CrossMark

ORIGINAL PAPER

Life cycle assessment of *N*-methyl-2-pyrrolidone reduction strategies in the manufacture of resin precursors

Brigitte M. Pastore[1] · Mariano J. Savelski[1] · C. Stewart Slater[1] · Frank A. Richetti[2]

Abstract A case study has been conducted on the reduction of *N*-methyl-2-pyrrolidone (NMP) solvent waste in the manufacture of polyimide and polybenzoxazole precursors. The evaluation includes the environmental and economic life cycle assessment of solvent recovery and solvent substitution strategies. A two-step distillation process proved effective in recovering 95 % of the NMP at a purity of 99.97 % from an aqueous waste stream comprised 17 % NMP, 0.5 % hydroxyethyl methacrylate, 0.5 % trifluoroacetic acid, and 0.5 % hydrochloric acid. Yearly operating costs were reduced by 83 %, with the greatest impact on the reduction in virgin NMP purchase and hazardous waste disposal cost. Even if a capital acquisition was needed, the recovery option would still result in a net present value at 10 years of 3.12 MM $US. The environmental life cycle assessment (LCA) showed that a 44 % reduction of total emissions is possible with the solvent recovery process, impacting the virgin NMP and hazardous waste disposal life cycle emissions the most. The efficiency in 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, thus generating significant life cycle emissions. Solvent substitutes dimethyl sulfoxide and sulfolane reduce life cycle emissions by 44 and 47 %, respectively, when they replace NMP in the process, even without a recovery operation, due to their greener manufacturing profile. Although, when the recovery systems for the solvent substitutes are incorporated into the design, no

further reductions in the environmental impact are seen. This demonstrates the need for a complete analysis of all the aspects of a greener design (including the recovery step), since the thermodynamic characteristics of the solvents are important when performing an LCA. Water reuse was also considered for the overall process, but not recommended due to the cost of recovering it from the waste stream to ultrapure water standards.

Introduction

The following case study focuses on the evaluation of green engineering practices to reduce the use of *N*-methyl-2-pyrrolidone (NMP) solvent in resin precursor manufacture. The study uses the production scenario at DuPont Corporation's Parlin, NJ plant as the base case. The solvent is used in the synthesis as the reaction medium. More specifically, NMP is used due to its thermal stability, dipolar aprotic properties, and ability to produce a high-molecular weight resin precursor (Ghosh 1996). The process generates significant NMP solvent waste, and strategies for solvent and water recovery and solvent substitution were investigated. The waste is produced in a resin precursor washing step where NMP solvent and other impurities are removed. Due to the nature of the batch washing process, this produces two aqueous wastes, one with significantly higher NMP/impurity levels than the other.

This case study poses challenges due to the waste stream's composition and recovery requirements, which make it unique from other published solvent recovery studies. As

✉ C. Stewart Slater
slater@rowan.edu

[1] Department of Chemical Engineering, Rowan University, Glassboro, NJ, USA

[2] DuPont, Parlin, NJ, USA

🌻 Springer

discussed later in the paper, the complex nature of the two waste streams represents the greatest challenges in performing an efficient separation. The hazardous stream has a low, but still significant, concentration of NMP, along with the monomer, hydroxyethyl methacrylate (HEMA), and dilute acids. In addition, the high purity standards required for solvent reuse make the separation process design more extensive. The thermodynamic properties of the mixture require a multistage approach for effective separation (Wankat 2012).

The resin precursor process is representative of typical manufacturing processes in the specialty and fine chemical industry. These processes require sequential batch reaction steps, followed by batch separation and purification steps. At each of these steps, inefficiencies in chemical, water, and energy use may occur (Slater and Savelski 2007). Addition of all inefficiencies of the process results in high volumes of waste and high waste per unit product. The specialty chemical sector which comprises subsectors such as resins, rubbers, fibers, and filaments (NAICS 3252); plastics and rubbers (NAICS 326); agrochemicals (NAICS 3253); pharmaceuticals (NAICS 3254); paints, coatings, and adhesives (NAICS 3255); and semiconductors (NAICS 3344) reported 2.6 billion kg of waste to the Toxic Release Inventory (TRI) in 2013. This waste consisted of organic solvents and associated chemicals (acids, bases, precursor chemicals, etc.) used in manufacturing operations (U.S. EPA 2015). The specialty chemical sector has one of the highest waste generation rates per kilogram of product produced (5–50 kg waste/kg product) which primarily comprises organic solvents (Sheldon 2011).

The use of organic solvents is a major source of waste in the specialty and fine chemical industries (Sheldon 2008). Solvents are used in unit processes to facilitate reactions and in various separation and purification operations. Processes that generate liquid waste streams containing solvents include crystallization, distillation, extraction, washing, and cleaning processes, as well as byproduct streams from inefficiencies in reactions. Solvents represent 80–90 % of the total mass in a typical pharmaceutical or fine chemical batch process (Constable et al. 2007b). The top organic solvents used in the specialty chemicals industry include toluene, methanol, 1, 2-dichloroethane, dichloromethane, xylene, n-hexane, and other toxic and hazardous solvents like NMP (U.S. EPA 2015). These solvents have varying degrees of toxicity to humans and animals and some are known or possible carcinogens or developmental toxins.

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 (Slater and Savelski 2009). 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 (Raymond et al. 2010). These life cycle 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 (Jimenez-Gonzalez and Constable 2011). Throughout their life cycle, organic solvents cause environmental pollution, thereby requiring approaches to reduction in use (Slater et al. 2012a, b; Raymond et al. 2010).

The environmental impact of solvent use is often ignored when developing a chemical manufacturing route. Use of a less harmful solvent (based on health, safety, and environmental factors) can reduce environmental impact (Henderson et al. 2011). Another approach is to recover solvent, for reuse, using separation techniques such as distillation or pervaporation (Slater and Savelski 2009). Solvent recovery and/or reduction often reduce the emissions associated with a chemical process (Raymond et al. 2010). Also, it is often economically favorable to recover spent solvent and reduce solvent use, as solvents are relatively expensive (Slater et al. 2012a, b).

NMP is typically used as a reaction medium, an extraction/purification solvent, a carrier solvent, and a stripping solvent (Jouyban et al. 2010) in the production of basic organic chemicals, along with specialty/fine chemical and pharmaceutical compounds, and polymeric materials (U.S. EPA 2015). NMP use is widespread 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 (Constable et al. 2007b). However, there are problems associated with NMP use and waste generation, as NMP is a suspected reproductive and developmental toxin (Reisch 2008). In addition, NMP use negatively impacts the environment through life cycle emissions from manufacture and disposal. Typically, work-ups for reactions using NMP require large quantities of water, generating aqueous NMP waste. This waste is typically disposed of using incineration, which requires additional fuel and creates NO_X emissions (Constable et al. 2007a, b).

NMP is used in polymer manufacturing because it is a thermally and chemically stable polar compound, with powerful solvent abilities. NMP is used as a solvent in the synthesis and processing of polymers for membranes, coatings, resins, plastics, and rubbers, for example, the synthesis of thermoresistant polymers such as polyamides, polyimides, polyethersulfones, and polyarylene ethers, and for the synthesis of polyurethanes (Figoli et al. 2014; Liaw et al. 2012; Ghosh 1996; Minges 1989; Alcalde et al. 2008; Liaw and Liaw 1997; Liou et al. 2002; Hergenrother 2003; Madbouly and Otaigbe 2009).

The use of NMP in polymer manufacturing presents issues because NMP is not consumed by synthesis and processing steps and exits the process as waste (Razali et al. 2015). The TRI shows that NMP waste generation in the polymer manufacturing industries has more than doubled over the past decade (U.S. EPA 2015). Although NMP waste generation is increasing in the polymer manufacturing industry, there are no published case studies on NMP recovery from these processes.

As mentioned previously, NMP use and waste generation is prevalent throughout the entire fine/specialty chemical sector. This is recognized as a problem because NMP use and disposal poses health and environmental risks. However, there is a lack of suitable replacements of lower risk and impact for NMP and other dipolar aprotic solvents (Constable et al. 2007a, b; Alfonsi et al. 2007; Jessop 2011). Therefore, NMP continues to be used throughout the specialty chemical sector. Typically, the NMP used in specialty chemical processes exits as aqueous waste, like in the resin precursor case study, and it is rarely recovered from these waste streams because the separation is said to be difficult and costly in terms of capital investment and energy consumption (Constable et al. 2007a, b; Pollet et al. 2011; Jessop 2011; Ji et al. 2011). However, there is limited literature providing a full analysis of NMP recovery from aqueous waste generated by specialty chemical processes.

There are no other published case studies on NMP recovery from fine/specialty chemical manufacture and only limited investigation of its recovery from aqueous waste in other commercial sectors. For instance, Gilles and Loehr (1994) mention the recovery of NMP from aqueous waste in the manufacture of semiconductors, but provide little detail on the process, and no analysis of the recovery operation. Higgins (1995) and Dahlgren (1995) discuss NMP recovery from aqueous waste from semiconductor manufacture in more detail, including brief descriptions of recovery designs and economic analyses. However, no environmental analysis is conducted. Recovery of NMP from aqueous waste generated from the extraction of coal has been proposed; however, recovery experiments were only performed on the laboratory scale and economic and environmental benefits were not determined (Renganathan et al. 1988; Pande and Sharma 2002). In the pharmaceutical and fine chemical industries, a literature survey has shown that NMP use is increasing; therefore, NMP waste generation is also increasing (Ashcroft et al. 2015). However, there are no published NMP recovery studies for the pharmaceutical or fine chemicals sectors. There are published studies on the separation of NMP and water, but these are preliminary studies and do not include an analysis of the implementation of this equipment for NMP recovery (Sunitha et al. 2013; Sato et al. 2012; Tsai et al. 2012; van Veen et al. 2011; Ghosh et al. 2006; Shao et al. 2014).

Since this case is representative of other specialty and fine chemical batch operations, the sustainable approaches will therefore have a potential broader impact.

Materials and methods

The approach to this case study was to use life cycle assessment (LCA) techniques to evaluate the base case and green engineering alternatives. Since the case study investigates new process modifications, an appropriate design/simulator was used. Solvent recovery systems were designed using Aspen Plus® v8.6 to reduce virgin NMP use and hazardous waste disposal. Aspen Plus is able to provide information on flow rates, purities, and utility needs. Solvent substitution was also investigated to find more benign solvents that could be used instead of NMP. Finally, other aspects of the process were designed, as described in subsequent sections, to reduce water use and non-hazardous wastewater disposal. Once the processes were designed, the information related to process flows, compositions, and energy usage was used in performing an LCA. The environmental and economic impacts of all alternative processes were evaluated using LCA and compared to the base case, with the overall goal of improving the base case.

The boundaries of the LCA, outlined in Fig. 1, 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. The current boundaries were chosen to focus on solvent use and waste issues, which is of primary concern at the plant. This approach is consistent with practices for analyzing solvent use in chemical and pharmaceutical manufacturing processes (Slater et al. 2012a, b; Raymond et al. 2010). The LCA boundaries also allow for analysis of water use and other waste issues associated with this process.

The LCA boundaries include the impact associated with the use of all chemicals entering the wash tank. This means that the manufacture of the raw materials: NMP, hydroxyethyl methacrylate (HEMA), trifluoroacetic acid (TFA), hydrochloric acid (HCl), and ultrapure water is included in the LCA. The disposal of the hazardous waste and non-hazardous wastewater is also included inside the LCA boundaries. The utility use from operation of the resin precursor washing process is accounted for in the LCA. However, the same utilities are also used in all alternative processes, so the impact from the washing process does not change for alternative processes. The additional utility use for alternative processes, from operation of recovery equipment, is included in the LCA of the alternative processes.

Three different types of LCAs were conducted to determine the environmental and economic impact of the base case and green alternative processes. Two types of environmental

Fig. 1 Current resin precursor
process with LCA boundaries
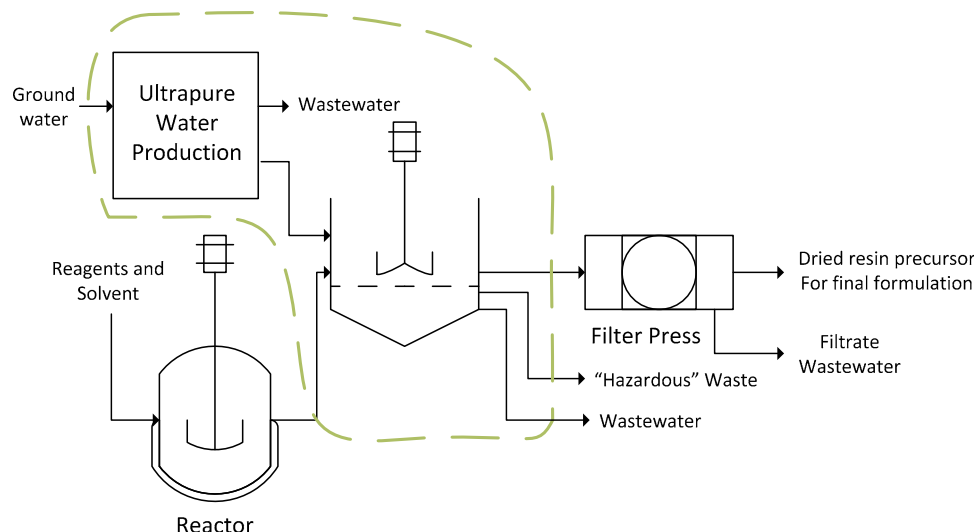
LCAs were conducted: one based on emissions to the environment and the other based on the ReCiPe endpoint H/A method (Goedkeep et al. 2009). An economic LCA was also conducted to determine the life cycle operating costs of the base case and alternative processes. The annualized quantities and life cycle inventories (LCIs) for raw materials, waste, and utilities were used to calculate the LCAs of the base case and alternative processes. The LCIs for raw material manufacture, waste disposal, and utility generation were determined on a 1 kg or 1 MJ basis. The LCIs for environmental emissions include the total emissions released to soil, water, and air. Specific CO_2 emissions, which are part of the total emissions, have been determined, as well. The LCIs for the ReCiPe endpoint method include single scores for human health, ecosystems, and resources. The economic LCIs include raw material, disposal, and utility costs.

The environmental LCIs for raw material manufacture, waste disposal, and utility generation were obtained using SimaPro® version 8. The economic LCIs were either provided by DuPont or found in literature (U.S. EIA 2015; ICIS 2008; Towler and Sinnott 2013). LCIs were found for the manufacture of NMP, TFA, HEMA, HCl, and ultrapure water; the generation of steam and electricity; and the disposal of hazardous waste and non-hazardous wastewater. Disposal of the hazardous solvent waste was modeled as incineration and disposal of the non-hazardous wastewater was modeled as being sent to a wastewater treatment plant.

Results and discussion

Base case

The resin precursor process manufactures liquid polyimide (PI) and polybenzoxazole (PBO) precursors that are cured by DuPont's customers to form PI and PBO resins for use in microelectronics, microelectromechanical systems, and other applications (Kirby 1992). Figure 1 shows that the current process (base case) includes a batch reactor for resin precursor synthesis, a tank for precipitation and washing of the resin precursor, a filter press for drying the solid resin precursor, and an ultrapure water production unit to produce water for washing. The washing process generates hazardous waste which contains water, NMP, and small quantities of reagents (HEMA, TFA, and HCl). Non-hazardous wastewater is also generated from the washing process which contains mainly water, with small quantities of NMP and reagents (HEMA, TFA, and HCl). The filtration step produces dried, solid resin precursor which is sent to a final formulation process. The final formulation involves dissolving the solid resin precursor in solvent with desired additives, such as adhesion promoters.

Life cycle analysis

The first step in analyzing the system is to determine the relevant LCIs for raw material manufacture, waste disposal, and utility generation (Table 1). The LCI data include total and CO_2 life cycle emissions; endpoint single scores for human health, ecosystems, and resources; and cost. Electricity and steam utility generation were modeled based on information relevant to the plant site. Hazardous waste disposal is based off of incineration of aqueous solvent waste with the same solvent composition as the base case hazardous waste. Energy is recovered from hazardous waste incineration and is used to generate steam. Table 1 shows that the total life cycle emissions associated with the manufacture of 1 kg of NMP, 4.22 kg, are significantly higher than those associated with the manufacture of 1 kg of average "generic" solvent, 2.05 kg, which

Table 1 Summary of LCIs used in the analysis of the base case and green alternative processes

Input/output (basis)	CO_2 emissions (kg)	Total life cycle emissions (kg)	Human health (mPt)	Ecosystems (mPt)	Resources (mPt)	Cost ($)
NMP (1 kg)	3.72	4.22	146	76.9	215	4.30
Ultrapure water (l kg)	0.00913	0.0115	0.315	0.172	0.229	0.0135
Electricity (1 MJ)	0.211	0.245	4.26	1.91	4.78	0.0314
Steam (1 MJ)	0.147	0.148	2.01	1.26	3.38	0.00682
Hazardous waste disposal (1 kg)	0.193	0.217	5.57	3.58	−8.71	0.532
Wastewater disposal (1 kg)	0.0275	0.0280	0.891	0.518	0.227	0.0105
HEMA (1 kg)	5.59	5.78	231	122	326	2.34
TFA (1 kg)	4.16	4.80	247	88.2	204	0.278
HCl (1 kg)	1.27	1.50	70.3	26.2	48.9	0.278
$Ca(OH)_2$ for neutralization (1 kg)	0.740	0.751	22.6	13.8	11.0	0.249

was obtained using SimaPro®. This shows that NMP manufacture has a high life cycle impact on the environment, even when compared to other solvents.

Evaluation of base case

The annualized values for raw material use and waste generation, within the LCA boundaries, were used to evaluate the base case (Table 2). The base case generates 1,077,000 kg/yr of hazardous waste which contains 81.5 wt% water, 17 wt% NMP, 0.5 wt% HEMA, 0.5 wt% TFA, and 0.5 wt% HCl. Non-hazardous waste is generated in a quantity of 3,232,000 kg/yr, containing 99.835 wt% water, 0.15 wt% NMP, 50 ppm HEMA, 50 ppm TFA, and 50 ppm HCl. The base case uses 183,200 kg/yr of virgin NMP and 4,110,000 kg/yr of ultrapure water. The NMP used in the base case is electronics grade, so it has a purity of 99.85 wt% and a maximum water composition of 300 ppm. This process also uses 16,160 kg/yr of minor reagents which includes HEMA, HCl, and TFA.

The base case generates 1,209,000 kg/yr of total life cycle emissions and 1,075,000 kg/yr of life cycle CO_2 emissions (Fig. 2). NMP manufacture accounts for 64 % of the total life cycle emissions, while hazardous waste disposal accounts for 19 % of the total emissions. 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 base case, respectively.

The endpoint single scores reveal that human health and resources are impacted the most and NMP manufacture is the main reason for this (Fig. 3.). NMP manufacture accounts for 83 % of the total endpoint score. Minor reagent manufacture, non-hazardous waste disposal, ultrapure water production, and hazardous waste disposal account for 8, 6, 3, and <1 % of the total endpoint indicator score, respectively. Hazardous waste disposal has a low impact on the total endpoint score because the resources score is negative. A negative value means that energy is recovered from the incineration process, thus saving fossil fuels.

The life cycle operating cost of the base case is 1,470,000 $/yr (Fig. 4). 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,

Table 2 Base case and NMP recovery system stream flow rates and compositions

Process stream	Total (kg/yr+)	Water (wt%)	NMP (wt%)	HEMA (wt%)	HCl (wt%)	TFA (wt%)	Other* (wt%)
Base case: NMP used	183,200						
Base case: hazardous solvent waste	1,077,000	81.5	17	0.5	0.5	0.5	
Base case: non-hazardous wastewater	3,232,000	99.835	0.15	0.005	0.005	0.005	
NMP recovery system: recovered NMP	173,400	0.03	99.97	Trace			
NMP recovery system: hazardous solvent waste	14,500	Trace	63.0	37.0			
NMP recovery system: non-hazardous waste	4,170,000	99.50	0.128	0.00388	0.00388	0.00388	0.360
NMP recovery system steam use (MJ/yr)	5,424,000						
NMP recovery system electricity use (MJ/yr)	175,400						

* Neutralization chemicals/products

+ Values for NMP Recovery system steam and electricity use are provided in MJ/yr

Fig. 2 Life cycle emissions for base case and alternative cases; here *Haz* hazardous, *HP* high pressure, *T* total life cycle emissions, CO_2 is life cycle CO_2 emissions, *NR* no recovery, *R* recovery
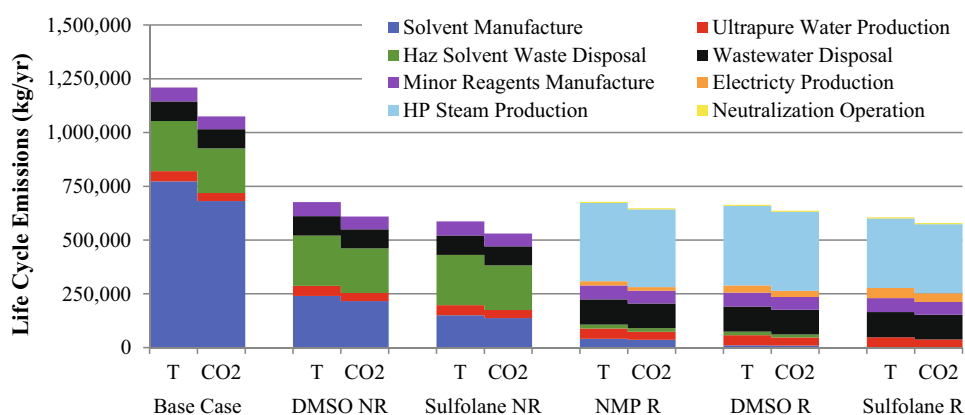
Fig. 3 ReCiPe endpoint single scores for the base case and alternative cases; here *Haz* hazardous, *HP* high pressure, *HH* human health, *E* ecosystems, *R* resources, *NR* no recovery, *R* recovery
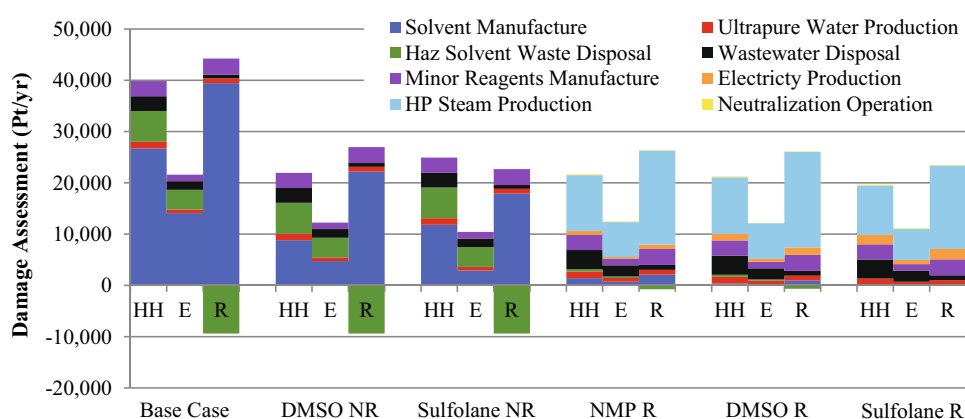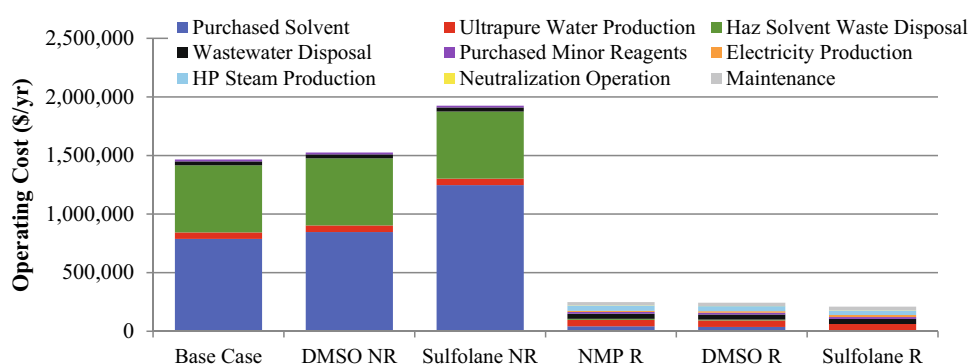
Fig. 4 Life cycle operating costs for base case and alternative cases; here *Haz* hazardous, *HP* high pressure, *NR* no recovery, *R* recovery

and minor reagents purchase account for 4, 2, and 1 % of the total operating cost, respectively.

From the evaluation of the base case, it was seen that NMP manufacture and hazardous waste disposal have the largest impacts on the LCA of the base case. The first green engineering approach focused on solvent recovery, to reduce virgin NMP use and hazardous waste generation. The next green engineering approaches focused on using solvents with lower LCA impact. Recovery of these solvents was also investigated in an attempt to find the lowest impact approach. Finally, water recovery was investigated to see if this further lowered the LCA impact of the base case.

NMP recovery

A preliminary analysis examined various techniques for the separation of NMP and water, which are the major components in the hazardous solvent waste. Distillation was investigated first because it is the most common method of solvent separation and the NMP-water system is homogeneous and non-azeotropic (Ramzan et al. 2008). The equilibrium data for the NMP-water system show that distillation is a feasible separation option at atmospheric pressure. However, other separation techniques were investigated because distillation can be energy intensive, resulting in high

operating costs and environmental impact (Ghosh et al. 2006; Sato et al. 2012; Constable et al. 2007a, b; Jessop 2011). This is a concern for the NMP-water system, because NMP has a high normal boiling point, 202 °C, and the solvent waste stream has a high water composition. Extraction was not considered for this separation because it introduces an extracting agent, which would need to be removed and recovered and limited data were available on NMP extraction from aqueous mixtures (Ghosh et al. 2006; Jessop 2011). Pervaporation was investigated as a lower energy alternative to distillation. However, pervaporation to dehydrate the NMP is not feasible for this case because water is the major component of the hazardous solvent waste (Chapman et al. 2008; Sunitha et al. 2013; Sato et al. 2012; Tsai et al. 2012; van Veen et al. 2011). Organic selective pervaporation, to remove NMP from the solvent waste stream, could not be modeled for this case because limited literature is available for similar aqueous NMP streams (Ghosh et al. 2006). The membrane options are also problematic since NMP has the potential to dissolve polymeric membranes, therefore requiring ceramic/inorganic membrane materials.

Since practical low-energy alternatives to distillation were not found, distillation was used in the NMP recovery system to remove water. However, since NMP and HEMA are both high boilers, NMP cannot be recovered in one distillation process. This adds a complexity to the design process. A second distillation step was used to remove HEMA from the concentrated NMP. Distillation was chosen for both separation steps because the same distillation column could be used, reducing capital costs. The two-step distillation process for recovering NMP from the hazardous solvent waste generated by the base case is shown in Fig. 5. The hazardous solvent waste accumulates in a holding tank, prior to treatment. The solvent waste is then fed to the packed distillation column, operated at atmospheric pressure. The distillate stream containing water, HCl, TFA, and trace amounts of NMP is neutralized and sent to a public wastewater treatment plant. The bottoms stream containing concentrated NMP (NMP, HEMA, and trace amounts of water) is sent to a holding tank. After the first distillation step is complete, the concentrated NMP in the holding tank is sent back to the distillation column used in the previous step. In the second distillation step, electronics grade NMP (to be reused in the resin precursor process) is produced in the distillate stream, while hazardous waste is produced in the bottoms stream.

The distillation system shown in Fig. 5 recovers 94.7 % of the NMP from the hazardous waste at a 99.97 % purity, with a water composition of 300 ppm (Table 2). The distillation process significantly reduces the need for virgin NMP and reduces hazardous waste generation. However, there is still some hazardous and non-hazardous waste generated by the recovery process (Table 2). Utilities to operate the recovery system, steam and electricity, as well as ancillary chemicals for waste neutralization are also needed. These are accounted for in the life cycle assessment.

The recovery process requires high-pressure steam to drive the boil-up of NMP and HEMA. The first distillation step is much more energy intensive than the second distillation step, as 87 % of the steam is used in the first step to evaporate 99.99 % of the water from the hazardous solvent waste stream and because almost 5.5 times more mass is removed in the first step.

The life cycle emissions associated with the current process (base case) and the process with NMP recovery are shown in Fig. 2. The case with NMP recovery generates 678,000 kg/yr of total life cycle emissions and 648,000 kg/yr of life cycle CO_2 emissions. This shows that recovery of NMP reduces total life cycle emissions by 44 % and reduces life cycle CO_2 emissions by 40 %. NMP recovery provides a significant reduction in life cycle emissions because virgin NMP use and hazardous waste generation are significantly reduced.

The ReCiPe endpoint single scores associated with the base case and case with NMP recovery are shown in Fig. 3. The single scores for human health, ecosystems, and resources for the case with NMP recovery are 21,700, 12,500, and 25,600 Pt/yr, respectively. This means that recovery of NMP reduces the scores for human health, ecosystems, and resources by 46, 42, and 27 %, respectively. NMP recovery provides a significant reduction in endpoint single scores because virgin NMP use and hazardous waste disposal, which have large impacts on the single scores for the base case, are drastically reduced. However, the resources score is not reduced as much as the human health and ecosystems scores mainly driven by steam generation needed to operate the distillation column reboiler. Steam generation requires fossil fuels, which explains having larger impact on resources than human health and ecosystems as shown in Fig. 3 and Table 1.

Figures 2 and 3 show that there is little room for further reduction of the environmental impact of NMP manufacture and hazardous solvent waste disposal because of the high recovery of NMP. However, Figs. 2 and 3 show that steam utilization in the NMP recovery has a significant impact on the environmental life cycle.

The life cycle operating costs associated with the base and NMP recovery cases are shown in Fig. 4. The case with NMP recovery has a life cycle operating cost of 248,900 \$/yr, which translates into reduction in the life cycle operating cost of 1,217,000 \$/yr or 83 %. This reduction is driven by a lower use of virgin NMP and lower waste generation (Fig. 4). The cost of steam and other utilities for operation of the NMP recovery equipment has a low impact on the economic life cycle.

Further economic analysis was conducted to evaluate NMP recovery based on both life cycle operating cost
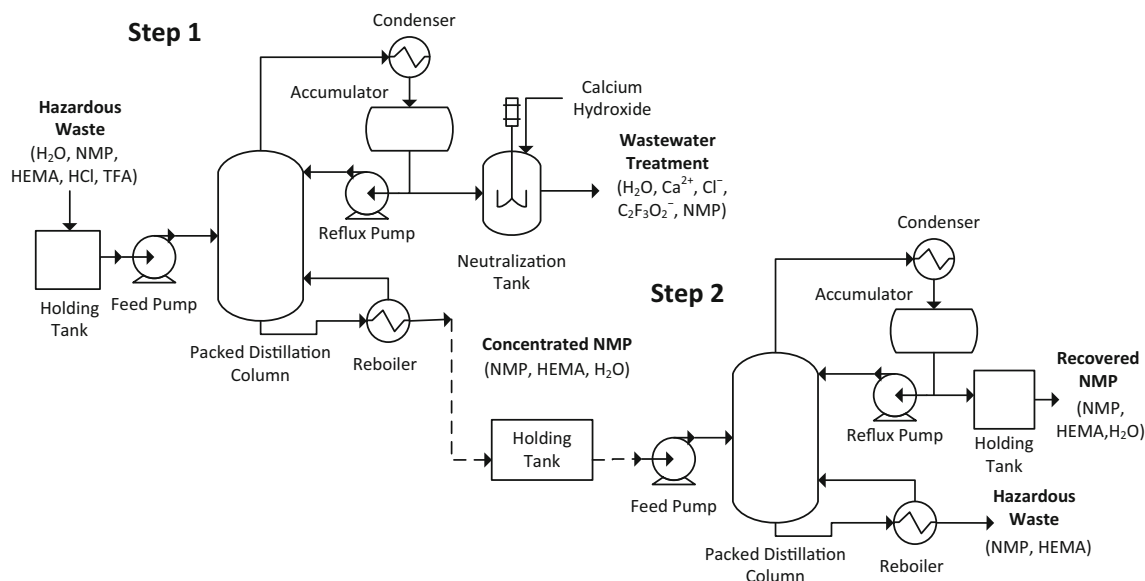
Fig. 5 NMP recovery system for hazardous solvent waste

savings and recovery equipment capital costs. Life cycle operating cost savings alone may not result in savings because capital equipment is also needed. The installed capital cost of the NMP recovery equipment, estimated using Aspen Capital Cost Estimator v8.4, is $1,497,000. To determine if NMP recovery is profitable, net present value (NPV) after 5 yr and NPV 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 (Towler and Sinnott 2013). The 5-yr NPV is $1,750,000 and the 10-yr NPV is $3,128,000. These results show that NMP recovery saves money in the long run, even though capital equipment must be purchased.

Solvent substitute selection

Although NMP has many beneficial properties, it has become a target for replacement and disuse due to its potentially harmful health effects. Also, NMP manufacture generates more life cycle emissions than the average solvent, and accounts for over 60 % of the total life cycle emissions associated with the resin precursor process. Potential solvent substitutes that could lower manufacturing carbon footprint and the human health/ecosystems risk were investigated.

Solvent selection guides were consulted to find other dipolar aprotic solvents because their properties are important in the manufacturing of resin precursors. The other dipolar aprotic solvents found are acetonitrile, dimethylformamide (DMF), dimethylacetamide (DMAc), dimethylsulfoxide (DMSO), sulfolane, and n,n'-dimethylpropylene urea

(DMPU) (Prat et al. 2014). Acetonitrile was not considered as a potential substitute for NMP because it is not a strong base, like is needed for the resin precursor synthesis (Alfonsi et al. 2007). DMPU was also not considered as a potential substitute because it produces low-molecular weight PI resin precursors (Ghosh 1996). However, DMF, DMAc, and DMSO have been found to be good solvents for PI resin precursor synthesis because acceptable molecular weights are achieved (Ghosh 1996). Sulfolane was also considered because it has comparable solubility and polarity properties to NMP, DMSO, DMF, and DMAc and has been found to be a good replacement for dipolar aprotic solvents in other applications (Tilstam 2012).

An analysis of the health, safety, environmental impacts, and physical properties of NMP and potential substitutes showed that DMSO and sulfolane are the best options. DMSO and sulfolane are less toxic than NMP, and are not suspected developmental and reproductive toxins. DMSO and sulfolane both have acceptable physical properties (vapor pressure, normal boiling point, flash point, ignition point, and decomposition temperature) for the resin precursor process and do not pose additional safety concerns. Table 3 also shows that the manufacture of DMSO and sulfolane has a much lower impact on the environment than NMP, based on life cycle emissions and endpoint indicator scores. The ReCiPe endpoint scores also show that the manufacture of DMSO has a lower human health impact compared to the manufacture of sulfolane, while the manufacture of sulfolane has a lower impact on ecosystems and resources. Another benefit of DMSO and sulfolane is that, like NMP, they do not form an azeotrope with water, making recovery through conventional distillation feasible.

Table 3 Summary of LCIs for NMP and potential solvent substitutes

Solvent	CO_2 emissions (kg)	Total life cycle emissions (kg)	Human health (mPt)	Ecosystems (mPt)	Resources (mPt)	Cost ($)
NMP (1 kg)	3.72	4.22	146	76.9	215	4.30
DMSO (1 kg)	1.18	1.31	48.1	25.9	121	4.62
Sulfolane (1 kg)	0.749	0.820	64.5	15.9	97.7	6.81

However, Table 3 also shows that DMSO and sulfolane are more expensive than NMP (Spectrum Chemical 2015).

Solvent substitution

NMP substitution with DMSO and sulfolane was investigated for the resin precursor process, with and without solvent recovery. In these analyses, it was assumed that DMSO and sulfolane could be substituted for NMP at a 1:1 mass ratio. It was also assumed that the LCIs for hazardous waste disposal are the same for all solvents. For the scenarios where DMSO and sulfolane are used without solvent recovery, the amounts of raw material use and waste generation are the same as for the base case. Therefore, changes in the life cycle impact of the resin precursor process are solely due to solvent manufacture.

Figure 2 shows that use of DMSO, without recovery, reduces total life cycle emissions by 44 % and life cycle CO_2 emissions by 43 %, compared to the base case. Substitution to sulfolane, without recovery, provides a 52 and 51 % reduction in total life cycle emissions and life cycle CO_2 emissions, respectively. Since the manufacture of sulfolane generates less life cycle emissions than the manufacture of DMSO, use of sulfolane provides the greatest reduction in life cycle emissions.

Figure 3 shows that substitution to DMSO reduces the single scores for human health, ecosystems, and resources by 45, 43, and 50 %, respectively. Use of sulfolane reduces the scores for human health, ecosystems, and resources by 37, 52, and 62 %, respectively. These results are consistent with the endpoint scores for the manufacture of DMSO and sulfolane. Use of DMSO provides the greatest reduction for the human health endpoint, while use of sulfolane provides the greatest reduction for the ecosystems and resources.

Figure 4 shows that use of DMSO, without recovery, increases the life cycle operating cost of the resin process by 4 %, while use of sulfolane, without recovery, increases the life cycle operating cost by 31 %. Use of DMSO and sulfolane increases the life cycle operating cost because these solvents are more expensive than NMP. DMSO is only slightly more expensive than NMP so life cycle operating costs are slightly increased; however, sulfolane is much more expensive than NMP so life cycle operating costs are greatly augmented. Replacement of NMP with DMSO results in losses of $298,000 after 10 yr. Substitution to sulfolane results in losses of $2,306,000 after 10 yr. These results show that it is not economically favorable to substitute NMP with DMSO and sulfolane, without solvent recovery. Therefore, the recovery of DMSO and sulfolane was investigated to evaluate the environmental and economic impact.

DMSO and sulfolane recovery systems were designed using Aspen Plus®. The DMSO recovery system is a two-step distillation process, similar to the NMP recovery system shown in Fig. 5. However, the DMSO distillation column is operated under vacuum to prevent the degradation of DMSO.

The DMSO distillation system recovers 95.7 % of the NMP from the hazardous waste stream at a purity of 99.98 wt% and a water composition of 150 ppm. There are still hazardous and non-hazardous wastes generated by the distillation system, and energy used for its operation (Table 4).

Figure 2 shows that use of DMSO with recovery provides a 45 % reduction in total life cycle emissions and a 41 % reduction in life cycle CO_2 emissions, compared to the base case. However, the DMSO recovery case is only slightly more favorable to the NMP recovery case. The recovery of DMSO presents higher life cycle emissions associated with electricity than the NMP recovery case driven by vacuum generation.

Figure 3 shows that the DMSO recovery case reduces the scores for human health, ecosystems, and resources by 47, 43, and 27 %, respectively. Similar to the life cycle emission results, the DMSO recovery case is only slightly more favorable to the NMP recovery case, exhibiting lower endpoint scores for solvent manufacture and higher endpoint scores for electricity generation.

The sulfolane recovery system varies from the other solvent recovery systems because only one distillation step is required as sulfolane has a higher boiling point than HEMA. In this distillation step, water, HCl, TFA, and HEMA are removed in the distillate, producing a bottoms stream containing 99.97 wt% sulfolane and trace water. The sulfolane recovery system includes all the equipment shown in the first distillation step in Fig. 5.

The sulfolane distillation system recovers 99.5 % of sulfolane, at a 99.97 % purity, and eliminates hazardous waste generation. However, the sulfolane recovery process

Table 4 Solvent substitute recovery system stream flow rates

Solvent substitute	Recovered solvent (kg/yr)	Solvent purity (wt%)	Hazardous waste (kg/yr)	Non-hazardous waste (kg/yr)	Recovery system steam use (MJ/yr)	Recovery system electricity use (MJ/yr)
DMSO	175,300	99.98	12,690	4,170,000	5,509,000	299,300
Sulfolane	182,300	99.97	0	4,176,000	4,818,000	421,500

still generates non-hazardous waste and requires electricity and steam for its operation (Table 4).

Figure 2 shows that the sulfolane recovery case provides a 50 % and a 46 % reduction in total life cycle emissions and life cycle CO_2 emissions, respectively. The sulfolane recovery case has lower life cycle emissions than the NMP and DMSO recovery cases because the sulfolane recovery process requires only one distillation step. Use of one distillation step results in higher solvent recovery and lower steam use compared to the NMP and DMSO recovery cases, which use two distillation steps. It also eliminates hazardous waste generation. Therefore, there are lower life cycle emissions associated with solvent manufacture, steam production, and hazardous waste disposal. However, the sulfolane recovery case uses the most electricity associated with vacuum operation. Therefore, the sulfolane recovery case is only slightly more favorable to the DMSO and NMP recovery cases.

Figure 3 shows that use of sulfolane with recovery reduces the scores for human health, ecosystems, and resources by 51, 48, and 33 %, respectively. The DMSO and sulfolane recovery cases show the same trend as the NMP recovery case, where the resources endpoint score is not reduced as much as human health and ecosystems.

Figure 4 shows that the sulfolane recovery case reduces the life cycle operating cost of the resin precursor process by 86 %, while the DMSO recovery case reduces the life cycle operating cost by 83 %. The sulfolane recovery case has the largest life cycle operating cost reductions, due to the one-step recovery design which reduces the operating costs associated with solvent purchase, hazardous waste disposal, and steam production. A further economic analysis was conducted to evaluate DMSO and sulfolane recovery based on both life cycle operating cost savings and recovery equipment capital costs. The DMSO and sulfolane recovery systems have installed capital costs of $1,477,000 and $1,565,000, respectively. The economic analysis showed that the DMSO recovery case saves 1.2 % more than the NMP recovery case after 10 yr, while the sulfolane recovery case saves 2.7 % more than the NMP recovery case after 10 yr. The DMSO and sulfolane recovery cases have similar cost savings to the NMP recovery case because all recovery cases have similar life cycle operating cost reductions and capital costs.

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. It is suggested that this analysis be performed in the early design phase of developing fine and specialty chemicals.

A typical assumption is that replacing a solvent with one carrying a lower manufacturing LCI would always make a process greener (Jessop 2011); however, in this case, the thermodynamics of the solvent substitute waste streams (high water composition and high b.p. of the solvent) require energy-intensive separations. The production of steam plays a significant role in the LCAs of the DMSO and sulfolane recovery cases, as it accounts for over 50 % of the total life cycle emissions and human health, ecosystems, and resources endpoint scores.

As shown in Fig. 2, solvent recovery is still favorable despite the high steam usage. The three solvent recovery approaches also show similar cost savings because virgin solvent purchase plays a small role in cost. It is recommended that the resin synthesis continues to use NMP; however, an NMP recovery system should be implemented. This alternative process provides comparable environmental and economic improvement to the DMSO and sulfolane recovery cases, while being the easiest to implement because the plant would not need to validate a different solvent for use in the resin precursor process. This is similar to the pharmaceutical industry, where replacing a solvent in an existing process would require re-registering of a process. In this case, using an alternative solvent would require extensive testing to ensure that there would be no negative impact in intermediate or final products. End-users may be hesitant of major process changes without full understanding of how it may impact the final product.

Water and solvent recovery

An evaluation of potential water recovery/reuse from the waste was also performed. The non-hazardous wastewater generated from the process comprises a 0.15 % NMP waste from resin precursor washing (which exists from the base case) and neutralized distillate of recovery step one (Fig. 5; Table 2). As stated previously, this is modeled in the life cycle assessment as being sent to a wastewater treatment facility. As shown in Figs. 2 and 3, the non-hazardous wastewater disposal constitutes 17 % of the life cycle emissions and 18 % of the operating cost for the NMP

recovery case. Therefore, designing a separate water recovery system has the potential to provide some reduction in emissions, with limited economic return. The main financial obstacle being the need to purify the wastewater to ultrapure "electronics grade" standards requiring a reverse osmosis and adsorption/ion exchange system (GE Power and Water 2015; Li et al. 2002; Dow Water Solutions 2015).

Our analysis shows that producing ultrapure water from the non-hazardous waste stream would reduce total life cycle emissions by 12 % more than the NMP recovery case. This is at the expense of an increase in cost of 68 % after 5 yr and 44 % after 10 yr, compared to the NMP recovery case. Even though membrane and sorption-based separations are low-energy processes, which reduce emissions, the capital cost of these water reuse processes outweighs the existing disposal method. Since this is not one of the alternative options, details of the design and its analysis are not presented here.

This water recovery evaluation points out the importance of looking at all the factors involved when performing a life cycle assessment. 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 an additional recovery process. However, if the plant were in another geographic region, the outcome could be different. For example, water supply issues in California are much more severe, and other locations may have tighter wastewater disposal guidelines (Griffin and Anchukaitis 2014). Therefore, while it may be a general guiding principle to consider zero-discharge options, each raw material to be recovered must be adequately evaluated for its potential environmental and economic impact based on the required separation processes needed. In this case, installing a water recovery system for use at this plant site would only net modest environmental returns at significant cost.

Discussion of process alternatives

This case study provides insight into the analysis of other manufacturing operations in the fine/specialty chemical industry. First, as pointed out in the introduction, NMP belongs to a class of solvents, dipolar aprotic compounds, used extensively in synthesis, extraction, and washing operations. Therefore, the solvent recovery operation described here has a great potential to be utilized throughout the entire sector, not just in resin precursor synthesis.

This particular case study demonstrates several important aspects of why a full LCA is necessary during the early design phase of a new process as well as when considering solvent substitutes or changes to an existing process. The two alternative solvents proposed had significantly lower environmental impacts based on several metrics. It would

appear on "face value" that a greener solvent alternative is better, but without a complete LCA, the design or retrofit exercise is missing an additional dimension necessary for an informed decision. This case study shows that without the recovery process the sole use of a greener solvent does not yield LCA improvements.

In addition, it is further shown that a common strategy of procuring water recovery may not result in such a great environmental or economic improvement. This is especially true for cases where the water supply and disposal costs are low, and the required purity is so high that further processing is required to allow for its reuse.

Conclusions

An analysis of green alternatives for resin precursor manufacture showed that NMP recovery from aqueous waste can be environmentally and economically beneficial. For this case study, NMP recovery would save the plant \$3,128,000 after 10 yr, while providing a 44 and 40 % reduction in total life cycle emissions and life cycle CO_2 emissions, respectively. Reductions of 46, 42, and 27 % to human health, ecosystems, and resources scores, respectively, are also achieved through NMP recovery. However, the reduction in environmental impact from NMP recovery is not as significant as for other solvents such as tetrahydrofuran and isopropanol (Slater et al. 2012a, b). The highly dilute nature of the NMP waste stream and the high boiling point of NMP cause a large quantity of high-pressure steam to be needed for the separation. Therefore, NMP recovery is much more energy intensive than generic solvent recovery.

An evaluation of alternative solvents showed that solvent selection/substitution requires thorough evaluation. In this case, it seems that substitution of NMP with DMSO and sulfolane could be environmentally beneficial because they are more benign solvents and their manufacture is less harmful to the environment. However, DMSO and sulfolane are high boiling solvents, like NMP, so their recovery from waste streams with large water compositions is also energy intensive. The LCAs show that steam generation has a large contribution to life cycle environmental impact, while virgin solvent manufacture does not. Therefore, the use of NMP, DMSO, and sulfolane in the resin precursor process, including solvent recovery, has similar environmental impacts. This case study shows that it is necessary to conduct an overall LCA, including solvent recovery, when evaluating alternative solvents/processes because many factors affect environmental impact.

The LCA performed in this case study showed that wastewater disposal and ultrapure water production do not present a significant contribution to the life cycle environmental impact of the overall resin precursor process. The

small environmental benefits from water recovery are not significant enough to outweigh the economic disadvantages.

Use of more energy efficient recovery systems could provide further reductions in environmental and economic life cycle impact and will be investigated in the future.

References

Alcalde R, Aparicio S, Davila MJ, Garcia B, Leal JM (2008) Liquid–liquid equilibria of lactam containing binary systems. Fluid Phase Equilibr 266:90–100

Alfonsi K, Colberg J, Dunn PJ, Fevig T, Jennings S, Johnson TA, Kleine HP, Knight C, Nagy MA, Perry DA, Stefaniak M (2007) Green chemistry tools to influence a medicinal chemistry and research chemistry based organisation. Green Chem 10:31–36

Ashcroft CP, Dunn PJ, Hayler JD, Wells AS (2015) Survey of solvent usage in papers published in Organic Process Research and Development 1997–2012. Org Process Res Dev 19:740–747

Chapman PD, Oliveira T, Livingston AG, Li K (2008) Membranes for the dehydration of solvents by pervaporation. J Membr Sci 318:5–37

Constable DJ, Dunn PJ, Hayler JD, Humphrey GR, Leazer JL, Linderman RJ, Lorenz K, Manley J, Pearlman BA, Wells A, Zaks A, Zhang TY (2007a) Key Green Chemistry Research Areas—a perspective from pharmaceutical manufacturers. Green Chem 9:411–420

Constable DJ, Jimenez-Gonzalez C, Henderson RK (2007b) Perspective on solvent use in the pharmaceutical industry. Org Process Res Dev 11:133–137

Dahlgren PE (1995) Solvent recycling for reuse in semiconductor manufacturing. 1995 International Symposium on Semiconductor Manufacturing, Austin, TX, September 1995, pp 205–209

Dow Water Solutions (2015) DOWEX MONOSPHERE MR-450 UPW. Available: http://www.dow.com/en-us/water-and-process-solutions. Accessed June 2015

Figoli A, Marino T, Simone S, Di Nicolo E, Li XM, He T, Tornaghi S, Drioli E (2014) Towards non-toxic solvents for membrane preparation: a review. Green Chem 16:4034–4059

GE Power and Water (2015) AG Series: Standard Brackish Water RO Elements. Available www.gewater.com. Accessed June 2015

Ghosh M (1996) Polyimides: fundamentals and applications. Marcel Dekker, New York

Ghosh UK, Pradhan NC, Adhikari B (2006) Pervaporation recovery of N-methyl-2-pyrrolidone from dilute aqueous solution by using polyurethaneurea membranes. J Membr Sci 285:249–257

Gilles DG, Loehr RC (1994) Waste generation and minimization in semiconductor industry. J Environ Eng 120:72–86

Goedkoop M, Heijungs R, Huijbregts M, De Schryver A, Struijs J, van Zelm R (2009) ReCiPe 2008: a life cycle impact assessment method which comprises harmonised category indicators at the midpoint and the endpoint level. Report I: Characterisation, 1st ed

Griffin D, Anchukaits KJ (2014) How unusual is the 2012–2014 California drought? Geophys Res Lett 41:9017–9023

Henderson RK, Jimenez-Gonzalez C, Constable DJ, Alston SR, Inglish GGA, Fisher G, Sherwood J, Binks SP, Curzons AD (2011) Expanding GSK's solvent selection guide—embedding sustainability into solvent selection starting at medicinal chemistry. Green Chem 13:854–862

Hergenrother PM (2003) The use, design, synthesis, and properties of high performance/high temperature polymers: an overview. High Perform Polym 15:3–45

Higgins (1995) Pollution prevention handbook. CRC Press, New York

ICIS (2008) Indicative Chemical Prices A-Z. http://www.icis.com/chemicals/channel-info-chemicals-a-z/. Accessed June 2015

Jessop PG (2011) Searching for green solvents. Green Chem 13:1391–1398

Ji P, Atherton J, Page MI (2011) Liquid ammonia as a dipolar aprotic solvent for aliphatic nucleophilic substitution reactions. J Org Chem 76:1425–1435

Jimenez-Gonzalez C, Constable DJ (2011) Green chemistry and engineering: a practical design approach. Wiley, New Jersey

Jouyban A, Fakhree MAA, Shayanfar A (2010) Review of pharmaceutical applications of N-methyl-2-pyrrolidone. J Pharm Pharm Sci 13:524–535

Kirby AJ (1992) Polyimides: materials, processing, and applications. Pergamon Press, New York

Li L, Quinlivan PA, Knappe DR (2002) Effects of activated carbon surface chemistry and pore structure on the adsorption of organic contaminants from aqueous solution. Carbon 40:2085–2100

Liaw DJ, Liaw BY (1997) Synthesis and properties of polyamides derived from 1,4-bis(4-aminophenoxy)-2-tert-butylbenzene. Macromol Sy 122:343–348

Liaw DJ, Wang KL, Huang YC, Lee KR, Lai JY, Ha CS (2012) Advanced polyimide materials: syntheses, physical properties and applications. Prog Polym Sci 13:907–974

Liou GS, Hsiao SH, Ishida M, Kakimoto M, Imai Y (2002) Synthesis and characterization of novel soluble triphenylamine-containing aromatic polyamides based on N, N'-bis(4-aminophenyl)-N, N'-diphenyl-1,4-phenylenediamine. J Polym Sci A 40:2810–2818

Madbouly SA, Otaigbe JU (2009) Recent advances in synthesis, characterization and rheological properties of polyurethanes and POSS/polyurethane nanocomposites dispersions and films. Progr Polym Sci 34:1283–1332

Minges ML (1989) Electronic materials handbook: packaging, vol 1. ASM International, Materials Park

Pande S, Sharma DK (2002) Ethylenediamine-assisted solvent extraction of coal in N-methyl-2-pyrrolidone: synergistic effect of ethylenediamine on extraction of coal in N-methyl-2-pyrrolidone. Energ Fuel 16:194–204

Pollet P, Eckert CA, Liotta CL (2011) Switchable solvents. Chem Sci 2:609–614

Prat D, Hayler J, Wells A (2014) A survey of solvent selection guides. Green Chem 16:4546–4551

Ramzan N, Degenkolbe S, Witt W (2008) Evaluating and improving environmental performance of HC's recovery system: a case study of distillation unit. Chem Eng J 140:201–203

Raymond MJ, Slater CS, Savelski MJ (2010) LCA approach to the analysis of solvent waste issues in the pharmaceutical industry. Green Chem 12:1826–1834

Razali M, Kim JF, Attfield M, Budd PM, Drioli E, Lee YM, Szekely G (2015) Sustainable wastewater treatment and recycling in membrane manufacturing. Green Chem

Reisch M (2008) Solvent users look to replace NMP. Chem Eng News 86:32

Renganathan K, Zondlo JW, Mintz EA, Kneisl P, Stiller AH (1988) Preparation of an ultra-low wash coal extract under mild conditions. Fuel Process Technol 18:273–278

Sato K, Sugimoto K, Shimotsuma N, Kikuchi T, Kyotani T, Kurata T (2012) Development of practically available up-scaled high-silica CHA-type zeolite membranes for industrial purpose in dehydration of *N*-methyl pyrrolidone solution. J Membrane Sci 409–410:82–95

Shao F, Hao C, Ni L, Zhang Y, Du R, Meng J, Liu Z, Xiao C (2014) Experimental and theoretical research on *N*-methyl-2-pyrrolidone concentration by vacuum membrane distillation using polypropylene hollow fiber membrane. J Membrane Sci 452:157–164

Sheldon RA (2008) Green and sustainable chemistry: challenges and perspectives. Green Chem 10:359–360

Sheldon RA (2011) Fundamentals of green chemistry: efficiency in reaction design. Chem Soc Rev 41:1437–1451

Slater CS, Savelski MJ (2007) A method to characterize the greenness of solvents used in pharmaceutical manufacture. Environ Sci Health 42:1595–1605

Slater CS, Savelski MJ (2009) Towards a greener manufacturing environment. Innov Pharm Technol 29:78–83

Slater CS, Savelski MJ, Hounsell G, Pilipauskas D, Urbanski F (2012a) Green design alternatives for isopropanol recovery in the celecoxib process. Clean Technol Envir 12:687–698

Slater CS, Savelski MJ, Moroz TM, Raymond MJ (2012b) Pervaporation as a green drying process for tetrahydrofuran recovery in pharmaceutical synthesis. Green Chem Lett Rev 5:55–64

Spectrum Chemical MGF Corp (2015) ACS Grade Solvents. Available: https://www.spectrumchemical.com/OA_HTML/Chemicals_Fine-Chemicals_ACS-Chemicals_ACS-Solvents.jsp?minisite=10020&respid=22372. Accessed May 2015

Sunitha K, Rani KY, Moulik S, Satyanarayana SV, Sridhar S (2013) Separation of NMP/water mixtures by nanocomposite PEBA membrane: part I. Membrane synthesis, characterization and pervaporation performance. Desalination 330:1–8

Tilstam U (2012) Sulfolane: a versatile dipolar aprotic solvent. Org Process Res Dev 16:1273–1278

Towler G, Sinnott R (2013) Chemical engineering design, 2nd edn. Butterworth-Heinenmann, Massachussettes

Tsai HA, Chen YL, Lee KR, Lai JY (2012) Preparation of heat-treated PAN hollow fiber membranes for pervaporation of NMP/H2O mixtures. Sep Purif Technol 100:97–105

U.S. Energy Information Administration (2015) Electricity Data Browser. http://www.eia.gov. Accessed June 2015

U.S. Environmental Protection Agency, Office of Environmental Information (2015) TRI.NET. http://www.epa.gov/tri/tridotnet/index.html. Accessed March 2015

van Veen HM, Rietkerk MDA, Shanahan DP, van Tuel MMA, Kreiter R, Castricum HL, ten Elshof JE, Vente JF (2011) Pushing membrane stability boundaries with HybSi® pervaporation membranes. J Membrane Sci 380:124–131

Wankat PC (2012) Separation process engineering, 3rd edn. Prentice Hall, New Jersey