

The Green Engineering Implications of the Replacement and Recovery of Dipolar Aprotic Solvents in Industrial Manufacturing

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Abstract—A case study has been conducted on the use of solvent substitutes and/or solvent recovery in a resin precursor manufacturing process. The current process uses the dipolar aprotic solvent *N*-methyl-2-pyrrolidone (NMP) as a synthesis reaction medium. NMP is associated with harmful environmental and health effects. Dimethylsulfoxide (DMSO) and sulfolane are also dipolar aprotic solvents with similar physical properties of NMP but are less harmful. With the substitution of NMP for DMSO or sulfolane in the resin precursor process, total life cycle emissions were reduced by 52% and 61%, respectively. Distillation processes were designed to evaluate the environmental impacts of recovering solvent from the waste. Total life cycle emissions were reduced by 63% when comparing the current operation using NMP with the case of the current operation with solvent recovery. There was no additional significant reduction on life cycle emissions for the cases with solvent recovery for DMSO or sulfolane. Thus, the importance of evaluating all green engineering options through a life cycle assessment is important to fully understand the environmental impact reduction each option possesses.

Index Terms—Solvent substitute, solvent recovery, green engineering, life cycle assessment.

I. INTRODUCTION

The following study discusses the substitution and recovery of *N*-methyl-2-pyrrolidone (NMP) for its uses as a solvent in the manufacture of specialty chemicals. A case study for the use of NMP in a polyimide (PI) and polybenzoxazole (PBO) resin precursor at the DuPont Parlin, NJ plant is used as a base case. NMP is a dipolar aprotic solvent that is used as a reaction medium for the synthesis of specialty chemicals, pharmaceuticals, and other fine chemicals [1], [2]. Dipolar aprotic solvents, such as NMP, are favorable for synthesis reactions, as they are strong basic solvents. During synthesis, a rapid exothermic acid-base reaction results, which becomes the driving force for the reaction [1]. The inherent issue coupled with solvent use in these synthesis reactions is the fact that the solvent is not consumed and typically is discharged as a hazardous waste stream. Emerging research on the health and environmental impacts of NMP and other dipolar aprotic solvents (e.g. dimethyl-acetamide and dimethylformamide) present a concern for the use and disposal of these solvents

[3]–[5]. Specifically, NMP, has been linked to negative effects to the human reproductive system [3].

Efforts have been made in the research of “greener” solvents to substitute in these industrial manufacturing applications. Such solvents have been considered for their lower health and environmental impacts. 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 provide 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), *n*, *n*-dimethylacetamide (DMAc), dimethyl-sulfoxide (DMSO), sulfolane, and *n*, *n*′-dimethylpropylene urea (DMPU) [6]. Acetonitrile was not considered as a potential substitute for NMP as Alfonsi et al (2007) found that it is a poor substitute for dipolar aprotic solvents [7]. DMPU was also not considered as a potential substitute because it is a poor solvent for synthesis of PI resin precursor [1]. However, DMF, DMAc, and DMSO have been found to be good solvents for PI resin precursor synthesis [1]. Sulfolane was considered as a potential substitute for NMP because it has comparable properties to NMP, DMSO, DMF, and DMAc [8]. It has also been found to be a good replacement for dipolar aprotic solvents in other applications [8].

As stated, the main concern associated with NMP use is its suspected developmental and reproductive toxicity [3]. The health risks associated with all potential substitutes (DMF, DMSO, DMAc, and sulfolane) were investigated to determine if any would be a safer alternative. However, DMF and DMAc are also suspected developmental and reproductive toxins [6]. Other health metrics were also investigated to compare the potential substitutes. Those considered are the lowest concentration to kill 50% population of test animals (LC50), threshold limit value (TLV), and skin permeability. These solvent characteristics are listed in Table I. Data have been obtained from each solvent’s respective safety data sheet, unless otherwise specified.

Based on health, DMSO and sulfolane are the best substitutes for NMP. Sulfolane is less toxic than NMP and has significantly lower skin permeability [8], [9], [15]. 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

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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, but they have higher toxicities than NMP, shown in Table I. These conclusions are consistent with the solvent selection guides, which show that DMF and DMAc are at least as hazardous to health as NMP [6]. The solvent selection guides also show that DMSO and sulfolane are less hazardous to health than NMP [6].

Physical properties related to health and safety were also considered when investigating potential substitutes for NMP. Such properties are listed in Table II. Data have been obtained from each solvent's respective safety data sheet, unless otherwise specified. Vapor pressure was considered

as it is an indication of the volatility of solvent. NMP or potential substitutes can cause harm when inhaled; thus, solvents with lower vapor pressures are considered more favorable. Flash point, ignition point, boiling point, and decomposition temperature were all considered to compare the thermal stability among potential substitutes. Additionally, the boiling point of a potential solvent be above 100 °C, which is the maximum operating temperature in the DuPont process. The solvents were then investigated to determine if an azeotrope with water could be formed. This gives an implication on the type of potential recovery processes for NMP or the solvent substitutes.

TABLE I: HEALTH DATA FOR NMP AND POTENTIAL SOLVENT SUBSTITUTES

	LC50	TLV	Skin Permeability
NMP	5,100 mg/m ³ 4 hr [9]	10 ppm (skin) AIHA [10]	171 mg/m ² /hr [8]
DMF	4,700 mg/m ³ 4 hr [11]	10 ppm (skin) ACGIH [12]	98 mg/m ² /hr [8]
DMAc	1,240 mg/m ³ 4 hr [13]	10 ppm (skin) ACGIH [13]	107 mg/m ² /hr [8]
DMSO	40,250,000 mg/m ³ 4 hr [14]	250 ppm (WEEL) [14]	176 mg/m ² /hr [8]
Sulfolane	12,000 mg/m ³ 4 hr [15]	No Data	0.2 mg/m ² /hr [8]

In typical manufacturing processing using dipolar aprotic solvents for synthesis reactions, the solvent is not consumed and is removed to a waste stream [16]. The waste solvent presents an environmental risk as it a hazardous organic waste and requires incineration. Waste containing the solvent commonly contains large quantities of water. The waste solvent (NMP in the case of the DuPont resin precursor process) is generally not separated from the

aqueous waste stream because of high capital costs and energy use. Incineration of the organic contaminated hazardous wastewater is the preferred treatment method. An additional amount of fuel is required because of the high water content. Incineration of the waste causes the generation of greenhouse gas pollutants such as CO₂ and NO_x [3].

TABLE II: PHYSICAL PROPERTIES OF NMP AND SOLVENT SUBSTITUTES

	NMP	DMF	DMAc	DMSO	Sulfolane
Vapor Pressure at 25 °C (kPa) [8]	0.050	0.37	0.13	0.06	0.0091**
Flash Point (°C)*	96	67	70	95	166
Ignition Point (°C)*	346	445	490	215	528
Boiling Point (°C)*	202	153	164	189	287
Decomposition Temperature (°C)	365	350	350	>189	220
Azeotrope with water	No	No	No	No	No

*at 1 atm; **at 30 °C

II. MATERIALS AND METHODS

Environmental and health impacts can be determined using the life cycle inventories (LCI) of NMP and each of the solvent substitutes. An LCI is a summary of all the emissions associated with a given process. In this case, the LCI of the manufacture or disposal of a given solvent on a 1 kg basis. This summary consists of all emissions released to soil, water, and air. In addition to emission data the LCI contains information on water and energy use. The cumulative energy demand (CED) is used to express the overall energy requirement for the desired manufacture or disposal process [17]. All LCIs have been generated using the life cycle assessment software SimaPro[®]. The LCIs for NMP, DMSO, and sulfolane on a 1 kg basis are provided in Table III. It can be seen that the manufacture of 1 kg of NMP generates 3.2 times and 5.1 times more emissions than DMSO and sulfolane, indicating it has the greatest negative

environmental impact of the dipolar aprotic solvents.

The environmental impact of the DuPont resin precursor process will be evaluated and compared with alternative processes. The base case life cycle emissions will be considered as those associated with the current processes using NMP and no solvent recovery methods. The life cycle emissions of alternative cases will also be conducted using the solvent substitutes DMSO and sulfolane. Life cycle emissions associated with the current processes will then be evaluated with solvent recovery. Similarly, life cycle emissions associated with the alternative cases with solvent substitutions of DMSO and sulfolane will also be evaluated with solvent recovery efforts. Solvent recovery processes have been designed and simulated using Aspen Plus[®]. The software tool is useful in determining separation system performance and operating requirements (e.g. utilities).

TABLE III: LCIS OF THE MANUFACTURE OF 1 KG OF NMP AND SOLVENT SUBSTITUTES

	NMP	DMSO	Sulfolane
Water Used (kg)	1.13E+04	3.38E+03	1.04E+03
Total Air Emissions (kg)	3.77E+00	1.19E+00	7.91E-01
CO ₂ (kg)	3.72E+00	1.18E+00	7.49E-01
CO (kg)	2.38E-03	1.00E-03	9.83E-04
CH ₄ (kg)	9.68E-03	5.31E-03	3.13E-03
NO _x (kg)	5.73E-03	1.98E-03	1.36E-03
NM VOC (kg)	1.88E-03	5.03E-04	1.09E-03
Particulate (kg)	2.08E-03	6.25E-04	3.73E-04
SO ₂ (kg)	7.45E-03	1.92E-03	3.59E-02
Total Water Emissions (kg)	4.51E-01	1.23E-01	2.82E-02
VOCs (kg)	4.69E-06	7.18E-07	7.33E-07
Total Soil Emissions (kg)	1.44E-03	3.54E-04	1.71E-04
Total Emissions (kg)	4.22E+00	1.31E+00	8.20E-01
CED (MJ)	8.97E+01	4.81E+01	3.73E+01

III. RESULTS AND DISCUSSION

A. Current Processes Solvent Substitution

The environmental and health impacts have been evaluated for the base case, as well as the comparison with the use of DMSO or sulfolane as a replacement for NMP. Thus, in this case, the focus is on the green engineering approach of the use of less hazardous raw materials. It has been assumed that DMSO and sulfolane can be substituted for NMP at a 1:1 mass ratio. The annualized flowrate of aqueous solvent waste associated with the DuPont resin precursor process is approximately 1,134,000 kg/yr. It is assumed that the amount of solvent present in the hazardous waste is equal to the amount of virgin solvent fed to the process. The weight percent of NMP in the aqueous wastewater is 17%. The remainder of the waste is approximately 82% water by weight percent and the balance is other minor reagents; however, the minor reagents have been considered negligible compared to the impact of the NMP. Thus, the waste will be considered as a binary waste stream. Water used in processing is ultrapure water (UPW). The LCI for UPW has been modeled to reflect the processes used to purify water at the DuPont plant.

The overall life cycle emissions associated for the cases of solvent use without recovery efforts can be evaluated

using (1).

$$LCE = \dot{m}_{\text{solvent}} LCI_{\text{solvent}} + \dot{m}_{\text{UPW}} LCI_{\text{UPW}} + \dot{m}_{\text{HW}} LCI_{\text{HW}} \quad (1)$$

where LCE is the total of a given life cycle emission (e.g. CO₂, NO_x) and is the sum of all associated emissions of the individual processes. In the current process, the LCIs of the solvent, water, and hazardous waste (HW) disposal (incineration) are included. The CED for hazardous waste incineration is negative because it is assumed that steam is generated as a byproduct off the process.

The annualized life cycle emissions for the current processes, using each solvent are shown in Fig. 1. The case for NMP reflects that of the process that is currently in operation. It can be seen that substituting solvents promotes a greener process. The current operation using NMP generates 2 times and 2.5 times more CO₂ annually than when DMSO or sulfolane were substituted, respectively. In addition, the total emissions are reduced by 52% and 61% when substituting DMSO and sulfolane, respectively. When NMP is used, the solvent manufacture accounts for 76% of the total emissions, while this is reduced to 50% and 38% for DMSO and sulfolane respectively. This confirms that the use of NMP in the current processes causes a high negative environmental impact.

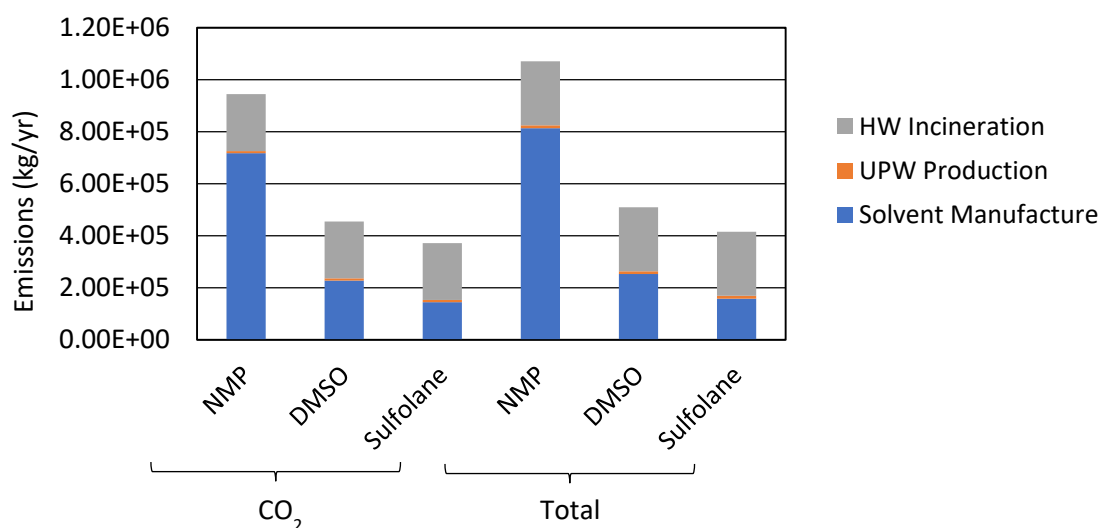


Fig. 1. The annual life cycle emissions for the current process using each solvent.

B. Current Processes Solvent Substitution and Recovery

Through solvent substitution alone, total process emissions were reduced by 61%. The environmental impact

of the process was decreased; however, a high volume of solvent was used in each case. Solvent recovery designs have been completed to further increase the green

implications of the process. In each case, the solvent recovery process was distillation. Table II shows that no solvent generates an azeotrope with water, thus distillation can give an effective separation. Table II also shows that NMP and DMSO have decomposition temperatures above their boiling points; however, the decomposition temperature of sulfolane is below its boiling point. Therefore, a vacuum distillation process is needed for the recovery of sulfolane.

The LCIs of nonhazardous waste disposal (1 kg basis) and steam and electricity (1 MJ basis) are required for the utilities of the distillation processes and are shown in Table IV. The distillation process recovers enough solvent such that waste from the process is considered nonhazardous. The total life cycle emissions of the process are calculated with (2).

$$LCE_r = (\dot{m}_{\text{solvent}} - \dot{r}_{\text{solvent}})LCI_{\text{solvent}} + \dot{m}_{\text{UPW}}LCI_{\text{UPW}} + \dot{m}_{\text{NHW}}LCI_{\text{NHW}} + S \cdot LCI_S + E \cdot LCI_E \quad (2)$$

where LCE_r is the total of a given emission for the process with solvent recovery. The mass of recovered solvent (\dot{r}_{solvent}) is removed from the LCE calculations as the solvent is reused. The mass flowrate of nonhazardous wastewater (NHW) and the energy requirement from steam (S) and electricity (E), as well as their respective LCIs are also included. Steam is required for the reboiler and electricity is required for the condenser and feed and reflux pumps. Electricity is also required for the vacuum pump for sulfolane recovery by vacuum distillation.

TABLE IV. LCIs FOR THE DISPOSAL OF NONHAZARDOUS WASTE AND THE GENERATION OF STEAM AND ELECTRICITY

	NHW	Steam	Electricity
Water Used (kg)	-8.96E-01	1.20E-03	1.61E+01
Total Air Emissions (kg)	2.77E-02	6.71E-02	9.75E-02
CO ₂ (kg)	2.75E-02	6.67E-02	9.57E-02
CO (kg)	2.27E-06	2.39E-05	6.49E-05
CH ₄ (kg)	2.43E-05	1.06E-04	4.58E-04
NO _x (kg)	5.74E-05	4.48E-05	8.57E-05
NM VOC (kg)	7.64E-07	5.67E-07	2.96E-05
Particulate (kg)	7.55E-07	8.03E-07	3.25E-05
SO ₂ (kg)	2.76E-05	2.31E-05	8.07E-04
Total Water Emissions (kg)	3.59E-04	3.23E-04	1.35E-02
VOCs (kg)	8.88E-11	3.62E-09	4.85E-08
Total Soil Emissions (kg)	3.04E-07	2.78E-06	1.75E-06
Total Emissions (kg)	2.80E-02	6.71E-02	1.11E-01
CED (MJ)	1.72E-01	1.19E+00	3.88E+00

The annual life cycle emissions for the processes solvent recovery are shown in Fig. 2. It can be seen that regardless of solvent, all processes with recovery have similar annual life cycle emissions. When compared to their respective processes without distillation for recovery, total emissions are reduced by 63%, 21%, and 3% when processing with NMP, DMSO, and sulfolane respectively. Solvent manufacture contributes a negligible amount to the total life cycle emissions, while the majority for processes with each solvent are dominated by steam generation for distillation. However, when comparing the original environmental

impact associated with NMP and no recovery to the case with recovery, it can be seen that the overall impact of the process with recovery is reduced greater or equal to the cases with solvent substitution and no recovery. Furthermore, there is no significant difference among NMP, DMSO, and sulfolane when comparing the cases with solvent recovery in terms of life cycle emissions. Solvent substitution may appear to have green implications on a process; however, it is important to conduct a life cycle assessment to understand the environmental impact of all potential green processing methods.

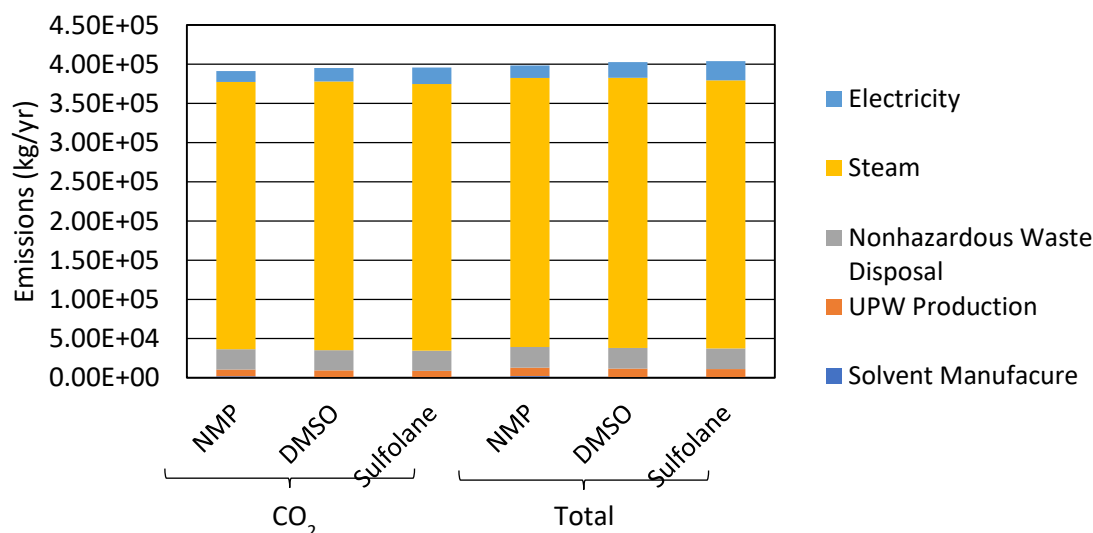


Fig. 2. The annual life cycle emissions for each solvent when distillation is used for solvent recovery.

IV. CONCLUSIONS

A life cycle assessment was used to understand the green implications of substituting a harmful organic solvent, NMP, with a less harmful alternative, DMSO or sulfolane. Potential solvent substitutes were selected with assistance of a solvent selection guide, and final options were chosen based on their reduced impact on human health and similar physical properties to NMP. In addition, distillation processes were evaluated to consider the green engineering practice of solvent recovery. By substituting DMSO or sulfolane for NMP in the DuPont resin precursor process, it was found that total life cycle emissions could be reduced by 52% and 61%, respectively. When applying solvent recovery by distillation, the total life cycle emissions of the current process using NMP were reduced by 63%. The cases with DMSO and sulfolane only saw further reductions of 21% and 3% when compared to their respective cases with no recovery. Among the cases for NMP, DMSO, and sulfolane with solvent recovery, there is no significant difference when comparing the life cycle emissions. It was revealed that the impacts associated with energy use in solvent recovery are less detrimental than solvent replacement. Thus, the importance of a life cycle assessment can be observed when considering the application of a green engineering practice for a new or existing operation.

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