.01E+03	1.85E+02	2.56E+02
SO_2 (lb/yr)	4.56E+03	2.34E+03	2.49E+03
Total Water Emissions (lb/yr)	2.73E+05	5.76E+04	9.05E+04
VOCs (lb/yr)	2.41E+00	3.56E-01	3.56E-01
Total Soil Emissions (lb/yr)	6.88E+02	1.16E+02	1.16E+02
Total Emissions (lb/yr)	**2.67E+06**	**1.49E+06**	**1.84E+06**
CED (MJ/yr)	1.56E+07	1.03E+07	1.46E+07

Table 114

Avoided life cycle emissions for Cases 2A-NMP and 2B-NMP

	Case 2A-NMP Avoided Emissions	**Case 2B-NMP Avoided Emissions**
Water Used (lb/yr)	4.52E+09	4.52E+09
Total Air Emissions (lb/yr)	9.52E+05	6.40E+05
CO_2 (lb/yr)	9.40E+05	6.33E+05
CO (lb/yr)	4.64E+02	-1.10E+03
CH_4 (lb/yr)	1.61E+03	1.22E+03
NO_X (lb/yr)	1.54E+03	-6.79E+02
NMVOC (lb/yr)	7.31E+02	5.57E+02
Particulate (lb/yr)	8.29E+02	7.58E+02
SO_2 (lb/yr)	2.22E+03	2.07E+03
Total Water Emissions (lb/yr)	2.15E+05	1.83E+05
VOCs (lb/yr)	2.05E+00	2.05E+00
Total Soil Emissions (lb/yr)	5.72E+02	5.72E+02
Total Emissions (lb/yr)	**1.17E+06**	**8.26E+05**
CED (MJ/yr)	5.30E+06	9.21E+05

Figure 24 shows the total and CO_2 life cycle emissions associated with Base Case 2, Case 2A-NMP, and Case 2B-NMP. The life cycle emissions due to NMP manufacture, minor reagent manufacture, ultrapure water production, hazardous solvent waste disposal, and wastewater disposal are shown. For Case 2A-NMP, the life cycle emissions due to the steam, electricity, and calcium hydroxide slurry used by the recovery system are also shown. For Case 2B-NMP, the life cycle emissions due to transportation and tolling operations are also shown. Cases 2A-NMP and 2B-NMP reduce the total life cycle emissions and CO_2 life cycle emissions of the current DuPont process because hazardous waste generation and virgin NMP manufacture are significantly reduced. However, Case 2B-NMP generates more life cycle emissions than Case 2A-NMP due to transportation of hazardous waste and recovered NMP.

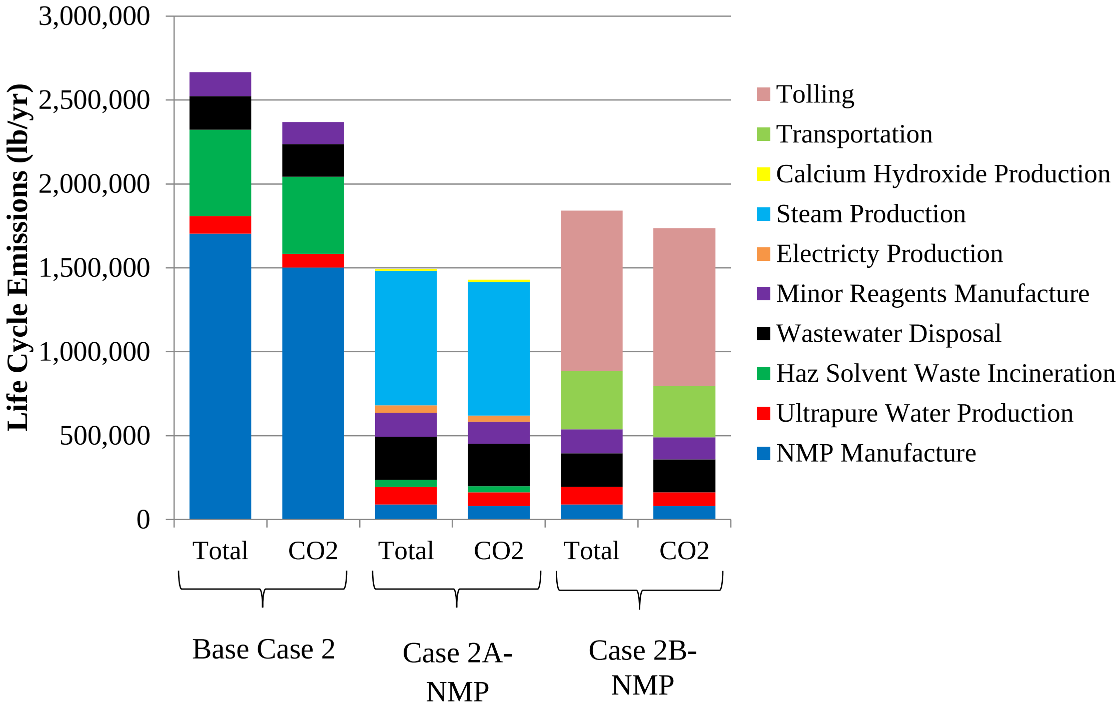


Figure 24. Total and CO_2 life cycle emissions for Base Case 2, Case 2A-NMP, and Case 2B-NMP

ReCiPe methodology was also used to calculate the environmental impact of Case 2B-NMP. The damage to human health, ecosystems, and resources caused by Base Case 2, Case 2A-NMP, and Case 2B-NMP is shown in Table 115. The reduction in damage from NMP recovery was calculated using Equation 12 and is shown in Table 116. The Case 2A-NMP approach to NMP recovery reduces the damage to human health, ecosystems, and resources by 46%, 42%, and 27%; respectively. The Case 2B-NMP approach reduces the damage to human health, ecosystems, and resources by 10%, 15%, and -9%; respectively.

Table 115

ReCiPe damage assessment for Base Case 2, Case 2A-NMP, and Case 2B-NMP

	Base Case 2	**Case 2A-NMP**	**Case 2B-NMP**
Human Health (mPt/yr)	3.99E+07	2.17E+07	3.60E+07
Ecosystems (mPt/yr)	2.16E+07	1.25E+07	1.83E+07
Resources (mPt/yr)	3.49E+07	2.56E+07	3.81E+07
Total (mPt/yr)	9.63E+07	5.98E+07	9.24E+07

Table 116

Avoided damage for Case 2A-NMP and Case 2B-NMP

	Case 2A-NMP Avoided Damage	**Case 2B-NMP Avoided Damage**
Human Health (mPt/yr)	1.82E+07	3.84E+06
Ecosystems (mPt/yr)	9.14E+06	3.30E+06
Resources (mPt/yr)	9.23E+06	-3.20E+06
Total (mPt/yr)	3.66E+07	3.94E+06

Figure 25 shows the damage to human health, ecosystems, and resources for Base Case 2, Case 2A-NMP, and Case 2B-NMP. The damage due to NMP manufacture, minor reagent manufacture, ultrapure water production, hazardous solvent waste disposal, and wastewater disposal are shown. For Case 2A-NMP, the damage due to the steam, electricity, and calcium hydroxide slurry used by the recovery system is also shown. For Case 2B-NMP, the damage due to transportation and tolling operations is also shown. Recovery of NMP reduces the damage to human health, ecosystems, and resources because hazardous waste generation and virgin NMP manufacture are significantly reduced. Figure 25 shows the same trend as Figure 24, where Cases 2A-NMP and 2B-NMP reduce environmental impact due to reduction in virgin NMP use and hazardous solvent waste disposal. However, both analyses show that Case 2B-NMP has a higher environmental impact due to transportation of materials to and from the Chicago facility.

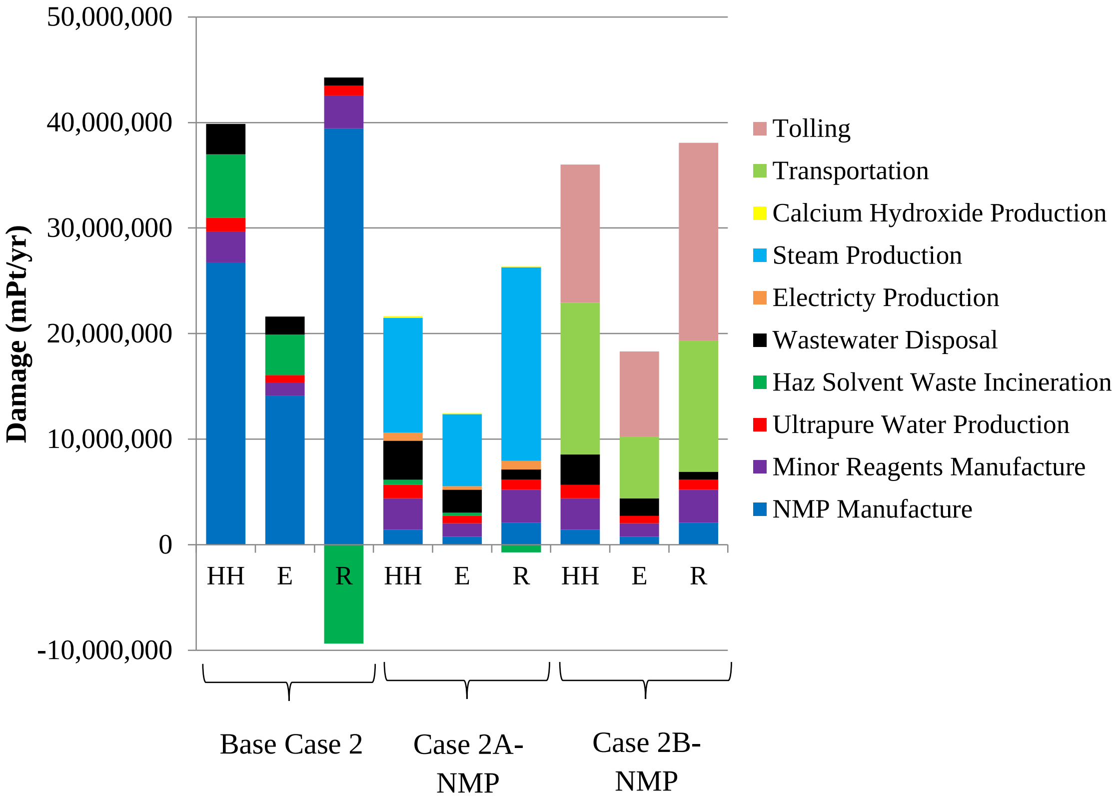


Figure 25. ReCiPe damage assessment for Base Case 2, Case 2A-NMP, and Case 2B-NMP; where HH is human health, E is ecosystems, and R is resources

The operating cost for Case 2B-NMP was calculated using Equation 45. This calculation includes the cost for tolling operations and transportation of hazardous waste and recovered NMP. As mentioned previously, the shipping requirements are 2,203,000,000 lb-mile/yr. The average cost to transport bulk materials by truck in the United States is 0.13 $/1,000 lb-mile [157]. The tolling cost (outside party processing charges) for NMP recovery was obtained from Clean Harbors. The average cost for

NMP recovery at Clean Harbors Chicago facility is based on the NMP composition in the waste stream. The tolling fees for NMP recovery, from waste streams with less than 5% dissolved solids and remaining components that are water or other low boiling solvents, is shown in Table 117. For Case 2B-NMP, the tolling fees are 2.35 \$/lb. Although this value is not based on the exact composition of the Parlin Plant waste stream, it is representative of NMP mixtures, and therefore is sufficient for this study.

$$\begin{aligned} Cost_{Case\ 2B} = {} & (m_{NMP} - r_{NMP}) \cdot Cost_{NMP} + m_{TFA} \cdot Cost_{TFA} + m_{HEMA} \cdot Cost_{HEMA} \\ & + m_{HCl} \cdot Cost_{HCl} + m_{UPW} \cdot Cost_{UPW} + m_{NHWW} \cdot Cost_{NHWW} \\ & + x_{shipping} \cdot Cost_{shipping} + m_{HW} \cdot Cost_{Tolling} \end{aligned} \tag{45}$$

In Equation 45, $Cost_{Case\ 2B}$ is the operating cost of Case 2B-NMP in \$/yr, $Cost_{shipping}$ is the cost to ship materials on a 1 lb-mile basis, m_{HW} is the mass of hazardous waste generated by the DuPont resin precursor process in lb/yr, and $Cost_{Tolling}$ is the tolling cost in \$/lb.

Table 117

Clean Harbors tolling fees, based on NMP composition in waste stream

NMP Composition (wt.%)	**Tolling Cost (\$/lb waste)**
> 80	1.03
70 – 79.9	1.15
60 – 69.9	1.35
50 – 59.9	1.55
40 – 49.9	1.75
30 – 39.9	1.95
20 – 29.9	2.15
10 – 19.9	2.35

The operating costs associated with Base Case 2, Case 2A-NMP, and Case 2B-NMP are shown in Table 118. Table 118 also shows the cost savings for Case 2A-NMP and Case 2B-NMP approaches to NMP recovery. The Case 2A-NMP approach reduces the operating costs of the DuPont process by 83%, while the Case 2B-NMP approach increases the operating cost of the DuPont process by 311%.

Table 118

Operating costs for Base Case 2, Case 2A-NMP, and Case 2B-NMP

	Base Case 2	**Case 2A-NMP**	**Case 2B-NMP**
Operating Cost ($/yr)	1,466,000	249,000	6,018,000
Cost Savings ($/yr)		1,217,000	-4,552,000
Percent Saved (%)		83	-311

Figure 26 shows the operating costs for Base Case 2, Case 2A-NMP, and Case 2B-NMP. The operating costs due to NMP manufacture, minor reagent manufacture, ultrapure water production, hazardous solvent waste disposal, and wastewater disposal are shown. For Case 2A-NMP, costs due to the steam, electricity, and calcium hydroxide slurry used by the recovery system and recovery system maintenance are also shown. For Case 2B-NMP, transportation and tolling costs are also included. The Case 2A-NMP approach to recovery of NMP results in significant operating cost savings because hazardous waste generation and virgin NMP manufacture are significantly reduced, and recovery system operating costs are low. The Case 2B-NMP approach significantly increases the operating cost of the DuPont process because the tolling cost is high (5,581,000 $/yr).

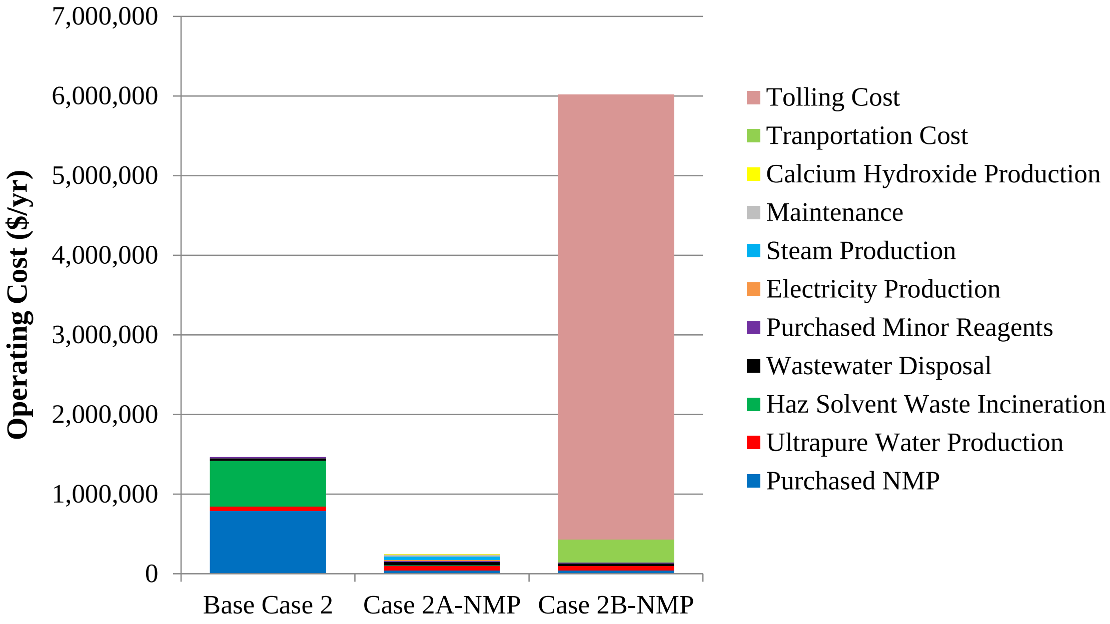


Figure 26. Operating costs for Base Case 2, Case 2A-NMP, and Case 2B-NMP

An economic analysis was conducted to further compare Cases 2A-NMP and 2B-NMP based on both operating cost and recovery equipment capital costs. Operating costs alone do not provide a fair comparison among the two approaches, as Case 2A-NMP requires the Parlin Plant to purchase capital equipment. To determine if Case 2A-NMP is economically favorable to Case 2B-NMP, net present value after 5 yr and net present value after 10 yr were calculated for Cases 2A-NMP and 2B-NMP. These calculations were performed using Equations 19-26, shown previously. Table 119 shows that Case 2A-NMP is profitable, while the Case 2B-NMP is not profitable. The Case 2A-NMP approach results in cost savings of $1,750,000 after 5 yr and $3,128,000 after 10 yr. The Case 2B-NMP approach results in additional costs of $15,261,000 after 5 yr and $22,848,000 after 10 yr.

Table 119

Economic analysis of Case 2A-NMP and Case 2B-NMP

	5 yr NPV ($)	**10 yr NPV ($)**
Case 2A-NMP	1,750,000	3,128,000
Case 2B-NMP	-15,261,000	-22,848,000

The evaluation of NMP recovery off-site (Case 2B-NMP) showed that it is not economically feasible to have NMP recovered from the hazardous waste by Clean Harbors at their solvent recycling facility. The tolling cost is expensive due to the low composition of NMP in the waste stream. The Case 2B-NMP approach did prove to be environmentally favorable compared to the current DuPont process with a 31% reduction in life cycle emissions, a 27% reduction in CO_2 emissions, and a 4 % reduction in damage. However, the Case 2A-NMP approach provides a greater reduction in environmental impact with a 44% reduction in life cycle emissions, a 40% reduction in CO2 emissions, and a 38% reduction in damage. The Case 2A-NMP approach also provides economic benefits, with savings of $3,128,000 after 10 yr. It is recommended to recover NMP for reuse on-site, at the Parlin Plant. Although capital equipment must be purchased, it is cheaper than paying transportation and tolling fees. The results show that the transportation costs are small in comparison to the tolling costs. Therefore, NMP recovery at a closer solvent recovery company would likely still not be economically feasible for this case. However, off-site NMP recovery could be economically feasible in other situations, if the waste contains a higher NMP composition.

Chapter 9

Case 2: Solvent Substitutes

Base Case 2-DMSO and Base Case 2-Sulfolane: Solvent Substitution

NMP substitution with DMSO and sulfolane, without solvent recovery, was investigated for the DuPont resin precursor process in Base Case 2-DMSO and Base Case 2-Sulfolane. It was assumed that DMSO and sulfolane could be substituted for NMP at a 1:1 mass ratio. Therefore, the annualized flow rate of raw materials and waste is the same as for the current DuPont process. The raw material use and waste generation associated with Base Case 2-DMSO and Base Case 2-Sulfolane are shown in Table 120.

Table 120

Raw material use and waste generation for Base Case 2-DMSO and Base Case 2-Sulfolane

	Quantity (lb/yr)
Solvent Substitute	404,000
Minor Reagents	36,000
HEMA	12,000
TFA	12,000
HCl	12,000
Ultrapure Water	9,062,000
Hazardous Waste	2,375,000
Wastewater	7,126,000
Process Steam	Constant for all processes
Electricity	Constant for all processes
Other Reagents	Outside of boundaries

The life cycle emissions associated with Base Case 2-DMSO and Base Case 2-Sulfolane are shown in Table 121, along with the life cycle emissions for Base Case 2. The life cycle emissions were calculated using Equation 7, where the LCI for hazardous solvent waste disposal is the same for all solvents. The current DuPont process has the highest life cycle emissions, with 2,670,000 lb/yr of total emissions and 2,370,000 lb/yr of CO_2 emissions. Substitution to DMSO reduces the life cycle emissions of the DuPont process to 1,490,000 lb/yr of total emissions and 1,340,000 lb/yr of CO_2 emissions. Use of sulfolane results in the least life cycle emissions with 1,290,000 lb/yr of total emissions and 1,170,000 lb/yr of CO_2 emissions. Table 121 also shows the reduction in life cycle emissions from substituting NMP with DMSO and sulfolane. Use of DMSO reduces the total life cycle emissions by 44% and the life cycle CO_2 emissions by 43%. Substitution to sulfolane provides the greatest reduction, with a 52% reduction in total emissions and a 51% reduction in CO_2 emissions.

Table 121

Life cycle emissions for Base Case 2, Base Case 2-DMSO, and Base Case 2-Sulfolane

	Base Case 2	**Base Case 2-DMSO**	**Base Case 2-Sulfolane**	**Base Case 2-DMSO Reductions**	**Base Case 2-Sulfolane Reductions**
Water Used (lb/yr)	5.24E+09	2.05E+09	1.10E+09	3.20E+09	4.14E+09
Total Air Emissions (lb/yr)	2.39E+06	1.35E+06	1.19E+06	1.04E+06	1.20E+06
CO_2 (lb/yr)	2.37E+06	1.34E+06	1.17E+06	1.03E+06	1.20E+06
CO (lb/yr)	1.14E+03	5.81E+02	5.74E+02	5.57E+02	5.64E+02
CH_4 (lb/yr)	4.26E+03	2.49E+03	1.61E+03	1.76E+03	2.65E+03
NO_X (lb/yr)	3.22E+03	1.70E+03	1.45E+03	1.51E+03	1.76E+03
NMVOC (lb/yr)	9.65E+02	4.09E+02	6.46E+02	5.56E+02	3.19E+02
Particulate (lb/yr)	1.01E+03	4.27E+02	3.25E+02	5.88E+02	6.89E+02
SO_2 (lb/yr)	4.56E+03	2.33E+03	1.60E+04	2.23E+03	-1.15E+04
Total Water Emissions (lb/yr)	2.73E+05	1.41E+05	1.02E+05	1.32E+05	1.71E+05
VOCs (lb/yr)	2.41E+00	8.04E-01	8.09E-01	1.60E+00	1.60E+00
Total Soil Emissions (lb/yr)	6.88E+02	2.49E+02	1.76E+02	4.39E+02	5.12E+02
Total Emissions (lb/yr)	2.67E+06	1.49E+06	1.29E+06	1.18E+06	1.37E+06
CED (MJ/yr)	1.56E+07	7.93E+06	5.95E+06	7.63E+06	9.61E+06

ReCiPe methodology was used to calculate the damage associated with Base Case 2-DMSO and Base Case 2-Sulfolane, shown in Table 122. The damage caused by using DMSO and sulfolane was calculated using Equation 10, where the damage score for hazardous solvent waste disposal is the same for all solvents. The current DuPont process causes the greatest damage, with 39,900,000 mPt/yr of damage to human health, 21,600,000 mPt/yr of damage to ecosystems, and 34,900,000 mPt/yr of damage to resources. Substitution to DMSO reduces the damage of the DuPont process to 21,900,000 mPt/yr of damage to human health, 12,300,000 mPt/yr of damage to ecosystems, and 17,600,000 mPt/yr of damage to resources. Use of sulfolane reduces the damage to 24,900,000 mPt/yr of damage to human health, 10,400,000 mPt/yr of damage to ecosystems, and 13,300,000 mPt/yr of damage to resources.

Table 122

ReCiPe damage assessment for Base Case 2, Base Case 2-DMSO, and Base Case 2-Sulfolane

	Base Case 2	**Base Case 2-DMSO**	**Base Case 2-Sulfolane**	**Base Case 2-DMSO Reductions**	**Base Case 2-Sulfolane Reductions**
Human Health (mPt/yr)	3.99E+07	2.19E+07	2.49E+07	1.79E+07	1.49E+07
Ecosystems (mPt/yr)	2.16E+07	1.23E+07	1.04E+07	9.35E+06	1.12E+07
Resources (mPt/yr)	3.49E+07	1.76E+07	1.33E+07	1.73E+07	2.15E+07
Total (mPt/yr)	9.63E+07	5.18E+07	4.87E+07	4.45E+07	4.76E+07

Table 122 also shows the reduction in damage from substituting NMP with DMSO and sulfolane. Use of sulfolane provides the greatest reduction in damage to ecosystems and resources, with reductions of 52% and 62%, respectively. Substitution to DMSO provides reductions of 43% and 50% to ecosystem and resource damage, respectively. However, use of DMSO provides the greatest reduction in human health damage, with a reduction of 45%, while use of sulfolane provides a 37% reduction in human health damage. Overall, use of sulfolane provides a 50% reduction in total damage, while use of DMSO provides a 46% reduction in total damage. These results are consistent with the life cycle emissions results, which showed that substitution of NMP to DMSO and sulfolane is favorable. Also, use of sulfolane is more favorable than use of DMSO.

The operating costs associated with Base Case 2-DMSO and Base Case 2-Sulfolane are shown in Table 123. The operating costs were calculated using Equation 16, where the cost to dispose of hazardous solvent waste is the same for all solvents. Table 123 shows that operating costs are not reduced from substituting NMP with DMSO and sulfolane. The operating cost of the current DuPont process is 1,466,000 $/yr. Substitution to DMSO increases the operating cost to 1,525,000 $/yr, while substitution to sulfolane increases the operating cost to 1,925,000 $/yr. This means that use of DMSO increases operating costs by 4%, while use of sulfolane increases operating costs by 31%. These results show that it is not economically favorable to substitute NMP with DMSO and sulfolane, without solvent recovery. Therefore, recovery of DMSO and sulfolane was investigated to evaluate the environmental and economic impact.

Table 123

Operating costs for Base Case 2, Base Case 2-DMSO, and Base Case 2-Sulfolane

	Base Case 2	**Base Case 2-DMSO**	**Base Case 2-Sulfolane**	**Base Case 2-DMSO Reductions**	**Base Case 2-Sulfolane Reductions**
Operating Cost ($/yr)	1,466,000	1,525,000	1,925,000	-59,000	-459,000

Case 2A-DMSO: DMSO Recovery Using Distillation

A recovery system was designed and evaluated for recovery of DMSO from the hazardous waste generated by the DuPont resin precursor process (Case 2A-DMSO). It was assumed that the hazardous waste contains the same composition of solvent, water, HCl, TFA, and HEMA as the hazardous waste currently generated, shown previously in Table 13. The approach to DMSO recovery is very similar to that of NMP recovery, previously described in Case 2A-NMP. Distillation is used to first remove the water and acids from the solvent waste, producing a stream containing mainly DMSO and HEMA. Distillation is used a second time to remove the HEMA, producing high purity DMSO. Similar to Case 2A-NMP, the binary interaction parameters for the DMSO-HEMA system were estimated using UNIFAC. The T-x-y diagram in Figure 27 shows that an azeotrope does not exists for the DMSO and HEMA system, so distillation is a feasible separation option for DMSO and HEMA. The same distillation column is used for both distillation steps, reducing capital costs.

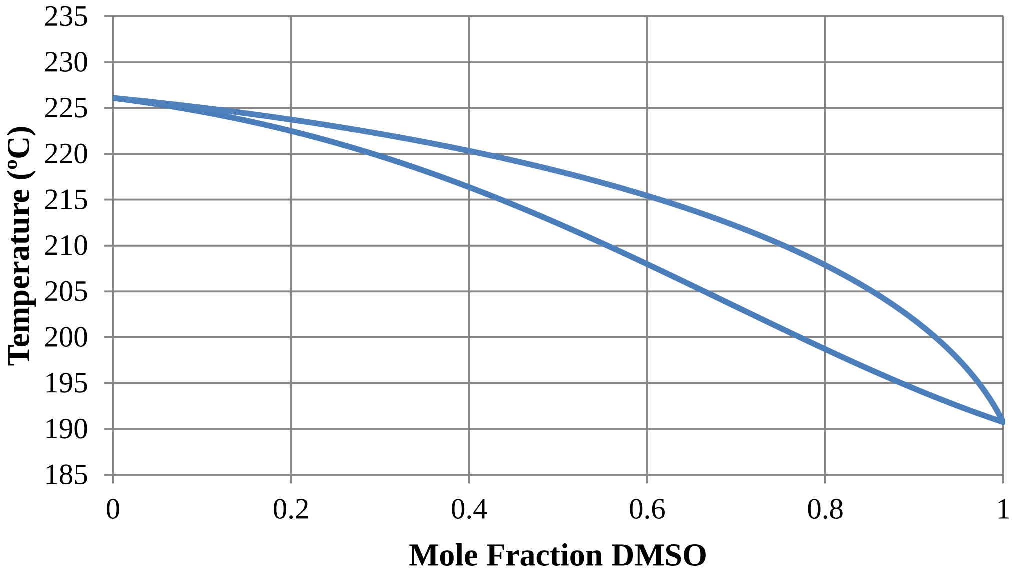


Figure 27. T-*x*-*y* equilibrium diagram for DMSO and HEMA system

The system to recover DMSO from the resin precursor process hazardous solvent waste is shown in Figure 28. This system is similar to the system designed in Case 2A-NMP. The hazardous solvent waste is sent to Holding Tank 1, where it accumulates. The solvent waste is then fed from Holding Tank 1 to the packed distillation column. The distillation column is operated under vacuum to prevent the degradation of DMSO. The distillate stream contains water with HCl, TFA, and trace amounts of DMSO. The distillate stream is neutralized and sent to a public wastewater treatment plant. The bottoms stream containing DMSO, HEMA, and trace amounts of water is sent to Holding Tank 2. After the first distillation step is complete, the concentrated DMSO in Holding Tank 2 is sent to the distillation column. In the second vacuum distillation step, high purity DMSO is produced in the distillate stream, while hazardous waste is produced in the bottoms stream. The desired specifications for recovered DMSO are assumed to be the same as for NMP. This means the DMSO must have a purity of 99.85 wt.% and a maximum water composition of 300 ppm. The recovered DMSO is sent to Holding Tank 3 for storage until it is used in the resin precursor process. The bottoms stream is disposed of as hazardous waste.

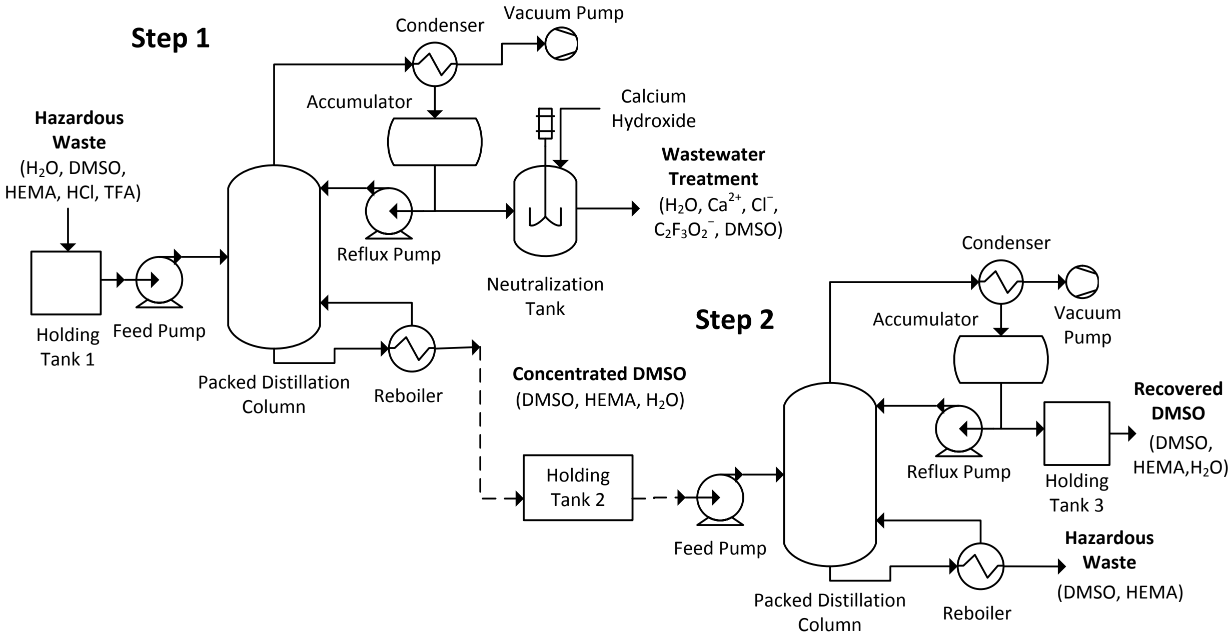


Figure 28. DMSO recovery system for DuPont's hazardous solvent waste

The distillation system shown in Figure 28 was designed to treat 2,375,000 lb/yr of hazardous solvent waste. The feed flow rate for the first distillation step was set to 2,855 lb/hr, resulting in an operating time of 832 hr/yr or 16 hr/week. The first distillation step is designed to run in weekly cycles that last for 16 hr. Holding Tank 1 is used to store the hazardous solvent waste required for 16 hr of operation of the first distillation step. Holding Tank 1 was designed to hold 5,500 gal of liquid and have a head space of about 20%. The total tank volume is 7,100 gal, with a diameter of 8.5 ft and a height of 16.75 ft. Holding Tank 1 was designed as a vertical flat bottomed storage tank, with specifications that are listed in Table 124. Holding Tank 1 was designed to be constructed of glass-lined carbon steel and have a corrosion allowance of 0.35 in. Once 5,500 gal of hazardous solvent waste is collected in Holding Tank 1, it is fed to the distillation column at a flow rate of 2,855 lb/hr for 16 hr. The hazardous solvent waste is fed using a centrifugal pump, with specifications listed in Table 124. The pump head was specified at 25 ft to ensure it would be able to send the solvent waste stream to the feed stage of the distillation column.

Table 124

Case 2A-DMSO Holding Tank 1 and feed pump specifications

Holding Tank 1		**Feed Pump**	
Material of Construction	Glass-lined Carbon Steel	Material of Construction	Stainless Steel
Diameter	8.5 ft	Liquid Flow Rate	7 gpm
Height	16.75 ft	Fluid Head	25 ft
Volume	7,100 gal	Power	0.125 hp
Corrosion Allowance	0.35 in	Pump Efficiency	70%
Design Pressure	15 psig	Design Pressure	50 psig
Design Temperature	150ºF	Design Temperature	150ºF

A distillation column was designed using Aspen Plus® for use in the step 1 and step 2 distillation processes. The distillation column design specifications are listed in Table 125. The distillation column was designed as a packed column, packed with 1.5 in ceramic Intalox saddles. The column was designed to be constructed out of glass-lined carbon steel and operated at 0.2 bar. The column has a packing height of 12 ft, a total column height of 18 ft, and a diameter of 4 ft. Table 126 shows the specifications for the reboiler and condenser. The reboiler heat transfer area was calculated assuming an overall heat transfer coefficient of 1,000 W/m^{2}·ºC and use of saturated steam at 16 bar (201ºC) for the first and second distillation steps [127]. Condenser heat transfer area was calculated assuming an overall heat transfer coefficient of 1,200 W/m^{2}·ºC and a cooling water temperature change of 15ºC [127]. The reboiler was designed as a kettle reboiler, while the condenser was designed as a TEMA heat exchanger.

Table 125

Case 2A-DMSO distillation column specifications

Distillation Column	
Material of Construction	Glass-lined Carbon Steel
Number of Stages	7
Feed Stage	3
Packing Material	1.5 in ceramic Intalox saddles
Height	18 ft
Packed Height	12 ft
Column Diameter	4 ft
Step 1 Reflux Ratio	1
Step 2 Reflux Ratio	5
Design Pressure	25 psig
Vacuum Design Pressure	-12 psig
Design Temperature	390ºF

Table 126

Case 2A-DMSO reboiler and condenser specifications

	Reboiler	**Condenser**
Material of Construction	Glass-lined Carbon Steel	Glass-lined Carbon Steel
Step 1 Duty	1,445 kW	-1,498 kW
Step 2 Duty	1,206 kW	-1,238 kW
Heat Transfer Area	430 ft^{2}	900 ft^{2}
Design Pressure	500 psig	50 psig
Design Temperature	390ºF	330ºF

The accumulator dimensions were calculated using the flow rate out of the condenser and a residence time of 10 min. The liquid flow rate through the reflux pump was the reflux flow rate. The vacuum pump flow rate was calculated using Equation 41. Table 127 shows the accumulator, reflux pump, and vacuum pump specifications. The accumulator has a diameter of 2.5 ft and a length of 10 ft, while the reflux pump has a liquid flow rate of 27 gpm. The distillate stream from the first distillation step is neutralized using calcium hydroxide slurry so it can be sent to a wastewater treatment plant. The calcium hydroxide slurry (15 wt.% calcium hydroxide) is pumped from the slurry holding tank to the neutralization tank. The slurry holding tank is designed to hold the quantity of slurry needed for 16 hr of operation of the first distillation step. The slurry holding tank was designed to hold 230 gal of slurry and have a head space of 20%, resulting in a diameter of 3 ft and a height of 8 ft. The slurry is pumped into the neutralization tank, to neutralize the acidic distillate stream. The neutralization tank was designed as an agitated vessel, with a residence time of 20 min [154]. The neutralization tank has a diameter of 2 ft and height of 6 ft. The specifications for the slurry holding tank, neutralization tank, and the slurry pump are listed in Table 128.

Table 127

Case 2A-DMSO accumulator, reflux pump, and vacuum pump specifications

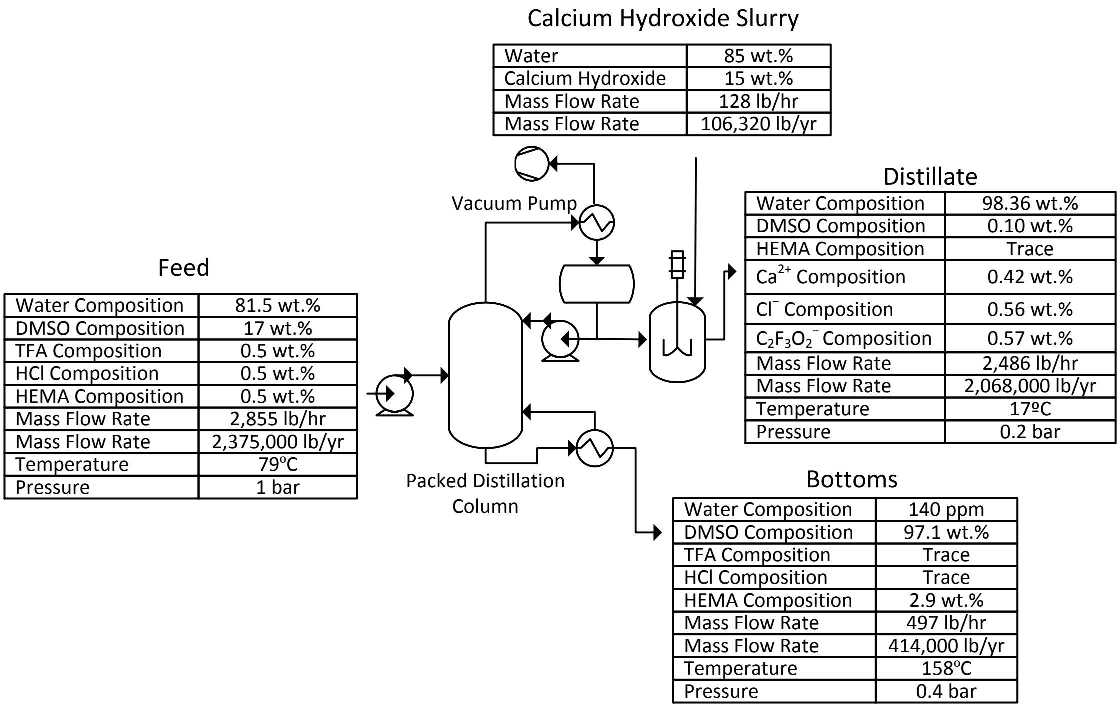
Accumulator		**Reflux Pump**		**Vacuum Pump**	
Material of Construction	Glass-lined Carbon Steel	Material of Construction	Stainless Steel	Material of Construction	Carbon Steel
Corrosion Allowance	0.35 in	Liquid Flow Rate	27 gpm	Gas Flow Rate	1,240 ft^3/min
Diameter	2.5 ft	Fluid Head	25 ft	Power	50 hp
Length	10 ft	Pump Efficiency	70%		
Volume	370 gal	Power	0.25 hp		
Design Pressure	50 psig	Design Pressure	50 psig		
Design Temperature	330ºF	Design Temperature	330ºF		

Table 128

Case 2A-DMSO neutralization equipment specifications

Slurry Holding Tank		**Neutralization Tank**		**Slurry Pump**	
Material of Construction	Stainless Steel	Material of Construction	Stainless Steel	Material of Construction	Stainless Steel
Corrosion Allowance	0.35 in	Corrosion Allowance	0.35 in	Liquid Flow Rate	0.5 gpm
Diameter	3 ft	Diameter	2 ft	Fluid Head	25 ft
Length	8 ft	Length	6 ft	Pump Efficiency	70%
Volume	420 gal	Volume	140 gal	Power	0.125 hp
Design Pressure	15 psig	Design Pressure	50 psig	Design Pressure	50 psig
Design Temperature	150ºF	Design Temperature	220ºF	Design Temperature	150ºF
		Agitator Power	5 hp		

The inlet and outlet streams for the first distillation step are shown in Figure 29. In the first distillation step, the hazardous solvent waste is fed to the distillation column. The bottoms stream contains 97.1 wt% DMSO, 2.9 wt.% HEMA, and 140 ppm water. The bottoms stream is sent to Holding Tank 2. The distillate stream contains water, acids, and DMSO. This stream neutralized with calcium hydroxide slurry, prior to sending to the wastewater treatment plant. The first distillation step recovers 99.5% of DMSO, which shows that a good separation is achieved.



Calcium Hydroxide Slurry

Water	85 wt.%
Calcium Hydroxide	15 wt.%
Mass Flow Rate	128 lb/hr
Mass Flow Rate	106,320 lb/yr

Feed

Water Composition	81.5 wt.%
DMSO Composition	17 wt.%
TFA Composition	0.5 wt.%
HCl Composition	0.5 wt.%
HEMA Composition	0.5 wt.%
Mass Flow Rate	2,855 lb/hr
Mass Flow Rate	2,375,000 lb/yr
Temperature	79°C
Pressure	1 bar

Distillate

Water Composition	98.36 wt.%
DMSO Composition	0.10 wt.%
HEMA Composition	Trace
Ca^{2+} Composition	0.42 wt.%
Cl^{-} Composition	0.56 wt.%
$C_2F_3O_2^{-}$ Composition	0.57 wt.%
Mass Flow Rate	2,486 lb/hr
Mass Flow Rate	2,068,000 lb/yr
Temperature	17ºC
Pressure	0.2 bar

Bottoms

Water Composition	140 ppm
DMSO Composition	97.1 wt.%
TFA Composition	Trace
HCl Composition	Trace
HEMA Composition	2.9 wt.%
Mass Flow Rate	497 lb/hr
Mass Flow Rate	414,000 lb/yr
Temperature	158°C
Pressure	0.4 bar

Figure 29. DMSO distillation step 1 stream flow rates and compositions

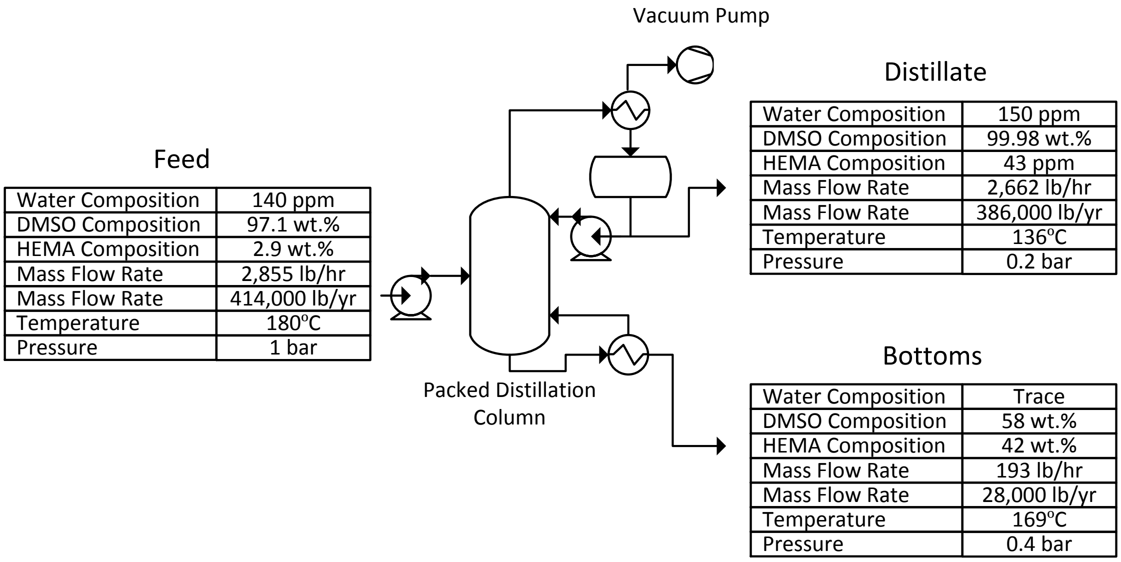
Holding Tank 2 was designed to store the bottoms from the first distillation step, prior to treatment in the second distillation step. As mentioned previously, the first distillation step is designed to run in weekly cycles that last for 16 hr. Therefore, Holding Tank 2 must store the concentrated DMSO produced from 16 hr of operation of the first distillation step. Holding Tank 2 was designed to store 1,000 gal of concentrated DMSO and have a head space of about 20%. The total tank volume is 1,300 gal, with a diameter of 4.75 ft and a height of 9.5 ft. Holding Tank 2 was designed as a vertical flat bottomed storage tank, with specifications that are listed in Table 129. Holding Tank 2 was designed to be constructed of glass-lined carbon steel and have a corrosion allowance of 0 in. Once 1,000 gal of concentrated DMSO is collected in Holding Tank 2, it is fed to the distillation column at a flow rate of 2,855 lb/hr for 2.8 hr. This flow rate was chosen so that the same size distillation column could be used for the second distillation step. The annual operating time of the second distillation step is 145 hr. The concentrated DMSO is fed using the feed pump, with specifications listed previously in Table 124.

Table 129

Case 2A-DMSO Holding Tank 2 specifications

Material of Construction	Glass-lined Carbon Steel
Corrosion Allowance	0 in
Diameter	4.75
Height	9.5
Total Volume	1,300 gal
Design Pressure	15 psig
Design Temperature	370ºF

The inlet and outlet streams for the first distillation step are shown in Figure 30. In the second distillation step, the concentrated DMSO is fed to the distillation column. The distillate stream contains the recovered high purity DMSO. The recovered DMSO has a purity of 99.98 wt.%, with a water composition of 150 ppm and a HEMA composition of 43 ppm. This stream is sent to Holding Tank 3, and is stored there until it is used in the resin precursor process. The bottoms stream contains 58 wt.% DMSO and 42 wt.% HEMA. This stream is disposed of as hazardous waste. The distillation system has a DMSO recovery of 96%.



Feed

Water Composition	140 ppm
DMSO Composition	97.1 wt.%
HEMA Composition	2.9 wt.%
Mass Flow Rate	2,855 lb/hr
Mass Flow Rate	414,000 lb/yr
Temperature	180°C
Pressure	1 bar

Distillate

Water Composition	150 ppm
DMSO Composition	99.98 wt.%
HEMA Composition	43 ppm
Mass Flow Rate	2,662 lb/hr
Mass Flow Rate	386,000 lb/yr
Temperature	136°C
Pressure	0.2 bar

Bottoms

Water Composition	Trace
DMSO Composition	58 wt.%
HEMA Composition	42 wt.%
Mass Flow Rate	193 lb/hr
Mass Flow Rate	28,000 lb/yr
Temperature	169°C
Pressure	0.4 bar

Figure 30. DMSO distillation step 2 stream flow rates and compositions

Holding Tank 3 was designed to store the recovered DMSO, prior to use in the resin precursor process. As mentioned previously, the second distillation step is designed to run in weekly cycles that last for 2.8 hr. Therefore, Holding Tank 3 must store the recovered DMSO from 2.8 hr of operation of the second distillation step. Holding Tank 3 was designed to hold 900 gal of DMSO and have a head space of about 20%. The total tank volume is 1,300 gal, with a diameter of 4.75 ft and a height of 9.5 ft. Holding Tank 3 was designed as a vertical flat bottomed storage tank, with specifications that are listed in Table 130.

Table 130

Case 2A-DMSO Holding Tank 3 specifications

Material of Construction	Glass-lined Carbon Steel
Corrosion Allowance	0 in
Diameter	4.75 ft
Height	9.5 ft
Total Volume	1,300 gal
Design Pressure	15 psig
Design Temperature	390ºF

The installed capital cost for the equipment in the DMSO distillation system, based on fourth quarter 2014 costs, was estimated using Aspen Capital Cost Estimator and is shown in Table 131. This cost includes the cost for equipment, piping, support structures, electrical work, insulation, and manpower. The total installed capital cost for the Case 2 DMSO distillation system is $1,477,000. Table 131 shows that the packed distillation column has the highest capital cost of all the equipment used in the DMSO recovery design, with a capital cost of $301,000. The condenser has the second highest capital cost ($192,000), followed by Holding Tank 1 ($170,000), the neutralization tank ($164,000), the accumulator ($151,000), and the reboiler ($150,000). The rest of the equipment have capital costs below $100,000.

Table 131

Case 2A-DMSO distillation system capital costs

Equipment	**Capital Cost ($)**
Holding Tank 1	170,000
Feed Pump	20,000
Packed Column	301,000
Reboiler	150,000
Condenser	192,000
Accumulator	151,000
Reflux Pump	23,000
Vacuum Pump	74,000
Slurry Holding Tank	51,000
Neutralization Tank	164,000
Slurry Pump	18,000
Holding Tank 2	81,000
Holding Tank 3	82,000
Total	1,477,000

The raw materials used, utilities used, and waste generated by the current DuPont resin precursor process and the DuPont process using DMSO with recovery is shown in Table 132. The steam energy use was calculated using Equation 34, while the condenser electricity use was calculated using in Equation 35. The electricity used by the feed, reflux, and vacuum pumps and the neutralization tank agitator were calculated using Equation 36. Table 132 shows that Base Case 2 uses 403,800 lb/yr of NMP, while Case 2A-DMSO uses 17,420 lb/yr of DMSO. This shows that virgin solvent use is decreased by 386,600 lb/yr. Hazardous waste generation is reduced by 2,347,000 lb/yr. However, non-hazardous wastewater generation is increased by 2,068,000 lb/yr. Also, 299,300 MJ/yr of electricity, 5,509,000 MJ/yr of steam, and 15,950 lb/yr of calcium hydroxide slurry is required for DMSO recovery.

Table 132

Raw material use, utility use, and waste generation for Base Case 2 and Case 2A-DMSO

	Base Case 2	**Case 2A-DMSO**
Solvent (lb/yr)	403,800	17,420
Minor Reagents		
HEMA (lb/yr)	11,880	11,880
TFA (lb/yr)	11,880	11,880
HCl (lb/yr)	11,880	11,880
Ultrapure water (lb/yr)	9,062,000	9,062,000
Hazardous Solvent Waste (lb/yr)	2,375,000	27,970
Non-hazardous Wastewater (lb/yr)	7,126,000	9,194,000
Electricity (MJ/yr)	0	299,300
Steam (MJ/yr)	0	5,509,000
Calcium Hydroxide Slurry (lb/yr)	0	15,950

The life cycle emissions of Case 2A-DMSO were calculated using Equation 8. This calculation includes the life cycle emissions from steam generation, electricity generation, and calcium hydroxide manufacture. The life cycle emissions for Base Case 2 and Case 2A-DMSO are shown in Table 133. The current DuPont process generates more life cycle emissions, with 2,670,000 lb/yr of total emissions and 2,370,000 lb/yr of CO_2 emissions. Case 2A-DMSO produces less life cycle emissions, with 1,460,000 lb/yr of total emissions and 1,400,000 lb/yr of CO_2 emissions. The reduction in life cycle emissions for Case 2A-DMSO was calculated using Equation 9 and is shown in Table 133. Case 2A-DMSO reduces the total life cycle emissions and life cycle CO_2 emissions by 45% and 41%, respectively.

Table 133

Life cycle emissions for Base Case 2 and Case 2A-DMSO

	Base Case 2	**Case 2A-DMSO**	**Avoided Emissions**
Water Used (lb/yr)	5.24E+09	5.41E+08	4.70E+09
Total Air Emissions (lb/yr)	2.39E+06	1.42E+06	9.78E+05
CO_2 (lb/yr)	2.37E+06	1.40E+06	9.66E+05
CO (lb/yr)	1.14E+03	6.64E+02	4.74E+02
CH_4 (lb/yr)	4.26E+03	2.68E+03	1.58E+03
NO_X (lb/yr)	3.22E+03	1.62E+03	1.59E+03
NMVOC (lb/yr)	9.65E+02	2.10E+02	7.55E+02
Particulate (lb/yr)	1.01E+03	1.59E+02	8.55E+02
SO_2 (lb/yr)	4.56E+03	2.44E+03	2.12E+03
Total Water Emissions (lb/yr)	2.73E+05	5.32E+04	2.20E+05
VOCs (lb/yr)	2.41E+00	2.78E-01	2.13E+00
Total Soil Emissions (lb/yr)	6.88E+02	9.18E+01	5.96E+02
Total Emissions (lb/yr)	**2.67E+06**	**1.46E+06**	**1.20E+06**
CED (MJ/yr)	1.56E+07	1.04E+07	5.18E+06

The damage caused by Case 2A-DMSO was calculated using Equation 11. This calculation includes the damage caused by steam generation, electricity generation, and calcium hydroxide manufacture. The damage to human health, ecosystems, and resources caused by Base Case 2 and Case 2A-DMSO is shown in Table 134. The current DuPont process causes more damage, with 39,900,000 mPt/yr of damage to human health, 21,600,000 mPt/yr of damage to ecosystems, and 34,900,000 mPt/yr of damage to resources. Case 2A-DMSO causes less damage, with 21,300,000 mPt/yr of damage to human health, 12,200,000 mPt/yr of damage to ecosystems, and 25,500,000 mPt/yr of damage to resources. The reduction in damage for Case 2A-DMSO was calculated using Equation 12 and are shown in Table 134. Case 2A-DMSO reduces the damage to human health, ecosystems, and resources by 47%, 43%, and 27%, respectively.

Table 134

ReCiPe damage assessment for Base Case 2 and Case 2A-DMSO

	Base Case 2	**Case 2A-DMSO**	**Avoided Damage**
Human Health (mPt/yr)	3.99E+07	2.13E+07	1.86E+07
Ecosystems (mPt/yr)	2.16E+07	1.22E+07	9.38E+06
Resources (mPt/yr)	3.49E+07	2.55E+07	9.41E+06
Total (mPt/yr)	9.63E+07	5.89E+07	3.74E+07

The operating cost associated with Base Case 2 and Case 2A-DMSO is shown in Table 135. The operating cost for Case 2A-DMSO was calculated using Equation 17. In Equation 17, the maintenance cost for the DMSO recovery system is 27,400 $/yr. The maintenance cost is 2.5% of the capital cost for all unit operations. The current DuPont process has an operating cost of 1,466,000 $/yr. Case 2A-DMSO reduces the operating cost to 242,700 $/yr. This is an 83% reduction in operating costs.

Table 135

Operating costs for Base Case 2 and Case 2A-DMSO

	Base Case 2	**Case 2A-DMSO**	**Savings**
Operating Cost ($/yr)	1,466,000	242,700	1,223,000

An economic analysis was conducted to evaluate Case 2A-DMSO, based on both operating cost savings and recovery equipment capital costs. This was done to determine if Case 2A-DMSO would save money. To determine if Case 2A-DMSO is profitable, internal rate of return (IRR), return on investment (ROI), payback time after tax, net present value after 5 yr, and net present value after 10 yr were calculated. These calculations were performed using Equations 19-27, shown previously. Table 136 shows that Case 2A-DMSO is profitable. Case 2A-DMSO results in cost savings of $1,781,000 after 5 yr and $3,165,000 after 10 yr.

Table 136

Economic analysis of Case 2A-DMSO

	IRR (%)	**ROI (%)**	**Payback time after tax (yr)**	**5 yr NPV ($)**	**10 yr NPV ($)**
Case 2A-DMSO	68.6	60.1	2.2	1,781,000	3,165,000

Case 2A-Sulfolane: Sulfolane Recovery Using Distillation

A recovery system was designed and evaluated for recovery of sulfolane from the hazardous waste generated by the DuPont resin precursor process (Case 2A-Sulfolane). It was assumed that the hazardous waste contains the same composition of solvent, water, HCl, TFA, and HEMA as the hazardous waste currently generated, shown previously in Table 13. The approach to sulfolane recovery is similar to that of NMP recovery, previously described in Case 2A-NMP. However, only one distillation step is required to recover high purity sulfolane. The T-*x*-*y* diagram in Figure 31, generated using estimated UNIFAC binary interaction parameters, shows sulfolane has a higher boiling point than HEMA. Figure 31 also shows that an azeotrope does not exists for the sulfolane and HEMA system, so distillation is a feasible separation option. In the sulfolane recovery design, distillation is used to remove the water, acids, and HEMA from the solvent waste, producing a stream containing high purity sulfolane.

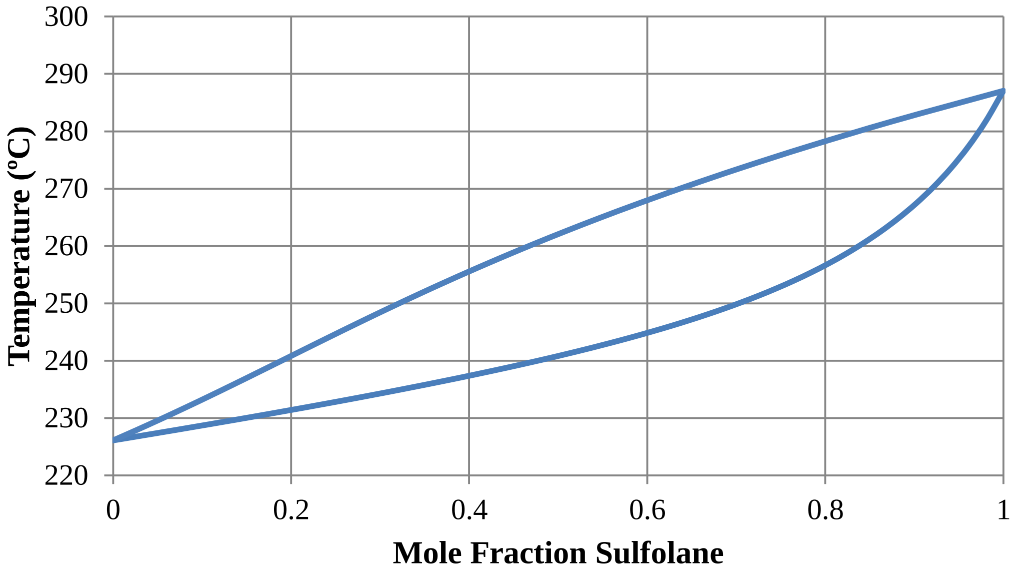


Figure 31. T-*x*-*y* equilibrium diagram for sulfolane and HEMA system

The system to recover sulfolane from the resin precursor process hazardous solvent waste is shown in Figure 32. This system is similar to the system designed in Case 2A-NMP, except only one distillation step is required. The hazardous solvent waste is sent to Holding Tank 1, where it accumulates. The solvent waste is then fed from Holding Tank 1 to the packed distillation column. The distillation column is operated under vacuum to prevent the degradation of sulfolane. The distillate stream contains water, HCl, TFA, HEMA, and trace amounts of sulfolane. The distillate stream is neutralized and sent to a public wastewater treatment plant. The bottoms stream contains high purity sulfolane, which is sent to Holding Tank 2 for storage until it is used in the resin precursor process. The desired specifications for the recovered sulfolane are assumed to be the same as for NMP. This means the sulfolane must have a purity of 99.85 wt.% and a maximum water composition of 300 ppm.

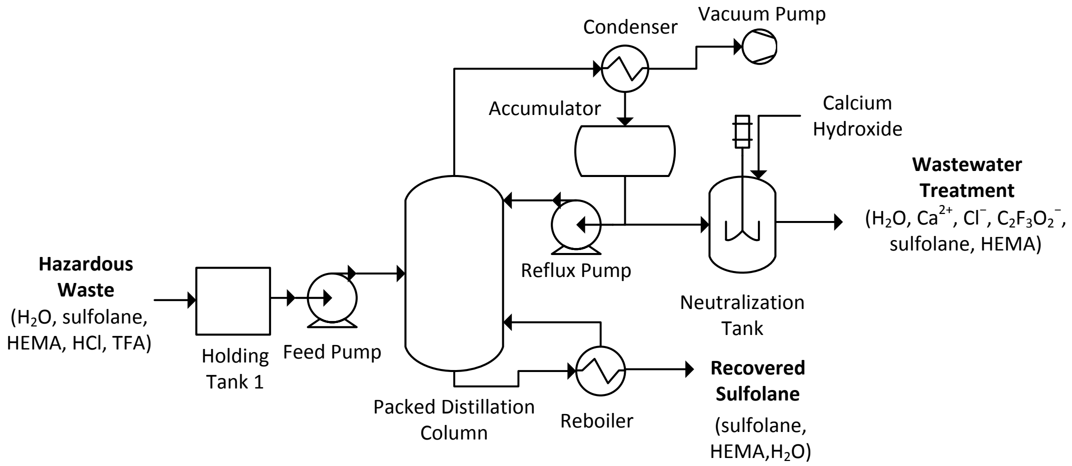


Figure 32. Sulfolane recovery system for DuPont's hazardous solvent waste

The distillation system shown in Figure 32 was designed to treat 2,375,000 lb/yr of hazardous solvent waste. The feed flow rate to the distillation column was set to 2,855 lb/hr, resulting in an operating time of 832 hr/yr or 16 hr/week. The distillation process is designed to run in weekly cycles that last for 16 hr. Holding Tank 1 is used to store the hazardous solvent waste required for 16 hr of operation of the distillation process. Holding Tank 1 was designed to hold 5,500 gal of liquid and have a head space of about 20%. The total tank volume is 7,100 gal, with a diameter of 8.5 ft and a height of 16.75 ft. Holding Tank 1 was designed as a vertical flat bottomed storage tank, with specifications that are listed in Table 137. Holding Tank 1 was designed to be constructed of glass-lined carbon steel and have a corrosion allowance of 0.35 in. Once 5,500 gal of hazardous solvent waste is collected in Holding Tank 1, it is fed to the distillation column at a flow rate of 2,855 lb/hr for 16 hr. The hazardous solvent waste is fed using a centrifugal pump, with specifications listed in Table 137. The pump head was specified at 25 ft to ensure it would be able to send the solvent waste stream to the feed stage of the distillation column.

Table 137

Case 2A-Sulfolane Holding Tank 1 and feed pump specifications

Holding Tank 1		**Feed Pump**	
Material of Construction	Glass-lined Carbon Steel	Material of Construction	Stainless Steel
Diameter	8.5 ft	Liquid Flow Rate	6 gpm
Height	16.75 ft	Fluid Head	25 ft
Volume	7,100 gal	Power	0.125 hp
Corrosion Allowance	0.35 in	Pump Efficiency	70%
Design Pressure	15 psig	Design Pressure	50 psig
Design Temperature	150ºF	Design Temperature	150ºF

A distillation column was designed using Aspen Plus® for use in the distillation process. The distillation column design specifications are listed in Table 138. The distillation column was designed as a packed column, packed with 1.5 in ceramic Intalox saddles. The column was designed to be constructed out of glass-lined carbon steel and operated at 0.05 bar. The column has a packing height of 8 ft, a total column height of 14 ft, and a diameter of 5 ft. Table 139 shows the specifications for the reboiler and condenser. The reboiler heat transfer area was calculated assuming an overall heat transfer coefficient of 1,000 $W/m^2 \cdot {}^{o}C$ and use of saturated steam at 20 bar (212ºC) [127]. Condenser heat transfer area was calculated assuming an overall heat transfer coefficient of 1,200 $W/m^2 \cdot {}^{o}C$ and a cooling water temperature change of 15ºC [127]. The reboiler was designed as a kettle reboiler, while the condenser was designed as a TEMA heat exchanger.

Table 138

Case 2A-Sulfolane distillation column specifications

Distillation Column	
Material of Construction	Glass-lined Carbon Steel
Number of Stages	5
Feed Stage	3
Packing Material	1.5 in ceramic Intalox saddles
Height	14 ft
Packed Height	8 ft
Column Diameter	5 ft
Reflux Ratio	1
Design Pressure	25 psig
Vacuum Design Pressure	-14 psig
Design Temperature	440ºF

Table 139

Case 2A-Sulfolane reboiler and condenser specifications

	Reboiler	**Condenser**
Material of Construction	Glass-lined Carbon Steel	Glass-lined Carbon Steel
Duty	1,448 kW	-1,557 kW
Heat Transfer Area	925 ft^2	935 ft^2
Design Pressure	500 psig	50 psig
Design Temperature	440ºF	200ºF

The accumulator dimensions were calculated using the flow rate out of the condenser and a residence time of 10 min. The liquid flow rate through the reflux pump was the reflux flow rate. Table 140 shows the accumulator and reflux pump specifications. The accumulator has a diameter of 2 ft and a length of 8 ft, while the reflux pump has a liquid flow rate of 5 gpm. The vacuum pump flow rate was calculated using Equation 41. Two vacuum pumps are required, with specifications shown in Table 140. The distillate stream is neutralized using calcium hydroxide slurry so it can be sent to a wastewater treatment plant. The calcium hydroxide slurry (15 wt.% calcium hydroxide) is pumped from the slurry holding tank to the neutralization tank. The slurry holding tank is designed to hold the quantity of slurry needed for 16 hr of operation of the distillation process. The slurry holding tank was designed to hold 230 gal of slurry and have a head space of 20%, resulting in a diameter of 3 ft and a height of 8 ft. The slurry is pumped into the neutralization tank, to neutralize the acidic distillate stream. The neutralization tank was designed as an agitated vessel, with a residence time of 20 min [154]. The neutralization tank has a diameter of 2 ft and height of 6 ft. The specifications for the slurry holding tank, neutralization tank, and the slurry pump are listed in Table 141.

Table 140

Case 2A-Sulfolane accumulator, reflux pump, and vacuum pump specifications

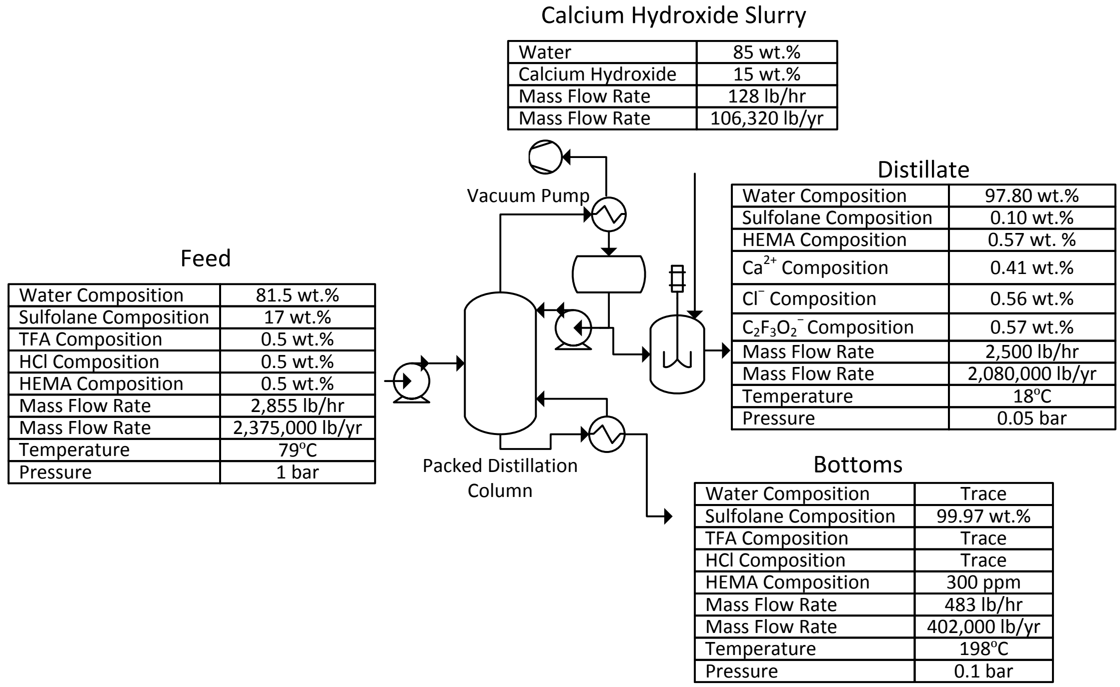
Accumulator		**Reflux Pump**		**Vacuum Pump**	
Material of Construction	Glass-lined Carbon Steel	Material of Construction	Stainless Steel	Material of Construction	Carbon Steel
Corrosion Allowance	0.35 in	Liquid Flow Rate	5 gpm	Gas Flow Rate	1,400 ft^3/min
Diameter	2 ft	Fluid Head	25 ft	Power	60 hp
Length	8 ft	Pump Efficiency	70%		
Volume	190 gal	Power	0.125 hp		
Design Pressure	50 psig	Design Pressure	50 psig		
Design Temperature	200ºF	Design Temperature	200ºF		

Table 141

Case 2A-Sulfolane neutralization equipment specifications

Slurry Holding Tank		**Neutralization Tank**		**Slurry Pump**	
Material of Construction	Stainless Steel	Material of Construction	Stainless Steel	Material of Construction	Stainless Steel
Corrosion Allowance	0.35 in	Corrosion Allowance	0.35 in	Liquid Flow Rate	0.5 gpm
Diameter	3 ft	Diameter	2 ft	Fluid Head	25 ft
Length	8 ft	Length	6 ft	Pump Efficiency	70%
Volume	420 gal	Volume	140 gal	Power	0.125 hp
Design Pressure	15 psig	Design Pressure	50 psig	Design Pressure	50 psig
Design Temperature	150ºF	Design Temperature	220ºF	Design Temperature	150ºF
		Agitator Power	5 hp		

The inlet and outlet streams for the distillation process are shown in Figure 33. In the distillation process, the hazardous solvent waste is fed to the distillation column. The bottoms stream contains high purity sulfolane. The recovered sulfolane has a purity of 99.97%, with 300 ppm HEMA and trace water. The recovered sulfolane is sent to Holding Tank 2, and is stored there until it is used in the resin precursor process. The distillate stream contains water, acids, HEMA, and sulfolane. This stream is neutralized with calcium hydroxide slurry, prior to sending to the wastewater treatment plant. The distillation process recovers 99.5% of sulfolane, which shows that a good separation is achieved.



Calcium Hydroxide Slurry

Water	85 wt.%
Calcium Hydroxide	15 wt.%
Mass Flow Rate	128 lb/hr
Mass Flow Rate	106,320 lb/yr

Feed

Water Composition	81.5 wt.%
Sulfolane Composition	17 wt.%
TFA Composition	0.5 wt.%
HCl Composition	0.5 wt.%
HEMA Composition	0.5 wt.%
Mass Flow Rate	2,855 lb/hr
Mass Flow Rate	2,375,000 lb/yr
Temperature	79°C
Pressure	1 bar

Distillate

Water Composition	97.80 wt.%
Sulfolane Composition	0.10 wt.%
HEMA Composition	0.57 wt. %
Ca^{2+} Composition	0.41 wt.%
Cl^- Composition	0.56 wt.%
$C_2F_3O_2^-$ Composition	0.57 wt.%
Mass Flow Rate	2,500 lb/hr
Mass Flow Rate	2,080,000 lb/yr
Temperature	18°C
Pressure	0.05 bar

Bottoms

Water Composition	Trace
Sulfolane Composition	99.97 wt.%
TFA Composition	Trace
HCl Composition	Trace
HEMA Composition	300 ppm
Mass Flow Rate	483 lb/hr
Mass Flow Rate	402,000 lb/yr
Temperature	198°C
Pressure	0.1 bar

Figure 33. Sulfolane distillation process stream flow rates and compositions

Holding Tank 2 was designed to store the recovered sulfolane, prior to use in the resin precursor process. As mentioned previously, the distillation process is designed to run in weekly cycles that last for 16 hr. Therefore, Holding Tank 2 must store the recovered sulfolane from 16 hr of operation of the distillation column. Holding Tank 2 was designed to hold 830 gal of sulfolane and have a head space of about 20%. The total tank volume is 1,100 gal, with a diameter of 4.5 ft and a height of 9 ft. Holding Tank 2 was designed as a vertical flat bottomed storage tank, with specifications that are listed in Table 142.

Table 142

Case 2A-Sulfolane Holding Tank 2 specifications

Material of Construction	Glass-lined Carbon Steel
Corrosion Allowance	0 in
Diameter	4.5
Height	9
Total Volume	1,100 gal
Design Pressure	15 psig
Design Temperature	440ºF

The installed capital cost for the equipment in sulfolane distillation system, based on fourth quarter 2014 costs, was estimated using Aspen Capital Cost Estimator and is shown in Table 143. This cost includes the equipment includes the cost for equipment, piping, support structures, electrical work, insulation, and manpower. The total installed capital cost for the Case 2A-Sulfolane distillation system is $1,565,000. Table 143 shows that the packed distillation column has the highest capital cost of all the equipment used in the sulfolane recovery design, with a capital cost of $364,000. The reboiler has the second highest capital cost ($207,000), followed by the condenser ($188,000), Holding Tank 1 ($170,000), vacuum pumps ($170,000), neutralization tank ($164,000), and accumulator ($113,000). The rest of the equipment have capital costs below $100,000.

Table 143

Case 2A-Sulfolane distillation system capital costs

Equipment	**Capital Cost ($)**
Holding Tank 1	170,000
Feed Pump	20,000
Packed Column	364,000
Reboiler	207,000
Condenser	188,000
Accumulator	113,000
Reflux Pump	20,000
Vacuum Pump (x2)	170,000
Slurry Holding Tank	51,000
Neutralization Tank	164,000
Slurry Pump	18,000
Holding Tank 2	80,000
Total	1,565,000

The raw materials used, utilities used, and waste generated by Base Case 2 and Case 2A-Sulfolane is shown in Table 144. The steam energy use was calculated using Equation 34, while the condenser electricity use was calculated using in Equation 35. The electricity used by the feed, reflux, and vacuum pumps and the neutralization tank agitator were calculated using Equation 36. Table 144 shows that the current process uses 403,800 lb/yr of NMP, while Case 2A-Sulfolane uses 1,881 lb/yr of sulfolane. This shows that virgin solvent use is decreased by 401,900 lb/yr. Hazardous waste generation is eliminated; however, non-hazardous wastewater generation is increased by 2,079,000 lb/yr. Also, 421,500 MJ/yr of electricity, 4,818,000 MJ/yr of steam, and 15,950 lb/yr of calcium hydroxide slurry is required for sulfolane recovery.

Table 144

Raw material use, utility use, and waste generation for Base Case 2 and Case 2A-Sulfolane

	Base Case 2	**Case 2A-Sulfolane**
Solvent (lb/yr)	403,800	1,881
Minor Reagents		
HEMA (lb/yr)	11,880	11,880
TFA (lb/yr)	11,880	11,880
HCl (lb/yr)	11,880	11,880
Ultrapure water (lb/yr)	9,062,000	9,062,000
Hazardous Solvent Waste (lb/yr)	2,375,000	0
Non-hazardous Wastewater (lb/yr)	7,126,000	9,205,000
Electricity (MJ/yr)	0	421,500
Steam (MJ/yr)	0	4,818,000
Calcium Hydroxide Slurry (lb/yr)	0	15,950

The life cycle emissions of Case 2A-Sulfolane were calculated using Equation 8. This calculation includes the life cycle emissions from steam generation, electricity generation, and calcium hydroxide manufacture. The life cycle emissions for Base Case 2 and Case 2A-Sulfolane are shown in Table 145. The current DuPont process generates more life cycle emissions, with 2,670,000 lb/yr of total emissions and 2,370,000 lb/yr of CO_2 emissions. Case 2A-Sulfolane produces less life cycle emissions, with 1,340,000 lb/yr of total emissions and 1,280,000 lb/yr of CO_2 emissions. The reduction in life cycle emissions for Case 2A-Sulfolane were calculated using Equation 9 and also are shown in Table 145. Case 2A-Sulfolane reduces the total life cycle emissions and life cycle CO_2 emissions by 50% and 46%, respectively.

Table 145

Life cycle emissions for Base Case 2 and Case 2A-Sulfolane

	Base Case 2	**Case 2A-Sulfolane**	**Avoided Emissions**
Water Used (lb/yr)	5.24E+09	4.71E+08	4.77E+09
Total Air Emissions (lb/yr)	2.39E+06	1.29E+06	1.10E+06
CO_2 (lb/yr)	2.37E+06	1.28E+06	1.09E+06
CO (lb/yr)	1.14E+03	6.34E+02	5.04E+02
CH_4 (lb/yr)	4.26E+03	2.60E+03	1.66E+03
NO_X (lb/yr)	3.22E+03	1.55E+03	1.67E+03
NMVOC (lb/yr)	9.65E+02	2.07E+02	7.58E+02
Particulate (lb/yr)	1.01E+03	1.52E+02	8.62E+02
SO_2 (lb/yr)	4.56E+03	2.65E+03	1.91E+03
Total Water Emissions (lb/yr)	2.73E+05	5.03E+04	2.23E+05
VOCs (lb/yr)	2.41E+00	2.49E-01	2.16E+00
Total Soil Emissions (lb/yr)	6.88E+02	7.79E+01	6.10E+02
Total Emissions (lb/yr)	**2.67E+06**	**1.34E+06**	**1.33E+06**
CED (MJ/yr)	1.56E+07	9.91E+06	5.65E+06

The damage caused by Case 2A-Sulfolane was calculated using Equation 11. This calculation includes the damage caused by steam generation, electricity generation, and calcium hydroxide manufacture. The damage to human health, ecosystems, and resources caused by the current process and the alternative process with sulfolane recovery is shown in Table 146. The current DuPont process causes more damage, with 39,900,000 mPt/yr of damage to human health, 21,600,000 mPt/yr of damage to ecosystems, and 34,900,000 mPt/yr of damage to resources. Case 2A-Sulfolane causes less damage, with 20,200,000 mPt/yr of damage to human health, 10,500,000 mPt/yr of damage to ecosystems, and 11,400,000 mPt/yr of damage to resources. The reduction in damage for Case 2A-Sulfolane were calculated using Equation 12 and are shown in Table 146. Case 2A-Sulfolane reduces the damage to human health, ecosystems, and resources by 51%, 48%, and 33%, respectively.

Table 146

ReCiPe damage assessment for Base Case 2 and Case 2A-Sulfolane

	Base Case 2	**Case 2A-Sulfolane**	**Avoided Damage**
Human Health (mPt/yr)	3.99E+07	1.97E+07	2.02E+07
Ecosystems (mPt/yr)	2.16E+07	1.11E+07	1.05E+07
Resources (mPt/yr)	3.49E+07	2.35E+07	1.14E+07
Total (mPt/yr)	9.63E+07	5.43E+07	4.21E+07

The operating cost associated with Base Case 2 and Case 2A-Sulfolane is shown in Table 147. The operating cost for Case 2A-Sulfolane was calculated using Equation 17. In Equation 17, the maintenance cost for the sulfolane recovery system is 31,600 $/yr. The maintenance cost is 2.5% of the capital cost for all unit operations. The current DuPont process has an operating cost of 1,466,000 $/yr. Case 2A-Sulfolane reduces the operating cost to 209,400 $/yr. This is an 86% reduction in operating costs.

Table 147

Operating costs for Base Case 2 and Case 2A-Sulfolane

	Base Case 2	**Case 2A-Sulfolane**	**Savings**
Operating Cost ($/yr)	1,466,000	209,400	1,257,000

An economic analysis was conducted to evaluate Case 2A-Sulfolane based on both operating cost savings and recovery equipment capital costs. This was done to determine if Case 2A-Sulfolane would save money. To determine if Case 2A-Sulfolane is profitable, internal rate of return (IRR), return on investment (ROI), payback time after tax, net present value after 5 yr, and net present value after 10 yr were calculated. These calculations were performed using Equations 19-27, shown previously. Table 148 shows that Case 2A-Sulfolane is profitable. Case 2A-Sulfolane results in cost savings of \$1,790,000 after 5 yr and \$3,214,000 after 10 yr.

Table 148

Economic analysis of Case 2A-Sulfolane

	IRR (%)	**ROI (%)**	**Payback time after tax (yr)**	**5 yr NPV (\$)**	**10 yr NPV (\$)**
Case 2A-Sulfolane	66.4	58.5	2.3	1,790,000	3,214,000

Case 2 Conclusion

The environmental and economic impact of Case 2A-NMP and Case 2 scenarios with solvent substitutes were compared to determine the best alternative to the current DuPont resin precursor process. Figure 34 shows the life cycle emissions associated with the current DuPont process and the green alternative process. In Figure 34, Base Case 2 is the current process. Base Case 2-DMSO reduces the total emissions by 44% and reduces the CO_2 emissions by 43%. Base Case 2-Sulfolane reduces the total emissions by 52% and reduces CO_2 emissions by 51%. Substitution of NMP with DMSO and sulfolane provides significant reductions in life cycle emissions because the manufacture of DMSO and sulfolane generate less life cycle emissions than the manufacture of NMP. Case 2A-NMP reduces total emissions and CO_2 emissions by 44% and 40%, respectively. Case 2A-DMSO reduces total emissions by 45% and reduces CO_2 emissions by 41%, while Case 2A-Sulfolane reduces total emissions by 50% and CO_2 emissions by 46%. These results show that Base Case 2-Sulfolane is the best option in terms of total and CO_2

life cycle emission reduction. However, all alternative processes provide similar reductions in life cycle emissions.

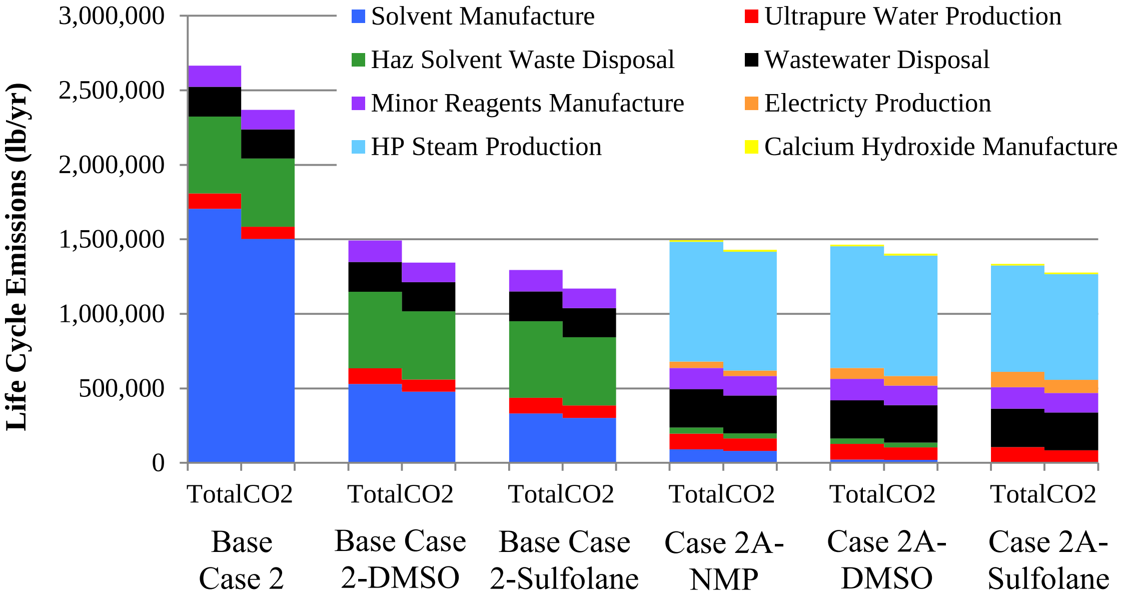


Figure 34. Total and CO_2 life cycle emissions for Case 2 approaches

Figure 35 shows the damage associated with the current DuPont process and the green alternative process. Base Case 2-DMSO reduces the damage to human health by 45%, reduces the damage to ecosystems by 43%, and reduces the damage to resources by 50%. Base Case 2-Sulfolane reduces the damage to human health, ecosystems, and resources by 37%, 52%, and 62%; respectively. Substitution of NMP with DMSO and sulfolane provides significant damage reduction because the manufacture of DMSO and sulfolane cause less damage than the manufacture of NMP. Case 2A-NMP reduces the damage to human health by 46%, reduces the damage to ecosystems by 42%, and reduces the damage to resources by 27%. Case 2A-DMSO reduces the damage to human health, ecosystems, and resources by 47%, 43%, and 27%; respectively. Case 2A-Sulfolane reduces the damage to human health by 51%, reduces the damage to ecosystems by 48%, and reduces the damage to resources by 33%. These results show that Case 2A-Sulfolane is the best option in terms of human health. Base Case 2-Sulfolane is the best option in terms of ecosystems and resources. However, all alternative processes provide similar damage reductions.

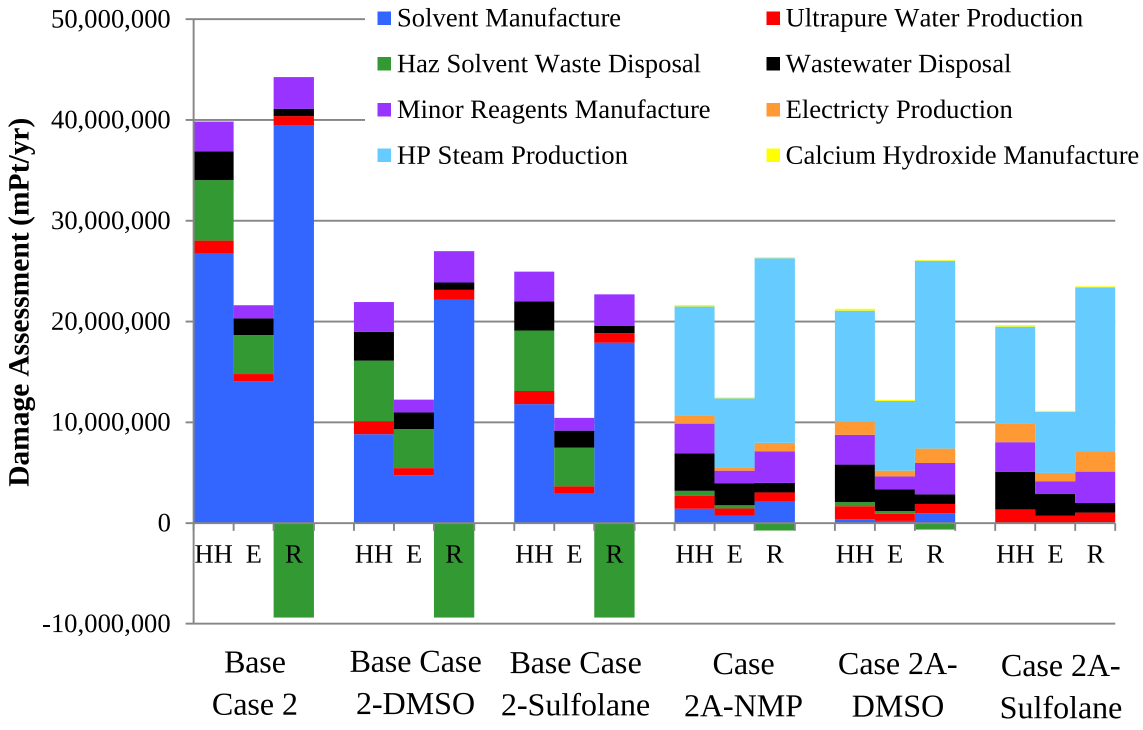


Figure 35. ReCiPe damage assessment for Case 2 approaches, where HH is human health, E is ecosystems, and R is resources

Figure 36 shows the operating costs associated with the current DuPont process and the green alternative process. Base Case 2-DMSO increases the operating cost by 4%, while Base Case 2-Sulfolane increases the operating cost by 31%. Substitution of

NMP with DMSO and sulfolane increases the operating costs because DMSO and sulfolane are more expensive than NMP. Case 2A-NMP reduces the operating cost by 83%. Case 2A-DMSO reduces operating cost by 83%, while Case 2A-Sulfolane reduces the operating cost by 86%. These results show that Case 2A-Sulfolane is the best option in terms operating cost savings. However, all recovery processes provide similar operating cost savings.

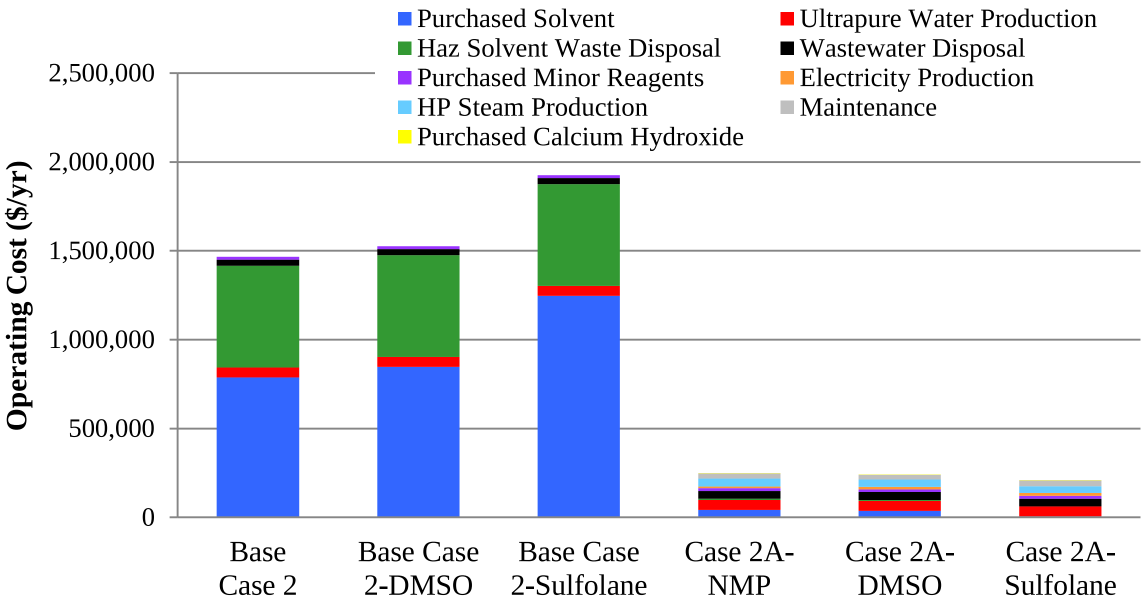


Figure 36. Operating costs for Case 2 approaches

An economic analysis was conducted to further evaluate the alternative processes based on both operating costs and capital costs. Operating costs alone do not provide a fair comparison among the alternative processes, as the recovery approaches require the Parlin plant to purchase capital equipment. To determine if the alternative processes are profitable, internal rate of return (IRR), return on investment (ROI), payback time after tax, net present value after 5 yr, and net present value after 10 yr were calculated for all alternative process. These calculations were performed using Equations 19-27, shown previously. Table 149 shows that all alternative process that use solvent recovery are profitable. Case 2A-NMP saves $3,128,000 after 10 yr, while Cases 2A-DMSO and 2A-Sulfolane save $3,165,000 and $3,214,000 after 10 yr, respectively. However, Base Case 2-DMSO and Base Case 2-Sulfolane increase costs by $298,000 and $2,306,000 after 10 yr, respectively. These results show that Case 2A-Sulfolane is the best option in terms of cost savings. However, all recovery processes provide similar savings.

Table 149

Economic analysis of Case 2 approaches

	IRR (%)	**ROI (%)**	**Payback time after tax (yr)**	**5 yr NPV ($)**	**10 yr NPV ($)**
Base Case 2-DMSO	n/a	n/a	n/a	-199,000	-298,000
Base Case 2-Sulfolane	n/a	n/a	n/a	-1,540,000	-2,306,000
Case 2A-NMP	67.3	59.2	2.2	1,750,000	3,128,000
Case 2A-DMSO	68.6	60.1	2.2	1,781,000	3,165,000
Case 2A-Sulfolane	66.4	58.5	2.3	1,790,000	3,214,000

Table 150 provides a summary of the evaluation of all alternatives to the current DuPont process. The summary shows that Base Case 2-Sulfolane is the best option in terms of total emission reduction, CO_2 emission reduction, and damage reduction. Case 2A-Sulfolane is the best option in terms of cost savings. However, Table 150 shows that Base Case 2-DMSO and Base Case 2-Sulfolane are not feasible because DuPont would lose money. The only feasible alternatives are the three solvent recovery approaches because DuPont would save money. These three approaches show similar cost savings and reduction in environmental impact, compared to the current DuPont process. Therefore, it is recommended that DuPont continues to use NMP; however, an NMP recovery system should be implemented at the Parlin Plant. This alternative process provides comparable environmental and economic improvement to the DMSO and sulfolane recovery cases, while being the easiest to implement. DuPont would not need to validate a different solvent for use in the resin precursor process.

Table 150

Overall comparison of Case 2 approaches

	Total Emission Reduction	**CO_2 Emission Reduction**	**Damage Reduction**	**10 yr NPV ($)**
Base Case 2-DMSO	44%	43%	46%	-298,000
Base Case 2-Sulfolane	52%	51%	50%	-2,306,000
Case 2A-NMP	44%	40%	38%	3,128,000
Case 2A-DMSO	45%	41%	39%	3,165,000
Case 2A-Sulfolane	50%	46%	44%	3,214,000

The results of the solvent substitute analysis show that it is important to perform the overall process LCA, including the recovery step, because many factors affect the sustainability of a process. Most researchers might assume that replacing a solvent with a more benign solvent or a solvent with a lower manufacturing LCI would always make a process greener. However, in this case, the thermodynamics of the solvent substitute waste streams make them difficult to separate, like the NMP waste stream. The solvent substitute waste streams have a large composition of water, so a large quantity of steam is required for operation of the distillation columns. The production of steam plays a significant role in the LCAs of the DMSO and sulfolane recovery cases, as it accounts for over 50% the total life cycle emissions and human health, ecosystems, and resources endpoint scores. Since steam generation has a large contribution to environmental impact, virgin solvent manufacture plays a small role. Therefore, the NMP, DMSO, and sulfolane recovery cases provided similar reductions in the environmental impact. The three solvent recovery approaches also show similar cost savings, due to virgin solvent purchase playing a small role in cost and similar utility and capital costs.

Chapter 10

Case 3: Solvent and Water Recovery

Introduction to Case 3

Two solvent and water recovery designs are described and evaluated. In the first design (Case 3A), water is recovered from the wastewater generated from resin precursor washing and NMP is recovered from the hazardous waste. In the second design (Case 3B), NMP is recovered from the hazardous waste and the wastewater generated from NMP recovery (neutralized distillate of Step 1) is combined with the wastewater generated from resin precursor washing. Water is then recovered from the combined wastewater. For Cases 3A and 3B, NMP is recovered from the hazardous waste using the Case 2A-NMP design. The scenarios for Cases 3A and 3B are shown in Figure 37. Since it is desired to reuse the recovered water in the resin precursor manufacturing process, the same standards that exist for the water quality in the process are used for the recovered water. The relevant specifications of the ultrapure water used in the DuPont resin precursor process are shown in Table 151. The specifications are similar to those of ASTM Type E-1 ultrapure water [158]. Ultrapure water was recovered to meet these specifications. This table includes only the parameters relevant to the ultrapure water recovery designs.

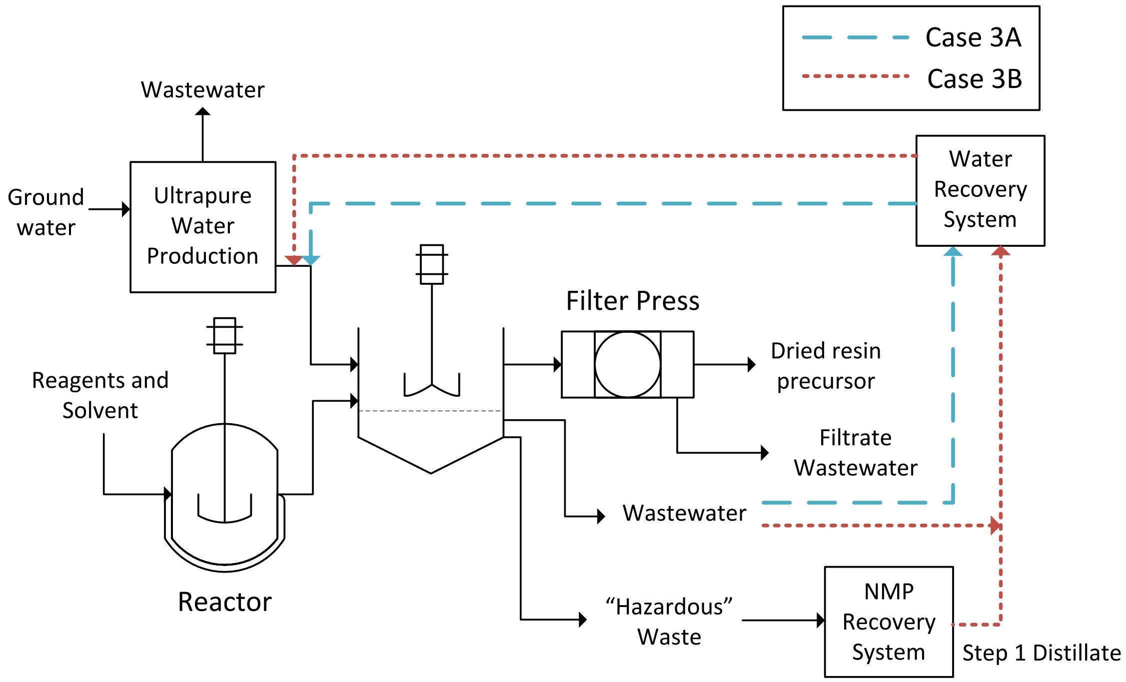


Figure 37. Water recovery Case 3A and Case 3B

Table 151

Ultrapure water specifications for ASTM type E-1 [158]

Parameter	Type E-1
Resistivity at 25°C (Mohm)	18.1
TOC (ppb)	5
Chloride (ppb)	0.1
Calcium (ppb)	0.05

Based on the standards to produce ultrapure water, water recovery and purification designs used in producing ultrapure water were investigated. These designs are similar for ultrapure water production processes used in pharmaceutical and semiconductor manufacturing industries [159, 160, 161, 162, 27, 28, 29, 163].

Case 3A: Ultrapure Water Recovery from Wastewater from Washing

In Case 3A, ultrapure water is recovered from the wastewater generated from washing the resin precursor. The composition and flow rate of this stream is shown in Table 152. Each week, several batches of wastewater are generated from washing. For design purposes, annualized flow rates were used, shown in Table 152. The yearly waste generation values were used to size the ultrapure water recovery system. Organic contaminants in the wastewater include NMP and HEMA, while ionic contaminants include HCl and TFA. The total organic carbon (TOC) present in the wastewater was calculated using Equation 46.

Table 152

Wastewater from washing composition and flow rate

Water Composition	99.835 wt.%
NMP Composition	1,500 ppm
TFA Composition	50 ppm
HCl Composition	50 ppm
HEMA Composition	50 ppm
Total Organic Carbon Composition	936 ppm
Mass Flow Rate (lb/yr)	7,126,000
Volumetric Flow Rate (gal/yr)	854,200

$$TOC = x_{nmp} \times \frac{CM_{NMP}}{MW_{NMP}} + x_{HEMA} \times \frac{CM_{HEMA}}{MW_{HEMA}} \qquad (46)$$

In Equation 46, TOC is the total organic carbon composition in ppm, x_{nmp} and x_{HEMA} are the compositions of NMP and HEMA in ppm, MW_{NMP} and MW_{HEMA} are the molar masses of NMP and HEMA in g/mol, and CM_{NMP} and CM_{HEMA} are the carbon mass per mole in NMP and HEMA in g/mol.

Normally in ultrapure water production systems there is a pretreatment stage to prepare the water for the primary treatment system, which typically consists of reverse osmosis (RO) and ion exchange processes [162]. Since the wastewater from washing contains few contaminants, which are known and consistent, pretreatment is not necessary. Primary treatment of the wastewater focuses on TOC removal, as the main contaminant in this wastewater stream is organic compounds. It is difficult to separate small organic compounds like NMP and HEMA from water; however, RO has been found to remove low molecular weight organics from water [164, 165]. RO was chosen as the first step in the ultrapure water recovery process to remove much of the NMP and HEMA contaminants, shown in Figure 38. RO also has a high rejection of ionic contaminants. After RO, the remaining organic and ionic contaminants are removed. Ions can be removed using ion exchange, while small amounts of organic compounds can be removed using activated carbon adsorption [162, 166, 167, 168]. Organic compounds can affect the efficacy of the ion exchange resin, so adsorption is performed before ion exchange, shown in Figure 38.

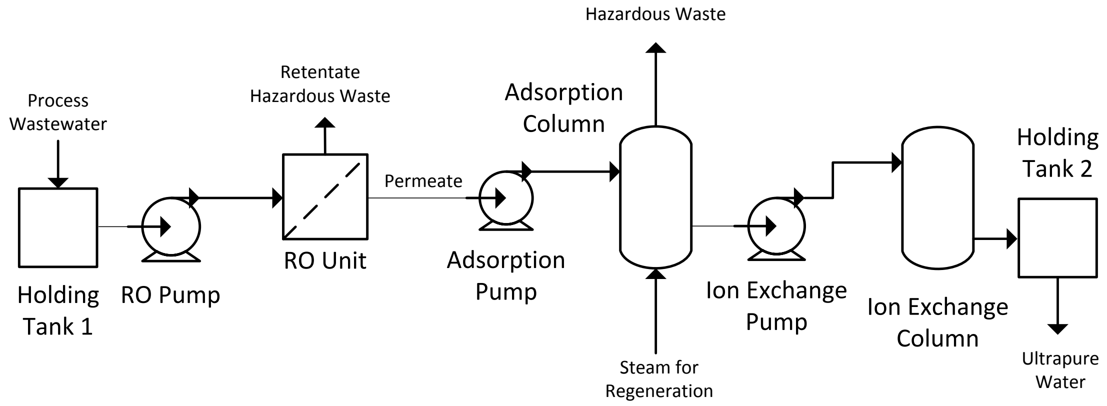


Figure 38. Case 3A ultrapure water recovery system

First, Holding Tank 1 was designed to store the wastewater from washing, prior to treatment to recover ultrapure water. Holding Tank 1 was designed to hold half of one week's worth of wastewater. This means that Holding Tank 1 would collect about 8,200 gal of wastewater and then the wastewater would be sent to the ultrapure water recovery system. After the wastewater is sent to the ultrapure water recovery system, 8,200 gal of wastewater would be collected in Holding Tank 1 and then treated. This cycle would be repeated every week. Holding Tank 1 was designed to hold 8,200 gal of wastewater and have a head space of about 20%. The total tank volume was 10,000 gal, with a diameter of 9.5 ft and a height of 19 ft. The capital cost of this holding tank was estimated using Aspen Capital Cost Estimator V8.4. Holding Tank 1 was designed as a vertical flat bottomed storage tank, with specifications that are listed in Table 153. Holding Tank 1 was designed to be constructed of stainless steel and have a 0.35 in corrosion allowance due to the TFA and HCl in the wastewater, which are corrosive chemicals. The total installed capital cost for Holding Tank 1 is $149,000, based on fourth quarter 2014 costs.

Table 153

Case 3A Holding Tank 1 specifications

Diameter	9.5 ft
Height	19 ft
Material of Construction	Stainless Steel
Corrosion Allowance	0.35 in
Design Temperature	150ºF
Design Pressure	15 psig

After 8,200 gal of wastewater is collected in the holding tank, it is sent to the ultrapure water recovery system for treatment. RO was chosen as the first step in the ultrapure water recovery process, shown in Figure 38. The wastewater is sent to the RO membrane system, which is composed of two membrane elements/modules in one pressure vessel. The retentate stream of the first RO module is sent as the feed to the second RO module. The two permeate streams are combined and sent to the next step in the water recovery process. Two RO membrane modules are used in series to increase the recovery of the RO system and reduce the hazardous waste produced. The RO system was designed to use the same membrane that DuPont uses in their existing RO system, which is used to produce ultrapure water for washing the resin precursor. This membrane is the GE DESAL® membrane AG8040F-400. It would be beneficial to use the same membrane because similar equipment could be used for the RO unit in the new ultrapure water recovery system as is used in the RO unit of the existing ultrapure water production system. Also, the DESAL® membrane is low energy, meaning it operates at a lower pressure than standard reverse osmosis membranes. This reduces environmental impact and cost. Specifications for the DESAL® membrane AG8040F-400 are listed in Table 154 [169].

Table 154

AG8040F-400 membrane specifications [169]

Permeate Flow Rate (gal/hr)	438
Minimum Salt Rejection (%)	99.0
Membrane Area (ft^2)	400
Maximum Operating Pressure (psi)	600
Element Length (ft)	3.33
Element Diameter (ft)	0.658

Since the rejection of NMP by the DESAL® membrane is not provided or available in literature, an experiment was conducted to determine the rejection of NMP. GE membrane AG2521TM was used in this experiment because the AG8040F-400 membrane is too large for Rowan University's RO unit. However, the AG2521TM membrane is the same material as the AG8040F-400 membrane, so they will have the same NMP rejection. The AG2521TM membrane was experimentally determined to have a 98.5% rejection of NMP, while operating at 300 psig. Similar rejection has been shown for small molecular weight organics at higher concentrations by Diltz *et al.* [170]. In the RO design, NMP rejection was assumed to be 98% to be conservative. It was also assumed that the rejection of HEMA was 98% because it is a small organic molecule like NMP. The rejection of HCl and TFA was assumed to be 99%, based off of the AG8040F-400 membrane specification sheet. Both RO modules were designed to operate at 300 psig because this was the condition that provided 98.5% rejection of NMP.

One drawback to using RO to remove the majority of the contaminants is the recovery. Recovery is the ratio of permeate flow to feed flow, which indicates the fraction of feed that is purified. The AG8040F-400 membrane specification sheet indicates a permeate flow rate of 438 gal/hr, with a recovery of 15% [169]. Recovery can be increased by decreasing the feed flow rate to the reverse osmosis unit or increasing the number of membranes. Permeate flux, and therefore permeate flow rate, remains relatively constant, so when feed flow rate is decreased the recovery increases. However, recovery cannot be too high, or concentration polarization could occur, which would cause membrane fouling and decreased effectiveness [171]. A recovery of 90% was chosen for the overall RO system to balance recovery with membrane performance. The feed flow rate to the first RO module was calculated using the permeate flow rates for both modules and recovery, shown in Equation 47. The permeate flow rate of both modules was 438 gal/hr, as specified in the membrane specification sheet. The feed flow rate into the first RO module was calculated to be 972 gal/hr.

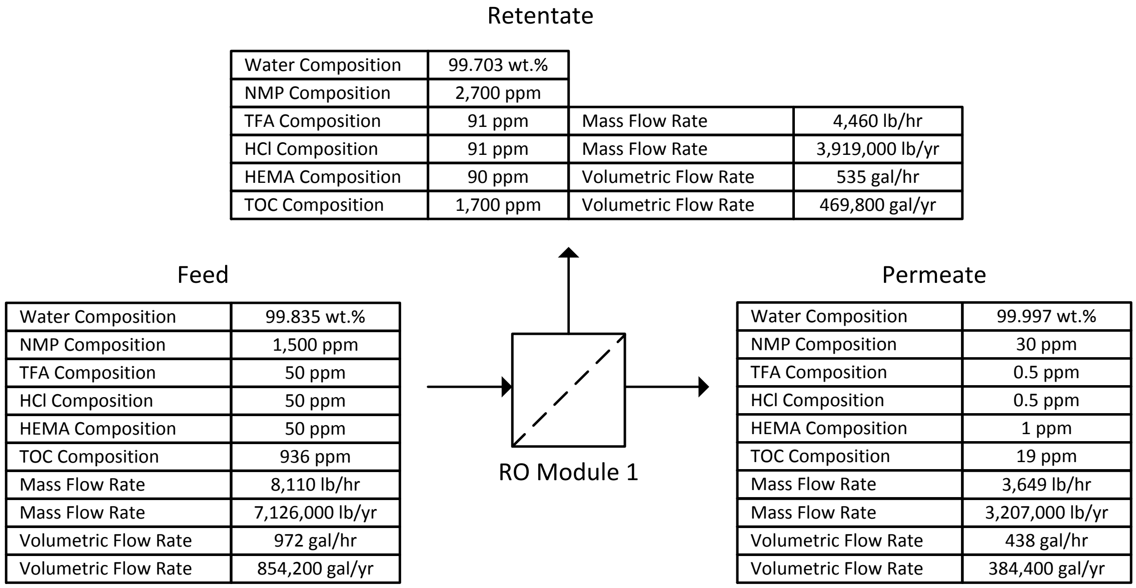
$$Q_{F1} = \frac{Q_{P1} + Q_{P2}}{0.9} \tag{47}$$

In Equation 47, Q_{F1} is the volumetric flow rate of the feed to the first RO element/module in gal/hr and Q_{P1} and Q_{P2} are the volumetric flow rate of the first and second permeate streams (438 gal/hr).

The operating time of each cycle of the RO unit was calculated using the volume of wastewater held in Holding Tank 1 and the hourly flow rate fed to the first RO module, shown in Equation 48. The operating time of each cycle of the RO unit was calculated to be 8.5 hr, for a total operating time of 880 hr/yr. The flow rate and composition of the wastewater after treatment with the first RO module is shown in Figure 39, along with the feed and retentate flow rates and compositions. The retentate stream from the first RO element/module is sent to the second RO module. The permeate stream of the first RO module is sent to the adsorption system, along with the permeate stream from the second RO unit. The flow rates and compositions of the feed and outlet streams for the entire RO unit are shown in Figure 40. As shown in Figure 40, the two permeate streams are combined and sent to the adsorption system. The retentate stream is hazardous waste, so it is sent off site for incineration.

$$t_{RO} = \frac{V_{wastewater}}{Q_{RO\ feed,hourly}} \tag{48}$$

In Equation 48, t_{RO} is the operating hours of the RO unit in hr/cycle, $V_{wastewater}$ is the volume of wastewater held in Holding Tank 1 in gal, and $Q_{RO\ feed,hourly}$ is the feed flow rate into the first RO module in gal/hr.



Retentate

Water Composition	99.703 wt.%		
NMP Composition	2,700 ppm		
TFA Composition	91 ppm	Mass Flow Rate	4,460 lb/hr
HCl Composition	91 ppm	Mass Flow Rate	3,919,000 lb/yr
HEMA Composition	90 ppm	Volumetric Flow Rate	535 gal/hr
TOC Composition	1,700 ppm	Volumetric Flow Rate	469,800 gal/yr

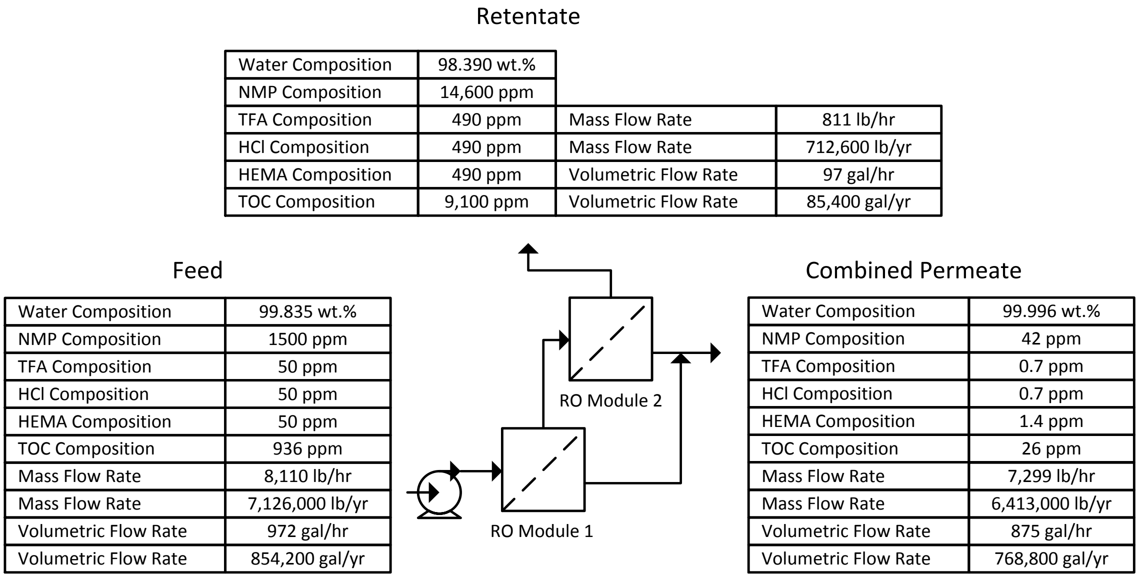
Feed

Water Composition	99.835 wt.%
NMP Composition	1,500 ppm
TFA Composition	50 ppm
HCl Composition	50 ppm
HEMA Composition	50 ppm
TOC Composition	936 ppm
Mass Flow Rate	8,110 lb/hr
Mass Flow Rate	7,126,000 lb/yr
Volumetric Flow Rate	972 gal/hr
Volumetric Flow Rate	854,200 gal/yr

Permeate

Water Composition	99.997 wt.%
NMP Composition	30 ppm
TFA Composition	0.5 ppm
HCl Composition	0.5 ppm
HEMA Composition	1 ppm
TOC Composition	19 ppm
Mass Flow Rate	3,649 lb/hr
Mass Flow Rate	3,207,000 lb/yr
Volumetric Flow Rate	438 gal/hr
Volumetric Flow Rate	384,400 gal/yr

Figure 39. Case 3A RO element/module 1 stream flow rates and compositions



Retentate

Water Composition	98.390 wt.%		
NMP Composition	14,600 ppm		
TFA Composition	490 ppm	Mass Flow Rate	811 lb/hr
HCl Composition	490 ppm	Mass Flow Rate	712,600 lb/yr
HEMA Composition	490 ppm	Volumetric Flow Rate	97 gal/hr
TOC Composition	9,100 ppm	Volumetric Flow Rate	85,400 gal/yr

Feed

Water Composition	99.835 wt.%
NMP Composition	1500 ppm
TFA Composition	50 ppm
HCl Composition	50 ppm
HEMA Composition	50 ppm
TOC Composition	936 ppm
Mass Flow Rate	8,110 lb/hr
Mass Flow Rate	7,126,000 lb/yr
Volumetric Flow Rate	972 gal/hr
Volumetric Flow Rate	854,200 gal/yr

Combined Permeate

Water Composition	99.996 wt.%
NMP Composition	42 ppm
TFA Composition	0.7 ppm
HCl Composition	0.7 ppm
HEMA Composition	1.4 ppm
TOC Composition	26 ppm
Mass Flow Rate	7,299 lb/hr
Mass Flow Rate	6,413,000 lb/yr
Volumetric Flow Rate	875 gal/hr
Volumetric Flow Rate	768,800 gal/yr

Figure 40. Case 3A RO system stream flow rates and compositions. Each element/module is shown separately, although they are connected in series in one pressure vessel.

Figure 40 shows that the RO unit produces 6,413,000 lb/yr of treated water and generates 712,600 lb/yr of hazardous waste. The operation of the RO feed pump requires 11,800 MJ/yr of electricity. The electrical power needed to run the RO pump was calculated using Equation 36, where the power drawn by the pump is 5 hp. The RO unit also requires membrane maintenance. In the design, it was assumed that both membrane modules are replaced every three months, which is the current practice for DuPont's existing RO system

The installed capital cost of the RO system was estimated by finding the cost of the feed pump, the pressure vessel housing, and the GE AG8040F-400 RO membranes. The installed capital cost of the feed pump and pressure vessel housing were estimated using Aspen Capital Cost Estimator. The feed pump was designed as a multistage centrifugal pump, so the desired inlet pressure could be achieved [127]. The pressure vessel was designed as a process vessel. The specifications of the multistage centrifugal pump and pressure vessel are listed in Table 155. The pump and pressure vessel were designed to be constructed of stainless steel due to the corrosive chemicals in the wastewater. The pump head was calculated using Equation 37, where it is assumed that the head due to friction is negligible. The size of the pressure vessel was chosen based off of the size of both membrane modules, when lined up end to end. The pressure vessel has a 0.35 in corrosion allowance due to the TFA and HCl in the wastewater, which are corrosive chemicals. The installed capital costs for the RO pump and pressure vessel housing are estimated to be $41,200 and $69,100; respectively. The cost of the GE AG8040F-400 reverse osmosis membrane is $826 [172]. The total installed capital cost for the reverse osmosis system is $112,000, based on fourth quarter 2014 costs.

Table 155

Case 3A RO pump and pressure vessel specifications

Pump Specifications		**Pressure Vessel Specifications**	
Material of Construction	Stainless Steel	Material of Construction	Stainless Steel
Liquid Flow Rate	16.5 gpm	Diameter	0.68 ft
Fluid Head	690 ft	Length	8.42 ft
Design Pressure	350 psig	Design Pressure	350 psig
Design Temperature	150ºF	Design Temperature	150ºF
Pump Efficiency	70%	Corrosion Allowance	0.35 in
Power	5 hp		

In order to remove the remaining NMP and HEMA from the wastewater, an activated carbon adsorption column was designed. The feed to the adsorption column is the combined permeate streams of the first and second RO modules; flow rate and composition shown in Figure 40. The adsorption column was designed to produce water with a TOC composition below 5 ppb. Since there are no existing studies on NMP removal from water, the design of the adsorption column was based off of experimental results with similar systems [173]. Li *et al*. used a variety of adsorbents to remove trichloroethylene (TCE) and methyl tertiary butyl ether (MTBE) from water [173]. Commercially available activated carbon, purchased from Nippon Kynol, was used as adsorbent. The results they obtained for MTBE adsorption by activated carbon was used in the adsorption design. MTBE was chosen as a more accurate representation of NMP and HEMA, as it has a more similar molecular structure that TCE. Li *et al.* found that the adsorption of MTBE by activated carbon at 298 K follows the Freundlich Isotherm, shown in Equation 49.

$$q = \frac{Kc^{1/n}}{1000} \tag{49}$$

In Equation 49, q is the mass of solute adsorbed in g divided by the mass of adsorbent in g, K is 0.141, c is the solute composition in the liquid phase in ppb, and $1/n$ is 0.634.

The mass of granular activated carbon needed for the adsorption process was calculated using Equation 50 [127]. To calculate the mass of required adsorbent, it was assumed that all organics (NMP and HEMA) have the same adsorption affinity. The compositions of NMP and HEMA were combined to calculate the composition of organic compounds. The inlet composition was calculated at 43 ppm or 43,000 ppb. This value was used to calculate q_1, using Equation 49. The outlet composition of organic compounds was set to 5 ppb, so q_2 could be calculated. The inlet flow rate to the adsorption column was set equal to the flow rate of the combined permeate stream of the RO system (7,299 lb/hr). The outlet flow rate (7,299 lb/hr) was calculated by subtracting the quantity of NMP and HEMA removed by the granulated activated carbon. The adsorption time was set to 17 hr, since the RO unit is run for 8.5 hr twice a week. This allows for the adsorption column to be regenerated once a week. It was assumed that 70% of the adsorption bed is loaded at the end of the adsorption phase of the cycle. It was calculated that 62 lb of granular activated carbon is needed for the adsorption process.

$$M_a = \frac{(F_1 y_1 + F_2 y_2) t_a}{(q_1 - q_2) f_L} \tag{50}$$

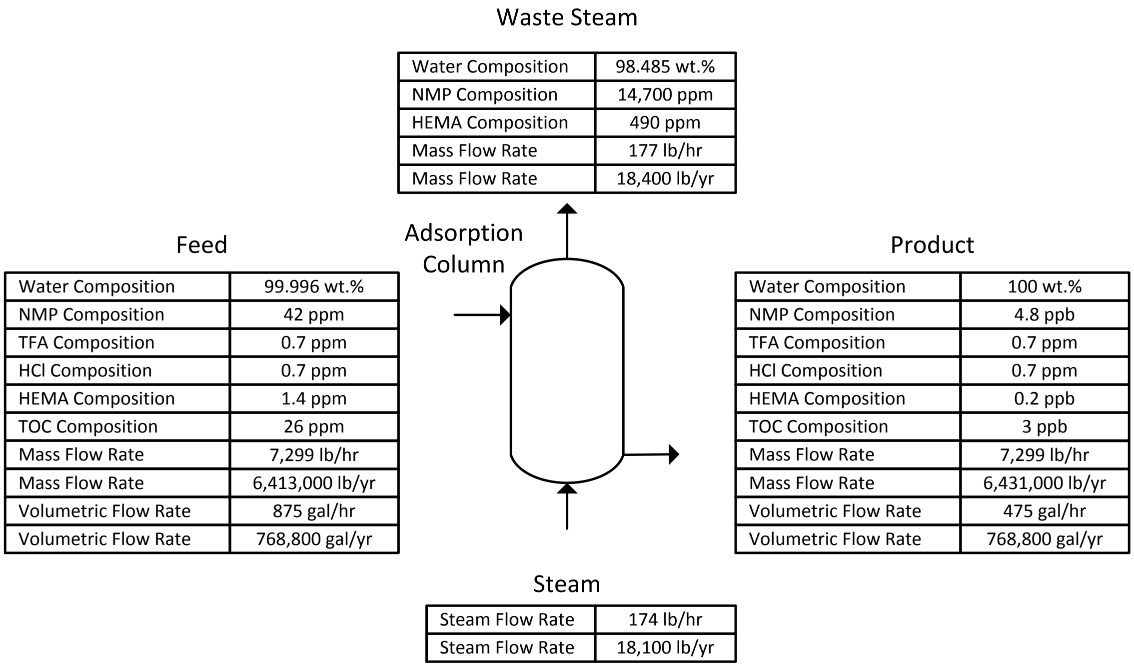
In Equation 50, M_a is the mass of adsorbent in the bed in lb, F_1 and F_2 are the inlet and outlet flow rates in lb/hr respectively, y_1 and y_2 are the inlet and outlet solute mass fractions in the liquid phase respectively, t_a is the time of adsorption in hr, q_1 and q_2 are the maximum and minimum loading factors (g solute/g adsorbent) respectively, and f_L is the fraction of the bed that is loaded at the end of adsorption phase of cycle [127].

The volume of packing in the adsorption column was calculated to be 0.83 ft^3 using the bulk density of granular activated carbon, 74.9 lb/ft^3 [174]. Using Equation 51, the column diameter and packing height were calculated to be 0.75 ft and 3 ft, respectively. To pack this volume of the adsorption column, 100 lb of activated carbon is needed. The total column height was set to 4 ft.

$$D = \left(\frac{V}{\pi}\right)^{1/3} \tag{51}$$

In Equation 51, D is the diameter of the column in ft and V is the volume of the column in ft^3. The aspect ratio of the column is 4:1.

As mentioned previously, the adsorption column is regenerated after 17 hr of operation. The regeneration process uses saturated steam at 250ºC (40 bar) to remove NMP and HEMA from the granular activated carbon. The regeneration time and steam flow rate were based off of experimental data for steam regeneration of activated carbon [175]. Kim *et al*. tested the regeneration of activated carbon after adsorption of the solvents n-hexane, MEK, and toluene. They found that each solvent was desorbed after 15 min with a maximum steam flow rate of 3.2 g/min. In the regeneration design, it was assumed that 2 hr would be adequate to fully regenerate the activated carbon. A longer regeneration time was chosen because the designed adsorption column is larger than the experimental unit used by Kim *et al*. It was also assumed that the same mass flux of steam used by Kim *et al.* would be adequate for regenerating the granular activated carbon. This means that a steam flow rate of 174 lb/hr for 2 hr is required to regenerate the activated carbon. The waste steam from regeneration is condensed and sent off site for incineration, since it is hazardous waste. The flow rates and compositions of the inlet and outlet streams of the adsorption column are shown in Figure 41.



Waste Steam

Water Composition	98.485 wt.%
NMP Composition	14,700 ppm
HEMA Composition	490 ppm
Mass Flow Rate	177 lb/hr
Mass Flow Rate	18,400 lb/yr

Feed

Water Composition	99.996 wt.%
NMP Composition	42 ppm
TFA Composition	0.7 ppm
HCl Composition	0.7 ppm
HEMA Composition	1.4 ppm
TOC Composition	26 ppm
Mass Flow Rate	7,299 lb/hr
Mass Flow Rate	6,413,000 lb/yr
Volumetric Flow Rate	875 gal/hr
Volumetric Flow Rate	768,800 gal/yr

Product

Water Composition	100 wt.%
NMP Composition	4.8 ppb
TFA Composition	0.7 ppm
HCl Composition	0.7 ppm
HEMA Composition	0.2 ppb
TOC Composition	3 ppb
Mass Flow Rate	7,299 lb/hr
Mass Flow Rate	6,431,000 lb/yr
Volumetric Flow Rate	475 gal/hr
Volumetric Flow Rate	768,800 gal/yr

Steam

Steam Flow Rate	174 lb/hr
Steam Flow Rate	18,100 lb/yr

Figure 41. Case 3A adsorption column stream flow rates and compositions

Figure 41 shows that the adsorption system produces 6,431,000 lb/yr of treated water. The activated carbon regeneration process requires 18,100 lb/yr (23,000 MJ/yr) of steam. This regeneration process generates 18,400 lb/yr of hazardous waste. The operation of the adsorption feed pump requires 600 MJ/yr of electricity, calculated using Equation 36. It was also assumed that the granular activated carbon is replaced after 25 regenerations. This means that the activated carbon must be replaced 2 times a year, so 200 lb/yr of granular activated carbon is used. The 200 lb/yr of spent activated carbon is disposed of as hazardous waste.

The installed capital cost of the adsorption unit was estimated by finding the cost of the adsorption column feed pump, the adsorption column, and the granular activated carbon packing. The installed capital cost of the feed pump and adsorption column, and the cost of the granular activated carbon packing were estimated using Aspen Capital

Cost Estimator. The feed pump was designed as a centrifugal pump and the adsorption column as a column for liquid adsorption. The specifications of the centrifugal pump and adsorption column are listed in Table 156. The pump and column were designed to be constructed of stainless steel due to the corrosive chemicals in the wastewater. The pump head was specified at 25 ft to ensure it would be able to send the permeate stream of the reverse osmosis system to the top of the adsorption column. The installed capital costs for the adsorption feed pump and column are estimated to be $21,600 and $63,100, respectively. Within Aspen Capital Cost Estimator, the adsorption column was specified to be packed with activated carbon, which was estimated to cost $50. It was assumed that the cost to pack 3 ft of the column with granular activated carbon is $50. The total installed capital cost for the adsorption system is $85,000, based on fourth quarter 2014 costs.

Table 156

Case 3A adsorption feed pump and column specifications

Pump Specifications		Adsorption Column Specifications	
Material of Construction	Stainless Steel	Material of Construction	Stainless Steel
Liquid Flow Rate	15 gpm	Diameter	0.75 ft
Fluid Head	25 ft	Height	4 ft
Design Pressure	50 psig	Packed Height	3 ft
Design Temperature	150ºF	Design Pressure	50 psig
Pump Efficiency	70%	Design Temperature	540ºF
Power	0.25 hp		

The LCI for the manufacture of granular activated carbon was estimated, since it would be required for the environmental analysis of Case 3A. SimaPro® was used to estimate the LCI for manufacture of granular activated carbon. Within SimaPro®, activated carbon was modeled as charcoal because charcoal is similar to activated carbon. Activated carbon is made by thermally treating charcoal; therefore, activated carbon and charcoal have similar LCIs [176]. The LCI for the manufacture of 1 lb of activated carbon is listed in Table 157. The ReCiPe damage assessment for activated carbon manufacture was also estimated using SimaPro® and is shown in Table 158.

Table 157

LCI for the manufacture of 1 lb of activated carbon

Water Used (lb)	7.26E+02
Total Air Emissions (lb)	3.14E+00
CO_2 (lb)	2.90E+00
CO (lb)	1.91E-01
CH_4 (lb)	4.05E-02
NO_X (lb)	7.61E-04
NMVOC (lb)	3.41E-04
Particulate (lb)	7.49E-04
SO_2 (lb)	2.61E-04
Total Water Emissions (lb)	9.99E-03
VOCs (lb)	3.99E-07
Total Soil Emissions (lb)	2.52E-04
Total Emissions (lb)	**3.15E+00**
CED (MJ)	3.12E+01

Table 158

ReCiPe damage assessment for the manufacture of 1 lb of activated carbon

Human Health (mPt)	15.19
Ecosystems (mPt)	59.68
Resources (mPt)	1.97
Total Damage (mPt)	76.84

The final step in the ultrapure water recovery system is ion exchange, which will remove the remaining ionic contaminants to produce ultrapure water. The ion exchange resin chosen for this design (Dowex Monosphere MR-450 UPW) is sold by Dow for use in ultrapure water production units [177]. It is a mixed bed ion exchange resin, where cations are exchanged with H^+ ions and anions are exchanged with OH^- ions. A mixed bed resin was chosen so all ionic contaminants would be removed. Even though the only known ionic contaminants are anions (chloride and trifluoroacetate) it is possible that cationic contaminants could be present. Since ultrapure water has stringent specifications, even a very small amount of cationic contaminants would result in ultrapure water that is out of specification. It is common to use mixed bed ion exchange as the final step in ultrapure water production [162]. The ion exchange resin in non-regenerable, meaning the resin is replaced after it is fully loaded with contaminant ions. Therefore, there is no regeneration step as in the carbon adsorption column design. Specifications for Dowex Monosphere MR-450 UPW ion exchange resin are shown in Table 159.

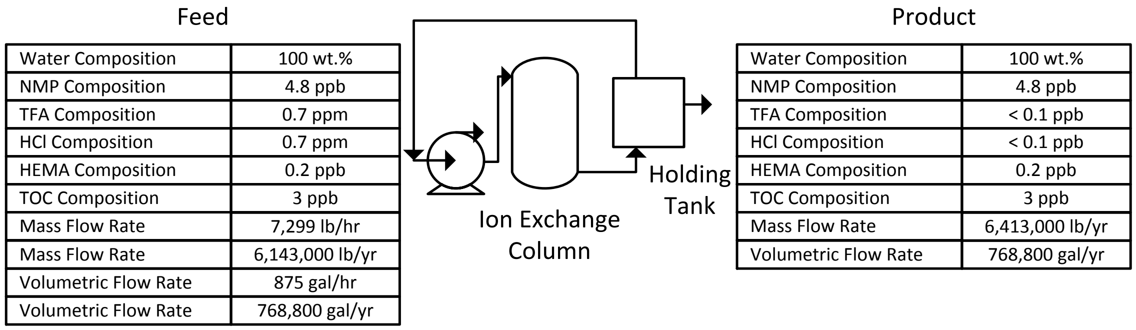
Table 159

Specifications for Dowex Monosphere MR-450 UPW ion exchange resin

Minimum Cationic Exchange Capacity	53.8 eq/ft^3
Minimum Anionic Exchange Capacity	28.3 eq/ft^3
Recommended Flow Rate	4-24 gpm/ft^2
Minimum Resin Bed Depth	2.6 ft
Minimum Cationic Exchange	99.7%
Minimum Anionic Exchange	95%

The ion exchange column was designed to treat the outlet of the adsorption column. The size of the column was calculated based on the volume of ion exchange resin required for treatment. For this design, the resin is replaced every 3 yr, as is recommended by Dow [177]. This means that the ion exchange bed must have the capacity for 3 yr of treatment. It was calculated that flow rates of TFA and HCl out of the adsorption column are 20.6 mmol/hr and 65.6 mmol/hr. In water, TFA dissociates into H^+ and $C_2F_3O_2^-$ (trifluoroacetate) and HCl dissociates in H^+ and Cl^-. So, 1 mol of TFA produces 1 mol of anionic contaminant (trifluoroacetate) and 1 mol of HCl produces 1 mol of anionic contaminant (chloride). The total molar flow rate of anionic contaminants into the ion exchange column is 86.2 mmol/hr or 75.7 mol/yr. To have a 3 yr capacity, the ion exchange column must exchange 227 mol of anions. Based on the anionic exchange capacity of the resin, 8.5 ft^3 of resin is required for the ion exchange column.

The diameter of the ion exchange was designed using a flow rate of 8 gpm/ft^2, which is within the recommended range. Since the inlet flow rate to the ion exchange column is set at 875 gal/hr, the diameter of the column must be 1.5 ft. The packed height of the column was set to 6 ft, to provide a resin volume of 10.6 ft^3 which is sufficient for 3 yr of operation. The total column height was set to 8 ft. The outlet of the ion exchange column is ultrapure water, which is sent to a holding tank. As mentioned previously the wastewater from washing is treated in batches that last 8.5 hr. After 8.5 hr, the entire batch of wastewater from washing is sent through the ion exchange and into a holding tank. However, the ultrapure water in the holding tank is recirculated back through the ion exchange until it is used in the resin precursor process. It is common practice to recirculate the water through the ion exchange unit multiple times to ensure all ions are removed [162]. The ultrapure water is recirculated into the ion exchange column at a flow rate of 875 gal/hr. The ion exchange column produces 6,413,000 lb/yr of ultrapure water. The inlet and outlet flow rates and compositions of the ion exchange column are shown in Figure 42.



Feed

Water Composition	100 wt.%
NMP Composition	4.8 ppb
TFA Composition	0.7 ppm
HCl Composition	0.7 ppm
HEMA Composition	0.2 ppb
TOC Composition	3 ppb
Mass Flow Rate	7,299 lb/hr
Mass Flow Rate	6,143,000 lb/yr
Volumetric Flow Rate	875 gal/hr
Volumetric Flow Rate	768,800 gal/yr

Product

Water Composition	100 wt.%
NMP Composition	4.8 ppb
TFA Composition	< 0.1 ppb
HCl Composition	< 0.1 ppb
HEMA Composition	0.2 ppb
TOC Composition	3 ppb
Mass Flow Rate	6,413,000 lb/yr
Volumetric Flow Rate	768,800 gal/yr

Figure 42. Case 3A ion exchange column flow rates and compositions

In the ion exchange system design, the feed pump is run continuously since the ultrapure water in the final holding tank is recirculated back to the ion exchange systems. The feed pump is designed to run for 7,200 hr/yr, while drawing 0.25 hp of electricity. Using Equation 36, it was calculated that the ion exchange system uses 4,800 MJ/yr of electricity. The ion exchange system also requires 10.6 ft^3 of ion exchange resin, which must be replaced every 3 yr. The density of the ion exchange resin is 44 lb/ft^3, so about 470 lb of ion exchange resin is needed to pack the column. The annualized quantity of ion exchange resin used is 156 lb (470 lb every 3 yr). The spent ion exchange resin waste is generated in a quantity of 156 lb/yr.

The installed capital cost of the ion exchange unit was estimated by finding the cost of the ion exchange column feed pump, the ion exchange column, and the ion exchange resin. The installed capital cost of the feed pump and column were estimated using Aspen Capital Cost Estimator. The feed pump was designed as a centrifugal pump and the column as a column for liquid adsorption. The specifications of the centrifugal pump and ion exchange column are listed in Table 160. The pump was designed to be constructed of stainless steel due to the corrosive chemicals in the wastewater, while ion exchange column was designed to be constructed of glass-lined carbon steel. Glass-lined carbon steel was chosen to prevent metal ions from leaching in to the treated water. The pump head was specified at 25 ft to ensure it would be able to send the outlet stream of the adsorption system to the top of the adsorption column. The installed capital costs for the ion exchange feed pump and column are estimated to be \$21,600 and \$117,900, respectively. The cost of the Dowex MR-450 UPW ion exchange resin was found to be 570 \$/ft^3, from Evoqua Water Technologies [178]. The cost to pack the ion exchange column is \$6,000. The total installed capital cost for the ion exchange system is \$146,000, based on fourth quarter 2014 costs.

Table 160

Case 3A ion exchange feed pump and column specifications

Pump Specifications		**Ion Exchange Column Specifications**	
Material of Construction	Stainless Steel	Material of Construction	Glass-lined Carbon Steel
Liquid Flow Rate	15 gpm	Diameter	1.5 ft
Fluid Head	25 ft	Height	8 ft
Design Pressure	50 psig	Packed Height	6 ft
Design Temperature	150ºF	Design Pressure	50 psig
Pump Efficiency	70%	Design Temperature	150ºF
Power	0.25 hp		

The LCI for the manufacture and disposal of ion exchange resin was estimated, since it would be required for the environmental analysis of Case 3A. SimaPro® was used to estimate the LCI for manufacture and disposal of ion exchange resin. The LCI for the manufacture of 1 lb of ion exchange resin was modeled as an average of the manufacture of 1 lb of cationic resin and the manufacture of 1 lb of anionic resin. This was done because the Dowex MR-450 UPW ion exchange resin consists of equal weights of cationic and anionic resin. The LCI for the disposal of 1 lb of ion exchange resin was modeled as an average of the disposal of 1 lb of cationic resin and 1 lb of anionic resin. The LCI for the manufacture and disposal of 1 lb of ion exchange resin is listed in Table 161. The ReCiPe damage assessments for ion exchange resin manufacture and disposal were estimated using SimaPro® and are shown in Table 162. Similar to the LCI, the damage caused by manufacture of 1 lb of ion exchange resin was modeled as an average of the damage caused by the manufacture of 1 lb of cationic resin and 1 lb of anionic resin. The damage caused by the disposal of 1 lb of ion exchange resin was also modeled as an average of the damage caused by the disposal of 1 lb of cationic resin and 1 lb of anionic resin.

Table 161

LCI for the manufacture and disposal of 1 lb of ion exchange resin

	Manufacture	**Disposal**
Water Used (lb)	5.31E+03	2.36E+02
Total Air Emissions (lb)	2.18E+00	1.12E+00
CO_2 (lb)	2.15E+00	1.12E+00
CO (lb)	2.34E-03	2.97E-04
CH_4 (lb)	1.15E-02	1.04E-04
NO_X (lb)	3.15E-03	9.13E-04
NMVOC (lb)	1.18E-03	8.34E-05
Particulate (lb)	8.30E-04	5.63E-05
SO_2 (lb)	5.53E-03	3.19E-04
Total Water Emissions (lb)	1.20E-01	1.96E-01
VOCs (lb)	9.82E-07	9.06E-08
Total Soil Emissions (lb)	3.14E-04	2.69E-05
Total Emissions (lb)	**2.30E+00**	**1.31E+00**
CED (MJ)	2.44E+01	4.45E-01

Table 162

ReCiPe damage assessment for the manufacture and disposal of 1 lb of ion exchange resin

	Manufacture	**Disposal**
Human Health (mPt)	48.85	15.43
Ecosystems (mPt)	55.52	9.41
Resources (mPt)	59.47	0.93
Total Damage (mPt)	130.84	25.77

As mentioned previously, the ultrapure water produced by the ion exchange column is sent into Holding Tank 2. This ultrapure water is recirculated back into the ion exchange column until it is used in the resin precursor process. Holding Tank 2 was designed to store the ultrapure water from one batch of wastewater from washing. For each batch of wastewater that is treated, 7,400 gal of ultrapure water is produced. Holding Tank 2 was designed to hold 7,400 gal of ultrapure water and have a head space of about 20%. The total tank volume was 9,300 gal, with a diameter of 9.25 ft and a height of 18.5 ft. The capital cost of Holding Tank 2 was estimated using Aspen Capital Cost Estimator. Holding Tank 2 was specified as a vertical flat bottomed storage tank. The specifications of the Holding Tank 2 are listed in Table 163. Holding Tank 2 was designed to be constructed of glass-lined carbon steel to prevent metal ions from leaching into the ultrapure water. The total installed capital cost for Holding Tank 2 is $172,000, based on fourth quarter 2014 costs.

Table 163

Case 3A Holding Tank 2 specifications

Diameter	9.25 ft
Height	18.5 ft
Material of Construction	Glass-lined Carbon Steel
Corrosion Allowance	0 in
Design Temperature	150ºF
Design Pressure	15 psig

The raw material use, utility use, and waste generation for Case 3A is shown in Table 164. The electricity used by the ultrapure water recovery system is the sum of the electricity used by the RO, adsorption, and ion exchange systems. The hazardous waste generated by the ultrapure water recovery system is the sum of the hazardous waste generated by the RO and adsorption systems. The material use, utility use, and waste generation from NMP recovery was found in Case 2A. Table 164 also provides comparison of the raw material use, utility use, and waste generation for Base Case 2 and Case 3A. Case 3A improves upon Base Case 2 by reducing virgin NMP use by 382,300 lb/yr and reducing hazardous waste generation by 1,612,000 lb/yr. Case 3A also reduces ultrapure water production by 6,413,000 lb/yr and reduces wastewater generation by 7,126,000 lb/yr. However, Case 3A requires electricity, steam, and other materials to operate the recovery equipment.

Table 164

Raw material use and waste generated by Base Case 2 and Case 3A

	Base Case 2	**Case 3A**
NMP (lb/yr)	403,800	21,530
Minor Reagents		
HEMA (lb/yr)	11,880	11,880
TFA (lb/yr)	11,880	11,880
HCl (lb/yr)	11,880	11,880
Ultrapure water (lb/yr)	9,062,000	2,649,000
Hazardous Waste (lb/yr)	2,375,000	0
Non-hazardous Waste (lb/yr)	7,126,000	0
UPW Recovery System		
Electricity (MJ/yr)	0	17,220
Steam (MJ/yr)	0	22,990
Hazardous waste (lb/yr)	0	731,000
Activated Carbon (lb/yr)	0	199
IE Resin (lb/yr)	0	156
Spent Activated Carbon (lb/yr)	0	199
Spent IE Resin (lb/yr)	0	156
Membranes (modules/yr)	0	8
NMP Recovery System		
Electricity (MJ/yr)	0	175,400
Steam (MJ/yr)	0	5,424,000
Calcium Hydroxide (lb/yr)	0	15,950
Wastewater (lb/yr)	0	2,067,000
Hazardous waste (lb/yr)	0	31,960

The life cycle emissions associated with Case 3A were calculated using Equation 52 and the values for raw material use, utility use, and waste generation in Table 164. Equation 52 includes the emissions associated with raw material use, waste disposal, water recovery system operation, and NMP recovery system operation.

$$
\begin{aligned}
LCE_{Case\ 3} = {} & (m_{NMP} - r_{NMP}) \cdot LCI_{NMP} + m_{TFA} \cdot LCI_{TFA} + m_{HEMA} \cdot LCI_{HEMA} \\
& + m_{HCl} \cdot LCI_{HCl} + (m_{UPW} - r_{UPW}) \cdot LCI_{UPW} + m_{NHWW} \cdot LCI_{NHWW} \\
& + S \cdot LCI_s + E \cdot LCI_E + m_{Ca(OH)2} \cdot LCI_{Ca(OH)2} + m_{HW} \cdot \frac{x_{NMP,HW}}{0.17} \\
& \cdot LCI_{HW} + m_{GAC} \cdot LCI_{GAC} + m_{IE\ Resin} \\
& \cdot (LCI_{IE\ Resin\ M} + LCI_{IE\ Resin\ D})
\end{aligned} \tag{52}
$$

In Equation 52, r_{NMP} and r_{UPW} are the masses of NMP and ultrapure water recovered in lb/yr. m_{HW} and m_{NHWW} are the mass of hazardous and non-hazardous wastewater generated by the Case 3 process in lb/yr. $x_{NMP,HW}$ is the mass fraction of NMP in the hazardous waste. S and E are the amount of steam and electricity used in the Case 3 process in MJ/yr. $m_{Ca(OH)2}$, m_{GAC}, and $m_{IE\ Resin}$ are the masses of calcium hydroxide, granulated activated carbon, and ion exchange resin used in lb/yr. $LCI_{Ca(OH)2}$, LCI_{GAC}, and $LCI_{IE\ Resin\ M}$ are the LCIs for the manufacture of calcium hydroxide, granulated activated carbon, and ion exchange resin on a 1 lb basis. $LCI_{IE\ Resin\ D}$ is the LCI for the disposal ion exchange resin on a 1 lb basis.

The life cycle emissions associated with Base Case 2 and Case 3A are shown in Table 165, along with the reduction in emissions for Case 3A. The current resin precursor process generates 2,670,000 lb/yr of total emissions and 2,370,000 lb/yr of CO_2 emissions. Table 165 shows that recovery of both ultrapure water and NMP reduces total life cycle emissions and CO_2 life cycle emissions by 1,420,000 lb/yr and 1,140,000 lb/yr, respectively. This is a 53% reduction in total emissions and a 50% reduction in CO_2 emissions.

Table 165

Life cycle emissions for Base Case 2 and Case 3A

	Base Case 2	**Case 3A**	**Case 3A Avoided**
Water Used (lb/yr)	5.24E+09	6.72E+08	4.57E+09
Total Air Emissions (lb/yr)	2.39E+06	1.21E+06	1.19E+06
CO_2 (lb/yr)	2.37E+06	1.19E+06	1.17E+06
CO (lb/yr)	1.14E+03	6.66E+02	4.72E+02
CH_4 (lb/yr)	4.26E+03	2.39E+03	1.86E+03
NO_X (lb/yr)	3.22E+03	1.17E+03	2.05E+03
NMVOC (lb/yr)	9.65E+02	2.26E+02	7.39E+02
Particulate (lb/yr)	1.01E+03	1.71E+02	8.43E+02
SO_2 (lb/yr)	4.56E+03	2.07E+03	2.49E+03
Total Water Emissions (lb/yr)	2.73E+05	4.21E+04	2.31E+05
VOCs (lb/yr)	2.41E+00	3.61E-01	2.05E+00
Total Soil Emissions (lb/yr)	6.88E+02	1.13E+02	5.75E+02
Total Emissions (lb/yr)	**2.67E+06**	**1.24E+06**	**1.42E+06**
CED (MJ/yr)	1.56E+07	9.42E+06	6.14E+06

The damage associated with Case 3A was calculated using Equation 53 and the values for raw material use, utility use, and waste generation in Table 164. Equation 53 includes the damage associated with raw material use, waste disposal, water recovery system operation, and NMP recovery system operation.

$$\begin{aligned} DS_{Case\ 3} = {} & (m_{NMP} - r_{NMP}) \cdot DS_{NMP} + m_{TFA} \cdot DS_{TFA} + m_{HEMA} \cdot DS_{HEMA} + m_{HCl} \\ & \cdot DS_{HCl} + (m_{UPW} - r_{UPW}) \cdot DS_{UPW} + m_{NHWW} \cdot DS_{NHWW} + S \cdot DS_{s} \\ & + E \cdot DS_{E} + m_{Ca(OH)2} \cdot DS_{Ca(OH)2} + m_{HW} \frac{x_{NMP,HW}}{0.17} \cdot DS_{HW} + m_{GAC} \\ & \cdot DS_{GAC} + m_{IE\ Resin} \cdot (DS_{IE\ Resin\ M} + DS_{IE\ Resin\ D}) \end{aligned} \tag{53}$$

In Equation 53, $DS_{Ca(OH)2}$, DS_{GAC}, and $DS_{IE\ Resin\ M}$ are the damage scores for the manufacture of calcium hydroxide, granulated activated carbon, and ion exchange resin on a 1 lb basis. $DS_{IE\ Resin\ D}$ is the damage score for the disposal ion exchange resin on a 1 lb basis.

The damage associated with Base Case 2 and Case 3A are shown in Table 166, along with the damage reduction for Case 3A. The current resin precursor process causes 39,900,000 mPt/yr, 21,600,000 mPt/yr, and 34,900,000 mPt/yr of damage to human health, ecosystems, and resources; respectively. Recovery of both ultrapure water and NMP reduces the damage to human health, ecosystems, and resources by 21,500,000 lb/yr, 11,100,000 lb/yr, and 10,700,000 lb/yr; respectively. This is a damage reduction of 54%, 52%, and 30% to human health, ecosystems, and resources; respectively. The ReCiPe damage results are similar to the life cycle emissions results, which both showed that recovery of NMP and ultrapure water significantly reduced the environmental impact of the resin precursor process.

Table 166

ReCiPe damage assessment for Base Case 2 and Case 3A

	Base Case 2	**Case 3A**	**Case 3A Avoided**
Human Health (mPt/yr)	3.99E+07	1.83E+07	2.15E+07
Ecosystems (mPt/yr)	2.16E+07	1.05E+07	1.11E+07
Resources (mPt/yr)	3.49E+07	2.42E+07	1.07E+07
Total (mPt/yr)	9.63E+07	5.29E+07	4.34E+07

An economic analysis was performed to determine if it is economically beneficial to recover ultrapure water and NMP. The installed capital cost of each part of the ultrapure water recovery system is shown in Table 167. Table 167 shows that Holding Tank 2 has the highest capital cost at $172,000, while Holding Tank 1 has the second highest capital cost at $149,000. The holding tanks have high capital costs because they are designed to store large volumes of liquid. The ion exchange has the third highest capital cost ($146,000), followed by the reverse osmosis system ($112,000) and the adsorption system ($85,000). The ion exchange system is expensive because the column is made of glass-lined carbon steel. The total installed capital cost of the ultrapure water recovery system is $664,000. The installed capital cost includes the cost for the equipment, piping, support structures, electrical work, insulation, and manpower.

Table 167

Installed capital cost for the Case 3A ultrapure water recovery system

	Installed Capital Cost ($)
Holding Tank 1	149,000
Reverse Osmosis System	112,000
Adsorption System	85,000
Ion Exchange System	146,000
Holding Tank 2	172,000
Total	**664,000**

The operating cost associated with Case 3A was calculated using Equation 54 and the values for raw material use, utility use, and waste generation in Table 164. Equation 54 includes the costs associated with raw materials, waste disposal, water recovery system operation, and NMP recovery system operation. In Equation 54, hazardous waste includes the hazardous waste generated by the NMP recovery system, hazardous waste generated by the water recovery systems, spent activated carbon, and spent ion exchange resin. The equipment maintenance cost for the ultrapure water recovery system was estimated as 2.5% of the installed capital cost of the unit operations of the ultrapure water recovery system (reverse osmosis, adsorption, and ion exchange) [127, 133]. The equipment maintenance cost for the ultrapure water recovery system is estimated to be 8,600 \$/yr. The maintenance cost for the NMP recovery system is 27,700 \$/yr, as mentioned in Case 2A-NMP.

$$\begin{aligned} Cost_{Case\ 3} = {} & (m_{NMP} - r_{NMP}) \cdot Cost_{NMP} + m_{TFA} \cdot Cost_{TFA} + m_{HEMA} \cdot Cost_{HEMA} \\ & + m_{HCl} \cdot Cost_{HCl} + (m_{UPW} - r_{UPW}) \cdot Cost_{UPW} + m_{NHWW} \\ & \cdot Cost_{NHWW} + S \cdot Cost_s + E \cdot Cost_E + m_{Ca(OH)2} \cdot Cost_{Ca(OH)2} \\ & + m_{HW} \cdot Cost_{HW} + m_{GAC} \cdot Cost_{GAC} + m_{IE\ Resin} \cdot Cost_{IE\ Resin} \\ & + n_{Membrane} \cdot Cost_{Membrane} + Cost_M \end{aligned} \tag{54}$$

In Equation 54, $Cost_{Ca(OH)2}$, $Cost_{GAC}$, and $Cost_{IE\ Resin}$ are the costs to purchase calcium hydroxide, granulated activated carbon, and ion exchange resin on a 1 lb basis. $n_{Membrane}$ is the amount of membranes used in modules/yr. $Cost_{Membrane}$ is the cost to purchase a membrane in \$/module. $Cost_M$ is the maintenance cost for the NMP and water recovery systems in \$/yr.

The operating costs associated with Base Case 2 and Case 3A are shown in Table 168, along with the operating cost savings and capital equipment costs for Case 3A. Table 168 shows that recovery of both ultrapure water and NMP saves 1,096,000 \$/yr in operating costs. Table 168 also shows the total capital cost of the NMP and water recovery systems is \$2,161,000.

Table 168

Capital and operating costs for Base Case 2 and Case 3A

	Recovery Equip Capital Cost ($)	Operating Cost ($/yr)	Savings ($/yr)	Percent Saved (%)
Base Case 2	0	1,466,000	0	0
Case 3A	2,161,000	370,000	1,096,000	75%

An economic analysis was conducted to compare the current resin precursor process to Case 3A based on recovery equipment capital costs and operating cost savings. The internal rate of return (IRR), return on investment (ROI), payback time after tax, net present value after 5 yr, and net present value after 10 yr were calculated using Equations 19-27, shown in Table 169. The economic analysis shows that ultrapure water and NMP recovery does show favorable economic metrics, as DuPont would save $886,000 after 5 yr and $2,159,000 after 10 yr.

Table 169

Economic analysis of Case 3A

	IRR (%)	ROI (%)	Payback time after tax (yr)	5 yr NPV ($)	10 yr NPV ($)
Case 3A	41%	38%	3.9	886,000	2,159,000

Case 3B: Ultrapure Water Recovery from Wastewater from Washing and Distillate

In Case 3B, ultrapure water is recovered from the wastewater generated from washing the resin precursor and proposed NMP recovery. The wastewater generated from proposed NMP recovery is the neutralized distillate of Step 1. The composition and flow rate of this combined wastewater stream is shown in Table 170. As mentioned in the previous section, several batches of wastewater are generated each week from washing. The neutralized Step 1 distillate from NMP recovery is also generated in weekly batches. For design purposes, annualized flow rates were used, shown in Table 170. The yearly waste generation values were used to size the ultrapure water recovery system for this case. The contaminants in the wastewater are similar to the previous case, except calcium ions are present from neutralization. Also, the acids are specified by their dissociated ions, since the distillate acids were neutralized. The total organic carbon (TOC) present in the wastewater was calculated using Equation 46.

Table 170

Wastewater from washing and NMP recovery composition and flow rate

Water Composition	99.509 wt.%
NMP Composition	1,322 ppm
$C_2F_3O_2^-$ Composition	1,319 ppm
Cl^- Composition	1,294 ppm
Ca^{2+} Composition	937 ppm
H^+ Composition	1.44 ppm
HEMA Composition	40.6 ppm
Total Organic Carbon Composition	822 ppm
Mass Flow Rate (lb/yr)	9,193,000
Volumetric Flow Rate (gal/yr)	1,102,200

Like Case 3A, the wastewater from washing and NMP recovery contains few contaminants, which are known and consistent, so pretreatment is not necessary. Primary treatment of the wastewater focuses on TOC removal, as organic compounds are a major contaminant in this wastewater stream. Reverse osmosis was again chosen as the first step in the ultrapure water recovery process to remove much of the NMP, HEMA, and ionic contaminants; shown in Figure 43. Like Case 3A, remaining organics will be removed using adsorption and then remaining ions will be removed using ion exchange, as shown in Figure 43.

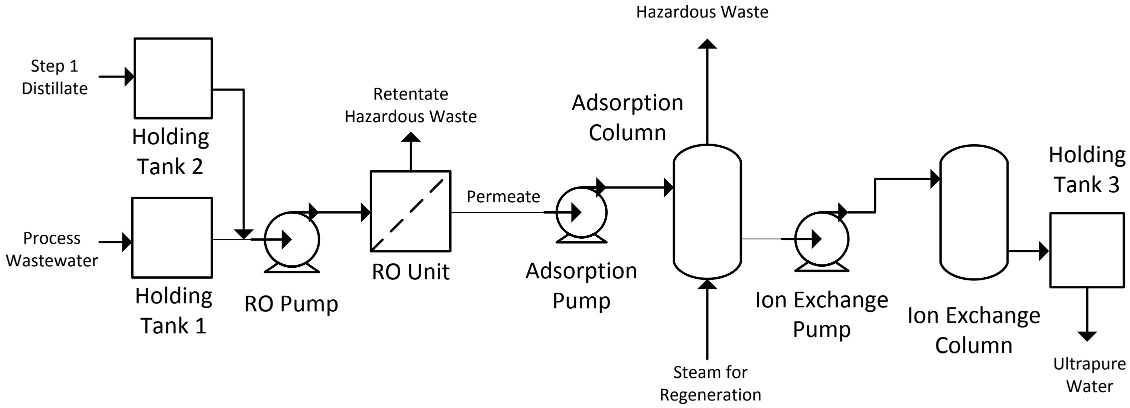


Figure 43. Case 3B ultrapure water recovery system

Like Case 3A, wastewater must be held prior to treatment in the ultrapure water recovery system. In this case, a holding tank is required to hold the neutralized distillated from Step 1 of the NMP recovery system and another holding tank is required to hold the wastewater from resin precursor washing. Holding Tank 2 is designed to hold the neutralized distillate which is generated in weekly batches of 40,000 lb/week (4,800 gal/week). Holding Tank 1 was designed to store the wastewater from washing. Holding Tank 1 is the same as Holding Tank 1 for the previous case. It was designed to hold half of one week’s worth of wastewater. This means that Holding Tank 1 would collect about 8,200 gal of wastewater and then the wastewater would be sent to the ultrapure water recovery system along with half of the wastewater from Holding Tank 2 (2,400 gal).

After the wastewater is sent to the ultrapure water recovery system, 8,200 gal of wastewater from washing would be collected in Holding Tank 1 and then sent to the ultrapure water recovery system along with 2,400 gal in Holding Tank 2. This cycle would be repeated every week.

Holding Tank 1 and Holding Tank 2 were designed to hold 8,200 gal and 4,800 gal of wastewater, respectively, and have a head space of about 20%. Holding Tank 1 had a total volume of 10,000 gal, a diameter of 9.5 ft, and a height of 19 ft. Holding Tank 2 had a total volume of 6,000 gal, a diameter of 8 ft, and a height of 16 ft. The capital cost of both holding tanks was estimated using Aspen Capital Cost Estimator. Both holding tank were designed as vertical flat bottomed storage tanks, with specifications that are listed in Table 171. Both holding tanks were designed to be constructed of stainless steel and have a 0.35 in corrosion allowance due to the TFA and HCl in the wastewater, which are corrosive chemicals. The total installed capital cost for Holding Tank 1 and Holding Tank 2 is $149,000 and $124,000, based on fourth quarter 2014 costs.

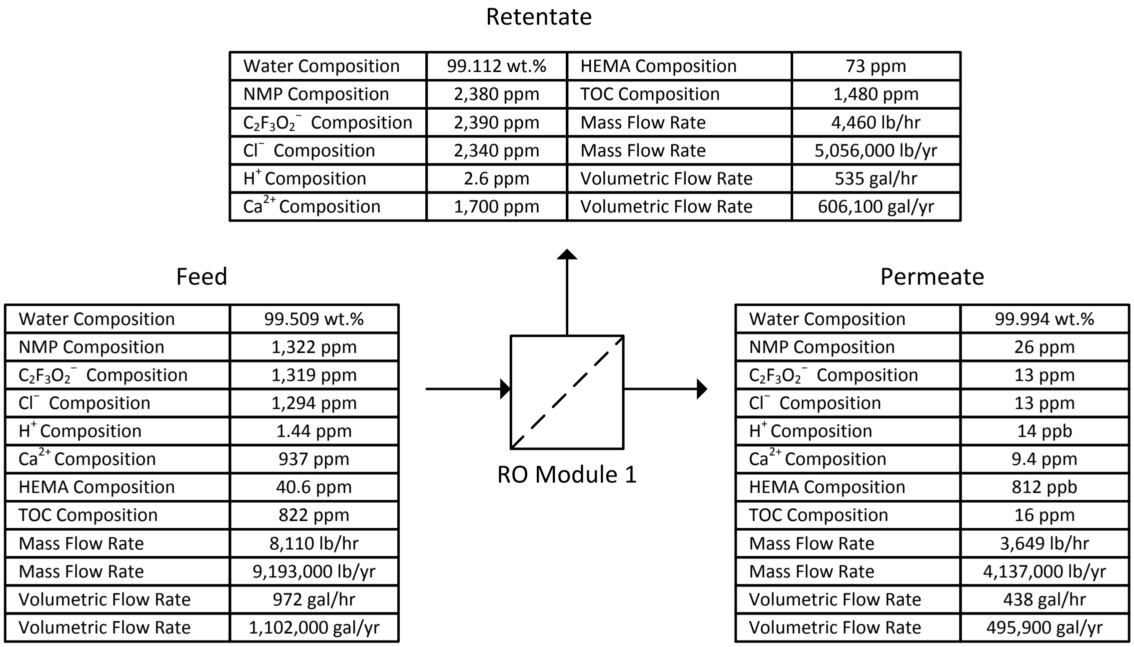
Table 171

Specifications for Holding Tanks 1 and 2

Holding Tank 1		**Holding Tank 2**	
Diameter	9.5 ft	Diameter	8 ft
Height	19 ft	Height	16 ft
Material of Construction	Stainless Steel	Material of Construction	Stainless Steel
Corrosion Allowance	0.35 in	Corrosion Allowance	0.35 in
Design Temperature	150ºF	Design Temperature	150ºF
Design Pressure	15 psig	Design Pressure	15 psig

The combined wastewater stream from resin precursor washing and NMP recovery is sent to the ultrapure water recovery system for treatment. Reverse osmosis was chosen as the first step in the ultrapure water recovery process, shown in Figure 43. The RO system was designed similarly to the previous case, where the RO membrane system consists of two RO elements/modules in one pressure vessel. The combined waste water stream is sent to the first RO module, and the retentate stream of the first RO module is sent as the feed to the second RO module. Two RO modules are used in series to increase the recovery of the RO system and reduce the hazardous waste produced. The GE DESAL® membrane AG8040F-400, specifications shown in Table 154, was also used for this design. The NMP and HEMA rejection by this membrane at 300 psig was assumed to be 98% and the rejection of ions was assumed to be 99%, as was assumed in the previous case. The recovery for the entire RO system was chosen to be 90%, as was done for the previous case. The feed flow rate to the first RO module was calculated using Equation 47, where the permeate flow rate is 438 gal/hr (specified in Table 154) and the recovery is 90%. The feed flow rate to the first RO module was calculated to be 972 gal/hr.

The operating time of each cycle of the RO unit was calculated using the volume of wastewater fed to the RO unit during one cycle and the hourly flow rate fed to the first RO module, shown in Equation 48. The volume fed to the first RO module during one cycle is the volume of liquid held in Holding Tank 1 and half the volume of liquid held in Holding Tank 2. The operating time of each cycle of the RO unit was calculated to be about 11 hr, for a total operating time of 1,130 hr/yr. The flow rate and composition of the wastewater after treatment with the first RO module is shown in Figure 44, along with the feed and retentate flow rates and compositions. The retentate stream from the first RO module is sent to the second RO module. The permeate stream is sent to the adsorption system, along with the permeate stream from the second RO unit. The flow rates and compositions of the feed and outlet streams for the entire RO system are shown in Figure 45. As shown in Figure 45, the two permeate streams are combined and sent to the adsorption system. The retentate stream is hazardous waste, so it is sent off site for incineration.



Retentate

Water Composition	99.112 wt.%	HEMA Composition	73 ppm
NMP Composition	2,380 ppm	TOC Composition	1,480 ppm
$C_2F_3O_2^-$ Composition	2,390 ppm	Mass Flow Rate	4,460 lb/hr
Cl^- Composition	2,340 ppm	Mass Flow Rate	5,056,000 lb/yr
H^+ Composition	2.6 ppm	Volumetric Flow Rate	535 gal/hr
Ca^{2+} Composition	1,700 ppm	Volumetric Flow Rate	606,100 gal/yr

Feed

Water Composition	99.509 wt.%
NMP Composition	1,322 ppm
$C_2F_3O_2^-$ Composition	1,319 ppm
Cl^- Composition	1,294 ppm
H^+ Composition	1.44 ppm
Ca^{2+} Composition	937 ppm
HEMA Composition	40.6 ppm
TOC Composition	822 ppm
Mass Flow Rate	8,110 lb/hr
Mass Flow Rate	9,193,000 lb/yr
Volumetric Flow Rate	972 gal/hr
Volumetric Flow Rate	1,102,000 gal/yr

Permeate

Water Composition	99.994 wt.%
NMP Composition	26 ppm
$C_2F_3O_2^-$ Composition	13 ppm
Cl^- Composition	13 ppm
H^+ Composition	14 ppb
Ca^{2+} Composition	9.4 ppm
HEMA Composition	812 ppb
TOC Composition	16 ppm
Mass Flow Rate	3,649 lb/hr
Mass Flow Rate	4,137,000 lb/yr
Volumetric Flow Rate	438 gal/hr
Volumetric Flow Rate	495,900 gal/yr

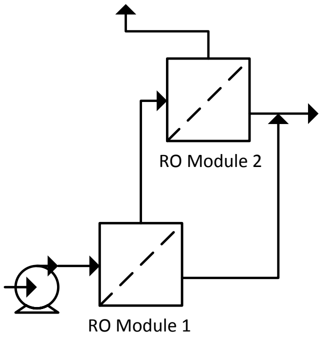
Figure 44. Case 3B RO element/module 1 stream flow rates and compositions

Retentate

Water Composition	95.166 wt.%	HEMA Composition	396 ppm
NMP Composition	12,900 ppm	TOC Composition	8,000 ppm
$C_2F_3O_2^-$ Composition	13,000 ppm	Mass Flow Rate	811 lb/hr
Cl^- Composition	12,800 ppm	Mass Flow Rate	919,300 lb/yr
H^+ Composition	14 ppm	Volumetric Flow Rate	97 gal/hr
Ca^{2+} Composition	9,300 ppm	Volumetric Flow Rate	110,200 gal/yr

Feed

Water Composition	99.509 wt.%
NMP Composition	1,322 ppm
$C_2F_3O_2^-$ Composition	1,319 ppm
Cl^- Composition	1,294 ppm
H^+ Composition	1.44 ppm
Ca^{2+} Composition	937 ppm
HEMA Composition	40.6 ppm
TOC Composition	822 ppm
Mass Flow Rate	8,110 lb/hr
Mass Flow Rate	9,193,000 lb/yr
Volumetric Flow Rate	972 gal/hr
Volumetric Flow Rate	1,102,000 gal/yr



Combined Permeate

Water Composition	99.991 wt.%
NMP Composition	37 ppm
$C_2F_3O_2^-$ Composition	19 ppm
Cl^- Composition	18 ppm
H^+ Composition	0.02 ppb
Ca^{2+} Composition	13 ppm
HEMA Composition	1.14 ppm
TOC Composition	23 ppm
Mass Flow Rate	7,299 lb/hr
Mass Flow Rate	8,274,000 lb/yr
Volumetric Flow Rate	875 gal/hr
Volumetric Flow Rate	991,900 gal/yr

Figure 45. Case 3B RO system stream flow rates and compositions. Each element/module is shown separately, although they are connected in series in one pressure vessel.

Figure 45 shows that the RO unit produces 8,274,000 lb/yr of treated water and generates 110,200 lb/yr of hazardous waste. The operation of the RO feed pump requires 15,200 MJ/yr of electricity. The electrical power needed to run the RO pump was calculated using Equation 36, where the power drawn by the pump is 5 hp. The RO unit also requires membrane maintenance. In the design, it was assumed that both membrane modules are replaced every three months.

The installed capital cost of the reverse osmosis unit was estimated by finding the cost of the feed pump, the pressure vessel housing, and the GE AG8040F-400 reverse osmosis membrane. The installed capital cost of the pressure vessel housing and pump are the same as the previous case because the equipment specifications are the same, listed in Table 172. The installed capital costs for the RO pump and pressure vessel housing are estimated to be $41,200 and $69,100; respectively. The cost of the GE

AG8040F-400 reverse osmosis membrane is $826 [172]. The total installed capital cost for the reverse osmosis system is $112,000, based on fourth quarter 2014 costs.

Table 172

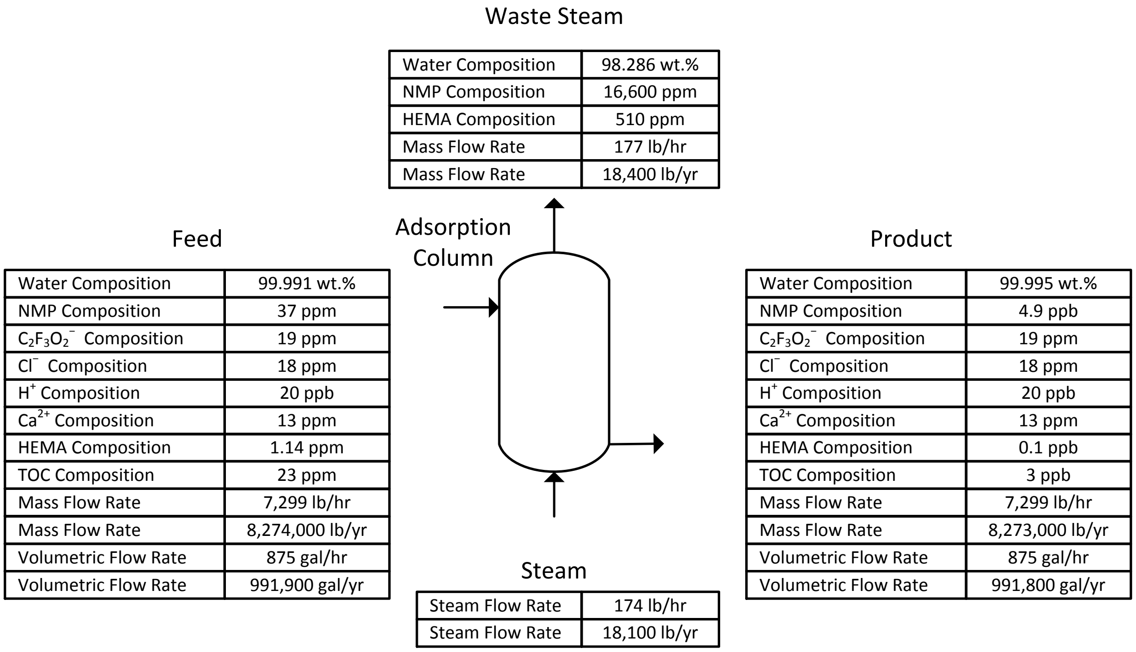
Case 3B RO pump and pressure vessel specifications

Pump Specifications		**Pressure Vessel Specifications**	
Material of Construction	Stainless Steel	Material of Construction	Stainless Steel
Liquid Flow Rate	16.5 gpm	Diameter	0.68 ft
Fluid Head	660 ft	Length	8.42 ft
Design Pressure	350 psig	Design Pressure	350 psig
Design Temperature	150ºF	Design Temperature	150ºF
Pump Efficiency	70%	Corrosion Allowance	0.35 in
Power	5 hp		

In order to remove the remaining NMP and HEMA from the wastewater, an activated carbon adsorption column was designed. The feed to the adsorption column is the combined permeate streams of the first and second RO modules; flow rate and composition shown in Figure 45. The adsorption column was designed to produce water with a TOC composition below 5 ppb. The design of the adsorption column was based off of experimental results by Li *et al*. which were used to design the adsorption column in the previous case. Li *et al.* found the adsorption of MTBE by activated carbon at 298 K follows the Freundlich Isotherm, shown previously in Equation 49. It was assumed that NMP and HEMA adsorption by activated carbon follows the same isotherm.

The mass of granular activated carbon needed for the adsorption process was calculated using Equation 50, assuming that all organics (NMP and HEMA) have the same adsorption affinity. The compositions of NMP and HEMA were combined to calculate the composition of organic compounds. The inlet composition was calculated at 38 ppm or 38,000 ppb. This value was used to calculate q_1, using Equation 49. The outlet composition of organic compounds was set to 5 ppb, so q_2 could be calculated. The inlet flow rate to the adsorption column was set equal to the flow rate of the combined permeate stream of the RO system (7,299 lb/hr). The outlet flow rate (7,299 lb/hr) was calculated by subtracting the quantity of NMP and HEMA removed by the activated carbon. The adsorption time was set to 22 hr, since the RO unit is run for 11 hr twice a week. This allows for the adsorption column to be regenerated once a week. It was assumed that 70% of the adsorption bed is loaded at the end of the adsorption phase of the cycle. It was calculated that 77 lb of granular activated carbon is needed for the adsorption process.

The volume of packing in the adsorption column was calculated to be 1.03 ft^3 using the bulk density of granular activated carbon, 74.9 lb/ft^3 [174]. Using Equation 51, the column diameter and packing height were calculated to be 0.75 ft and 3 ft, respectively. To pack this volume of the adsorption column, 100 lb of granular activated carbon are needed. The total column height was set to 4 ft. As mentioned previously, the adsorption column is regenerated after 22 hr of operation. The regeneration process uses saturated steam at 250ºC (40 bar) to remove NMP and HEMA from the activated carbon. The regeneration time and steam flow rate were based off of experimental data for steam regeneration of activated carbon, as was done for the previous case [175]. In the regeneration design, it was assumed at a steam flow rate of 174 lb/hr for 2 hr would regenerate the activated carbon. The waste steam from regeneration is condensed and disposed of as hazardous waste. The flow rates and compositions of the inlet and outlet streams of the adsorption column are shown in Figure 46.



Waste Steam

Water Composition	98.286 wt.%
NMP Composition	16,600 ppm
HEMA Composition	510 ppm
Mass Flow Rate	177 lb/hr
Mass Flow Rate	18,400 lb/yr

Feed

Water Composition	99.991 wt.%
NMP Composition	37 ppm
$C_2F_3O_2^-$ Composition	19 ppm
Cl^- Composition	18 ppm
H^+ Composition	20 ppb
Ca^{2+} Composition	13 ppm
HEMA Composition	1.14 ppm
TOC Composition	23 ppm
Mass Flow Rate	7,299 lb/hr
Mass Flow Rate	8,274,000 lb/yr
Volumetric Flow Rate	875 gal/hr
Volumetric Flow Rate	991,900 gal/yr

Product

Water Composition	99.995 wt.%
NMP Composition	4.9 ppb
$C_2F_3O_2^-$ Composition	19 ppm
Cl^- Composition	18 ppm
H^+ Composition	20 ppb
Ca^{2+} Composition	13 ppm
HEMA Composition	0.1 ppb
TOC Composition	3 ppb
Mass Flow Rate	7,299 lb/hr
Mass Flow Rate	8,273,000 lb/yr
Volumetric Flow Rate	875 gal/hr
Volumetric Flow Rate	991,800 gal/yr

Steam

Steam Flow Rate	174 lb/hr
Steam Flow Rate	18,100 lb/yr

Figure 46. Case 3B adsorption column stream flow rates and compositions

Figure 46 shows that the adsorption system produces 8,273,000 lb/yr of treated water. The activated carbon regeneration process requires 18,100 lb/yr (23,000 MJ/yr) of steam. This regeneration process generates 18,400 lb/yr of hazardous waste. The operation of the adsorption feed pump requires 760 MJ/yr of electricity, calculated using Equation 36. It was also assumed that the granular activated carbon is replaced after 25 regenerations. This means that the activated carbon must be replaced 2 times a year, so 200 lb/yr of granular activated carbon is used. The 200 lb/yr of spent activated carbon is disposed of as hazardous waste.

The installed capital cost of the adsorption unit was estimated by finding the cost of the adsorption column feed pump, the adsorption column, and the activated carbon packing. The installed capital cost of the adsorption system designed in this case is the same as the previous case because the equipment specifications are the same, listed in Table 173. The installed capital costs for the adsorption feed pump and column are estimated to be $21,600 and $63,100, respectively. The cost to pack 3 ft of the adsorption column was estimated to be $50. The total installed capital cost for the adsorption system is $85,000, based on fourth quarter 2014 costs.

Table 173

Case 3B adsorption feed pump and column specifications

Pump Specifications		**Adsorption Column Specifications**	
Material of Construction	Stainless Steel	Material of Construction	Stainless Steel
Liquid Flow Rate	15 gpm	Diameter	0.75 ft
Fluid Head	25 ft	Height	4 ft
Design Pressure	50 psig	Packed Height	3 ft
Design Temperature	150ºF	Design Pressure	50 psig
Pump Efficiency	70%	Design Temperature	540ºF
Power	0.25 hp		

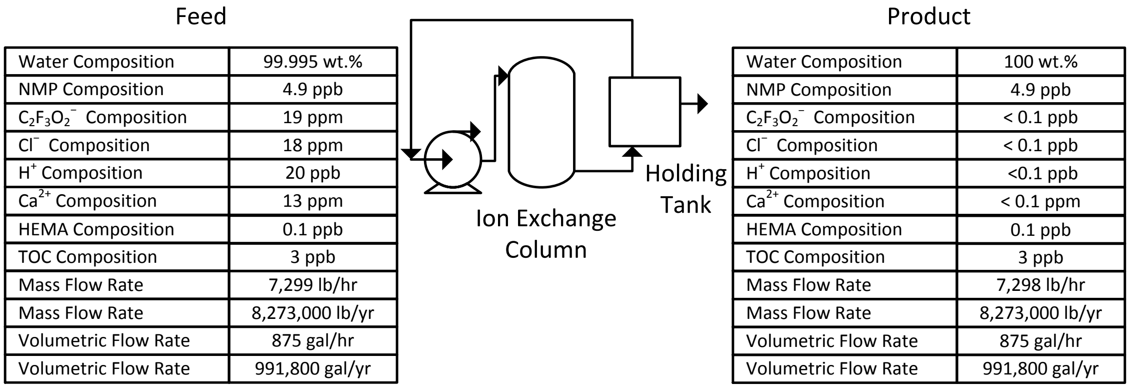
The final step in the ultrapure water recovery system is ion exchange, which will remove the remaining ionic contaminants to produce ultrapure water. The Dowex Monosphere MR-450 UPW ion exchange resin was also chosen for this design. A mixed bed resin was chosen so anionic and cationic contaminants would be removed. As mentioned previously, the ion exchange resin in non-regenerable, meaning the resin is replaced after it is fully loaded with contaminant ions. Therefore, there is no regeneration step as in the carbon adsorption column design. Specifications for the Dowex Monosphere MR-450 UPW ion exchange resin are shown previously in Table 159. The ion exchange column was designed to treat the outlet of the adsorption column, shown in Figure 46. A larger composition of ionic contaminants is present in the inlet stream to the ion exchange than in the previous case. It was calculated that the flow rates of $C_2F_3O_2^-$, Cl^-, and Ca^{2+} out of the adsorption column are 0.548 mol/hr, 1.75 mol/hr, and 1.09 mol/hr; respectively. The total molar flow rate of anionic contaminants into the ion exchange column is 2.29 mol/hr or 2,601 mol/yr, while the molar flow rate of cationic contaminants is 2.18 mol/hr or 2,466 mol/yr.

The diameter of the ion exchange was designed using a flow rate of 8 gpm/ft^2, which is within the recommended range. Since the inlet flow rate to the ion exchange column is set at 875 gal/hr, the diameter of the column must be 1.5 ft. Using an aspect ratio of 4:1, the packed of the height column was calculated to be 6 ft, resulting in 10.6 ft^3 of resin. The total column height was set to 8 ft, as was done in the previous case. Unlike the previous case, this volume of resin is not sufficient for 3 yr since more ions are present in the inlet stream to the ion exchange. The number of weeks that the ion exchange resin would last was calculated using Equation 55. This calculation was based off of the anions present in the wastewater because the anionic portion of the mixed bed will be spent before the cationic portion. It was calculated that the resin would last for 5.7 weeks, which was rounded down to 5.5 weeks since the resin cannot be replaced while the system is operating. Since the ultrapure water recovery system is run in two batches a week, the resin can be replaced mid-week while the ion exchange system is not operating. This means that the resin is replaced about 9.5 times a year.

$$t_{resin} = \frac{anionic\ capacity \times V_{bed}}{\dot{n} \times t_{RO}} \tag{55}$$

In Equation 55, t_{resin} is the time the resin lasts in weeks, $anionic\ capacity$ is $\frac{28.3\ eq}{ft^3}$, V_{bed} is the resin bed volume in ft^3, $\dot{n}$ is the inlet flow rate of anions in $\frac{eq}{hr}$, and t_{RO} is the operating hours of the reverse osmosis unit in hr/week.

The outlet of the ion exchange column is ultrapure water, which is sent to Holding Tank 3. As mentioned previously the wastewater from washing is treated in batches that last 11 hr, twice a week. After 11 hr, the entire batch of wastewater from washing is sent through the ion exchange system and into Holding Tank 3. However, the ultrapure water in Holding Tank 3 is recirculated back through the ion exchange until it is used in the resin precursor process, to ensure all ions are removed. The ultrapure water is recirculated into the ion exchange column at a flow rate of 875 gal/hr. The ultrapure water would not be recirculated back into the ion exchange column while the ion exchange resin is replaced. The ion exchange column produces 7,298 lb/hr or 8,273,000 lb/yr of ultrapure water. The inlet and outlet flow rates and compositions of the ion exchange column are shown in Figure 47.



Feed	
Water Composition	99.995 wt.%
NMP Composition	4.9 ppb
$C_2F_3O_2^-$ Composition	19 ppm
Cl^- Composition	18 ppm
H^+ Composition	20 ppb
Ca^{2+} Composition	13 ppm
HEMA Composition	0.1 ppb
TOC Composition	3 ppb
Mass Flow Rate	7,299 lb/hr
Mass Flow Rate	8,273,000 lb/yr
Volumetric Flow Rate	875 gal/hr
Volumetric Flow Rate	991,800 gal/yr

Product	
Water Composition	100 wt.%
NMP Composition	4.9 ppb
$C_2F_3O_2^-$ Composition	< 0.1 ppb
Cl^- Composition	< 0.1 ppb
H^+ Composition	<0.1 ppb
Ca^{2+} Composition	< 0.1 ppm
HEMA Composition	0.1 ppb
TOC Composition	3 ppb
Mass Flow Rate	7,298 lb/hr
Mass Flow Rate	8,273,000 lb/yr
Volumetric Flow Rate	875 gal/hr
Volumetric Flow Rate	991,800 gal/yr

Figure 47. Case 3B ion exchange column flow rates and compositions

In the ion exchange system design, the feed pump is run continuously since the ultrapure water in the final holding tank is recirculated back to the ion exchange systems. The feed pump is designed to run for 7,200 hr/yr, while drawing 0.25 hp of electricity. Using Equation 36, it was calculated that the ion exchange system uses 4,800 MJ/yr of electricity. The ion exchange system also requires 10.6 ft^3 of ion exchange resin, which must be replaced every 5.5 weeks. The density of the ion exchange resin is 44 lb/ft^3, so about 470 lb of ion exchange resin is needed to pack the column. The annualized quantity of ion exchange resin used is 4,400 lb (470 lb every 5.5 weeks). The spent ion exchange resin waste is generated in a quantity of 4,400 lb/yr.

The installed capital cost of the ion exchange unit was estimated by finding the cost of the ion exchange column feed pump, the ion exchange column, and the ion exchange resin. The installed capital cost of the ion exchange system is the same as the previous case because the equipment specifications are the same, listed in Table 174. The installed capital costs for the ion exchange feed pump and column are estimated to be \$21,600 and \$117,900, respectively. The cost to pack the ion exchange column is

$6,000. The total installed capital cost for the ion exchange system is $146,000, based on fourth quarter 2014 costs.

Table 174

Case 3B ion exchange feed pump and column specifications

Pump Specifications		**Ion Exchange Column Specifications**	
Material of Construction	Stainless Steel	Material of Construction	Glass-lined Carbon Steel
Liquid Flow Rate	15 gpm	Diameter	1.5 ft
Fluid Head	25 ft	Height	8 ft
Design Pressure	50 psig	Packed Height	6 ft
Design Temperature	150ºF	Design Pressure	50 psig
Pump Efficiency	70%	Design Temperature	150ºF
Power	0.25 hp		

As mentioned in the previous section, the ultrapure water produced by the ion exchange column is sent to Holding Tank 3. This ultrapure water is recirculated back into the ion exchange column until it is used in the resin precursor process. Holding Tank 3 was designed to store the ultrapure water recovered from one batch of combined wastewater from washing and NMP recovery. For each batch of combined wastewater that is treated, 9,600 gal of ultrapure water is produced. Holding Tank 3 was designed to hold 9,600 gal of ultrapure water and have a head space of about 20%. The total tank volume was 11,700 gal, with a diameter of 10 ft and a height of 20 ft. The capital cost of Holding Tank 3 was estimated using Aspen Capital Cost Estimator. Holding Tank 3 was specified as a vertical flat bottomed storage tank. The specifications of Holding Tank 3 are listed in Table 175. Holding Tank 3 was designed to be constructed of glass-lined carbon steel to prevent metal ions from leaching into the ultrapure water. The total installed capital cost for Holding Tank 3 is $181,000, based on fourth quarter 2014 costs.

Table 175

Case 3B Holding Tank 3 specifications

Diameter	10 ft
Height	20 ft
Material of Construction	Glass-lined Carbon Steel
Corrosion Allowance	0 in
Design Temperature	150ºF
Design Pressure	15 psig

The raw material use, utility use, and waste generation for Case 3B are shown in Table 176. The electricity used by the ultrapure water recovery system is the sum of the electricity used by the RO, adsorption, and ion exchange systems. The hazardous waste generated by the ultrapure water recovery system is the sum of the hazardous waste generated by the RO and adsorption systems. The material use, utility use, and waste generation from NMP recovery was found in Case 2A-NMP. Table 176 also provides comparison of the raw material use, utility use, and waste generation for Base Case 2 and Case 3B. Case 3B improves upon Base Case 2 by reducing virgin NMP use by 382,300 lb/yr and reducing hazardous waste generation by 1,405,000 lb/yr. Case 3B also reduces ultrapure water production by 8,274,000 lb/yr and eliminates wastewater generation. However, Case 3B requires electricity, steam, and other materials for operation of the recovery equipment.

Table 176

Raw material use and waste generated by Base Case 2 and Case 3B

	Base Case 2	**Case 3B**
NMP (lb/yr)	403,800	21,530
Minor Reagents		
HEMA (lb/yr)	11,880	11,880
TFA (lb/yr)	11,880	11,880
HCl (lb/yr)	11,880	11,880
Ultrapure water (lb/yr)	9,062,000	788,500
Hazardous Waste (lb/yr)	2,375,000	0
Non-hazardous Waste (lb/yr)	7,126,000	0
UPW Recovery System		
Electricity (MJ/yr)	0	20,810
Steam (MJ/yr)	0	22,990
Hazardous waste (lb/yr)	0	937,700
Activated Carbon (lb/yr)	0	199
IE Resin (lb/yr)	0	4,411
Spent Activated Carbon (lb/yr)	0	199
Spent IE Resin (lb/yr)	0	4,411
Membranes (modules/yr)	0	8
NMP Recovery System		
Electricity (MJ/yr)	0	175,400
Steam (MJ/yr)	0	5,424,000
Calcium Hydroxide (lb/yr)	0	15,950
Wastewater (lb/yr)	0	0
Hazardous Waste (lb/yr)	0	31,960

The life cycle emissions associated with Case 3B were calculated using Equation 52 and the values for raw material use, utility use, and waste generation in Table 176. Equation 52 includes the emissions associated with raw material use, waste disposal, water recovery system operation, and NMP recovery system operation. The life cycle emissions associated with Base Case 2 and Case 3B are shown in Table 177, along with the reduction in emissions for Case 3B. The current resin precursor process generates 2,670,000 lb/yr of total emissions and 2,370,000 lb/yr of CO_2 emissions. Table 177 shows that recovery of both ultrapure water and NMP reduces total life cycle emissions and CO_2 life cycle emissions by 1,480,000 lb/yr and 1,230,000 lb/yr, respectively. This is a 56% reduction in total emissions and a 52% reduction in CO_2 emissions.

Table 177

Life cycle emissions for Base Case 2 and Case 3B

	Base Case 2	**Case 3B**	**Case 3B Avoided**
Water Used (lb/yr)	5.24E+09	6.79E+08	4.57E+09
Total Air Emissions (lb/yr)	2.39E+06	1.15E+06	1.25E+06
CO_2 (lb/yr)	2.37E+06	1.14E+06	1.23E+06
CO (lb/yr)	1.14E+03	6.63E+02	4.75E+02
CH_4 (lb/yr)	4.26E+03	2.37E+03	1.89E+03
NO_X (lb/yr)	3.22E+03	1.04E+03	2.18E+03
NMVOC (lb/yr)	9.65E+02	2.29E+02	7.36E+02
Particulate (lb/yr)	1.01E+03	1.70E+02	8.44E+02
SO_2 (lb/yr)	4.56E+03	2.01E+03	2.55E+03
Total Water Emissions (lb/yr)	2.73E+05	3.86E+04	2.34E+05
VOCs (lb/yr)	2.41E+00	3.65E-01	2.04E+00
Total Soil Emissions (lb/yr)	6.88E+02	1.13E+02	5.75E+02
Total Emissions (lb/yr)	**2.67E+06**	**1.18E+06**	**1.48E+06**
CED (MJ/yr)	1.56E+07	9.28E+06	6.28E+06

The damage associated with Case 3B was calculated using Equation 53 and the values for raw material use, utility use, and waste generation in Table 176. Equation 53 includes the damage associated with raw material use, waste disposal, water recovery system operation, and NMP recovery system operation. The damage associated with Base Case 2 and Case 3B are shown in Table 178, along with the damage reduction for Case 3B. The current resin precursor process causes 39,900,000 mPt/yr, 21,600,000 mPt/yr, and 34,900,000 mPt/yr of damage to human health, ecosystems, and resources;

respectively. Recovery of both ultrapure water and NMP reduces the damage to human health, ecosystems, and resources by 22,500,000 lb/yr, 11,600,000 lb/yr, and 10,900,000 lb/yr; respectively. This is a damage reduction of 57%, 54%, and 31% to human health, ecosystems, and resources; respectively. The ReCiPe damage results are similar to the life cycle emissions results, which both showed that recovery of NMP and ultrapure water significantly reduces the environmental of the resin precursor process.

Table 178

ReCiPe damage assessment for Base Case 2 and Case 3B

	Base Case 2	**Case 3B**	**Case 3B Avoided**
Human Health (mPt/yr)	3.99E+07	1.74E+07	2.25E+07
Ecosystems (mPt/yr)	2.16E+07	9.99E+06	1.16E+07
Resources (mPt/yr)	3.49E+07	2.40E+07	1.09E+07
Total (mPt/yr)	9.63E+07	5.13E+07	4.50E+07

An economic analysis was performed to determine if it is economically beneficial to recover ultrapure water and NMP. The installed capital cost of each part of the ultrapure water recovery system is shown in Table 179. Table 179 shows that Holding Tank 3 has the highest capital cost at $181,000, while Holding Tank 1 has the second highest capital cost at $149,000. The ion exchange has the third highest capital cost ($146,000), followed by Holding Tank 2 ($124,000), the reverse osmosis system ($112,000) and the adsorption system ($85,000). The holding tanks have high capital costs because they must be able to store a large volume of liquid. The ion exchange system is expensive because the column is made of glass-lined carbon steel. The total installed capital cost of the ultrapure water recovery system is $797,000. The installed capital cost includes the cost for the equipment, piping, support structures, electrical work, insulation, and manpower.

Table 179

Installed capital cost for the Case 3B ultrapure water recovery system

	Installed Capital Cost ($)
Holding Tank 1	149,000
Holding Tank 2	124,000
Reverse Osmosis System	112,000
Adsorption System	85,000
Ion Exchange System	146,000
Holding Tank 3	181,000
Total	**797,000**

The operating cost associated with Case 3B was calculated using Equation 54 and the values for raw material use, utility use, and waste generation in Table 176. Equation 54 includes the costs associated with raw materials, waste disposal, water recovery system operation, and NMP recovery system operation. In Equation 54, hazardous waste includes the hazardous waste generated by the NMP recovery system, hazardous waste generated by the water recovery systems, spent activated carbon, and spent ion exchange resin. The equipment maintenance costs for the ultrapure water and NMP recovery systems are estimated to be 8,600 $/yr and 27,700 $/yr, respectively.

The operating costs associated with Base Case 2 and Case 3B are shown in Table 180, along with the operating cost savings and capital equipment costs for Case 3B. Table 180 shows that recovery of both ultrapure water and NMP saves 1,011,000 $/yr in operating costs. Table 180 also shows the total capital cost of the NMP and water recovery systems is $2,294,000.

Table 180

Capital and operating costs for Base Case 2 and Case 3B

	Recovery Equip Capital Cost ($)	**Operating Cost ($/yr)**	**Savings ($/yr)**	**Percent Saved (%)**
Base Case 2	0	1,466,000	0	0
Case 3B	2,294,000	455,000	1,011,000	69%

An economic analysis was conducted to compare the current resin precursor process to Case 3B based on recovery equipment capital costs and operating cost savings. The internal rate of return (IRR), return on investment (ROI), payback time after tax, net present value after 5 yr, and net present value after 10 yr were calculated using Equations 19-27, shown in Table 181. The economic analysis shows that ultrapure water and NMP recovery does show favorable economic metrics, as DuPont would save $561,000 after 5 yr and $1,748,000 after 10 yr.

Table 181

Economic analysis of Case 3B

	IRR (%)	**ROI (%)**	**Payback time after tax (yr)**	**5 yr NPV ($)**	**10 yr NPV ($)**
Case 3B	35%	34%	4.7	561,000	1,748,000

Case 3 Conclusion

Figure 48 shows the total and CO_2 life cycle emissions associated with each raw material, waste disposal, and utility used by the resin precursor process, within the LCA boundaries, for the current and alternative processes. The life cycle emissions due to NMP manufacture, minor reagent manufacture, ultrapure water production, hazardous solvent waste disposal, and wastewater disposal are shown. The life cycle emissions due to steam and electricity used by the recovery systems are also shown. Emissions due to activated carbon manufacture, ion exchange resin manufacture, calcium hydroxide manufacture, and spent ion exchange resin disposal are listed under other recovery operation. The current resin precursor process has the most total life cycle emissions and life cycle CO_2 emissions. NMP recovery reduces total life cycle emissions and life cycle CO_2 emissions by 44% and 40%, respectively. Life cycle emissions are significantly reduces from NMP recovery because hazardous waste generation and virgin NMP manufacture are significantly reduced. The Case 3A approach to NMP and water recovery reduces total emissions by 53% and CO_2 emissions 50%. Case 3B reduces total and CO_2 emissions by 56% and 52%, respectively. Case 3B results in the lowest total life cycle emissions and CO_2 life cycle emissions because virgin NMP manufacture, ultrapure water production, hazardous solvent waste disposal, and wastewater disposal are all reduced. However, Case 3B is only slightly better than Case 2A-NMP in terms of life cycle emission reduction.

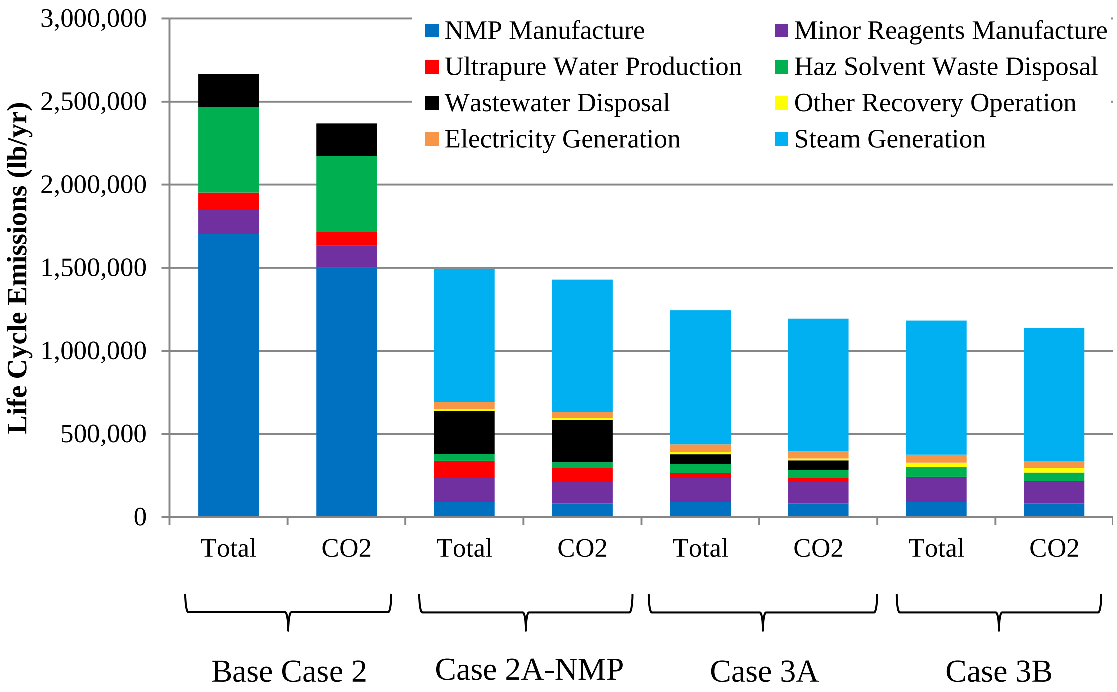


Figure 48. Total and CO_2 life cycle emissions for Base Case 2 and Cases 2A-NMP, 3A, and 3B

Figure 49 shows the damage to human health, ecosystems, and resources for each part of the resin precursor process, within the LCA boundaries, for the current and alterative processes. The damage due to NMP manufacture, minor reagent manufacture, ultrapure water production, hazardous solvent waste disposal, and wastewater disposal are shown. The damage due to steam and electricity used by the recovery systems are also shown. Damage due to activated carbon manufacture, ion exchange resin manufacture, calcium hydroxide manufacture, and spent ion exchange resin disposal are listed under other recovery operation. The current resin precursor process has the most damage to all endpoints. NMP recovery reduces the damage to human health by 46%, reduces the damage to ecosystems by 42%, and reduces the damage to resources by 27%. NMP recovery significantly reduces damage because hazardous waste generation and virgin NMP manufacture are significantly reduced. Case 3A provides reductions of 54%, 52%, and 31% to human health, ecosystems, and resources; respectively. Case 3B reduces damage to human health, ecosystems, and resources by 56%, 54%, and 31%; respectively. Case 3B has the least damage because virgin NMP manufacture, ultrapure water production, hazardous solvent waste disposal, and wastewater disposal are all reduced. However, Case 3B is only slightly better than Case 2A-NMP in terms of damage assessment.

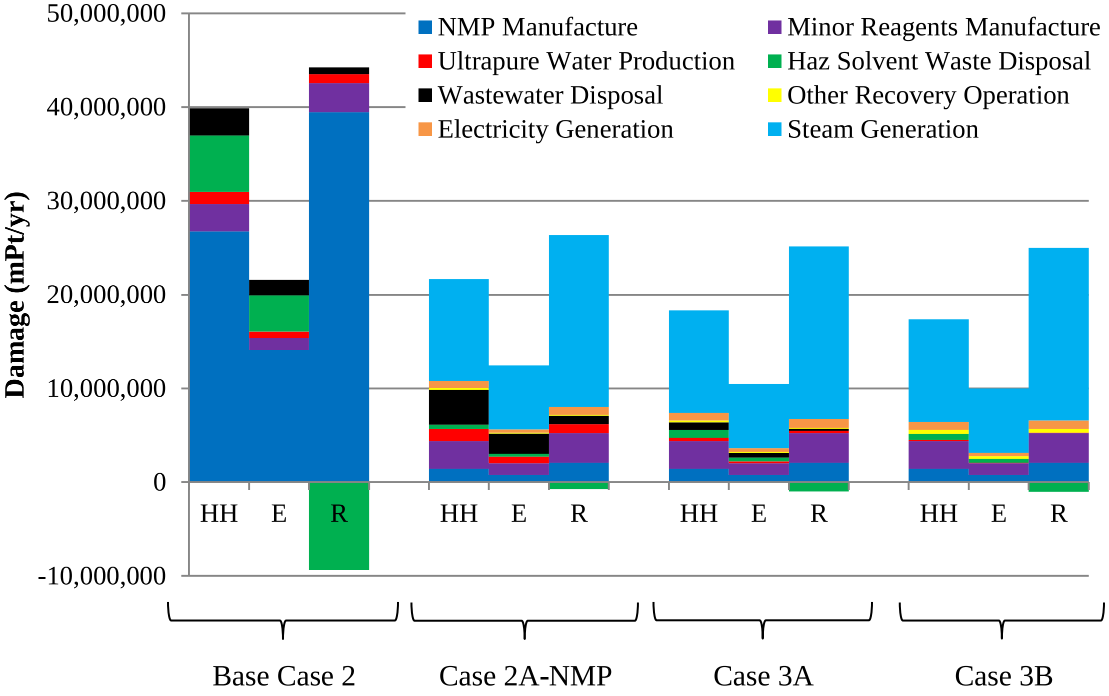


Figure 49. ReCiPe damage assessment for Base Case 2 and Cases 2A-NMP, 3A, and 3B; where HH is human health, E is ecosystems, and R is resources

Figure 50 shows the operating costs for raw material use, waste disposal, and utility use for the current and alterative processes, within the LCA boundaries. The operating costs due to NMP manufacture, minor reagent manufacture, ultrapure water production, hazardous solvent waste disposal, and wastewater disposal are shown. The costs due to steam and electricity used by the recovery systems are also shown. Operating costs due to activated carbon, ion exchange resin, membrane module, and calcium hydroxide purchase; spent activated carbon and ion exchange resin disposal; and equipment maintenance are all included within maintenance. Case 2A-NMP reduces the operating costs by 83%. NMP recovery has a significant reduction in operating costs because hazardous waste generation and virgin NMP manufacture are significantly reduced. Case 3A reduces the operating cost by 75%, while Case 3B reduces the operating cost by 69%. The addition of ultrapure water recovery does not provide further cost savings because it is expensive to dispose of the retentate hazardous waste and maintain the ion exchange system. These results show that Case 2A-NMP is the best option in terms of operating cost savings.

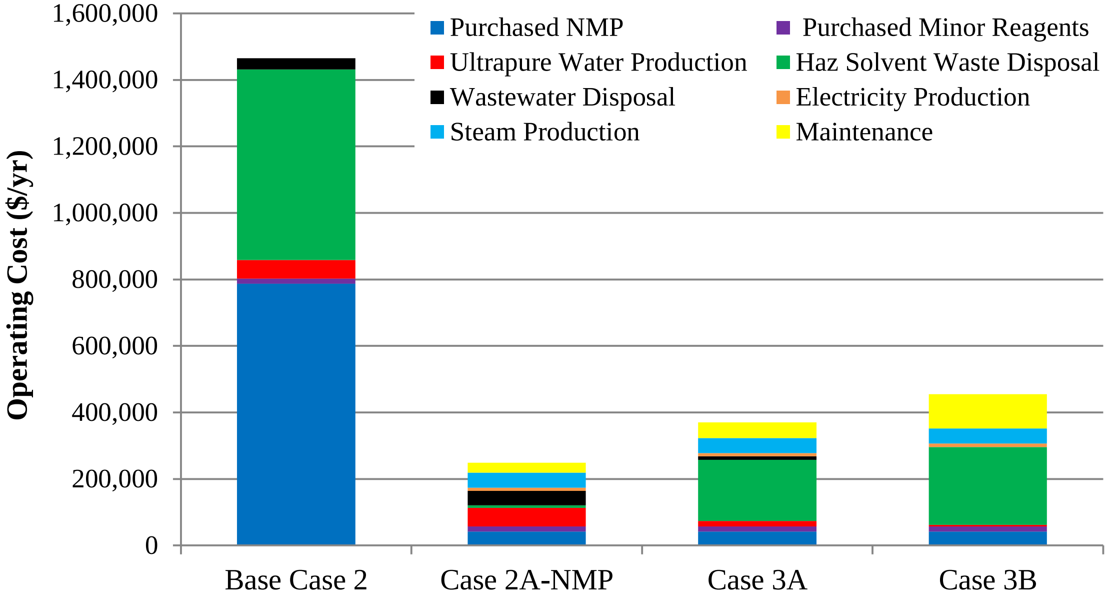


Figure 50. Operating costs for Base Case 2 and Cases 2A-NMP, 3A, and 3B

An economic analysis was conducted to further evaluate the alternative processes based on both recovery equipment capital costs and operating cost savings. To determine if the alternative processes are profitable, IRR, ROI, payback time after tax, net present value after 5 yr, and net present value after 10 yr were calculated for all alternative process. These calculations were performed using Equations 19-27, shown previously. Table 182 shows that Cases 2A-NMP, 3A, and 3B are all profitable. Case 2A-NMP saves $1,750,000 after 5 yr and $3,128,000 after 10 yr. Case 3A saves $886,000 and $2,159,000 after 5 yr and 10 yr, respectively. Case 3B saves $561,000 after 5 yr and $1,748,000 after 10 yr. These results show that Case 2A-NMP is the best option in terms of cost savings.

Table 182

Economic analysis of Cases 2A-NMP, 3A, and 3B

	IRR (%)	**ROI (%)**	**Payback time after tax (yr)**	**5 yr NPV ($)**	**10 yr NPV ($)**
Case 2A-NMP	67%	59%	2.2	1,750,000	3,128,000
Case 3A	41%	38%	3.9	886,000	2,159,000
Case 3B	35%	34%	4.7	561,000	1,748,000

Table 183 provides a summary of the evaluation of Cases 2A-NMP, 3A, and 3B. The summary table shows that Case 3B is the best option in terms of total emission reduction, CO_2 emission reduction, and damage reduction. However, Case 2A-NMP would save DuPont the most money. It is recommended that DuPont only recovers NMP from the resin precursor process. Although the addition of ultrapure water recovery to

NMP recovery showed a slight reduction of environmental impact, additional 12% reduction in total emissions and additional 10% reduction in total damage; the economic analysis showed that NMP recovery alone is the most profitable. It is not a good option to invest in ultrapure water recovery because only small environmental gains will be achieved, while money will be lost. The economic analysis shows that even if existing water treatment equipment is used, money would not be saved due to high operating costs. It is expensive to treat the wastewater found in Case 3A and Case 3B to ultrapure specifications.

Table 183

Overall comparison of Cases 2A-NMP, 3A, and 3B

	Total Emission Reduction	**CO_2 Emission Reduction**	**Damage Reduction**	**10 yr NPV ($)**
Case 2A-NMP	44%	40%	46%	3,128,000
Case 3A	53%	50%	54%	2,159,000
Case 3B	56%	52%	56%	1,748,000

This water recovery evaluation points out the importance of looking at all the factors involved when performing an LCA. While it is worthwhile to consider water reuse, the purity standards required, combined with the availability of an economical supply and disposal method, do not justify water recovery. In this case, installing a water recovery systems for use at this plant site, would only net some environmental returns, while increasing cost. However, this could be different for other plant sites. For example, other geographic locations may have more severe water supply issues or tighter wastewater disposal guidelines.

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