

Evaluation of Solvent Recovery Options for Economic Feasibility through a Superstructure-Based Optimization Framework

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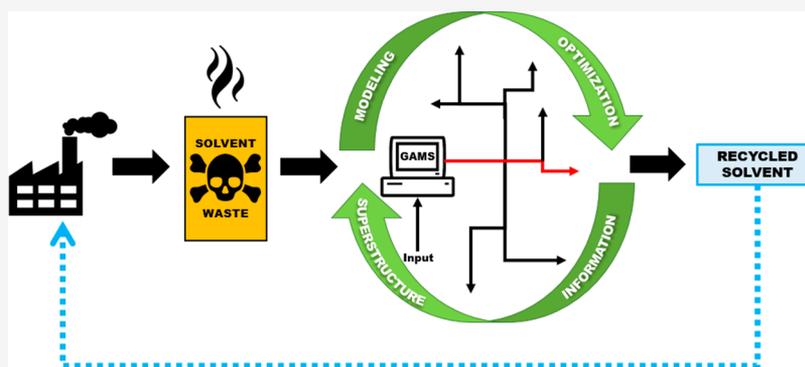
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ABSTRACT: As the chemical market continues to expand, environmental concerns have increased due to excessive disposal of organic solvents. To date, there is no comprehensive mitigation plan to completely handle such a volume of solvent waste generated annually by the chemicals sector. These organic solvents can account for up to 90% of the process by mass and are often discarded after a single use. Incineration, the most widely used process for solvent disposal, is not a green method because of the release of harmful pollutants and greenhouse gases to the environment. A systematic framework for solvent recovery has been developed to overcome the drawbacks of the existing disposal methods. This framework uses a superstructure-based approach that considers the simultaneous comparison of multiple separation technologies for solvent recovery. The viability of this framework was tested using two representative case studies of varying complexities. These case studies were analyzed and formulated as mixed-integer nonlinear programming optimization problems. In both cases, solvent recovery is an economically favorable choice to conventional incineration. Herein, we demonstrate the capability of our solvent recovery framework to obtain economically viable solvent recovery pathways.

1. INTRODUCTION

In 2017, the chemical industry was the world's second-largest manufacturing industry and is projected to double between 2017 and 2030.¹ However, waste generation and emission from poor solvent selection and processing inefficiencies in the chemical industry have led to a growing concern for chemical releases, exposures, environmental impacts, and health safety.¹ The United States Environmental Protection Agency (US EPA) has estimated that solvent emissions resulting from the chemical market growth can reach up to 10 million metric tons of carbon dioxide equivalent, which accounts for up to 62% of the total emission in 2017.² This amount of chemical emission will lead to a substantial increase in the Global Warming Potentials (GWP), a metric developed to measure the amount of energy that emissions can absorb for a given period.³ The pharmaceutical industry, for instance, relies heavily on solvents in both the synthesis of API (active pharmaceutical ingredient) and the dilution of API for ease of processing. Organic solvent use can account for as much as 90% of the process by mass and often disposed of after one cycle because of purity concerns,

which is not a sustainable practice.^{4–7} A large quantity of solvent waste and emission can occur as a result. These events are caused by inefficient mixing, synthesis pathways, insufficient reaction time, inappropriate technologies, quality of raw materials, inaccurate measurements, and control anomalies.^{4,8} As a response to the growing concern for chemical waste and environmental impacts, the global environmental initiative has given rise to legislation and policies put forth by regulatory agencies from around the world.^{1,9–13} Additional work is in progress by several researchers to address environmental management,^{14,15} sustainability indicators,^{16–19} controllability,^{20,21} and multi-

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stakeholder decision-making²² for the greater benefit of society, thus supporting the global environmental initiative and the United Nations Sustainable Development Goals of responsible consumption and production as well as climate action.^{23,24} This study proposes an optimization framework to address the economic challenges in implementing waste recovery in chemical processes.

One term commonly used by industry is known as the E-factor, which is a way to quantify the amount of waste (nonwater) produced per unit product, shown by Equation 1.²⁵

$$\text{E-factor} = \frac{\text{Total mass of Waste Produced}}{\text{Total mass of Products Produced}} \quad (1)$$

A low E-factor represents a minimal waste produced by a given process. Table 1 presents the typical E-factors for various

Table 1. Generic E-Factors in Major Chemical Industries^{25,26}

industry	tons of product/year	E-factor
oil refining	10 ⁶ –10 ⁸	<0.1
bulk chemicals	10 ⁴ –10 ⁶	<1–5
fine chemicals	10 ² –10 ⁴	5–50
pharmaceuticals	10–10 ³	25–100

industries. The pharmaceutical industry uses many organic solvents for the production of active pharmaceutical ingredients. The amount of waste corresponds to the multistep reactions, separations, and purifications steps involved. In addition to the purity requirements and solvent-intensive nature of the processes used, the pharmaceutical industry's E-factor remained the highest among the major sectors in the chemical industry. Since 2007, the reported overall E-factor from the four major industries remains unchanged.²⁶ This fact suggested that material recovery practices in the chemical industry are not implemented regularly to create a considerable change in these E-factor values. With the expansion of the chemical market, a better waste recovery method is needed to reduce these values.

There are several options to handle solvent wastes. One possibility is on-site solvent disposal, which consists of direct release into air and water or injection into the ground via injection wells below the lowest available source of drinking water.^{27,28} When disposing solvent vapor into the air, industrial scrubbers are used to reduce pollution. Regulations have forced industries to control the allowable concentration of emissions. Conversely, off-site solvent disposal involves using a third party to handle the waste. Solvents are typically not reused in the pharmaceutical industry because of purity concerns. Instead, the used solvents are sold to sectors with less stringent regulations or fuel blending operations.⁸ For disposal of wastes, either on-site or off-site incineration can be used. This method is proven to thermally decompose the volatile organic compounds (VOC) with efficiencies up to 99.99% and recover energy, but a constant feed flow is required to achieve complete combustion and maintain efficiency.^{29–31} Although incineration is the most widely used solvent disposal process, it is not considered a "green" method as it can release harmful chemicals such as acidic gases, particulates, and other pollutants into the atmosphere.^{13,32} Some consequences of these releases include human exposure to carcinogens, adverse effects on respiratory health, and contaminations of dioxins

and heavy metals in the food chain.³³ Incineration is known to produce approximately 6.7 kg CO₂/kg organic carbon, which along with other solvent disposal methods, contributes negatively toward the emission statistics and consequently increases environmental risks and concerns.^{33,34} Recovery methods are being considered to improve the greenness and overall sustainability of processes in the pharmaceutical and fine chemical industries.¹³ Multiple unique greenness analysis methods were developed in the past decade^{35–40} to identify economic, environmental, and process efficiency indicators. Although these methods can eventually lead to sustainability and improve process efficiency and cost, there has not been an integrated method that accounts for factors concerning the environment,^{13,41} safety, and economics.^{42–45} Nationwide data from the US EPA's Toxic Release Inventory (TRI) database were analyzed for the years 2007–2017 to observe the cumulative solvent waste from the past decade from solvent-consuming industries.⁴⁶ As shown in Figure 1, the general

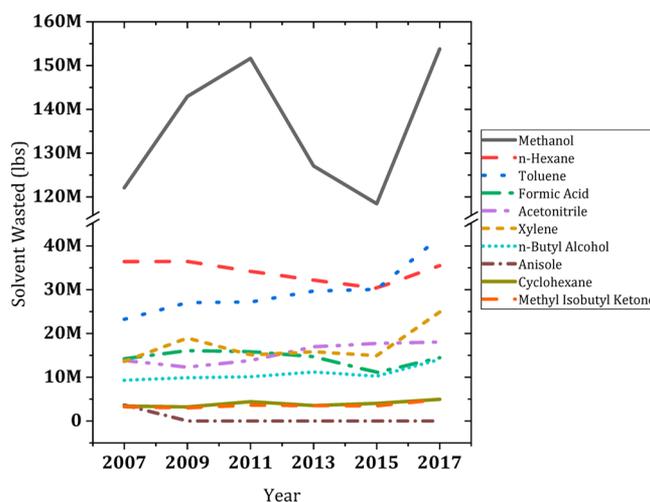


Figure 1. Top 10 US EPA TRI waste solvents in the United States between 2007 and 2017. In the beginning of 2015, the US EPA has published a revision for solvent waste recycling under Subtitle C of the Resource Conservation and Recovery Act (RCRA), which redefines the hazardous waste by allowing exclusion from the RCRA regulation as long as chemical wastes are sent to an RCRA facility or verified recycler of hazardous waste.⁴⁷ This act provides strong encouragement for solvent recovery. However, the chemical waste trend following 2015 continues to rise despite the revision because there is a higher quantity of solvent waste generated from the increasing chemical demand.

chemical waste trend for the top 10 most wasted solvents has been relatively consistent with minor fluctuations between values. The TRI database only reports solvent wastes that are considered detrimental to the environment and human health, so it excludes more benign solvents such as acetone and ethanol.

The rising trend is expected to raise the global toxic chemical waste and emission simultaneously. The motivation to practice sustainable solvent waste handling can be increased by examining economic factors such as the cost of fresh feed and incineration. For example, the purchase cost of 45 million kg of methanol is \$124.7 million, while the cost of disposal via incineration is \$47.3 million.³⁴ Hence, incineration can account for one-third of the original price of purchase. Although incineration can recover energy, the emissions

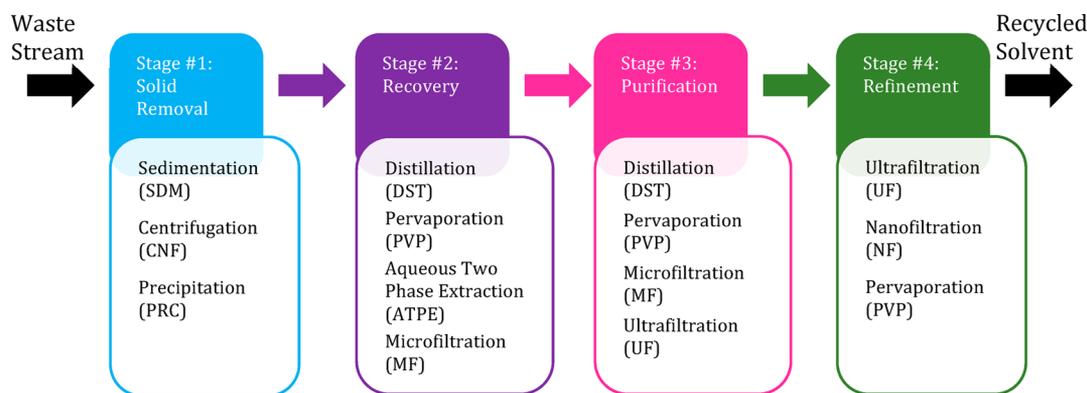


Figure 2. General steps for recovery and purification of solvents.

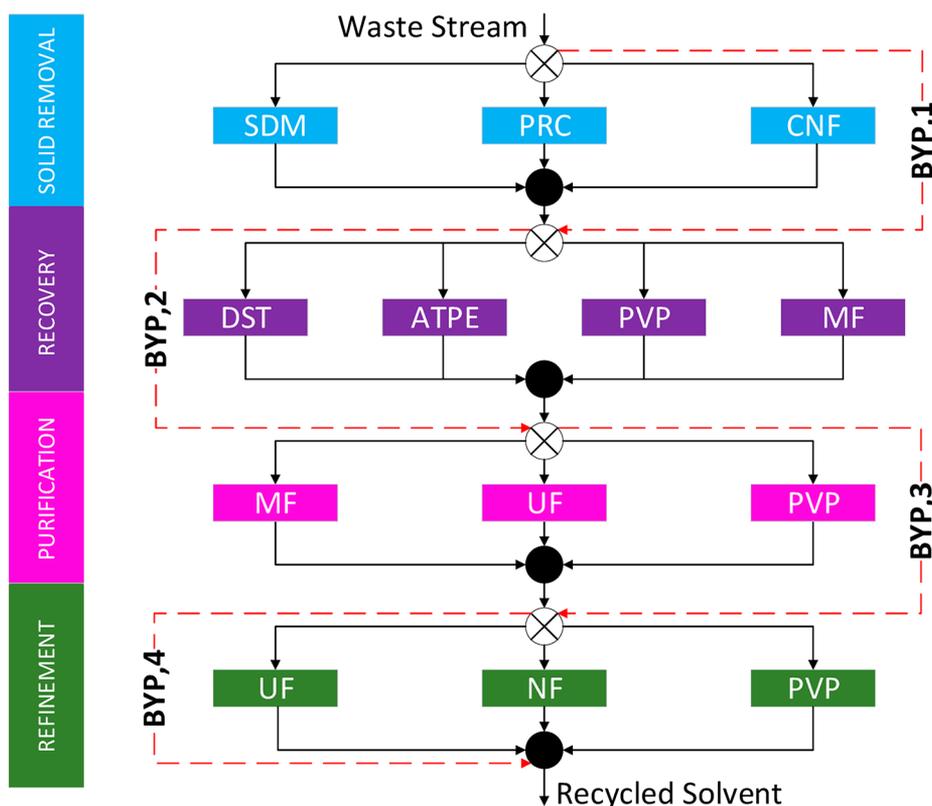


Figure 3. Generic solvent recovery superstructure containing multiple technology options. The acronyms SDM, PRC, CNF, DST, ATPE, PVP, MF, UF, and NF represent gravity sedimentation, precipitation, distillation, aqueous two-phase extraction, pervaporation, microfiltration, ultrafiltration, and nanofiltration, respectively. Bypass (BYP) streams are used if a given stage is not applicable or the desired purification is met.

cannot be controlled and are subsequently released into the environment.⁴⁸

Optimization has always been an integral part of the design of any process, yet it is one of the most time-consuming steps because a large amount of information collection and analysis are required for each process pathway. One-by-one analysis of these pathways is often infeasible within the design time frame. A practical solvent recovery framework will help aid in designing sustainable processes by recycling materials, reducing emissions, and enhancing the economics of chemical processes.^{49–52} The framework proposed in this study is applicable to a multitude of solvent-utilizing industries because it starts from the very basics such as the physical properties of the components involved, driving forces of the recovery, and purification technologies, then extends to broader metrics such

as process economics and environmental impacts. Although solvent recovery is a multistakeholder problem, this study focuses primarily on enhancing solvent recovery from an economic standpoint.

2. MATERIALS AND METHODS

2.1. Designing a Framework for Process Evaluation.

As an initial step in designing the solvent recovery framework, we collected information on common solvents properties, separation technologies, and their corresponding driving force, material, and energy requirements. Commonly used separation technologies such as sedimentation, decantation, distillation, aqueous two-phase extraction, pervaporation, and nanofiltration were considered and applied to case-specific solvent recovery challenges for economic and environmental impact

analysis.^{53,54} These results were compared to the waste stream incineration model to demonstrate the feasibility of solvent recovery from both economic and environmental standpoints. All separation technologies were modeled according to mathematical equations found in typical engineering textbooks and research articles.^{42–44,55–63}

2.2. Annualized Cost Evaluation. The analysis of each separation technology was divided into material and energy balances, design, constraints, capital cost, and operating cost.^{55,64} Capital cost was evaluated with a Capital Recovery Factor (CRF) of 0.11. This value was used to account for cost annualization, assuming a plant life of 25 years. Operating cost encompasses five major categories: materials, utilities, labor, consumables, and overhead cost. The materials cost included any raw materials added to the process, which may consist of added chemicals required for the solvent recovery. The utility cost included the electricity, steam, or cooling water needed. The labor cost for a continuous process was calculated for a 330 day work year at a rate of \$30/hour. The consumables cost accounts for materials that can be depleted, degraded, or require periodic replacement. The overhead cost is due to project management. All equations, parameters, and constraints for each technology were implemented in the General Algebraic Modeling System (GAMS) version 30.2.0 and modeled separately as nonlinear programming (NLP) problems, where cost minimization is the objective.^{65,66} The [Supporting Information](#) contains all equations used for relevant technologies in this study.

2.3. Constructing an Optimization Model. Designing a solvent recovery process is a complex task because multiple stages of separation are required, with several technologies being applicable at each stage. [Figure 2](#) depicts this complexity in decision-making. The solvent recovery process typically goes as follows: solid removal, recovery, purification, and refinement. The solid removal stage is designed to remove solid particles that may be present in the waste stream. Dissolved solid impurities present in the original waste stream may be removed through precipitation. The recovery stage contains separation technologies to recover the majority of the solvents in the waste stream. The purification stage utilizes technology similar to that of the recovery stage, but the majority of the impurities associated with the original waste stream have been eliminated from the recovery stage. Solvents with higher purity are anticipated. A refinement stage may be used to further meet the standards set forth by the user. The selection of solvent recovery technology is dependent on factors such as process efficiency, chemical waste characteristics, capital and operating cost, and environmental impacts. If a solvent recovery process is unable to achieve the desired specification and operates at a cost that significantly exceeds the price of disposal, then incineration may be employed to eliminate the waste stream and recover some energy at the expense of emission. However, based on the disadvantages discussed previously, the selection of incineration as a waste processing method is unlikely.

A superstructure optimization approach was used to develop the framework for solvent recovery, which identifies and considers alternative options at any stage of a given process rather than through one direct pathway.^{42–45,65,67,68} [Figure 3](#) illustrates a proposed solvent recovery superstructure. For solvent recovery, this method begins with waste stream specification and desired purity. Chemical waste streams are unique and do not necessarily have to adhere to the

technologies listed. In some cases, solid particles are present in the waste stream. This scenario will require a solid removal stage that may consider technology options such as gravity sedimentation, decantation, centrifugation, or precipitation to remove the solids or dissolved solids. The first stage of recovery may include technologies such as distillation, pervaporation, aqueous two-phase extraction, and microfiltration. Additional recovery stages can be used to separate other components present within the waste stream. The purification stage may consider distillation, pervaporation, microfiltration, and ultrafiltration. In all major steps, a bypass may be used if the technology options are not applicable to reach the desired purity.

We combined the NLP technology models in GAMS as Mixed-Integer Nonlinear Programming (MINLP) problems and assessed the optimal solvent recovery path from the solvent recovery superstructure. MINLP is an optimization approach that uses a series of linear and nonlinear equations and continuous and integer (binary) variables.^{65,69} The linear and nonlinear equations consist of material and energy balance, design equations that are specific to a given technology, and constraints. The developed mathematical models for each technology are in the supporting document. Binary variables are represented as either active (1) or inactive (0). In the case of using an MINLP approach to select a process path, the chosen technology is assigned an “active” status and a value of “1”. Technologies that are less economically favorable in the optimization problem are given an “inactive” status and a value of “0”. The use of binary variables can help illustrate whether a specific technology from a case-specific superstructure is selected once optimality is reached. This optimal condition is determined by an objective function, which mathematically describes the desired goals (minimize cost, maximize solvent recovery, and reduce waste). Therefore, solvent recovery is inherently a multistakeholder problem. The solution to the MINLP was determined through the Branch-And-Reduce Optimization Navigator (BARON), a global optimization solver that uses a branch-and-reduce algorithm, which analyzes upper and lower bounds associated with each pathway and converges on a solution.^{70–72} The combined modeling, multistakeholder formulation, and superstructure optimization approach will allow the system to choose one optimal path out of many, rather than restricting the evaluation to a single separation and recovery pathway, as observed in most simulation packages.

2.4. Modeling Selective Superstructure for Case-Studies Evaluation. The viability of the generalized solvent recovery superstructure, as shown in [Figure 3](#), was determined through case studies of waste accumulation in the major sector in the chemical industry. We fully defined the flow rate and physical properties of the waste stream components before applying the solvent recovery framework. On the basis of the relevance of the separation technology to the physical properties of the components, we reduced the size of the superstructure and adjusted the technology stages accordingly. For example, if there is no solid or dissolved solid present in the original waste stream, the solid removal stage is not considered. The reduced case-specific superstructure was then modeled in GAMS using equations from the [Supporting Information](#). In GAMS, we first defined “sets,” which contain relevant separation technology assignments, stream numbers, and components. The necessary parameters, colored in red text in the [Supporting Information](#), were specified according to

property estimations and thermodynamics data. All relevant variables for cost estimation, technology design, and logical statements were defined. The specified parameters and defined variables were inputted into the design and cost equations. The binary variables were implemented as logical equations shown in eq 2.

$$\sum y_j = 1, \forall y_j \in \{0, 1\}, j \in \{1, 2, 3, .0.\} \quad (2)$$

The binary variable “ y ” represents the selection of a specific pathway in a superstructure. The subscript “ j ” refers to the stream number. The GAMS codes for the case studies are available in the [Supporting Information](#).

2.5. Technologies for Solvent Recovery. The basis of this section is to provide insight into different technologies that were modeled as a part of the case studies presented in Section 3.

2.5.1. Solid Removal. Gravity sedimentation (SDM) allows partial separation of solids suspended in liquid to settle by gravity. Sedimentation is affected by the solid particle size, liquid viscosity, solution density, and particle characteristics. At a higher concentration of solids, particles may collide with each other and combine (floculate), effectively enhancing the rate of sedimentation.⁷³ At a low concentration of solids, solid particles are generally too far apart to settle at a constant rate.⁵⁷

Decantation (DCT) operates on an idea similar to gravity sedimentation, but the terminology is applicable for liquid–liquid separation. For a feed stream containing a dispersion of immiscible fluids at different density, a decanter acts as a tank to give sufficient time for the immiscible fluids to either settle or rise to their respective phases. As the fluid travels through the decanter, three layers can be observed: clear dense liquid at the bottom phase, a dispersion of two immiscible fluids in the middle phase, and clear light liquid at the top phase. Decantation can be carried out as either continuous or batch operation.⁶¹

Centrifugation (CNF) is a form of forced sedimentation that subjects materials (liquids or solids) of different density to centrifugal force. This operation can be carried out continuously and have a short retention time, which means that heavier material will settle relatively fast and consequently leave the centrifugation unit within a matter of seconds.⁵⁷ Centrifugation is chosen when gravity sedimentation is not sufficient, meaning that the density difference between the substances of interest is as low as 100 kg/m^3 ,^{61,74,75} which is close to the point of neutral buoyancy. When a particle is neutrally buoyant in the liquid, it remains stationary within a given space until a force is applied to the particle. The disadvantage of centrifugation relates to the amount of power required to force particle sedimentation. If the density difference between the substances of interest is high, then simple gravity sedimentation or decantation is preferred due to the low energy requirement.

Precipitation (PRC) is typically used as an initial purification step used to remove the product, impurities, and contaminations through the addition of solvents, salts, or polymer, modification of temperature, or adjustment of pH. This event occurs as a result of a shift in phase equilibrium. In antisolvent precipitation, a solvent is added to a liquid mixture containing the dissolved substance. The dissolved material within a liquid mixture can precipitate if its solubility within the new liquid mixture is low. Ideally, the dissolved material should not be miscible with the antisolvent, while the

antisolvent should be highly miscible with the original mixture. A similar mechanism is observed when salt is added. The precipitates (solids) obtained at the end of this process are usually fine powders that are difficult to filter. Therefore, centrifugation is used to remove the precipitate from liquid.^{57,76} The antisolvent, depending on thermodynamics properties, used can be recovered by means of other liquid–liquid separation such as distillation or membrane.

2.5.2. High-Temperature Separation. Distillation (DST) is a technique that separates chemical compounds based on relative volatility at a given temperature and pressure. Multicomponent separation is possible, with the volatile substances as the light key and less volatile substances as the heavy key. A distillation column may include either random packing, structured packing, or trays stacked above one another in an enclosed cylindrical shell to facilitate intimate contact between vapor and liquid phases. A typical distillation operation employs counter-current contact of vapor and liquid streams. The feed stream is first sent into the column at a specified point. At steady-state operation, the liquid content travels downward from the condenser through the packing or trays, while vapor flows upward through the liquid phase. The liquid content that reaches the bottom of the distillation column is partially vaporized in a reboiler, while the remaining liquid (the phase rich in heavy key) is removed from the distillation unit as the bottom product. This partial reboiler provides one of the major driving forces that separate light key from the heavy key in a distillation operation. The vapor content derived from the partial reboiler travels through the falling liquid and into a condenser, which converts vapor into liquid (phase rich in light key). Depending on the chosen reflux ratio, some of the condensed liquid is sent back into the column (reflux) to provide liquid overflow, while the remainder is recovered as the top product (distillate) that mostly contains light key components.^{57,66,77,78}

2.5.3. Membrane Processes. Membrane processes are a separation technique that relies on semipermeable material with a pressure driving force from the feed stream to perform the desired component separation. The materials that diffuse through a porous membrane exit as permeate, and the remainder exit the membrane unit as the retentate. The permeate stream contains materials that have been allowed to flow through the membrane freely, while the retentate stream flows through the unit and becomes more concentrated with the rejected component.⁵⁷ Diffusion is the leading factor in molecular transport through a porous membrane, and this means that the size of the material of interest will greatly affect its permeability through the membrane.^{56,79} The membrane process selected, such as **microfiltration (MF)**, **ultrafiltration (UF)**, and **nanofiltration (NF)**, is determined by the particle, molecular size, charge, and physicochemical state of the material of interest.^{56,58,80,81} The nominal pore sizes of the membranes are as follows: microfiltration (0.1–10 μm), ultrafiltration (10–100 nm), and nanofiltration (1–10 nm).⁸² Despite the differences in the names, the inherent nature of these separations is the same, in that they each require some external pressure to drive the permeate stream through a semipermeable membrane that is selective to specific particle sizes. However, the separation mechanism for nanofiltration is also dependent on the membrane structure and its interaction with the molecules.⁸³ Depending on the nature of the process, the efficiency of membrane separation is

Table 2. List of Separation Technologies for Solvent Recovery, the Main Driving Forces, and Important Specifications

technology	principle/driving force	specifications and important conditions	literature sources
Physical Separation			
precipitation (PRC)	charge solubility	antisolvent availability and requirements, temperature, pH change	57,76
sedimentation (SDM) or decantation (DCT)	density gradient, settling velocity	size, density, tank depth, residence time	57,92
centrifugation (CNF)	settling velocity centrifugal force	size, density, angular speed, the ratio of centrifugal to gravitational force and settling distance	57,74,93
High-Temperature Separation			
distillation (DST)	relative volatility	relative volatility >1.05 heat of vaporization and energy requirements	57,61,77,78
Membrane Processes			
membranes	particle/molecular size/permeability, sorption/diffusion pressure	pore size, mol. wt. cutoff, average flux, pressure gradient, types of membranes – MF, UF, NF, and RO	57, 58, 80, 81
pervaporation (PVP)	sorption/diffusion, partial pressure	heat of vaporization, chemical potential gradient, pressure gradient, average flux, membrane selectivity	57, 94, 95
Liquid–Liquid Extraction			
liquid–liquid extraction (LLE)	selective partitioning of solutes	partition coefficient, the solubility of solutes, low solubility of the added solvent in water	57, 60, 61, 92, 96, 97
aqueous two-phase extraction (ATPE)	partitioning of solute, bioselectivity	solubility, composition of two phases, molecular weight	63, 86–88, 98

characterized by flux, solute rejection, recovery, or permselectivity of the solute.^{57,83}

Pervaporation (PVP), one of the major membrane processes, is used to separate liquid mixture through contact with a nonporous permselective membrane. Unlike MF, UF, and NF, this separation technology typically requires preheating the feed mixture to aid in the effective separation of the desired component. By lowering the permeate partial pressure through either vacuum or sweep gas, the permeate solubilizes in the membrane, then diffuses through the membrane and evaporates upon exit. This permeate gas becomes a liquid through a condenser. Unlike distillation, this rate-driven process can resolve azeotropes like a system of ethanol and water through a hydrophilic membrane. The term “hydrophilic membrane” refers to a system that has a strong affinity for water. This type of membrane is selected to remove water from the organic phase. The opposite, a “hydrophobic membrane”, has a stronger affinity for organic compounds and hence is used to remove organic compounds from water.⁵⁷

2.5.4. Liquid–Liquid Extraction. Liquid–liquid extraction (LLE) typically employs an extraction technique that removes desired components or dissolved impurities from a liquid phase by contact with a second immiscible liquid phase. The feed stream enters the extraction unit and comes in contact with a fresh solvent stream. The component of interest within the feed stream solubilizes into the solvent phase and exits as the extract. The remainder of the feed stream exits the extraction unit as the raffinate. The selected liquid phases for extraction contrast each other through polarity. For instance, an organic liquid stream (nonpolar) may contain impurities that are more soluble in aqueous conditions (polar). LLE can be used by washing the organic liquid stream with water. Subsequently, decantation, which is the physical separation of the solvent-rich phase (extract) and the water-rich phase (raffinate), is employed according to density difference.^{57,61} The partition and selectivity coefficients determine the efficiency of an LLE process. The partition coefficient is the ratio of the chemical of interest in both phases, while the selectivity coefficient is the ratio of the partition coefficient of two chemical species. The high selectivity coefficient corresponds to an easier separation.⁶¹ LLE has been applied

to the processing of petrochemicals, biomolecules, wastewater, coal and wood-derived chemicals, pharmaceuticals, food, and agricultural products.⁵⁷ In comparison to distillation, LLE is generally a cheaper approach to separation, as long as the desired result can be accomplished with low energy consumption and that the relative volatility of the two components is less than 1.05.⁶¹ Relative volatility describes the ease of separation between two liquids. The relative volatility of 1 suggests that component 1 has the same vapor pressure as component 2; thus, separation through distillation is not possible at the given temperature and pressure.

Aqueous two-phase extraction (ATPE) is a type of liquid–liquid extraction that can be applied to the separation and recovery of biomolecules, such as proteins, to prevent denaturation.⁸⁴ ATPE system typically consists of liquid polymers, salts, low molecular weight alcohols, surfactants, and ionic liquids.^{63,85–87} This method relies on the molecular weight, miscibility of each component, and the concentration of hydrocarbon and inorganic salt added. ATPE can handle high liquid capacity, be low in cost and processing time, and achieve the desired purification and concentration specification without additional step.⁸⁸ Besides the specified difference in configuration between ATPE and LLE, the driving force behind the separation remains similar. However, in a polymer–salt or a polymer–polymer system, the partition coefficient can be modified based on hydrophobicity, pH, and temperature of the system^{63,84,87} and for biological molecules, the partition coefficient can be as high as 30–45.^{89,90}

2.5.5. Waste Disposal. Incineration (INCIN) is a process employed to eliminate waste through combustion reaction, typically to recover energy. A waste stream enters the incinerator along with air and fuel gas. Other incinerators may utilize steam. A chemical reaction takes place, driven by elevated temperatures, to convert waste to gaseous products. These products exit the incinerator along with ash/residues. The heat produced from these products may be used for steam production. This technology can be used for a variety of waste disposal needs, such as solvents, plastics, and municipal wastes. The major disadvantages of this method are the environmental concerns. Emissions from incineration may be toxic and are often regulated by government agencies. It also eliminates the

opportunity to recycle and reuse materials, adding to the environmental impact. The biggest advantage is the opportunity for energy recovery for another process.^{31,32,48,91} The driving forces and crucial specifications required for each of the technologies are summarized in Table 2. Detailed equations and parameters specified are available in the Supporting Information.

3. RESULTS AND DISCUSSIONS

Despite the existing efforts to encourage sustainable solvent waste management, the rapid expansion of the chemical market caused the total amount of chemical waste to increase and exceed the reported waste values from the years 2007–2017.^{46,47} One possible mitigation plan requires the strategic implementation of solvent recovery in all chemical processes. Separation technologies were represented as mathematical models and compared simultaneously against incineration through a systematic superstructure-based optimization problem and case analyses of solvent waste issues in a range of chemical industries. Our results demonstrated that implementing solvent recovery is more economically viable than incinerating chemical wastes (see Tables 3 and 4). However, the cost of implementing recovery processes remained a more costly approach than purchasing fresh solvent in most instances. These results demonstrated the importance of the trade-offs between process economics, environmental impacts, resource recovery, and reuse.

Table 3. Optimization Results from GAMS for Recovering IPA from a Binary Mixture of IPA and Water from Case Study 1

solvent recovery pathways	annualized cost (millions \$/year)	prices (\$/kg IPA processed)
ATPE–UF1–SDM	0.452 ^a	0.12 ^a
PVP1–UF2	0.524	0.14
DST–PVP2	0.862	0.25
incineration	8.10	2.01

^aThis solution was obtained through a relaxed purity constraint (60% purity with 90% IPA recovery requirements). This solution failed to converge at the specified purity constraint of 99.5%

Table 4. Feasible Optimization Results from GAMS for the Recovery of DME in Case Study 2

solvent recovery pathways	annualized cost (millions \$/year)	prices (\$/kg processed)
FLT–PVP–UF	0.330	4.13
SDM–PVP–UF	0.329	4.12
CNF–PVP–UF	0.330	4.12
incineration	14.6	108.18

3.1. Case Study 1: Pharmaceutical Waste Stream. In our previous work, we have examined a case of isopropanol (IPA) recovery from the celecoxib waste stream.⁹⁹ The celecoxib process produces the API for an arthritic medication known as Celebrex.³⁴ As the study was published in 2012, the process chemistry, flows, and concentrations have since changed. However, for modeling solvent recovery, this case study serves as a classic representative case for the recovery of solvents from a pharmaceutical waste stream because centrifugation and drying are two of the most common pharmaceutical purifications steps following a multi-stage synthesis process. Figure 4 displays the celecoxib synthesis

and purification diagram. Although this pharmaceutical process possesses a relatively low E-factor of 9.0, life cycle analysis (LCA) has determined that there is 2.19 kg total emissions/kg IPA used. These emissions include both air (1.65 kg total/kg IPA produced) and water (0.538 kg total/kg IPA produced). Air emission consists of 98.8% carbon dioxide, with the remainder being carbon monoxide, methane, nitric oxide, sulfur dioxide, and other particulates. Water emission consists of organic compounds and inorganic salts.

3.1.1. Process Conditions. The celecoxib synthesis process emits three separate waste streams containing (i) IPA/water washes, (ii) mother liquor (filtrate), and (iii) dryer distillates. A simplified solvent recovery optimization was performed around the dryer distillate waste, where minor impurities were neglected. Azeotropic points are anticipated at 87.7 wt % and 80.37 °C, which means that separation solely through distillation will not be able to achieve the desired purity.¹⁰⁰ Before modeling the IPA recovery case study, we assumed a waste stream feed basis of 1000 kg/h, where IPA is 51% by weight and the rest is water. Impurities were excluded to simplify the preliminary analysis. If the impurity is present within the original waste stream, then an additional stage of purification is required. The purification technology selection is dependent on the physical property of the impurity. If there are dissolved solids present, then precipitation may be used. In the case of the dryer distillates, the impurities are methanol and ethanol. Both of the components do form an azeotrope with water. Once the organic is fully separated from water, then a membrane process can be used to remove methanol and ethanol from the organic mixture containing isopropyl alcohol, ethanol, and methanol. The targeted IPA recovery and water purity were set to 99.5% IPA and 99% water, respectively.

Figure 5 illustrates a proposed selective superstructure for the recovery of IPA from a binary mixture of IPA/water. We excluded the solid removal stage from the final superstructure because solid impurity is not present. The recovery of IPA from the dryer distillate waste stream is attainable through 3 separate pathways containing 5 unique processing units and 23 streams. Aqueous two-phase extraction, pervaporation, and distillation were considered as part of the recovery stage, followed by additional separation technologies for further purification. The flow of the waste stream through the superstructure is handled through logical constraint equations consisting of binary variables. Each pathway consists of recovery steps, followed by purification to meet the specified recovery and purity requirements. The first possible recovery path, aqueous two-phase extraction (ATPE), requires the addition of hexane and salt to effectively separate IPA from water, resulting in two separate phases containing IPA/hexane and sodium chloride/water. An ultrafiltration (UF1) operation can be used to separate and recycle hexane from IPA/hexane mixture. The separation of solid salt and water is possible through decantation, which allows salt recycling for reuse in ATPE technology. Water has a higher affinity for the salt, while IPA separates into the hexane layer. The second IPA recovery path utilizes membrane technology such as pervaporation and ultrafiltration, which have relatively low energy requirements. The third method, which is more energy-intensive, uses distillation and pervaporation to reach recovery specifications. For the distillation of an IPA/water mixture, water is the heavy key with a normal boiling point of 100 °C, while IPA is light key with a normal boiling point of 82.5 °C. Pervaporation was

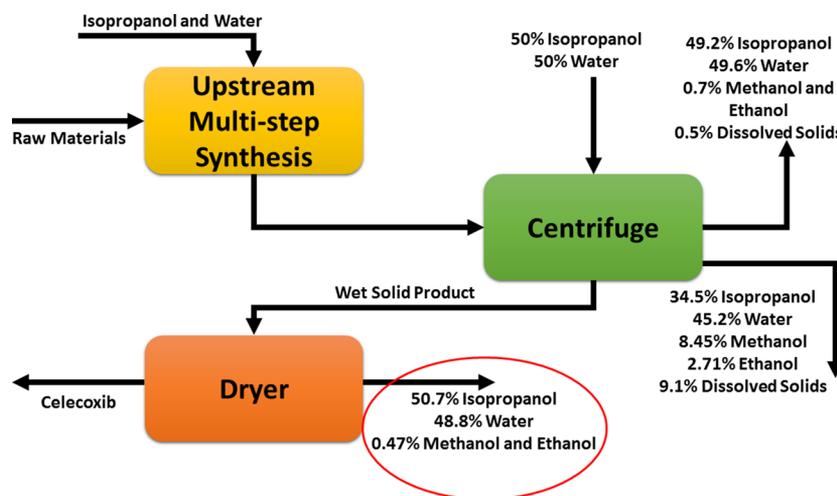


Figure 4. Celecoxib synthesis, purification, and possible waste streams.⁹⁵ The circled stream is used as the entering waste in our recovery superstructure.

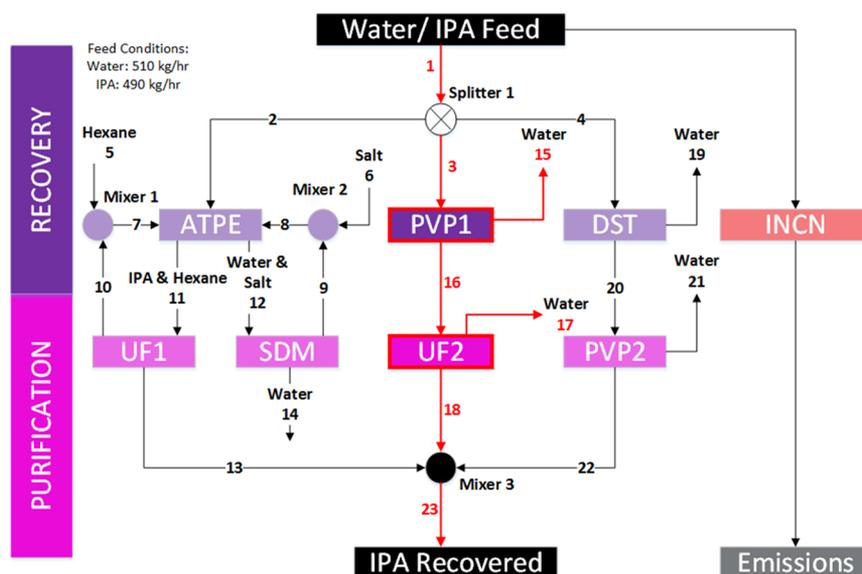


Figure 5. Superstructure of possible solvent recovery methods to separate IPA from a pharmaceutical waste stream containing a mixture of IPA and water. ATPE, UF, SDM, PVP, DST, and INCN represent aqueous two-phase extraction, ultrafiltration, sedimentation, pervaporation, distillation, and incineration, respectively. Recycle streams are also included. The optimal pathway has been selected through GAMS.

implemented to effectively separate the distillate stream since there is an azeotropic point at 87.7 wt % and 80.37 °C.

3.1.2. Analysis. Table 3 presents a result summary of the combined GAMS model and cost comparison of the individual solvent recovery pathways. The pharmaceutical waste stream optimization model consists of 258 equations, 238 variables, and 3 discrete variables. BARON solution converged within 2.48 s with an optimality gap of 1.00×10^{-9} . The optimized solvent recovery pathway is selected as PVP1–UF2, which meets the purity requirement and has the lowest annualized cost of \$524 000 and requires \$0.14/kg solvent recovered. Figure 6 depicts the cost distribution of the optimal pathway. The annualized capital costs, overhead, consumables, labor, and utility contribute 47, 26, 13, 10, and 4% of the total cost, respectively. The ATPE–UF1–SDM pathway was unable to meet the desired recovery and purity requirement; thus, the solution becomes infeasible. However, it is possible to relax the constraint on purity to allow the solution to converge to a

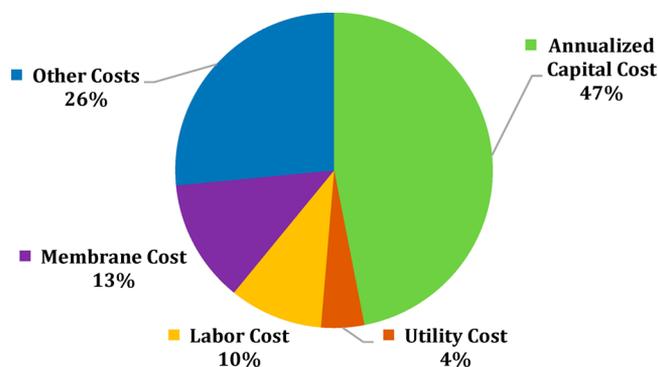


Figure 6. Cost distribution of the optimal solvent recovery pathway (PVP–UF1) for recovering IPA from Case Study 1.

feasible point. In this case, ATPE can only recover up to 90% of the original IPA with 60% purity. The final IPA recovered through the ATPE pathway cannot be reused because low

toluene). Although DME and EME are classified as organic compounds, there are potentials for hydrogen bonds to occur with water because of the oxygen present along the chain.¹⁰⁴ This phenomenon increases the miscibility of DME and EME in the aqueous phase. The use of decantation to separate the aqueous and organic layer will not be valid and thus not considered for this case study. Anhydrous salt, which consists entirely of cation (positively charged ion) and anion (negatively charged ion), is ideal for separating water from an organic layer because of its natural tendency to draw in moisture from the environment to become a hydrated salt. The water molecules present in the waste stream will bind loosely with the salt after a solid–liquid separation step has been applied.

Three possibilities of solid–liquid separation were considered: filtration (FLT), gravity sedimentation (SDM), and centrifugation (CNF). The decision regarding the three choices is dependent on the settling velocity of the salt particles after mixing. For instance, gravity sedimentation will not be feasible if the solid present in a liquid mixture is classified as colloidal particles. Centrifugation, although capable of enhancing sedimentation rate, is impractical in cases where solid particles are considerably denser than the fluid medium. The hydrated salt recovered can be dried to become anhydrous and reused in the solvent recovery process again, since water is loosely held to the salt molecules. Following the removal of the aqueous phase, we considered four unique processing paths for organic separation. Although distillation in a sequence was reported to be successful,⁴⁸ our relative volatility calculation indicated that the relative volatility of DME to EME is 1.06. This number is close to 1.05, which is the minimum recommended relative volatility threshold for distillation.¹⁰⁵ Therefore, the distillation pathway was compared against the less energy-intensive processes such as pervaporation and ultrafiltration and traditional incineration. Following splitter 2, the first recovery pathway utilizes two distillation columns in series. The stream enters the first distillation column at 11.36 kg/h. Toluene has the highest boiling point of the three components, with a relative volatility of 1.17. This component is the heavy key and exits as the bottom product of DST1, while DME and EME mixture is the light key and exit DST1 at the top as the distillate. The distillate from DST1 is fed into a second distillation (DST2). A reflux ratio of 10:1 was used to address the similarity in DME and EME boiling points of 85 and 87 °C, respectively.⁴⁸ In DST2, DME is the light key with a relative volatility of 1.017, while the bottom product is EME. The top stream is composed of 95% DME and 0.03% EME at 3.16 kg/h, while the bottom stream is composed of pure EME at 1.26 kg/h. The second major recovery pathway utilizes a pervaporation system followed by ultrafiltration. The waste stream enters the pervaporation system at 11.36 kg/h. The desired permeate, DME and EME, are vaporized while toluene flows downstream and exits as the retentate. The permeate stream then enters an ultrafiltration unit (UF) where the DME and EME are separated based on size. DME exits the system at 95% purity with a flow rate of 3.16 kg/h. Splitter 3 allows for additional pathways to be considered. The waste stream processed by pervaporation unit may either enter the ultrafiltration (UF) or distillation (DST2) unit and vice versa for the first distillation (DST1).

The case-specific superstructure contains 29 streams, which include solid removal and recovery stages. The technologies

include filtration (FLT), gravity sedimentation (SDM), and centrifugation (CNF), followed by either distillation in sequence (DST) or membrane processes such as pervaporation (PVP) and ultrafiltration (UF), for separating the organic mixtures of toluene, DME, and EME. The criteria for determining the best method of recovery involved cost minimization.

3.2.2. Analysis. Table 4 displays the optimization results from GAMS, which contain the annual operating costs for three feasible pathways and the price per kg processed. Although there are 12 possible solvent recovery pathways, the low relative volatility value between DME and EME chemicals has made the DST1–DST2 pathway infeasible, eliminating distillation pathways from consideration. The specialty chemical waste stream optimization model consists of 673 equations, 582 variables, and 6 discrete variables. BARON solution converged within 11.36 s with an optimality gap of 0.01. The optimal solvent recovery pathway to recover DME from a waste stream containing 21.3% DME, 1.3% EME, 41.3% toluene, and 36.1% water will require removal of water through anhydrous salt, solid separation, pervaporation, ultrafiltration. These operations require a cost of \$330,000/year at an annual solvent recovery rate of 53.9 tons/year of water, 55.5 tons/year of toluene, 1.6 tons/year of EME, 25.8 tons/year of DME. Both the annualized costs and unit prices are similar for FLT–PVP–UF, SDM–PVP–UF, and CNF–PVP–UF pathways. This observation is attributed to the labor cost and overhead being the highest cost contributor. The capacities of the separation units were calculated based on a small flow rate (17 kg/h), which scales to a lower cost. The price of incinerating the DME waste stream is \$14.6 million/year, a considerable increase from the three feasible recovery pathways.

Figure 8 displays the total cost distribution for the feasible pathways in GAMS. The overhead (other) cost contributes to

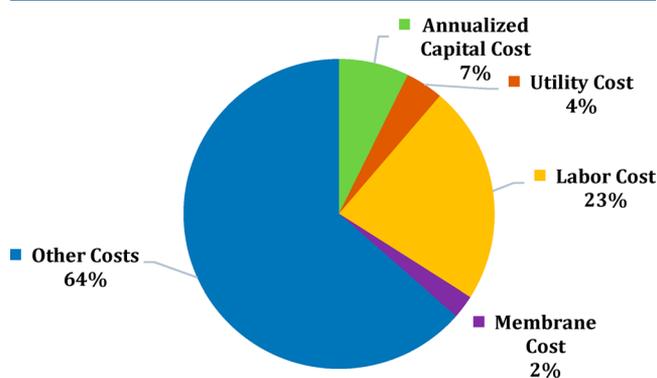


Figure 8. Cost distribution for the optimal recovery pathway to recover DME in Case Study 2.

the majority of the total cost, followed by the labor costs. The annualized capital, consumable, and utility costs are attributed to the equipment capacity being reduced to handle a low waste stream flow rate. However, the required operational cost per kg of solvent recovered is considerably larger than that of the pharmaceutical waste stream case study because each process equipment has a minimum capacity requirement. Continuous solvent recovery at a low flow rate is not a viable option unless the wastes are stored at a satellite accumulation area and then processed in larger quantities. The complete combustion of the solvent waste containing toluene, DME, and EME is expected

to result in 239 tons/year of CO₂ released into the atmosphere. Such release is equivalent to greenhouse gas emissions from 584 000 miles, driven by an average passenger vehicle.¹⁰²

A sensitivity analysis of the feasible solutions was performed by varying the waste feed flow rate and operating hours of the solvent recovery process. Figure 9 demonstrates the reduction

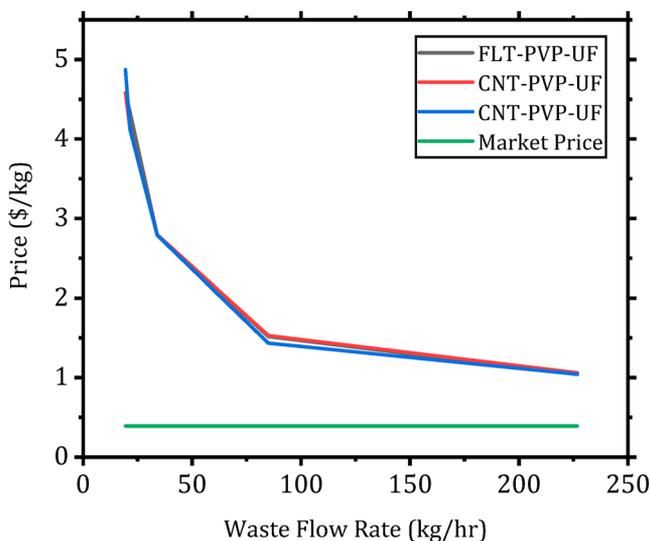


Figure 9. Sensitivity analysis of prices as a function of waste feed for Case Study 2 (DME recovery).

in the cost of recovering solvents and changes to the optimal solution as the waste flow rate increases. The change in the waste flow rate affects the capital cost calculations. Given that we used unique systems of nonlinear equations for each separation technology, the estimation of capital costs does not scale proportionally with other processes. However, the prices of solvent recovered through the three feasible solutions do asymptotically approach \$1/kg. In comparison to the market price of \$0.39/kg solvent, solvent recovery will appear as a less favorable option at the chosen condition. However, the multistakeholder nature of solvent recovery problems requires a compromise between environmental impacts and economics. Although purchasing fresh solvent may be economically favorable in this case, disposing of solvent through conventional disposal methods will negatively impact the overall environmental sustainability.

From both case studies, a similar trend between optimal solvent recovery and incineration was observed for the recovery of organic solvent from a waste stream, where it is more economically viable to recover solvent than to incinerate. Solvent recovery also allows material reuse within the process as opposed to the degradation option associated with incineration. Such a trade-off between economics and environmental impact should be considered, given that solvent recovery is a multistakeholder problem. In the recovery of the DME case study, we observed an instance when solvent recovery is more expensive than purchasing the fresh solvent. Depending on the values of the decision-maker, utilizing solvent recovery is a preferable option because materials are recovered and harmful emissions are reduced.

There are two major limitations to the proposed solvent recovery framework. First, if the solvent concentration in the waste stream is too low (between 1 and 5% of the overall waste stream mass), then recovery will be costlier than disposing of

solvents. For example, if we have an oil waste with many additive products and a small fraction of mixed solvents (hexane and octane), then processes like distillation, membrane separation, and extraction will not be able to perform the desired separation at a reasonable cost. In this case, using one of the primary waste disposal methods is preferred. Second, we have found from the sensitivity analysis of Case Study 2 that the magnitude of the waste stream flow rate can drastically influence the price of recovery. If the flow rate of the waste stream is too low, then the cost to recover the solvents will be larger. The design equations used for our mathematical models are based on industrial-scale equipment. The solvent recovery framework can remain usable to recover solvents at a reasonable cost, as long as the flow rate is increased and the yearly operating hour is reduced. Physically, this action would equate the solvent waste being stored at a satellite accumulation area and later sent to a recovery process.

There is an uncertainty of approximately $\pm 30\%$ associated with all results due to possible variations in material types, costs, and specified parameters. For example, the ATPE process requires salt and hexane to perform the desired purification; however, if other types of systems are selected (polymer–salt, polymer–polymer) or the chemical property of the waste stream is different, then the annual total cost of operation will likely change. This uncertainty is tolerable for the preliminary design phase. The error associated with the process selection aspect of this work propagates in the same way as does typical process design. The result and uncertainty from one process unit would transfer to the next unit, continuing until the desired product is obtained.

While commercial simulation software, such as Aspen, can provide detailed analyses of a specific flowsheet, it does not have the capability to compare multiple options at once. By using GAMS, we have the flexibility to simultaneously evaluate multiple solvent separations and recovery technologies through its optimization capability. The user can write their own equations, introducing limits on crucial process variables and integrating codes with powerful optimization solvers. The models formulated and solved using GAMS are independent of the industry to which it is applied and can be easily adapted for any solvent consuming process where recovery and recycling are the desired steps to enable good manufacturing practices. Our work will help narrow down the number of possible options and give a reasonable cost estimate for implementing solvent recovery. The uncertainty from the solutions resulting from this work can be reduced further during the detailed design phase.

4. CONCLUSIONS

We developed a superstructure-based solvent recovery framework that considers a stage-wise analysis of multiple technologies. The robustness of this framework was tested in two case studies of varying complexities involving the recovery of isopropanol from a pharmaceutical waste stream and dimethoxyethane from a specialty chemical waste stream. Common solvent properties, separation technologies, and solvent waste information were collected to obtain the necessary information for solving the solvent recovery-related case study. Multiple solvent recovery options were analyzed simultaneously in GAMS to determine the optimal separation pathways. Selecting solvent recovery as the primary waste handling practice will not always yield economically favorable results, as evidenced by the specialty chemical waste stream

case study. However, an adjustment to the operating flow rate and hours can considerably reduce the total price of solvent recovery. From both economic and environmental standpoints, incineration is a costly approach in solvent waste handling that can also release unwanted substances into the environment. Solvent recovery is a preferable option because materials are recovered and harmful emissions are reduced. Such a trade-off relationship between economics and environmental impact should be considered, given that solvent recovery is a multistakeholder problem. Additional case studies will be conducted in future studies for other solvent-consuming industries, such as polymers, oil, and metals. These analyses can further refine the solvent recovery framework that we have developed to consider other separation technologies and techniques not included in this paper. In subsequent studies, life cycle analysis of the recovery pathways will be conducted to pair with the economic evaluations presented in this study. The systematic framework developed in this study has demonstrated viability to be applied to all cases involving solvent recovery.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.iecr.9b06725>.

Summary of previous green engineering optimization work, detailed model equations, modeling parameters specification, relative volatility estimation, additional emission data from the US EPA Toxic Release Inventory, and the mentioned GAMS code (PDF)

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Notes

The authors declare no competing financial interest.

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