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ENHANCING SUSTAINABLE PROCESS DESIGNS THROUGH STRATEGIC MATERIAL UTILIZATION AND WASTE MINIMIZATION APPROACHES

by

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Dedications

For mom and dad and the sacrifices you both have made to ensure that I could become who I am today. For my little sister, my family, and my cat (Yuki).

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Abstract

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Doctor of Philosophy in Chemical Engineering

Sustainability is a growing concern as resources are continually depleted for various applications without adequate renewal plans. The resulting impacts on the ecosystem, health, and resource circularity are often overlooked. This research analyzes improvement opportunities at each major stage in a product's life cycle. Raw material acquisition, product synthesis, process waste management, and the fate of a material in the end-of-life phases were examined. The viability of utilizing renewable resources has been demonstrated in this work by extracting bio-based chemicals from underutilized renewable resources at a commercial scale and transforming the extracted resources into polymeric materials. The optimization of raw material acquisition and process waste management have been accomplished via a superstructure-based approach that is modeled as MINLP optimization problem. Even though process sustainability can be achieved with strategic usage of renewable resources and recovery, the fate of post-consumer materials also poses major concerns regarding releases and emissions if left unmitigated. The guidelines surrounding the manufacturing and end-of-life phases of a material introduced in this work, backed by experimental and computational findings, can be used to effectively design environmentally conscious processes, inventions, and materials without sacrificing costs.

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Chapter 1

The Inherent Flaws in the Life Cycle of Existing Products

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Sustainability, a term introduced in 1987, is a state that ensures that the present needs of the human population do not negatively impact the ability of the future generation to exist, meet their needs, and prosper [1]. In engineering applications, sustainability can be achieved by implementing design considerations for process efficiency, environmental impact, and safety [1]. Diwekar has developed a framework that considers the green-engineering approach at all design stages, which involves green processes and energy, clean products, and environmentally friendly practices, to help minimize short-term and long-term environmental impacts [2]. Although the implementation of such practice is feasible in theory, the existing applications of this framework are not commonly practiced because of the convenience of using readily available resources and eliminating waste through direct release and incineration. This reliance on convenience is not sustainable and can be detrimental to the environment, despite meeting the required economic and social growth.

In reality, the state of sustainability is relative, in which some processes may meet more requirements than others [3]. It is practically impossible to fulfill all the requirements without sacrificing some aspects. The Earth has been seen as the natural system boundary containing many systems, processes, and biological species that continuously interact to exchange materials, energies, and ideas [1]. Often, when man-made processes are designed with considerations for sustainability, full circularity is not easily achieved because the impacts of one sub-process may create problems in other aspects. For instance, renewable polyethylene from ethanol, specifically from sugarcane, can present a sustainable solution to reducing the reliance on fossil fuels in the material production sector [3]. However, the demand for polyethylene is significant enough to compete with the current applications of sugarcane. A large fraction of sugarcane production must be dedicated to generating ethanol for polyethylene synthesis to fulfill the current demands using a greener approach. This scenario thus highlights a case when a green process is not necessarily sustainable. The use of bio-derived resources can also be deterred from the "Food vs. Fuel" argument. Food supply may be decreased considerably to establish a biofuel production process successfully. Therefore, alternative sources must be selected carefully to avoid diverting resources from essential processes.

In process engineering, the common design goal is achieving the production targets with maximized efficiency and minimized cost. However, the sustainability of these processes is usually brought into question because of the conflicting factors surrounding economics, social, safety, and environmental impacts [4]. Shifting the objective toward one category (economics) may cause other objectives to suffer (e.g., environment). Multi-objective optimization is typically used to address these trade-off relationships by providing the ability to seek optimal solutions within reasonable constraints [4]–[8].

Even with the added complexity in problem formulation, achieving circularity in process design remains challenging. From a life cycle perspective, a man-made material undergoes a material acquisition and extraction stage, followed by manufacturing, distribution, usage, and end-of-life management [9]. The material acquisition and extraction stage focuses on obtaining the initial materials needed to synthesize the required product [3].

1.1 Linear Economic Scheme

The concept of a linear economy holds that products are made from existing resources and disposed at the end of their uses with no consideration for recycling [10]. Currently, manufacturers identify consumer needs, synthesize, and modify products from easily acquired resources. In turn, natural resources are consumed while waste and pollution are generated. Petroleum is generally used for fuel and energy generation and as a feedstock for synthesizing chemicals and synthetic materials for many applications found in modern-day households [11]–[13]. Petroleum and natural gas have also created many products and materials, including polyethylene, polyesters, synthetic rubber, lubricants, pesticides, and resins [12], [14]. However, the declining availability of petroleum is forecasted to considerably disrupt the global economy because alternative resources are generally unable to fulfill the gap for energy generation and match properties in material applications [13]. Approximately 99% of the feedstock for global plastic products is made from petroleum-based chemicals, and the remainder is from bio-based materials [15]. It becomes clear that this market possesses low resource sustainability because petroleum is available in limited supplies and consumed significantly faster than generated.

One notable transition effort, hydraulic fracturing or “fracking,” has been widely used in the US to address the energy generation gap [16]. However, despite the effectiveness of this method in reducing energy prices and providing additional feedstock for chemicals and materials production, environmental concerns have been raised regarding freshwater resources being contaminated with radioactive, inorganic, and organic materials [16]–[18].

Additionally, post-consumer treatment of spent products (the end-of-life stage) is prioritized based on cost, with minimal consideration for environmental impacts and circularity. This observation is evidenced in the plastic management sector. The increased demands for plastics and, consequently, an increase in global plastics production have considerably increased the number of spent plastics, out of which over 90% are either landfilled or incinerated [15]. It is more convenient and cheaper to destroy or bury the generated waste than to spend additional resources to recover the products at a significantly lower quality. However, the current methods for handling post-consumer waste are also susceptible to releasing toxic chemical additives and greenhouse gases and inflicting detrimental effects on air, water, soil, organisms, and public health. An improvement to the existing infrastructure for plastics management is needed to limit chemical releases and exposure, creating environmental concerns [19], [20]. An economic benefit is observed more often with the treatment of wastes that are not heavily contaminated with foreign substances [21]. The issue with this linear economy also stems from the beginning of the life cycle of a material because manufacturers do not generally consider the end-of-life stage of the product if it can be eliminated through incineration or buried in a landfill.

1.2 Achieving a Circular Economy

The state of a circular economy requires that products are used to their maximum value and that resources from previous uses are recovered or reused as much as possible [3]. This condition is achievable if the design process of a product is created with considerations for every stage in the life cycle. Judicious selection of material used in the manufacturing process should be considered to minimize waste, avoid excessive energy usage, minimize steps (reduce process units by process intensification), and limit the presence of hazardous substances [3]. Numerous novel bio-based materials have been synthesized and demonstrated to have comparable properties to petroleum-derived materials to address the inevitable decline in the availability of petroleum and natural gas for material production [22]–[27]. Therefore, the extraction of bio-based chemicals is not a new concept. Research efforts have been made toward finding sustainable feedstocks to yield products derived from natural materials with competitive economics and properties compared to existing petroleum-based products [22], [28]–[32].

The chemicals used to create these novel materials have been extracted from plants primarily at the lab scale, ranging between supplements, pharmaceuticals, and food product formulations [33]–[37]. The practicality of commercializing these materials relies on obtaining the feedstock at a much larger scale without sacrificing economic viability and natural resource regeneration [3]. The manufacturing process should be sustainable in the sense that the process is energy efficient, can be sustained by renewable resources, utilizes minimal resources, and leaves a minimal carbon footprint. These criteria should not negatively impact the product quality to ensure sustainability between the customer and the manufacturer. In 2017, the amount of solvent waste from the manufacturing process in the chemical industry reached over 3.8 billion lbs and was expected to rise as a function of the expanding market [38]. In this case, solvent recovery is required to further enhance the sustainability of process designs. Implementing such a process is often costly and time-consuming, unlike conventional waste disposal. Therefore, the raw material acquisition and product manufacturing stages are two of the most critical stages as they ultimately decide the existence of a product that may become an environmental, economic, or social burden later in the life cycle of a material. The distribution and use stage may be sustainable if the properties of the product can directly improve the convenience of another process, such as lightweight containers for more accessible transport and minimizing the distance between the distribution center and the consumers. The end-of-life (EoL) stage should consider recycling or treating waste when possible. Reuse is preferred if the material remains in good condition after usage. The incineration and landfilling of wastes should be minimized to ensure circularity [3]. As can be seen, it is difficult to achieve all of the objectives without sacrificing some aspect of convenience or sustainability.

We hypothesize that a sustainable process can be achieved with strategic optimization of each major stage in the life cycle of a material. This work analyzes and proposes solutions to the sustainability challenges involving plastic recycling, raw material acquisition, and waste management. Specifically, we developed a systematic framework for the optimization of large-scale bio-based chemical extraction to be used in polymer synthesis applications, optimized solvent recovery for industrial processes, tracked and estimated harmful chemical releases in the EoL waste management stage, and provided alternative solutions to achieve a sustainable circular economy in modern process design.

The **overarching hypothesis** of this dissertation is that **strategic optimization of practices and resource allocation in process engineering can enhance global environmental and resource sustainability**.

The following sub-hypotheses are defined to highlight specific challenges addressed in this dissertation:

Hypothesis 1: The production of bio-based chemicals and materials can be increased without sacrificing cost and disrupting commercial needs when the source is underutilized and can be replenished in a reasonable timeframe.

Hypothesis 2: The sustainability of manufacturing processes can be improved with a comparative assessment framework that can significantly reduce the time from process design to implementation.

Hypothesis 3: Better material management can be achieved by preventive actions and mitigation strategies that lead to higher recovery rates.

In the following sections of this Chapter, challenges that led to the existence of Hypotheses 1 – 3 are reviewed. First, in Section 1.3, raw material acquisition at the commercial scale is identified, leading to two analyses: (1) involving the commercial-scale isoflavone extraction from soybean meal and (2) using impure extracts as a material feedstock. In Section 1.4, challenges and recent advances regarding the treatment of chemical solvent waste are identified. Lastly, Section 1.5 analyzes the current infrastructure of end-of-life waste management, paving the research toward closing the material loop and achieving a circular economy.

1.3 Chemical Extraction and Bio-Based Material Synthesis

The needs for the commercialization of bio-based chemical extractions stem from the rapidly declining nonrenewable resource reserves. The challenges associated with the successful commercialization of bio-based materials are driven by the high price of raw material acquisition compared to petroleum-based products. Plastic is a prime example of a material class typically derived from petroleum-based monomers. This material has been widely used as a substitute for metal, paper, and glass since 1976. Plastic production is expected to triple by 2050, exceeding one billion metric tons annually [39]. The heavy reliance on fossil-based resources for plastic production is expected to significantly impact the environment and process economics.

Despite the advantages of using bio-based chemicals, petroleum-derived chemicals remain the primary source for polymer production because of the inexpensive prices related to acquiring this raw material and the lack of political support for bio-based chemicals [12]. Over 90% of epoxy resins manufactured today stem from bisphenol A (BPA), which is an estrogen antagonist, endocrine disrupter, and a human carcinogen derived from petroleum [40], [41]. This chemical is favored among applications such as coatings, adhesives, composites, food containers, and plastic bags. The aromatic content and π-π stacking allow BPA-based materials to exhibit high thermal and structural stability and excellent mechanical properties [40]. A suitable replacement for BPA is required for applications involving large amounts of human contact because of potential leaching [42]–[44]. The annual growth rate of bio-based polymers can increase to 10-20% if oil prices and the availability of bio-based chemicals increase [45]. Selecting bio-based chemicals for polymer production can aid in shifting the reliance on petroleum sources to renewable biomass. However, the challenges associated with the successful implementation of bio-based materials are due to the high price of raw materials and sub-par performance compared to petroleum-based products [46].

Although bio-based polymer research is still relatively new, numerous bio-based materials with mechanical and thermal properties comparable to petroleum-derived materials have been synthesized [22]–[27]. Bio-based polymers are produced using biomass-derived monomers that may biodegrade, depending on the chemical and structural stability [47]. One significant advantage of such material is that it does not contribute extraneous greenhouse gas emissions to the atmosphere because the reaction steps required to produce the starting molecule are unnecessary [46]. For example, lignin, a byproduct and waste of the pulp and papermaking industry, has been explored as a potential chemical derivative because of its inherently high thermal and structural properties and abundance of hydroxyl groups for functionalization [24], [48], [49]. Lignin derivatives such as vanillin, vanillyl alcohol, and guaiacol have also been used to produce novel polymer resins for adhesives, coating, flame retardant, high-performance, and composite applications [22], [27], [30], [50]. Alternatively, similar reaction chemistry and chemical modification can be performed on many other chemicals derived from renewable resources, including soybean, betulin, citrus peels, and other underutilized resources.

The commercial-scale extraction of natural chemicals from renewable resources can prove advantageous as more renewable chemicals become available for existing applications and the design of novel materials with unique properties and reduced toxicity.

In addition, bio-based chemical extraction can minimize or eliminate the reaction steps that would have otherwise been required.

We identified soybeans as a promising candidate to demonstrate a solution to the commercialization challenge. In 2018, the US produced over 125 million metric tons of soybeans, accounting for more than one-third of the global soybean production [51]. Specialty chemicals can be extracted from soybeans without consuming the original material. The soybeans in post-production may be dried and redirected toward the animal feed industry. The extracted chemicals, isoflavone aglycones, may then be used in nutraceuticals, beverages, food, and cosmetics. Additionally, these chemicals can be used as a polymer derivative that exhibits comparable properties to petroleum-derived polymers. Birch bark, a byproduct of the forest industry, is another strong candidate as a bio-based feedstock. From Sweden alone, approximately 1 to 2 million m^3 of birch bark is produced yearly [52]. This material is used as a low-grade fuel, with up to 30% of its dry weight being betulin [52], [53]. A similar approach can be employed to extract and purify betulin from birch bark. However, these extraction processes are not applicable on the industrial scale [54], [55]. The successful commercialization of bio-based chemical extractions can add tremendous value to underutilized renewable resources. The increase in bio-based chemical accessibility can pave the way for the commercialization of promising bio-based materials synthesized on the lab scale and shift the reliance away from conventional petroleum-derived chemicals.

1.4 Introduction to Solvent Recovery

Solvents are an integral part of industrial processes. Almost all industrial processes rely on solvents at varying levels. The pharmaceutical industry is one of the major consumers of solvents for its active pharmaceutical ingredient (API) purification and refinement processes [56], [57]. Furthermore, the importance of solvents can be extended to the food, cosmetics, nutraceuticals, biofuels, paints, and fine chemical industries [58]–[65]. The continuous growth in demand for solvents has inadvertently increased waste generation. For example, the pharmaceutical industry generates approximately 25 – 100 kg of waste per kg of a product [66]. The forefront of this generation issue is the inefficiencies associated with industrial processes and the poor solvent selection criteria [67]. Undeniably, solvents are excessively used to achieve desired purities and quantities of products. Therefore, the increasing trends in waste solvent generation have necessitated process intensification methods such as solvent recovery to curb the growing environmental, health, and safety concerns.

Incineration, offsite, and onsite disposal techniques have been the conventional waste handling methods practiced by most industries. However, these methods present challenges regarding the emissions, safety, handling, and fate of the waste solvents within the ecosystem. The annual Disability-Adjusted Life Years (DALY) associated with transportation for offsite disposal has been estimated to be 0.35 – 35.03 [68]–[70]. Incineration is typically a more expensive waste management technique because it requires high energy input to maintain continuous operation. The thermal destruction capability by incineration is highly effective at reducing solvent waste volume. However, chemicals resulting from the combustion of solvents can be hazardous to the surrounding ecosystem

[20], [71]–[74]. Offsite and onsite disposals are not energy-intensive, but the waste solvents are prone to leakage into the nearby water supply and land, contaminating the affected resources [75], [76].

Thus, solvent recovery presents a better mitigation option than conventional disposal methods due to lower implementation costs and fewer emissions [77], [78]. The recovery and reuse of organic waste solvents are essential to improving the sustainability and circularity of industrial processes. The use of conventional waste handling methods tends to increase the overall energy and ecological footprint of a given industry [68], [73], [79]–[81]. Over the years, governmental policies have been enacted to help industries practice the disposal of hazardous waste solvents to reduce their life cycle impacts. The Resource Conservation and Recovery Act (RCRA) was implemented to promote industrial sustainability. This act encourages environmentally sound methods for managing waste. It establishes a national framework for hazardous waste control by mandating the United States Environmental Protection Agency (US EPA) to develop regulations, guidelines, and policies that ensure the safe handling of hazardous waste and its reuse. Based on the RCRA requirements, solvent recovery presents an opportunity that fosters a robust industrial sustainability backbone by ensuring responsible management practices [67], [77], [82], [83].

The implementation of solvent recovery processes comes with various challenges. In the modern-day capitalistic economy, process cost has been the driving force for most industrial policies because it determines if solvent recovery can be used in waste management. Technology selection is another challenge that should be considered when designing a solvent recovery process because different technologies can perform similar tasks. Therefore, selecting technologies that can achieve the required specification at minimum cost can be challenging without systematic evaluation. Furthermore, the need to integrate a sustainability metric that quantitatively evaluates the greenness of solvent recovery processes has not been extensively investigated. Lastly, solvent waste characteristics are a major concern for most industries when considering recycling and reuse options within the same process. However, there is a hidden opportunity for research and development to devise better solutions to every challenge.

Several metrics have been developed to help assess the sustainability of industrial processes. The E-factor quantifies the amount of waste generated per kilogram of a product obtained. Solvents have been used in the pharmaceutical field for the past 25 years (Sheldon, 2007; Sheldon, 2017). The American Chemical Society Green Chemistry Institute Pharmaceutical Roundtable (ACS-GCIPR) has adopted the Process Mass Intensity (PMI) as the benchmark for evaluating the greenness of pharmaceutical processes [85]. However, these metrics are mass-dependent and usually do not account for the energy demand along the supply chain of processes. Emissions in gaseous states have also been represented in carbon dioxide equivalent (CO_2-eq). CO_2 persists in the atmosphere and traps heat for an extended period. The release of other chemicals is compared directly to CO_2 based on a 100-year global warming potential (GWP), in which CO_2 is assigned a reference value of 1. The release of 1 kg of methane is equivalent to 25 kg of CO_2 released into the atmosphere [86]. Other substances, such as 1 kg of sulfur hexafluoride, may equate up to 22,800 kg of CO_2 released [87]. The difference in CO_2-eq values is dependent on the ability of a substance to absorb energy and its persistence in the atmosphere concerning CO_2 [88]. In solvent-intensive operations, fugitive emissions, spills, and evaporations can create gaseous phase emissions that can negatively impact the environment over time. Therefore, CO_2-eq is valuable in evaluating the impacts of process waste (E-factor).

1.4.1 Supporting Legislation for Solvent Recovery

Solvent recovery may have begun as early as the Industrial Revolution, as the production of chemicals has shifted to larger scales [89]. However, the focus on material recovery has been treated as a secondary rather than a primary objective. The primary goals of any chemical company have always been to obtain a product with high yield and purity with minimal expenditure. Many small companies did not have a proper solvent recovery system because the production process was too expensive, complex, and required a workforce to maintain and operate [89]. Until the mid-1970s, contaminated solvents were treated as liquid waste and then discarded in the ground or water sources because the solvents could evaporate over time, leaving behind dissolved contaminants.

Burying hazardous waste has severely harmed the surrounding land and water because the waste containments are susceptible to corrosion, causing leaks over time [90], [91]. Dumping hazardous waste in the local water source also creates an issue involving the accumulation of toxic pollutants. One of the most notable events that sparked the creation of the US Environmental Protection Agency was the incident involving the Cuyahoga River fire in 1969 [92], [93]. A spark from a train track ignited debris on the surface of the Cuyahoga River, propagating the flames along the surface of the polluted river. This event increased public awareness and flaws regarding the viability of the existing waste management and eventually led to the creation of the US EPA.

Additionally, the continuous growth of the economy and population led to an increase in production scale to meet demand, leading to a rise in waste generation. The need to develop mitigation plans becomes paramount as a result. In 1965, the chemical industry in the US produced over four million tons of chemicals. The boost in production resulted in the generation and release of many toxic by-products, which were unregulated. By 1973, the total amount of unregulated solids was 144 million tons [94]. Due to unrestrictive disposal, severe health and environmental issues were associated with water and air pollution. For example, the 30 inches of rain in early 1978 resulted in the overflow of the Stringfellow Acid Pits, culminating in releasing over a million gallons of contaminated water into the Glen Avon community [93], [95]. Table 1 summarizes the various legislations that supported solvent recovery, the agencies that enacted them, and their major features.

Table 1

Legislations that Gave Recognition to Hazardous Waste and Promoted Solvent Recovery

Legislation/Act/Policy	Agency	Features
Environmental Action Program (1973)	European Community (EC)	Established the first environmental framework by focusing on finding solutions to waste, toxicity, and non-biodegradability issues
Polluter Pays Principle (1973)	European Community (EC)	Charged polluters with clean-up costs and also advocated for greener production processes
The Framework Directives on Waste (1975)	European Community (EC)	Defined what "waste" and "disposal" are and proposed various disposal methods. It also advocated for the recovery and recycling of chemical waste by outlining the basic disposal requirements needed to protect human health and the environment
The Resource Conservation and Recovery Act (1976)	United States Congress	Mandated the US EPA to promulgate regulations controlling mainly hazardous solid waste from "cradle to grave."
Environmental Action Program (1977)	European Community (EC)	This legislation was enacted to reduce the quality of non-recoverable waste, promote recovery, recycling, and reuse of waste, and proper management practices for the disposal of non-recoverable waste
Hazardous and Solid Waste Amendment (1984)	United States Congress	Banned the disposal of hazardous liquid waste via landfills, provided guidelines to disposal facilities on how to handle hazardous liquid waste
Environmental Protection Law (1989)	National People's Congress, China	Enacted to provide environmental standards, monitoring, planning, pollutant discharge, and pollution control. It further provided the administrative, criminal and civil liabilities for the infringement of the environmental laws
The Waste Framework Directive (2008)	European Union (EU)	Laid down basic waste management principles. Presented a 5-step hierarchical benchmark for waste management, namely, prevention, reuse, recycling, recovery, and disposal
Environmental Protection Law (2015)	National People's Congress, China	Sets forth a stringent legal framework, stresses the need for scientific and technological advancement to solve environmental issues

Note. This table was adapted from [590]

1.4.2 Resource Conservation and Recovery Act (RCRA)

In late 1976, US Congress passed environmental legislation called the Resource Conservation and Recovery Act (RCRA) [96]. The act was established to ensure economically sound and environmentally safe disposal of hazardous waste, primarily solids. This act ensured that these hazardous wastes were regulated from cradle-to-grave.

The US EPA established benchmarks for generators, transporters, and disposers of hazardous waste through RCRA. However, the initial administration and implementation of RCRA had its challenges. For example, while US EPA mandated that individual states establish their hazardous waste program to complement RCRA, there was inadequate knowledge of hazardous waste sites' number, location, and cleanup costs across the nation [94], [97].

The 1976 RCRA became a source of hope to citizens and institutional bodies such as the American Chemical Society (ACS), advocating for mitigation plans to safely dispose of hazardous solid wastes. However, this hope was short-lived. The vast “secured” landfills that contained solid waste began to leach toxic substances into the surrounding groundwater [97]. Furthermore, the ACS indicated that wastes generated by laboratories were of varying characteristics and predominantly liquid. These wastes were not well captured in the RCRA. As a result, there was an amendment in the RCRA act in 1984 known as the Hazardous and Solid Waste Amendment (HSWA) [98], [99]. This amendment paved the way for the proper regulation of liquid hazardous waste. For waste generators, the HSWA meant direct disposal to landfill sites was not cost-effective as there was an immediate ban on releases into these sites. Therefore, incineration and other recovery methods for the solvent and its reuse became the most economical way to handle solvent-containing liquid waste [100]–[103]. The treatment of chemical waste before disposal resulted in solvent recovery gaining popularity among chemical industries.

1.4.3 European Union (EU) Hazardous Waste Legislation

Various legislations have been enacted by the European Community (EC) to help mitigate hazardous waste accumulation [104]. However, during the 1970s, there was a surge in enacting these legislations [105] due to public awareness of the negative environmental impacts of industrialization growth [106]. Furthermore, the geographic proximity of countries meant that each member state was affected directly by the environmental practices of the other. For example, the pollution of the river Rhine in Switzerland directly affected the Netherlands downstream, leading to the harmonization of the independent member-state legislation [107], [108].

The Environmental Action Program (EAP) in 1973 was the first framework established by the EC to help address environmental issues [109]. This legislation aimed to find solutions to eliminate waste accumulation problems within the EC. The first EAP was followed by the second in 1977. While the first EAP was mainly used to establish the need for the harmonization of environmental policies by the participating countries, the second EAP was explicitly focused on three main objectives, namely: 1) the prevention and reduction of quality non-recoverable waste, 2) the recycling, recovery, and reuse of waste for raw materials and energy, and 3) proper management and disposal of non-recoverable waste. In addition, recovering waste for reuse was one of the pillars that helped industries rethink their waste disposal methods by resorting to more environmentally friendly options [110]–[112].

Other legislation, such as the 1973 Polluter Pay Principle (PPP), encouraged proper waste disposal. The 1975 Framework Directives on Waste (FDW) was the first hazardous waste-related legislation passed by the EC [104]. The 1983 disappearance of a shipment of barrels containing waste dioxins transported from Italy triggered the Transfrontier Movement of Hazardous Waste (TMHW). This event presented a benchmark for the shipment of waste across the EC. However, the need to recover hazardous waste for reuse was highly encouraged due to the dangers associated with transportation. The Waste Framework Directive (WFD) is the current management principle being implemented by the European Union (EU) [113]–[115]. This directive strongly encourages the recovery of hazardous waste solvents for reuse.

1.4.4 Other Environmental Protection Policies

Economic growth has been the main emphasis of the Chinese government. However, this increased growth directly scales with the burdens of environmental issues. Environmental protection was incorporated into the constitution when revised in 1978, leading to the enactment of the Environmental Protection Law (EPL) [116]. This law helped regulate pollution by making a general provision for handling industrial waste [117], [118]. However, there was no stringent adherence to the enacted policies due to the liberality in its implementation. In addition, specific details of the various ways to handle waste were not indicated and defined within the law; in fact, some referred to it as a “trial and error” framework [119], [120]. Therefore, the law had a major revision in 1989, providing environmental standards, monitoring, planning, pollutant discharge declaration, and industry registration [118]. Thus, these reforms helped improve the scope of the EPL. However, some of the provisions within the law indicated that industries could still dispose of hazardous chemicals into the ecosystem as long as they paid the associated fees [118].

Therefore, solvent recovery was still not promoted within the law reformations. The implementation of a revised EPL in 2015 has raised awareness of the detrimental effects of the irresponsible disposal of hazardous waste into the environment [117], [118], [120], [121]. The amended EPL is more stringent on releasing waste into the environment and strongly supports solvent recovery.

The Australian Standard 1940 (AS1940) is critical in guiding the safe handling and storage of flammable and combustible liquids. This standard helps industries enact good industrial practices that minimize the risks associated with solvent waste handling by promoting solvent recovery [122], [123]. The Canadian Environmental Protection Act (CEPA), enacted in 1999, is the legislation that helps regulates the management of hazardous waste recycling and disposal. The CEPA sets criteria and standards to assess environmentally friendly ways of hazardous waste materials. It promotes the export and import of hazardous waste based on set guidelines [124], [125]. Rapid industrialization in Japan during the 1960s and 1970s resulted in high economic growth, generating hazardous wastes such as organic solvents. To curb the growing concerns posed by these wastes, the Japanese government amended the Waste Management and Public Cleansing Act in 1970, which offered comprehensive steps to dispose of waste safely [126]. In addition, Japan currently has a waste management act that advocates for resource utilization, promoting solvent recovery by industries [126].

1.4.5 Evolution of Solvent Recovery Technologies

As can be seen, there is tremendous emphasis on chemical recovery and minimizing hazardous waste disposal in most countries worldwide. However, it is essential to devise efficient recovery methods to ensure these practices are implemented to their fullest potential. To this end, we present an overview of solvent recovery practices.

1.4.5.1 Conventional Solvent Recovery Practices. From the late 1930s to the early 1970s, solvent recovery was practiced on more minor scales to remove contaminants from chemical solvents [89]. However, the drive to advance solvent recovery was heavily focused on economic profit. Distillation has, historically, been the most commonly used technique because of its ability to separate components from a fluid mixture at a wide range of flow rates, regardless of the initial concentration, and with high purity [127]. Flash, steam, fractional, extractive, and azeotropic distillation were the most common distillation types to remove contaminants from solvent waste [128]–[131]. Additional processing steps, such as carbon adsorption, have been reported to improve the final appearance of the solvent. Flash distillation is a single-stage process that partially vaporizes the liquid feed under vacuum or atmospheric pressure in a column, creating two phases in thermodynamic equilibrium [128]. Steam distillation does not require vacuum-like flash distillation. However, this method subjects the solvent waste to high temperatures, which may cause the impurities and non-volatile substances to react, decompose or change the quality of the distilled product. Water is mixed with the organic solvent waste and heated to a boil, creating a vapor mixture of water and organic solvent. The gaseous phase substance is condensed into liquid and separated from water in the downstream process [132]. Fractional distillation is used to separate multiple volatile components from a waste mixture if azeotropes are not present, i.e., components do not possess similar boiling points. The liquid waste feed is heated to a high temperature and fed into the fractionation column.

Volatile components travel toward the top of the column and condense at different locations based on their boiling points [129], [133]. Extractive distillation separates close boiling components and azeotropes by introducing a new, relatively non-volatile component to serve as an entrainer. The newly added component does not form an azeotrope with any other substance in the mixture, allowing easier separation between the components in the original mixture [131]. Azeotropic distillation also introduces an entrainer. However, this component can form new azeotropes with other components from the mixture of interest. The newly formed azeotropes can be separated into another distillation column and recovered for reuse [130]. The distillation process requires high energy usage despite the separation capabilities, which significantly affects the operation costs. Alternative options to the conventional solvent recovery methods are later discussed in Section 1.4.8.

1.4.6 Solvent Selection and its Influence on Recovery

Solvent recovery technology selection is a function of the solvent choices selected for use during the process. The resulting waste stream establishes the properties of the final streams, altering the recovery methods required to recover valuable materials. Poor solvent selection may lead to low production yield, difficulty in separation, and excess material consumption. Many companies such as AstraZeneca, Pfizer, GlaxoSmithKline (GSK), and Sanofi have taken the necessary steps to publish their guides on solvent selection [134]–[136]. The solvent selection guides were later enhanced to consider safety, health, environmental impacts (SHE), and process requirements to ensure that green chemistry is incorporated at every design stage. The latest solvent selection guide has been designed with inspiration from other companies, including a database of 272 known, new, and green solvents typically used in processes. Solvents were grouped and differentiated based on chemical functionality and categorized into different solvent classes such as acid, alcohol, alkene, ester, hydrocarbon, amine, and aromatics [137]. In addition, seven SHE categories from AstraZeneca: health, air impact, water impact, life cycle analysis, flammability, static potential, and VOC (volatile organic carbon) potentials, were included. Some solvents may take on the characteristics of one or more classes because of the functional groups present, enhancing the solubility of the desired solutes. Classifying the solvent system during the design or recovery phase provides a better understanding of the physical properties and chemical interactions that may cause a change in density, affinity toward a specific substance, or solution stability. Solvents can thus be analyzed and compared based on their physical and chemical properties, safety, health, and environmental impacts to suit the process needs [137].

When designing a solvent-intensive process, it is crucial to consider the factors listed in the solvent selection guide to ensure that the process objective can be achieved efficiently and does not adversely impact the environment. GSK solvent selection guide provides scoring assessments based on available data for a selected list of solvents on incineration, recycling, biotreatment, VOC emissions, aquatic impact, air impact, health hazard, exposure potential, flammability & explosion, reactivity, and life cycle analysis. Each category is assigned a score of 1 (least green) to 10 (most green), with unique criteria. For instance, the VOC emission score is determined according to vapor pressure and risk of spillage and loss during storage, transport, and waste management of a specific solvent.

Solvents with a low boiling point are rated lower due to the increased volatility [134]. The high vapor pressure of individual solvents also negatively impacts other factors such as biotreatment, VOC emissions, air, exposure potential, flammability, and explosion. For a given solvent, scores are determined through various evaluation metrics recommended by the GSK solvent selection guide. The individual scores are combined into a geometric mean, resulting in a composite (overall) score for waste, environment, health, and safety categories.

Other groups, such as the ACS-GCIPR, contributed a solvent selection tool that considers the properties of individual solvents and identifies a shortlist of solvents appropriate to a process needs [138]. Slater and Savelski developed a solvent selection table in collaboration with Bristol-Myers Squibb and the US EPA to compare green solvents and process routes based on 12 environmental parameters [139]. The Innovative Medicines Initiatives (IMI)-CHEM21 contributed a solvent selection tool that analyzes and ranks classical solvents used within the pharmaceutical industry. Unlike the previous tools, the CHEM21 selection guide is not generalized for all applications by default. Additional criteria and solvent lists are needed in other applications [140].

A solvent selection guide should be considered in the design stage to improve the recyclability of a chemical solvent. Table 2 provides the recommended criteria to improve the greenness of a process. However, it is not necessary to satisfy all criteria to ensure recyclability. The “Waste” categories present the largest impact on the ease of recycling in the solvent end-of-life phase. The chosen solvent should ideally have low miscibility with water, low vapor pressure, high boiling point, and no reactivity with other substances. This solvent can easily be separated from a mixture through conventional separation techniques. These considerations ultimately provide the ease of separation and purification. For instance, in the design phase, a process engineer may intentionally choose a multi-component system with significantly different boiling points and no azeotropes over the solvents with close boiling points and azeotropes. The solvent selection guide generally favored high boiling point solvents in the recycling score because it correlates with a lower vapor pressure at the given operating temperature than solvents with a lower boiling point [134]. Consideration of environmental and human health hazards can also influence the outcome of the process by allowing the process engineer to account for the potential releases and implement the necessary mitigation strategies.

Table 2

A Summary of Solvent Selection Criteria Required to Maximize Solvent Recycling Potentials and Minimize Impacts on the Environment, Health, and Safety [134], [136], [141]

Categories	Criteria
Waste	Low water miscibility and can be separated from water easily Easily separable from a mixture of multiple solvents Low vapor pressure and high boiling point
Environment	Low photochemical ozone creation potential (POCP), odor score (high vapor pressure → low score) Low toxicity (acute and chronic) toward the environment and aquatic species can biodegrade
Health	Low carcinogenic, mutagenic effects, and not considered harmful to reproductive health Solvents exposure level falls within the occupational exposure limits (OEL)
Safety	Low flammability and explosivity (based on boiling point, flash point, and auto-ignition temperature) Low to no intrinsic reactivity of solvents (self-reaction, thermal decomposition, reaction with acidic or basic reagents, forms peroxide over time)

Isoni *et al.* (2016) created an LCA-based methodology called Q-SA√ESS to further assist in decision-making in the manufacturing stage of a chemical process by using a cradle-to-grave analysis. The general hierarchy of green processes begins with using no solvent as the most green, followed by water, renewable solvent, and petroleum-based solvents as the least green option. Q-SA√ESS method uses metrics such as carbon footprint, acidification potential, eutrophication, human toxicity, the total energy used per batch, and the product obtained per batch to evaluate the safety, health, and environmental impacts of the organic solvents used [142]. These categories are scored according to the ACS-GCIPR solvent selection guide [143]. Trade-off relationships between social, environmental, and economic factors were observed, creating complexity in decision-making. Although social and environmental impacts are important to consider, economic profit has the largest influence on the final decision of a company [142]. Therefore, an acceptable balance between social, environmental, and economic factors should be decided at the process design stage to ensure efficient recovery.

Judicious solvent selection in the initial design stage serves as a preventive strategy. At the same time, recovery processes exist to minimize process waste that was generated as a result of the existing chemical processes. Depending on the process, a combination of dissolved solids, suspended solids, chemical impurities, and multiple solvent components could be present in multiple phases in the waste stream. Therefore, solvent recovery processes should be designed according to the components and properties of the waste stream unique to the process. The most significant obstacle to date is selecting the most appropriate separation and purification technologies to recover valuable solvents at the desired purity level.

1.4.7 Solvent Recovery in Practice

Earlier solvent recovery methods stressed the development of separation and purification technologies for solvent recovery and their implementation. For example, Blaney (1986) proposed various technologies that could be used to treat hazardous waste solvents [144]. Technologies such as sedimentation, filtration, centrifugation, flotation, and evaporation were proposed. Lau and Koenig (2001) also indicated that applying solvent recovery techniques during machine cleaning, dry cleaning, and screen cleaning can help reduce the cost of industrial processes by using a case study associated with a Chemical Waste Treatment Center (CWTC) in Hong Kong [145]. However, recovery costs became predominant as industries sought to cut down production costs.

Recently, there have been efforts to develop emerging technologies, including sustainability indicators, and apply computational tools and optimization methods due to technological advancements. For example, García *et al.* (2013) presented an extensive study on the recovery of organic waste solvents using pervaporation technology. They studied an aqueous solvent mixture of n-butanol, dichloromethane, and sodium chloride and observed a 100% rejection rate of sodium chloride when a pervaporation unit with a hydrophobic membrane is used, followed by a hydrophilic membrane [146]. Therefore, the permeate from the first stage consisting of n-butanol (50 – 90% wt.), dichloromethane (5 – 45% wt.), and water (5 – 20% wt.) served as the feed to the second pervaporation unit. The resulting permeate comprises 97.6 % wt. of water and 2.4% wt. of n-butanol, while

100 % dichloromethane is retained by the membrane. Pervaporation, therefore, has a higher capability of recovering organic waste solvents from wastewater streams and thus should be one of the key technologies industries should consider as a recovery option due to the greenness of the process. Raymond *et al*. (2010) presented a life cycle assessment approach to pharmaceutical waste solvent treatment. Their work estimated the life cycle inventories using SimaPro® and EcoSolvent software [78]. Based on three case studies, they also compared off-site disposal (base case) with on-site incineration (with energy recovery) and solvent recovery. They observed that the life cycle assessment of solvent recovery should be done from a cradle-to-grave perspective rather than gate-to-gate.

Ooi *et al.* (2019) proposed a Computer-Aided Molecular Design (CAMD) framework that simultaneously factors solute extraction and solvent recovery. They aim to design solvents that can be recovered with low economics, environmental impacts, and health hazard [147]. Their framework can systematically predict, estimate, and design solvents in separation processes by analyzing their molecular properties. Their approach follows similar techniques to Chea *et al.* (2020), which screens for existing separation technologies, determines the best recovery pathway combinations, identifies crucial parameters, and determines costs. However, this framework extended beyond cost and targeted safety and health criteria. An objective function was formulated, considering weighting factors for the multiple objectives. The authors concluded that process performance and overall cost savings could be improved by selecting solvent recovery methods with consideration for their intended application [147]. Wang and Lakerveld presented a systematic approach to optimize continuous crystallization process conditions, solvent selection, and recycling in pharmaceutical applications. The Perturbed-Chain Statistical Associating Fluid Theory (PC-SAFT) method of continuous mapping was used to simplify the optimization from a mixed-integer non-linear programming problem (MINLP) to a non-linear programming problem (NLP). The PC-SAFT identifies thermodynamic parameters and can estimate the effects of interaction parameters for unique solvents with limited data [148]. Table 3 summarizes some previous work done in solvent recovery and the limitations associated with each work. The limitations of the various works suggest that a systems-level approach to solvent recovery presents a better and holistic methodology where there is a convolution of all prior techniques implemented.

Table 3

Previous Studies on Solvent Recovery with Features and Limitations

Reference	Features	Limitations
[145]	Evaluated the economic feasibility of the solvent recycling process. Presented some industrial activities from which solvent usage can be minimized	No comparison of alternate technologies for the recycling process. Analysis based on mass balance, no energy balance
[149]	Presented a statistical analysis of estimating life cycle data inventory associated with separating waste solvents via distillation.	No sensitivity analysis using the estimated parameters for the LCI
[78]	Demonstrated the need to perform a life cycle assessment on pharmaceutical solvents. They further applied solvent recovery to API manufacturing by considering the entire supply chain of the process.	Case-specific studies. No process design of the solvent recovery options and alternatives
[150]	Coupled distillation with pervaporation and demonstrated that over 92% of emissions associated with solvent recovery and incineration could be reduced when recovering isopropyl alcohol (IPA) from water	Process and solvent specific. Only binary mixture was considered; no multi-component analysis
[151]	Coupled a constant volume distillation with pervaporation and demonstrated the recovery of tetrahydrofuran (THF) from water compared to azeotropic distillation.	Alternate technologies should have been considered aside from pervaporation and distillation
[152]	Developed a software toolbox to assess binary solvent recoverability from both the economic and environmental perspectives	Only distillation and pervaporation technologies were considered. Only binary solvents were considered; no multi-component solvents
[153]	Implemented the box and quadratic programming approach to minimize the energy required for the distillation-based solvent recovery process in the semiconductor industry. About 40% of energy savings can be made based on the developed energy-efficient distillation system as compared to conventional sequences	No comparison with other distillation configurations and no alternate technologies. Distillation is an energy-intensive process. No LCA analysis
[148]	Proposed a methodology for solvent selection and recycling for crystallization. This was achieved by transforming an MINLP problem into an NLP using the PC-SAFT methodology	No economic and sustainability assessment of the process
[147]	Proposes a CAMD approach for the selection of solvents with higher recoverability properties. Focus on the Safety, Health, and Environmental (SHE) impact of the solvent generated	Only energy balance is incorporated in the CAMD approach.
[77]	Generated a generic superstructure for solvent recovery and implemented an MINLP approach to minimize the cost associated with the process.	Case studies were specific. No LCA or sustainability assessment

1.4.8 Emerging Trends in Designing Solvent Recovery

According to the US EPA, energy recovery proved to be the most typical form of hazardous waste management (22.0%) in 2019, followed by landfills, contributing 18.3%. Solvent Recovery ranks 8th with a percentage contribution of 3.5%. Figure 1 suggests that minimum efforts are directed toward the implementation of solvent recovery by the chemical industry. Ever since the enactment of major legislation by the US, EU, and China, industries and academia, have dedicated considerable research efforts to finding alternative treatment methods [96], [97], [144]. Recent advances in hazardous waste disposal indicate a gradual transition from conventional treatment techniques, such as deep injection wells and incineration, to modern recovery and reuse methods.

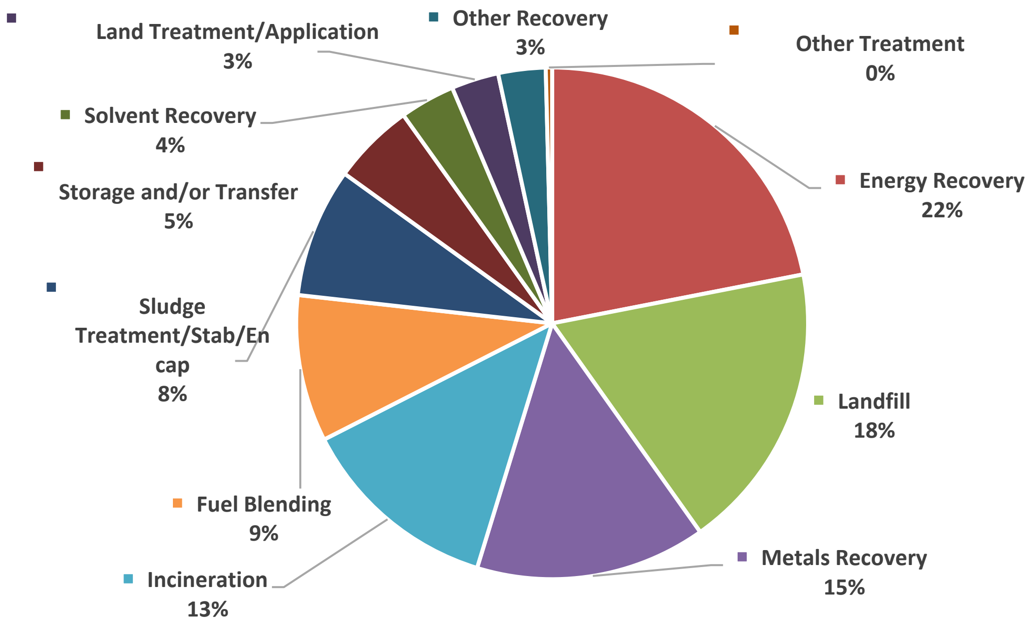

Figure 1. Top 12 hazardous waste management techniques in 2019 (total tons managed: 6,613,468) [154]

Membrane separation technologies began to find usage in scientific research and various industries in the 1970s [155], [156]. This method has been implemented primarily in wastewater treatment and desalination to remove solutes and produce high-purity water. Membrane separation may use pressure as a driving force to separate the component of interest through either polymeric or ceramic membranes as they permeate. Other components that do not diffuse through the membrane can exit as the retentate. Microfiltration, ultrafiltration, nanofiltration, and reverse osmosis are prime examples of pressure-driven membrane separation. Alternatively, membrane separation may also be osmotically-driven, which uses osmotic pressure as the driving force. Forward and pressure-retarded osmosis are typically used to perform osmotically-driven membrane processes [157].

Despite the popularities in water-based applications, organic solvent-resistant membranes are an emerging option for separating organic solvents [158]. Compared to distillation, the relatively low energy consumption allows membranes to serve as an alternative option in solvent recovery [158]. Liquid-liquid extraction is also gaining importance by proving its viability as an alternative to distillation and various uses in bio-based product applications. In some cases, the components in chemical solvent waste may be heat-sensitive and become susceptible to creating unwanted by-products. The presence of azeotropes and a similar boiling-point mixture may also deter distillation and encourage liquid-liquid extraction as a separation option. The chemical solvent of interest may have its impurities extracted using another immiscible solvent with a strong affinity for the impurities. First, the two immiscible solvents are mixed to provide sufficient contact time between the impurities and the extracting solvent. Then, the two phases can separate and be collected according to density difference. Multiple extraction cycles may be used with fresh extracting solvent to reduce the impurity levels after the initial extraction [129], [159]. Table 4 displays the alternative strategies that can be used to recover chemical solvents and the advantages and disadvantages of selecting each method. In deciding the most optimal solvent recovery technique for a waste mixture, the limitation of the solvent feed system should be identified. For instance, ethanol and water are known to form an azeotrope with each other [160]. Therefore, distillation is less favorable than other techniques that can break the azeotropes with minimal energy cost.

Table 4

Conventional Solvent Recovery Technologies, Driving Forces, Important Specifications, and Key Advantages and Disadvantages, Recreated from [77]

Technology	Principle/ Driving Force	Specifications and Important Conditions	Advantages	Disadvantages	Literature Sources
Physical Separation					
Precipitation	Charge solubility	Antisolvent, supersaturation, temperature, pH change	Low cost, selective removal possible, high yield, can remove dissolved solids	Impurities, coprecipitates	[159], [161]–[163]
Sedimentation or Decantation	Density gradient, Settling velocity	Size, density, tank depth, residence time	Effective at removing dense particles, cheap to implement	Require large space, must be designed based on maximum volume, and cannot remove dissolved solids	[159], [164], [165]
Centrifugation	Settling velocity Centrifugal force	Size, density, angular speed, the ratio of centrifugal to gravitational force, and settling distance	Effective at removing low-density and colloidal particles in a shorter time frame than sedimentation	Energy-intensive, cannot remove dissolved solids, generates high heat, and poses a safety hazard when processing volatile solvents	[159], [166]–[169]
High-Temperature Separation					
Distillation	Relative volatility	Relative volatility > 1.05 Heat of vaporization and energy requirements	Designed for a large variety of flow rates, it can separate a homogeneous fluid mixture	Energy-intensive, difficult to separate azeotropes unless a modification is made	[127], [133], [159], [170], [171]
Membrane Processes					
Membranes	Particle/molecular size/permeability Sorption/Diffusion Pressure	Pore size, Mol. Wt. Cut-off, average flux, Pressure gradient, type of membranes – M.F., U.F., NF, and R.O.	Lower energy requirement than distillation, highly selective with products, break azeotropes	Fouling, cannot operate at high temperatures and may not be compatible with all solvents	[156], [159], [172]–[174]
Pervaporation	Sorption/Diffusion Partial pressure	The heat of vaporization, chemical potential gradient, pressure gradient, average flux, membrane selectivity	Can break azeotropes, separate close-boiling point mixture, lower energy requirement than distillation,	Low-permeate flow rate, reduced membrane stability	[151], [159], [175]–[177]
Liquid-Liquid Extraction					
Liquid-liquid Extraction	Selective partitioning of solutes	Partition coefficient, the solubility of solutes, low solubility of the added solvent in water	Extracts dissolved solids from solvents, high selectivity, separates azeotrope mixture, does not require high temperature	Solvent-intensive, requires, limited by solubility	[133], [159], [164], [178]–[181]
Aqueous Two-Phase Extraction	Partitioning of solute, bioselectivity	Solubility, the composition of two phases, molecular weight	Highly practical with separating bioproducts	Macromolecule partition differently than smaller molecules	[182]–[186]

1.4.9 Process Intensification

Solvent recovery technology selection does not necessarily need to adhere to conventional methods. The theory of process intensification aims to optimize the existing processes by condensing multiple methods into fewer units or steps without sacrificing the efficiencies or changing the driving forces. Effects such as reduced equipment size, energy consumption per product mass, and by-product formation may be achieved [187]. There is no single definition that can fully describe process intensification. However, the general principle holds that the intensified process should maximize the effectiveness of molecular events, provide a similar processing experience for all molecules, optimize the driving forces and the associated surface area of contact, and maximize the synergistic effects between the combined processes. No extra chemicals, solvents, or equipment should be used in the new process. The overall size of the process would ideally be reduced due to combining multiple functions [188]–[190]. Process synthesis can, therefore, be improved using process intensification as long as the requirements and limitations are specified.

Process intensification can be performed with interest in the spatial, thermodynamic, functional, and temporal domains. The spatial domain aims to create a structure that would minimize randomness in a process. Thus, a controlled process can be directed to reach the desired outcome consistently. The thermodynamic domain aims to optimize the transfer of energy at various stages to minimize energy dissipation and waste. The functional domain seeks to synergize the traits from different processes into one unit. Yadav *et al.* (2021) designed an intensified process to extract algae oil and convert the biomass to biodiesel using CO_2 and methanol. This intensification was done by premixing the algae extract stream with methanol solvent before sending the material in for transesterification. Supercritical CO_2 was added [191]. The temporal domain modifies the time scale of the process to create the possibility of obtaining the product at a smaller timescale. One instance of timescale manipulation occurs when a continuously stirred tank is fed periodic feed, oscillating liquid volume and changing the mixing characteristic similar to a plug-flow reactor. The conversion of a batch to a continuous process may also be treated as a case of time-scale manipulation [190].

The approaches to process intensification can be applied to all design scales. In engineering design, multi-functional reactors, hybrid separators, alternative energy sources, and specially designed equipment have been introduced. Specifically, with solvent recovery, separators such as dividing-wall column, membrane distillation, pervaporation, membrane adsorption, adsorptive distillation, and liquid membrane can be viable choices [151], [175], [176], [192]–[197]. A dividing wall column is an alternative to conventional distillation that uses a longitudinal partition wall to separate multiple components in one unit. This method provides a considerable advantage over traditional distillation column-in series and in parallel because it requires less energy and space to operate. An existing distillation column can be retrofitted to include a dividing wall to reduce up to 20 – 50% operation and capital cost [198] while achieving multi-component separation. [194]. Membrane distillation combines the separation functions of reverse osmosis and evaporation into one unit by using a porous membrane to transfer volatile components in the liquid feed to the permeate side as vapor, followed by condensation into the liquid phase. This method has effectively rejected 100% ions, macromolecules, colloids, cells, and other non-volatile substances using temperature as the driving force. The operating temperature and pressure of membrane distillation remain lower than conventional membrane and distillation processes, creating a safer environment for heat-sensitive materials. Pervaporation combines the idea of permselective and evaporation to separate the component of interest based on its permeability through the membrane. The liquid feed enters the pervaporation unit and comes in contact with a dense membrane. The vacuum is pulled on the permeate side as a driving force for separation. Materials permeate through the membrane in the vapor phase, which later gets condensed into a liquid. This method is less energy-intensive than conventional distillation and can break azeotropes and separate components with similar boiling points [77], [175]. Membrane adsorption uses a polymeric membrane to allow specific substances to selectively adsorb onto the surface through functional groups present on the membrane. Sorbent may be incorporated as part of the membrane to enhance the adsorption capability. This method has removed contaminants from drinking water [199]. Adsorptive distillation adds selective adsorbents into the distillation feed to remove impurities, azeotropes, and components with similar relative volatilities [187]. Chang 2020 discusses using green solvents in extraction and liquid membrane (LM), an emerging technology promoting solute removal and solvent extraction into one unit. LM can reduce the energy requirement and provide non-equilibrium mass transfer and greater solute diffusion coefficients than solid membranes. Although promising at the lab scale, LM has not been used in large-scale applications due to poor membrane stability. The performance of using green organic solvents, conventional organic solvents, and a mixture of the two was compared. While green organic solvents can help achieve similar efficiency as conventional solvents, this cost may present the largest barrier to using a green organic solvent. Food security may also be affected because they are derived from agricultural commodities extracted from plants (palm oil, soybean oil, sunflower oil, coconut oil, etc.) [193]. The temperature-swing molecular imprinting technology designed by Voros *et al.* (2019) can extract bio-based compounds and recover solvents at over 97% efficiency [200]. Kisszekelyi *et al.* (2019) implemented a synthesis and separation hybrid using a flow reactor with an in-line membrane separation unit to recover catalysts and solvents in reaction applications. Their reaction achieved up to 95% yield while recovering 100% of the catalysts and 50% of the solvents. Challenges involving products precipitating during membrane separation were reduced by adding heat, followed by a subsequent crystallization in the collection vessel to purify the products further [201]. The examples shown merely represent a small pool of the intensified solvent recovery processes that have been implemented.

Selecting the most viable process intensification option for optimizing solvent recovery processes may be as complex as designing a new solvent recovery system because of the lack of precedent, data, simulations, and safety concerns on the proposed process [189]. Lutze *et al.* (2010) have created a framework for minimizing the feasible process intensification search space based on a six-step method [202]. This framework requires that the designer (1) defines the objectives, process scenario, and constraints, (2) collects information about the process and identifies limitations, (3) creates mathematical models to describe the process, (4) synthesizes a superstructure that encompasses all of the possible intensified processes and incorporates logical constraints and binary variables, (5) uses shortcut methods or semi-rigorous simulations to eliminate infeasible options, and (6) performs a multi-objective optimization on the feasible intensified process methods. The selected intensified process may be validated through experiments [202]. It should be noted that intensifying a process does not need to satisfy every criterion in the existing definition. However, the process viability, sustainability, and net profit can be expected to shift greatly toward a favorable outcome with each successful process intensification.

Solvent recovery is one of the alternative approaches to improving the sustainability and greenness of industrial processes. However, the design of an effective recovery process requires a systems-level approach. In the subsequent sections, we discuss some key elements that can help improve the integration of solvent recovery into industrial processes.

1.4.10 Energy-Efficient Ways for Solvent Recovery

Energy usage is one of the paramount factors to consider when designing solvent recovery systems. Higher energy consumption during the recovery process tends to reduce the attractiveness of its implementation by industries. In addition, energy from non-renewable sources tends to increase the overall carbon footprint of the process. Thus, there is a need to improve the energy demand of the process to make it economically and environmentally viable for implementation. Earlier implementation of the solvent recovery process by Case and Toy (1987) indicated an energy-efficient, activated carbon stripping system to recover 2721 kg/h of toluene-naphtha-lactane solvent mixture. They showed that preheating the water before being used for steam generation by the boiler unit improved the energy demand of the recovery process by reducing the amount of steam required [203]. Recent works predominantly explore the use of distillation columns for the recovery of used industrial solvents. Tremendous research has been conducted in separation processes using distillation to improve the energy efficiency of distillation processes. Chaniago *et al.* (2015) proposed an enhanced distillation system to recover a waste solvent mixture comprising isopropanolamine, water, monoisopropanolamine, methyl diglycol, n-methylformamide, 1-piperazineethanol, photoresist in the semiconductor industry. They observed that by thermally coupling the distillation columns in sequence and implementing a heat pump, about 40% of energy savings were made compared to conventional methods [153]. They presented further advanced combinations of the distillation units in sequence, which achieved the required outlet solvent specifications at a reduced reboiler heat duty.

The use of Switchable Hydrophilicity Solvents (SHSs) for industrial processes has begun to gain attention in the past decade [204]–[206]. The idea with SHSs is to "switch" the hydrophobicity and hydrophilicity of solvents in the presence of water and CO_2 [204]. These unique physicochemical properties of certain nitrogenous organic solvents present a new frontier for distillation-free solvent utilization and recovery processes. Thus, with increased pressure on distillation, which is an energy- and cost-intensive process, the use of SHSs presents an energy-efficient way of designing solvent recovery processes. Expanding the research to find non-nitrogenous organic solvents that exhibit this "switchable" property should be vital to improving solvent-based processes and recoveries. Membrane processes also present cheaper alternatives to energy-intensive technologies. For example, White and Nitsch (2000) presented a solvent recovery of lube oil filtrates using a polyimide membrane, which was later commercialized [207]. Given that fewer boiling processes are associated with the implementation of membrane processes, they should be preferred to distillation in terms of energy efficiency.

Implementing solvent recovery presents an opportunity to reduce manufacturing costs, improve the greenness of the process, and reduce the emissions and environmental impacts associated with industrial processes. With increasingly stringent governmental regulations for hazardous waste disposal, solvent recovery offers industries a greener alternative to meet these legislations. A superstructure-based approach for designing solvent recovery systems presents a decisive advantage over sequential methods because it can simultaneously analyze multiple options. The interconnections between the separation and purification technologies are preserved, while sequential design targets the specific needs using conventional schemes and one-at-a-time analysis. The sequential method may not always reach the global optimum, leaving room for improvement. Sustainability metrics can be an indicator for assessing the chosen process viability. In cases when improvements are needed, there are opportunities to optimize recovery processes further. For instance, direct process modification can solve the specific limitations in the process by targeting the areas of interest and crucial bottlenecks. Alternatively, process intensification combines the functionality of two or more separation technologies by reducing the equipment sizes without drastically changing the process characteristics, which can help reduce the fixed costs and land footprint. The overall benefits of solvent recovery highlight the need for a paradigm shift from traditional waste handling methods to environmentally friendly and green alternatives. Energy resource utilization is always immensely at the forefront of industrial decisions. The emergence of switchable hydrophilicity solvents could greatly improve the architecture of energy demands for solvent recovery processes. The rise in data generation at a geometric rate indicates that AI/ML has become an indispensable tool for industrial research. Advances in ML/AI can help with critical steps in addressing solvent recovery processes in industries.

1.5 Challenges with Plastic Recycling and the Unintentional Releases

In the end-of-life stage, a low material recovery rate presents the largest obstacle to achieving a circular economy. Plastics, for instance, have proven to be essential in applications ranging from packaging, storage, vehicles, and insulation because of their low cost, versatility, durability, and low weight [15]. As a result, global plastic production was estimated to reach 360 million tons in 2018 [208], and this demand continues to rise annually. However, the current plastic end-of-life (EoL) management methods, which scale with the plastic production rate, are not sustainable and are prone to releasing toxic chemical additives into the surrounding environment [209], [210].

Incineration and landfilling process over 90% of the spent plastics [211] and are generally considered the preferred methods for waste handling. These methods are not favorable because the materials are either thermally decomposed or buried with other waste materials [74], [81], [212], [213]. The consequences of these processes can emit unwanted substances detrimental to human health and the environment. An improvement to the existing infrastructure is needed to limit chemical release and exposure resulting from municipal plastic waste.

The life cycle of plastic encompasses three major phases: production, use, and end-of-life. The production phase begins with raw material, monomer synthesis, and polymerization with chemical additives to create plastic for consumer use. The use phase generates plastic wastes, which are processed through the end-of-life phase. The fate of these plastic wastes is dependent on the following pathways: (1) recovering, (2) incineration, (3) landfilling, and (4) littering [209]. Plastic recovery, the most favorable end-of-life pathway, encompasses mechanical, chemical, and energy recycling [214]–[218]. Alternatively, incineration thermally decomposes plastic waste, releasing energy, greenhouse gas, and other pollutants into the environment [219], [220]. Although air pollution control technologies have been developed to reduce environmental impacts, incineration is an irreversible process that can aid in depleting natural resources such as fossil fuels [221]. Landfilling uses an area of land to accumulate unwanted waste, while littering is the improper disposal of waste. Both methods result in pollution problems and contamination of water supplies [219], [222]. The waste from landfilling and littering may be reduced through chemical, mechanical, and biodegradation. A perfectly circular economy can be achieved if incineration, landfilling, and littering are eliminated. However, a circular economy cannot be achieved until the current technological efficiencies, operation costs, incentives, and legislation support associated with plastic recycling are improved [209], [223], [224]. The efficiency problems are correlated to unwanted chemical additive migration, emission, leaching, degradation, and exposure following plastics manufacturing. Therefore, it is crucial to examine the existing flaws in the current end-of-life material recovery infrastructure before the traditional linear production paradigm can be shifted into a circular economy structure.

1.5.1 Municipal Solid Waste Composition

The MSW composition is shown in Figure *2*a. Papers, metals, glasses, and plastics are the primary components considered for recycling. The US EPA has estimated that over

35.7 million tons (32.4 billion kg) of plastic waste were generated in the United States in 2018. The municipal plastic waste is composed of 14.8% polyethylene terephthalate (PET), 17.7% high-density polyethylene (HDPE), 2.4% polyvinyl chloride (PVC), 24.1% low-density polyethylene (LDPE), 0.3% polylactic acid (PLA), 22.8% polypropylene (PP), 6.3% polystyrene (PS), and 11.7% other plastics by weight. Up to 3 million tons (2.7 billion kg) (~8.4%) of the waste plastics were successfully recycled, 75.8% were landfilled, and 15.8% were incinerated [211]. Recycled plastics are generally reprocessed into pellets to be used as raw materials for new plastics.

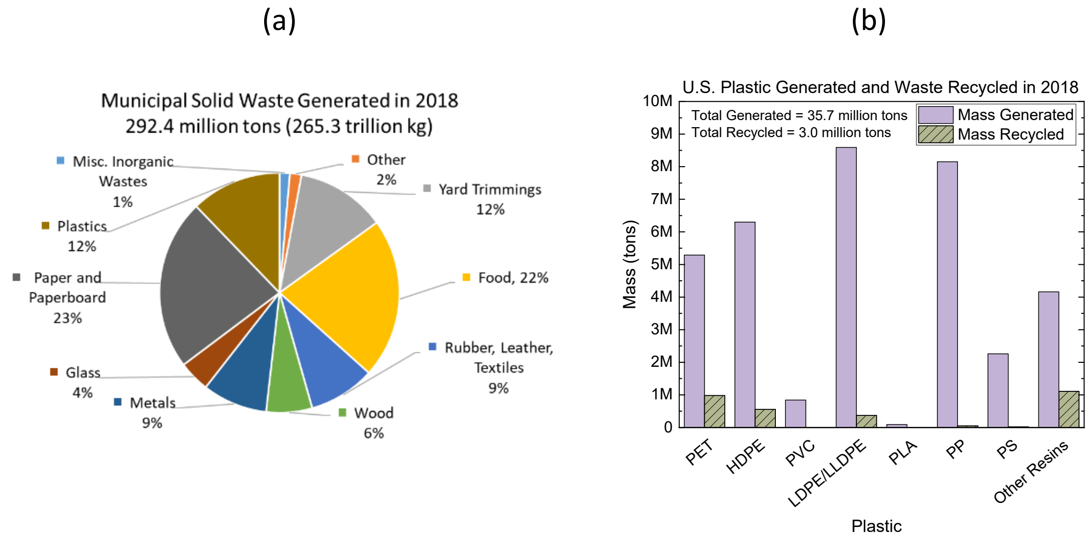

Figure 2. (a) Municipal solid waste (MSW) composition in 2018 and (b) Plastic Waste Composition in the United States in 2018. The overall recycling rate equates to 8.4%. The main plastic waste includes polyethylene terephthalate (PET), high-density polyethylene (HDPE), polyvinyl chloride (PVC), low-density polyethylene (LDPE), polylactic acid (PLA), polypropylene (PP), polystyrene (PS), and other uncategorized types

Similar EoL pathways were reported by the United Nations, in which 9% of the global plastics wastes were recycled, 79% were landfilled, and 12% were incinerated by weight [225]. This concerning fact suggests improving the existing plastics processing infrastructure to minimize excess environmental accumulation and toxic exposure. Figure 2b illustrates the typical plastic waste collected as part of the MSW in 2018 [211]. The plastic waste categories coincide with polymer resin identification codes 1 through 7, with the addition of polylactic acid (PLA). Most of the recycling efforts have been allocated toward recovering PET, HDPE, LDPE, and a select group of uncategorized plastics.

1.5.2 General Plastic Wastes Treatment Methods

Mechanical recycling is the most common method utilized throughout the United States because of its low operational costs and high reliability. To date, this method is considered physical recycling, in which plastic is ground down and then reprocessed for the original use or to produce new material [226]. The recycling process begins with the separation and sorting of the collected materials. First, the plastics are sorted based on shape, density, size, and type. Next, the sorted plastics may be condensed into bales and transported to a separate facility for reprocessing. Finally, a washing step is typically employed to remove organic contaminants present on the surface of the collected plastics [21]. Various physical recycling techniques can be used depending on the plastic types and properties. Each mechanical recycling method has drawbacks that decrease the quality of the final recycled plastics. For example, Augier *et al.* (2007) recycled composite waste (PVC and wood fiber) up to five times without requiring any added materials. The molecular weight of PVC decreased from chain scission induced by shear stress from each recycling iteration [227]. Jin *et al.* (2013) reported that LDPE's complex viscosity increases during extrusion, reducing material processability. This increase is caused by crosslinking throughout the LDPE chain from reactive carbon radicals [228]. Aurrekoetxea *et al.* (2001) showed reprocessing reduced the molecular weight and increased the crystallinity of recycled polypropylene. Young's modulus and yield stress increased from the high crystallinity. The decreased molecular weight reduces elongation at break and fracture toughness [229]. These challenges during EoL recycling decrease the usage rate of recycled plastics. Downcycling is often the fate of mechanically recycled plastics that do not meet the requirement of manufacturers [15], [230]. This action repurposed the recycled plastics to form lower-value products, including building materials, packaging, fillers, and textiles [230].

Incineration uses a large amount of energy to thermally decompose MSW (e.g., plastics), releasing energy, greenhouse gases, and other pollutants into the environment through combustion [219], [220]. Furthermore, the incineration of MSW may produce other byproducts, such as soot particles (e.g., PM2.5) and bottom ash residues that may act as carrier agents to transfer toxic chemicals to the environment. In addition, the composition of the incineration products depends highly on the materials fed into the process [231]. Although air pollution control technologies have been developed to reduce environmental impacts, incineration irreversibly converts plastics into other forms that are no longer usable from a closed-loop system standpoint [74], [221], [232].

Landfilling has been debated as both an impediment to further improvement in recycling and a necessity for storing nonrecoverable materials. Nonbiodegradable materials such as many plastics may persist within the landfills for many years, creating an accumulation of solid waste and occupying land space [233]. In addition, this waste management practice can potentially lead to air and land pollution problems and contamination of water supplies. These consequences originate from rainfall and groundwater seeping through the landfill containment barriers [219], [222].

As can be seen, the flaws in the existing recycling infrastructure and the heavy reliance on non-sustainable waste management techniques have led to an unacceptable recycling rate. Chemical recycling is a viable alternative to processing wastes that are not recycled through physical means. The chemically recycled plastics are often converted to oil, hydrocarbon, and other monomeric components that can be used as raw materials for new substances. For instance, de la Puente *et al.* (2002) performed fluid catalytic cracking (FCC) at 500°C in the presence of various commercial catalysts using toluene as a solvent [234]. Hajekova and Bajus used a two steps thermal cracking method for LDPE and PP waste [235]. One polymer type was decomposed in a batch reactor at 450°C into wax/oil products. Then, the wax/oil products were dissolved in heavy naphtha to produce steam-cracking feedstock. Vicente *et al.* (2009) reported that HDPE recycling could be accomplished through thermal cracking in the presence of phenol [236]. Achilias *et al.* (2008) recycled PE (LDPE and HPDE) and PP using dissolution/precipitation methods with various solvents and non-solvents, as well as catalytic pyrolysis using fluid catalytic cracking (FCC) [237]. They also performed catalyst and non-catalyst pyrolysis of PS waste in a fixed-bed reactor using commercial waste products as feedstock. The pyrolysis oil fraction could be polymerized into virgin polystyrene [237]. Although the methods described are promising, chemical recycling is not a standardized practice because of legislative, economic, and technical hardships in various regions worldwide [238]. A modification to the existing EoL infrastructure is needed to maximize material recovery and maintain a circular economy while reducing waste and unintentional environmental releases.

1.6 Dissertation Summary

The conventional material flow of product manufacturing generally exhibits a linear structure because it is in the best interest of the manufacturer to create a long-lasting product that serves the consumer's needs. This mentality tends to result in products that persist in the end-of-life stage for many decades after disposal. For instance, in comparison to incineration and landfilling, minimal plastic products were recycled because these wastes do not meet the requirements or are difficult to separate from other impurities. A circular economy can be achieved if a product is designed considering every stage within the life cycle. This research aims to modify the process design paradigm by strategically adding sustainable practices throughout the life cycle of a material. Specifically, we aimed to enhance (1) the material extraction and acquisition stage by commercial-scale extraction and the subsequent product synthesis, (2) chemical processes by minimizing material waste, and (3) end-of-life waste management by proposing alternative recycling strategies.

The remaining chapters are structured as follows: Chapter 2 presents the characterization methods used throughout this work. Specialized techniques are further elaborated on in the relevant chapters. Chapter 3 proposes a sustainable solution in the beginning stage of the life cycle of a material using a systematic framework to extract resources from renewable feedstocks commercially. Chapter 4 shows the viability of using the extracted resources to synthesize polymeric materials for various applications. Chapter 5 applies a similar systematic approach as Chapter 3 to managing waste throughout a process. Chapter 6 examines the movement of waste products post-consumer use and tracks the potential releases. Generic scenario analyses and other hypothetical waste treatments are presented with recommendations. Chapter 7 describes an ongoing approach to simplify recovery method designs and release estimations described in Chapters 5 and 6, respectively. Finally, Chapter 8 concludes with remarks on achieving a sustainable and circular economy in process design. Figure 3 illustrates a mind map containing the logical flow between the chapters presented in this dissertation.

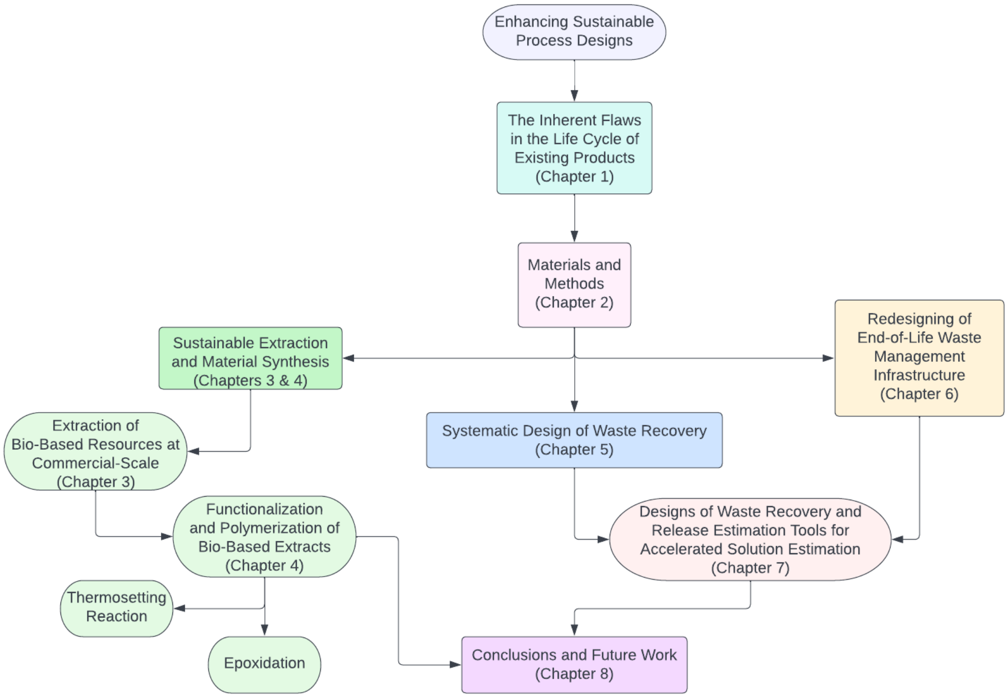

Figure 3. Overview of the full scope and connectivity between each topic covered in this work

Chapter 2

Materials and Methods

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This section serves as a reference for the general procedures used in this study. Experimental and computational techniques are separated as Sections 2.1 and 2.2, respectively. Specialized techniques used for specific studies are excluded from this Chapter and explained in the relevant chapters.

2.1 Experimental Techniques

2.1.1 Nuclear Magnetic Resonance (NMR)

NMR was used to verify the molecular structure of all products synthesized or extracted. Proton (H)-NMR traces were acquired from Bruker Avance Core NMR Spectrometer for this research. The general sample preparation procedure involves dissolving approximately 20 mg of the substance in 1 mL of deuterated solvent (chloroform). All NMR spectra were analyzed in ACD/1D NMR Processor.

2.1.2 High-Performance Liquid Chromatography (HPLC)

High-performance liquid chromatography was used to separate and quantify different chemicals in the powdered birch extract. The mobile phase composition, adapted after a method reported by Maji *et al.* (2014), was selected to be 94% acetonitrile (ACN) with 0.1% acetic acid and 6% water (0.1% acetic acid by volume) [239]. This composition was held as an isocratic flow of 1 mL per minute [240]. The XTerra MS C18 Column was chosen as the stationary phase, a reversed-phase silica-packed column. Non-polar molecules contained within the extract, such as the triterpenoid molecules, are expected to interact with the stationary phase and exhibit a longer retention time. All samples were analyzed at a column temperature of 25°C over 20 minutes. The wavelength of detection chosen from the photodiode array detector (PDA) was 210 nm, based on the absorbance intensity of the triterpenoid standards. The resulting chromatogram was analyzed in the Waters Alliance e2695 Separations Module for the concentration of betulin, betulinic acid, and lupeol, with the remaining peaks classified as unknown.

2.1.3 Advanced Polymer Chromatography (APC)

Waters AQUITY Advanced Polymer Chromatography was used to determine the molecular weight distributions of materials extracted and synthesized. This instrument is calibrated with polystyrene standards with a molecular weight range between 474 – 2,500,000 g/mol and a dispersity of 1.15. A series of ACQUITY APC columns were maintained at 40°C during all sample runs. The number average molecular weight (M_n) represents the total weight of the polymer sample divided by the total number of polymer molecules. The weight-average molecular weight (M_w) considers the number of molecules present and the weight of each molecule. Dispersity (Đ) is the ratio of M_w to M_n. A dispersity value of one signifies that the polymer sample is monodispersed, which indicates that the molecular weight distribution consists of one value [241].

2.1.4 Thermogravimetric Analysis (TGA)

The thermal stability of the polymers was measured using a TA Instruments Discovery Series Thermogravimetric Analyzer (TGA) 550. This instrument records observable changes in the mass of any materials as a function of temperature or time, which can be useful in identifying material decomposition, dehydration, or oxidation. For this research, the initial decomposition temperature ($T_{5\%}$), the temperature at 50% weight loss ($T_{50\%}$), maximum decomposition temperature (T_{max}), and char content (%) were reported. Approximately 5-10 mg samples were placed in a platinum pan, equilibrated to 40°C, and heated to 700°C at a rate of 10°C/min in a nitrogen-rich atmosphere (40 mL/min balance gas flow rate and 25 mL/min sample gas flow rate). These values aid in establishing the upper-temperature limit for operations.

2.1.5 Differential Scanning Calorimetry (DSC)

TA Instruments Discovery Series Differential Scanning Calorimeter (DSC) 2500 was used to observe thermal transitions such as glass transition, crystallization, phase changes, melting, and curing kinetics as a function of temperature. DSC measures the temperature difference between a sample pan and a reference (empty) pan at a specified heating rate in both inert (N_2) and oxidative (air) atmospheres to calculate the heat flow in and out of the material of interest. Samples between 5-10 mg were placed in an aluminum pan and sealed using a crimper press. Based on the TGA results and to avoid decomposition, the samples were heated from room temperature to a specified temperature below the $T_{5\%}$ at a rate of 10°C/min. The second thermal cycle subjects the samples to -10°C at a rate of 25°C/min. The final heating cycle subjected the samples to the chosen temperature at 10°C/min. Endothermic heat flow is characterized on the plots by a downward trend, and vice versa for exothermic heat flow. The glass transition temperature (T_g) of a material is characterized by an inflection point, which indicates the temperature when the material transitions from a glassy to a rubbery state [241].

2.1.6 Dynamic Mechanical Analysis (DMA)

A dynamic mechanical analysis (DMA) was performed using TA Instruments DMA 850 on each sample. This technique applies oscillatory strain to a material at a given frequency and temperature and reports the resulting stress developed by the material. For each material, Young's modulus (E'), a measure of elasticity, and loss modulus (E''), a measure of energy dissipation as heat, can be obtained as a function of temperature. The T_g of a material can be obtained at the maximum point of tan δ, which is a ratio of the loss modulus to Young's modulus [242]. All samples were run at a frequency of 1 Hz, amplitude of 10 μm, and a heating rate of 2°C/min.

2.1.7 Epoxy Equivalent Weight Titration

The epoxy equivalent weight (EEW) was determined through ASTM D1652, which involves the titration of a solution containing a known amount of the epoxy sample of interest, dichloromethane, and tetraethylammonium bromide in glacial acetic acid solution, and crystal violet indicator using a 0.1 N perchloric solution in glacial acetic acid solution [243]. EEW is necessary for epoxy curing, as it indicates the amount of reactive epoxy group for a given mass of epoxy resin. One reactive epoxy group will crosslink with one amine hydrogen group provided by the curing agent. This curing process begins with a nucleophilic attack of the amine nitrogen on the terminal carbon of the epoxy group, which opens the oxirane (epoxy) ring [244], [245]. One of the primary amine hydrogens would then react with the oxygen in the epoxy group. One secondary amine hydrogen remains after this event, which can continue to react with another epoxy molecule. All chemicals were purchased from VWR Chemicals.

2.1.8 Hydroxyl Value Titration

Hydroxyl value titration was performed using ASTM 222-17, a standard test method for hydroxyl groups using acetic anhydride acetylation [246]. This method helps determine the number of hydroxyl groups attached to primary and secondary carbon atoms in aliphatic, alicyclic, and phenolic compounds. The reactivity of unrefined biomass, obtained as part of this research, can be determined because this reaction targets hydroxyl groups in the chemical mixture. A given sample is acetylated in a solution of acetic anhydride in pyridine at reflux temperature and under constant agitation for 1.5 hrs. The excess reagent is later hydrolyzed with water, forming acetic acid. The acids are then titrated with a standard sodium hydroxide solution. The hydroxyl content is calculated from the difference in the titration of a blank and sample solutions. The blank solution follows the same setup as a regular sample. However, no sample is added for the acetylation reaction. Pyridine ACS grade (suitable for Karl Fischer Reagent) was purchased from Fisher Scientific. This chemical was mixed with ACS grade (>99.0%) acetic anhydride, obtained from Fluka Analytical, to prepare the acetylation reagent per the ASTM 222-17. The sodium hydroxide solution used for titration was diluted to 0.5 N from a 50% w/w solution purchased from VWR Chemicals.

2.1.9 Fourier-Transformed Infrared Spectroscopy (FTIR)

Fourier Transformed Infrared Spectroscopy was used to confirm the chemical structure of substances (solid and liquid) purchased and synthesized in this work. Physically, each sample is held in place while an IR source is directed at the sample. The spectrometer records frequencies that allow the sample to absorb the IR light. Each chemical absorbs infrared radiation at specific wavelengths, causing a change in its dipole moment. The vibrational energy level of the chemical is then shifted from the ground to the excited state. High peak intensity corresponds relatively to the amount of a specific chemical group within the sample. Additionally, based on the sample, the attenuated total reflection (ATR) assessor was used to capture the mid-infrared (MIR) spectra at 4000 – 400 cm^{-1} (2.5 – 25μm) through a Thermo Scientific Nicolet 6700 FTIR. Alternatively, near-infrared (NIR) was used to analyze chemical structure in the near-infrared region at 12,500 – 4000 cm^{-1} (0.7 – 2.5 nm) through a Thermo Scientific Nicolet iS50 FTIR [247].

2.2 Computational Techniques

2.2.1 General Software

General Algebraic Modeling System (GAMS) is a language used to model mathematical programming and optimization problems. GAMS modeling, at minimum, requires fully defining sets, parameters, variables, equations, and a solver. Sets are building blocks representing any category related to a specific problem. For example, the typical sets in process design would include technology, stream number, and components. Parameters are values that are specified or calculated. Variables are fully customizable objects that may take the form of either "decision" or "objective." Decision variables are expressed algebraically as part of an equation. The objective variable typically exists as a single object in which the entire model is used to determine this value. This object can be found as part of the objective function.

Many solvers are available for use with GAMS, which are determined based on the programming model [248]. SuperPro Designer is a modeling program designed to model and optimize batch and continuous processes from over 140 unit operations that include, but are not limited to, biotech, pharmaceutical, specialty chemical, food processing, and wastewater treatment [249]. This program contains a database of chemical components and mixtures that are readily available, including material and energy balances, sizing, costing equations, economic evaluation, environmental impact assessment, and scheduling of batch operations. Although SuperPro Designer provides a high level of detail, GAMS provides a faster screening estimation of processes. Therefore, in this dissertation, SuperPro Designer is used post-GAMS analysis in process synthesis-related work.

2.2.2 Process Synthesis

The process design methodology in this work first defines the objective functions with specific goals. For example, in solvent recovery, we aimed to maximize material recovery while minimizing both process costs and environmental impacts [77]. This step identifies the solvent waste streams and process constraints to establish the feed stream characteristics and limitations. Feed stream information such as solvent identity and composition, possible azeotropes, impurity types, and quantities proves valuable in future calculations. The limitations identified may include temperature limits to avoid degradations, equipment types available for usage, and the minimum purity and recovery requirement. Process synthesis typically employs two methods involving (1) sequential methods and (2) superstructure-based optimization.

2.2.2.1 Sequential Method. The sequential method uses past engineering designs and decisions to generate a process flow sheet. The primary process is designed one at a time to achieve a specific goal irrespective of the decisions made in the previous stages [250]. Some prominent examples may include reactor networks, gas cleaning systems, and heat recovery networks [133], [251]. The existing systems and networks serve as a general starting point and can be modified to fit the process needs. Many unique combinations of process units may also be possible because process design is partially dependent on the creativity of the engineers. However, such an approach can be time-consuming because alternative methods are not being compared simultaneously.

2.2.2.2 Superstructure Optimization Approach. A superstructure-based optimization approach is a powerful alternative method that has been used in process synthesis because it considers all of the possibilities to perform the desired process and connects the techniques between the stages [77], [251]–[255]. The superstructure-based optimization is formulated as mathematical equations, including constraints, logical constraints between units and stages, and process unit models [251]. The generation of a superstructure begins with the problem formulation, followed by generation and finding a solution to the optimization problem [256]. For example, Chea *et al.* 2020 have developed a generic superstructure-based solvent recovery framework that uses a stage-wise approach to separate and purify waste solvent from a chemical process. This solvent recovery framework is illustrated in Figure 4. By default, a superstructure approach considers traditional and emerging technologies without imposing special restrictions. However, technology restrictions may be included as needed based on the property of the waste solvent. For instance, distillation may be excluded from consideration because the waste solvent contains components with similar boiling points or form azeotropes.

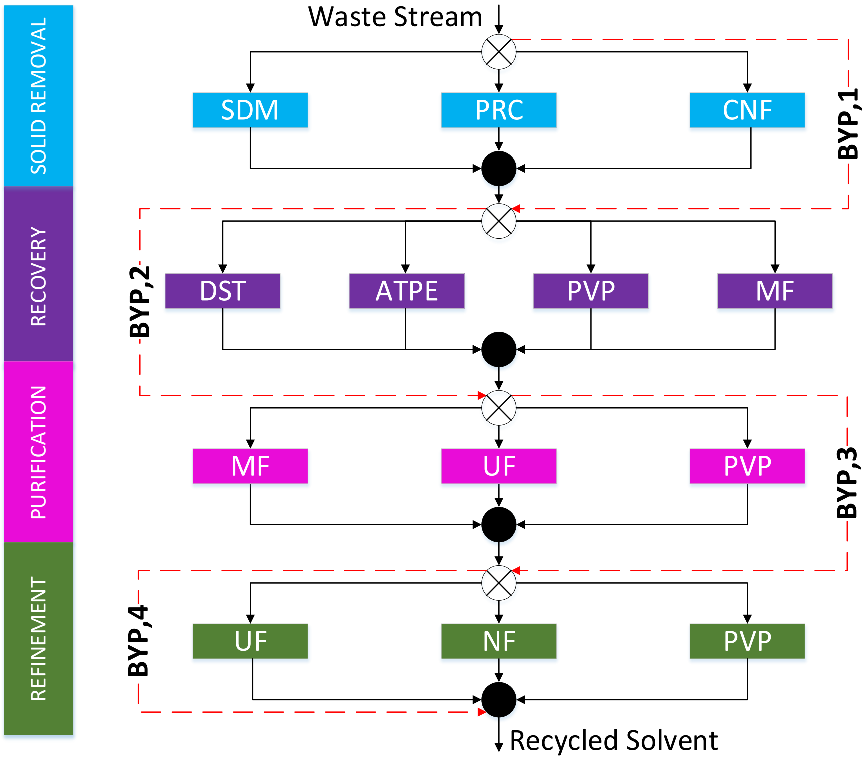


Figure 4. A generic solvent recovery superstructure. The acronyms represent the following: Sedimentation (SDM), Precipitation (PRC), Centrifugation (CNF), Distillation (DST), Aqueous Two-Phase Extraction (ATPE), Pervaporation (PVP), Microfiltration (MF), Ultrafiltration (UF), Nanofiltration (NF).

The superstructure generation method identifies all possible technologies for performing a specific task. The technologies may be grouped at various stages according to their characteristics. In cases like solvent recovery, multiple stages may be required to purify the solvent waste of interest. The interconnections between the technologies at each stage should also be included to show the relationships and possible interactions with the previous stages. Each technology presented in the superstructure can be represented in the optimization model as mathematical equations that include designs, user-specified and typical constraints, costs, and environmental impacts. These calculations can be customized and incorporated into the model based on the interest. The superstructure-based optimization problem can be solved as either mixed-integer non-linear (MINLP) or linear programming (MILP) because the decisions to choose between alternative technology for a given stage are represented by integer variables [257]. This method analyzes all non-constrained options simultaneously and selects the best combination of technologies that satisfy the objectives [77], [252], [253], [253], [256]. The process design engineer may also exclude technologies deemed infeasible or unavailable to reduce the number of calculations in the analysis. Figure 5 summarizes the solvent recovery superstructure methodology and the necessary steps to acquire the most feasible design. This method provides flexibility by allowing simultaneous comparison of potential options with reasonable approximation at the screening level stage. Detailed design pathways can be compiled as a shorter list based on the constraints set forth by the designer.

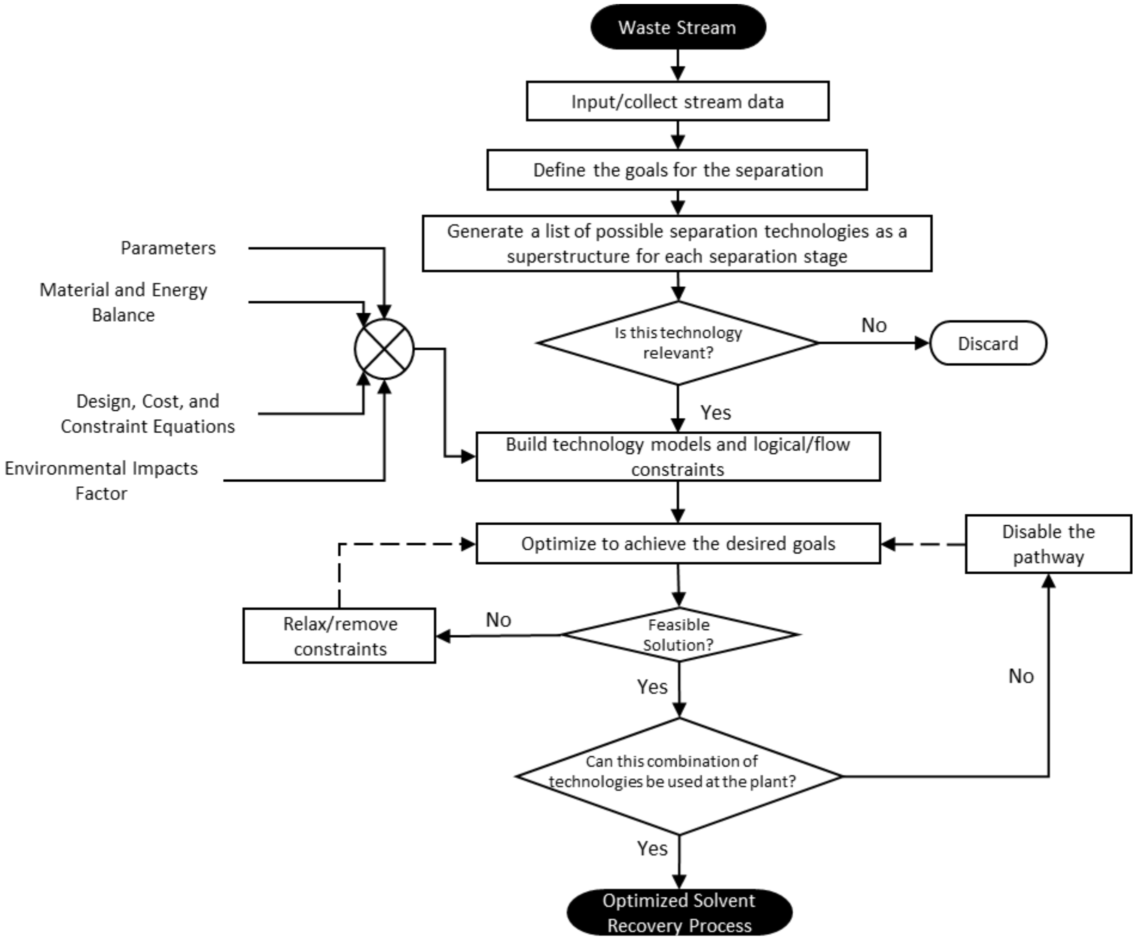


Figure 5. The recommended flow path for optimizing solvent recovery processes using the superstructure approach. The diamond-shaped decision box is implemented via binary (1-Yes/0-No) selection variables, enabling the logical flow constraints for active/inactive technologies and their corresponding stream flows.

2.2.3 Economic Analysis

Economic assessment is a crucial component of any design process to ensure viability. Such estimation should be performed in the early stages of design because there is greater flexibility in changing the initial concept over a process already in operation. However, retrofitting an existing process to implement solvent recovery is also feasible. Both cases ultimately determine the cost of installing, maintaining, and operating a solvent recovery system. If the projected cost and payback period of solvent recovery for a given waste stream is deemed unfavorable, further optimization can be performed by comparing alternative options based on the initial assessment. In some instances, the capital cost required to implement a solvent recovery system may be too high due to low waste volume. Savelski *et al.* (2017) identified this challenge and completed a relevant case study on the economic and environmental feasibility of solvent recovery at an active pharmaceutical ingredient production facility. They concluded that recovering solvent from one instance of waste would net negative costs. However, a flexible recovery design combining low-volume waste streams into larger quantities can lead to more favorable results. Their life cycle impact assessment also demonstrated that impacts on human health, ecosystems, and resources are unavoidable but can be drastically reduced by recovering the materials and reducing the need to create and manufacture new raw materials [258]. Chea *et al.* (2020) expanded upon the work by creating a generic and systematic approach to determine the economic feasibility of solvent recovery methods at a large scale. They presented two test cases of solvent waste processing from different sectors in the chemical industry (pharmaceutical and specialty chemicals) at the screening phase before design. The screening phase examines many options and narrows the possibilities to the most favorable candidates for further analyses. The outcome of the economic analysis of the selected solvent recovery processes generally favors recycling instead of using waste incineration and purchasing fresh solvents. The recovered materials can also reduce process waste and unwanted chemical releases, reducing the E-factor of the process and environmental impacts [77].

The cost estimation of solvent recovery processes can be approached using multiple methods. The quickest way of plant cost assessment with ±25% accuracy can be made by scaling the capital cost of a process with the capacity [250]. The capacity of the unit can be calculated according to chemical engineering principles, design equations, and common constraints. Equation (1) describes the cost scaling method, where C_i represents the estimated capital cost based on the new capacity, Q_i, while C_0 and Q_o represent the standard cost and capacity, respectively. The exponent n is the scaling factor that can vary depending on the type of process. However, in the chemical industry, $n = 0.6$ is considered an average [133]. This exponent is always less than 1.0 because larger equipment generally costs less at a specific capacity than smaller equipment.

$$C_i = C_0 \left(\frac{Q_i}{Q_o}\right)^n \tag{1}$$

Standard cost and capacity data are not always available, especially if the process is novel. A step count method has been reported, which can allow an order-of-magnitude cost estimate of the overall process by correlating the total capital cost to the number of functional units with considerable costs in a plant N, total plant capacity Q, and the reactor conversion rate s of product per mass fed to the unit. The reactor conversion rate can be treated as the expected recovery fraction in estimating the solvent recovery process sequence. Equations (2) and (3) describe the correlation, with 60,000 metric tons/yr as the threshold [133], [259].

$$Q \geq 60{,}000\,\frac{metric\ tons}{yr}; C = 4320\ N\ \left(\frac{Q}{s}\right)^{0.675} \tag{2}$$

$$Q < 60{,}000\,\frac{metric\ tons}{yr}; C = 380{,}000\ N\ \left(\frac{Q}{s}\right)^{0.3} \tag{3}$$

The cost scale and the step count methods should be used to provide screening level estimation for determining the process viability. The uncertainty of the estimated capital cost can be further reduced by creating a list of required parts and equipment, considering material types, the fabrication process, and the labor required. A direct vendor price is also a valid option because it provides the actual cost tailored toward a specific process condition and purpose of the equipment. The solvent recovery unit installation cost conservatively can be estimated as 100% of the capital cost [152].

In addition to the capital cost of the equipment, variable costs, fixed costs, revenues, and profits are the remaining essential components of the total process cost. Variable costs are defined as costs that scale according to the plant output and operation, including raw materials, utilities, consumables, disposals, packaging, and shipping. The fixed costs, including labor, overhead, maintenance, taxes, insurance, and rent, do not change with the plant output and operation. Labor cost can be considered a variable cost if treated to be scalable to the working capacity of a processing unit [77]. Equation (4) displays a method to approximate the number of laborers required to operate a technology under a different capacity. The standard number of labors ($N_{labor,std}$) corresponds to the standard capacity (Q_{std}) and vice versa for the scaled number of labors (N_{labor}) and new capacity (Q_{new}). The overhead cost in solvent recovery processes primarily consider research and development and general administrative costs. Research and development involving material recovery may account for up to 15% of the total process revenue, while the general administrative cost may be assumed to be a minimum of 65% of the calculated labor cost [133].

$$N_{labor}Q_{std} = N_{labor,std}Q_{new} \tag{4}$$

The process revenues are typically contributed by the main products and by-products [133]. However, process waste may contain valuable materials (e.g., solvents) that can be recovered, provided that the substance meets the minimum standards for reuse. This standard may vary between different sectors. For instance, the pharmaceutical industry may require a more stringent requirement for solvent reuse than the paint industry [77]. Nevertheless, recovered solvents have values and can improve the overall process viability. This value is a function of the solvent purity obtained through the separation and purification techniques.

Raw materials are substances used in the process, which may include solvents. Consumables include materials that require regular replacement, including membranes, acids, bases, and adsorbents. Solvents are typically treated as a consumable. However, in solvent recovery processes, solvents can be treated as raw materials that can be recovered in large quantities. The price of raw materials and consumables can be calculated by multiplying the price ($/mass unit) by the input rate. The largest uncertainty with raw material pricing originates from fluctuating prices over time, constantly altering the total process cost. The raw material price sometimes becomes higher than the final product, rendering the process infeasible and unnecessary [260]. Although assuming an average price is possible, this approach does not fully represent the market's volatility. Future trends must be evaluated based on the price history of the material of interest through a deterministic and stochastic approach [261]. This approach is shown in Equation (5), where $P_{material,i}$ is the price of the material at time i, $P_{material,i-1}$is the material price in the previous time step, $\sigma_{material}$ is the standard deviation of the price, $\overline{X}_{material}$ is the average price, and RAND is a random function that produces a set of values within a normal distribution.

$$P_{material,i} = P_{material,i-1}\left(1 + RAND * \sigma_{material} + \overline{X}_{material}\right) \quad (5)$$

Utilities include fuel, steam, cooling water, electricity, and other gas required to maintain operation. Likewise, with other variable costs, utility cost is subjected to price volatility, which requires a similar stochastic approach to estimating the cost of the materials [262]. Utility pricing can be estimated using statistical forecasting methods such as interval, density, threshold, and point. Statistical forecasting considers the random nature of the price possibilities and suggests a prediction interval with a calculated probability. Interval forecast uses probabilistic intervals to account for the possibility of price fluctuation in the future. The forecasted value of the utility price falls within an interval with a specific probability. Density forecast predicts utility pricing through a probability integral transform (PIT). The densities of utility prices can be generated and evaluated for quality by calculating the average Continuous Ranked Probability Scores (CRPS). A threshold forecast can determine a critical price point that no longer yields a profitable process. The accuracy of the utility price through threshold forecast is less important than determining a specific price threshold that cannot be exceeded. Point forecast predicts the utility price at a given time using the average of the forecasted price [262]–[264].

Waste disposal costs are considered when materials produced from a given process cannot be recycled or sold. In general, chemical processes and solvent recovery do not have 100% efficiency and thus generate waste. However, organic chemical solvents contain a large amount of stored energy within the chemical bonds, thus reducing energy costs. By knowing the heat of combustion, the waste solvent value ($/mass unit) can be approximated using Equation (6), where ΔH_C^o is the heat of combustion and P_F is the price of fuel ($/energy unit) [133].

$$C_{WFW} = P_F * \Delta H_C^o \tag{6}$$

The evaluation of fixed and variable costs is the minimum calculation required to estimate the preliminary cost of the solvent recovery process. However, other techniques such as cost-volume-profit, break-even, and cash flow analysis may be incorporated to acquire more information regarding process viability [265]. Short-term cost projection can be determined through cost-volume-profit analysis by analyzing the relationship between the output and the changes in revenues, process cost, and profit. In solvent recovery, the revenue generated may include recovered solvents sold to other industries. Other sources of revenue are expected to come from the main process. The process cost accounts for the variable and fixed costs to operate the process. Profit may be determined by the amount of solvent sold to other industries and money saved by reusing the recovered solvents. The economic viability with recovery should occur where the recovered material can offset new purchases.

Chapter 3

A Systems Approach to Bio-Based Materials Acquisition

Texts and figures are reproduced and adapted with permission from J. D. Chea, A. L. Lehr, J. F. Stanzione, and K. M. Yenkie, "Evaluation of isoflavone extraction options at commercial scale," Biofuels Bioprod Bioref, p. bbb.2411, Jul. 2022, DOI: 10.1002/bbb.2411.

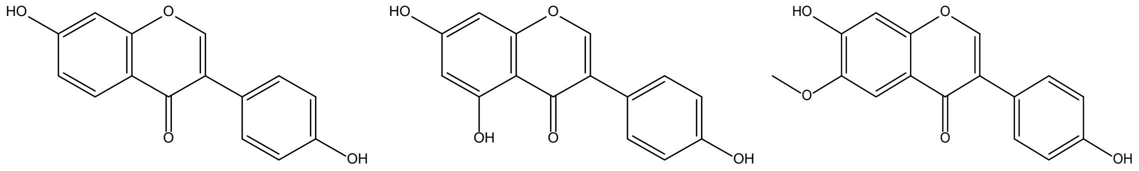
Resource sustainability concerns keep increasing due to the continuous use of natural materials without reclamation. Efforts are ongoing to find sustainable feedstocks for naturally-derived products with competitive economics and properties. However, there is no established methodology for commercializing the extraction of chemicals from renewable sources. This work examined soybeans as a potential bio-based feedstock to generate isoflavones commercially. The isoflavones content in soybeans has proven beneficial in the nutraceuticals industry for their anti-inflammatory and cancer inhibition properties and in the materials sector due to their inherent chemical functionality and thermal resistance. Currently, isoflavone extraction is only optimized at the lab scale. Thus, we present a superstructure-based framework to screen isoflavone extraction methods and assess their viability at a commercial scale. This method allows simultaneous comparison of alternative technologies using mixed-integer non-linear programming optimization to determine the most economical pathway. Internal material recovery greatly enhances viability at the commercial scale by reducing annual operating costs and environmental footprint. Therefore, this work presents a powerful tool for systematically comparing extraction pathways and accessing their commercial feasibility. The successful implementation of commercial-scale extraction of isoflavones has tremendous potential for generating additional revenue for US soy farmers. Isoflavones can produce bio-based polymers and composites and are used in dietary supplements, cosmetics, and nutraceuticals. Similar works can be applied to extract other natural materials from renewable feedstocks and increase the production of bio-based products.

3.1 Evaluation of Isoflavone Extraction Options at Commercial Scale

Sustainability is a growing concern as resources are continually depleted for various applications without renewal plans. Therefore, the need for alternative and sustainable feedstocks becomes a necessity as the availability of petroleum-derived resources becomes scarcer. The challenge to meet the inevitable increase in demand for bio-based feedstocks can be addressed by developing commercially scalable, highly efficient, and environmentally friendly chemical extraction methods and subsequent chemistries to transform the extracts into higher value-added products, if needed [266]. Prominent examples of this practice include synthesizing poly(lactic acid) (PLA) [267] and using bioethanol as an alternative fuel and solvent [268]. In addition, lignin derivatives such as vanillin and vanillyl alcohol have been used to produce novel polymer resins for adhesives, coatings, flame retardants, high-performance, and composite applications [22], [27], [30], [49], [50], [269]. Alternatively, reaction chemistries and chemical modifications can be performed on other chemicals derived from renewable resources, including soybeans, citrus peels, flowers, roots, and other underutilized resources [132]. Such possibilities can create an opportunity to expand the bio-based economy and support the large-scale production of renewably sourced materials and chemicals [270]. However, petroleum-derived chemicals and materials remain the primary choices for consumer goods because they have already been well-established in the current marketplace, creating a challenge for bio-based alternatives [12]. The successful transition of bio-based chemicals as the primary feedstock for chemicals and materials, as opposed to petroleum-based chemicals, may aid in shifting the reliance from non-renewable petroleum sources to renewable bio-based sources. Moreover, extracted natural chemicals also present a unique advantage over their synthesized counterparts; namely, complete elimination of costly synthesis and purification steps as many such chemicals can be utilized without further modifications, which can reduce overall carbon emissions and industrial hazards [46]. To highlight this critical and timely paradigm shift in chemicals and materials manufacturing, we present an extraction case study to assess the feasibility of extracting soy isoflavones from soybean meal at the commercial-scale by following a superstructure-based approach to determine the most feasible processing pathway option.

Soybeans are one of the most abundantly grown crops worldwide. In 2018, the United States produced over 125 million metric tons of soybeans, accounting for more than one-third of the global soybean production [51]. The majority of soybean and other soy-based products are exported from the United States to other countries, making soybean the second-largest cash crop in the United States [51]. Soy-derived products are forecasted to be valued at $355.05 billion with a CAGR of 6.8% by the year 2028 [271]. Approximately 85% of American-grown soybeans are pressed to produce soybean oil, while the remaining soybean contents are converted to soybean meal [272]. Nearly 97% of defatted soybean meal in the United States is sent to the agricultural sector for animal feed [273]. Soybean meals contain phytochemicals, also known as isoflavones, which account for approximately 0.15 wt% of the product [274]. In conjunction with the high volumes of soybean meal produced yearly, we hypothesize that these phytochemicals could be extracted to produce over 187,500 metric tons of value-added, bio-based platform chemicals while also recycling high protein soybean meal back to the animal feed supply chain [275]. In 2018, the isoflavone market size equated to $13.9 billion, with the potential to expand to $30 billion by 2027 with a CAGR of 13.7%, suggesting that the demands for these isoflavones continue to be relevant in the coming years [276].

Isoflavones are phytoestrogens, a group of bioactive polyphenolic compounds from plants that can behave as estrogen agonists and antagonists [277]. These chemicals are found naturally in legumes such as soybeans, chickpeas, peanuts, and other fruits and vegetables [278]. Isoflavones are used as nutraceuticals to provide antioxidant-related health benefits [279]. They also exhibit weak estrogenic activity because of their similarities to 17-β-estradiol, a major female sex hormone [280]. After ingestion, isoflavones metabolize into equol, a chemical used to protect against certain hormone-related cancers and alleviate symptoms associated with menopause and osteoporosis [281]–[283].



Daidzein Genistein Glycitein

Figure 6. Structures of isoflavone aglycones commonly found in soybeans

The extracted soy isoflavones (daidzin, genistin, and glycitin) occur naturally as a glucoside, defined as the state of being bound to a glucose molecule [284]. This bond can be separated through fermentation or digestion, where isoflavone glucosides become aglycones (daidzein, genistein, and glycitein) [285]. Figure 6 depicts the chemical structures of the major isoflavones found in soybeans. The extraction of soy isoflavones from soybean meal is a process that has been optimized at the lab scale with little consideration for costs or the environment, as they generally involve the use of large quantities of organic solvents [286]–[288]. As a result, alternative isoflavone extraction processes have been proposed, such as supercritical fluid extraction and ultrasonic-assisted methods [289]–[292]. More recently, an eco-friendly isoflavone extraction method has been developed, which uses water as the extracting solvent in conjunction with conventional agitation and separation techniques [289]–[293]. However, side-by-side comparisons of multiple processing pathways remain challenging as simulating each extraction and purification pathway can be time-consuming and lead to suboptimal solutions. Alternatively, a simultaneous analysis methodology can provide a comparative assessment of the different extraction pathways, supporting faster decision-making regarding process feasibility, technology commercialization, and economic viability. Thus, if an extraction pathway for a bio-based chemical or chemicals is proven economically viable, a larger quantity of renewable materials and chemicals can be obtained.

The main content of this chapter has been organized into four sections. Section 3.2 presents a brief overview of the methodology behind the superstructure development, the recovery/abstraction and purification technologies relevant to isoflavone extraction, and the optimization problem formulation. Section 3.3 presents the results from the superstructure optimization study, breakeven economic analyses, and an environmental footprint evaluation. Section 3.4 concludes with our findings and recommendations regarding bio-based chemical extraction processes.

3.2 Materials and Methods

3.2.1 Designing a Framework for Process Evaluation

This study optimizes the extraction of isoflavones from soybean meal. The isoflavone extraction process design was completed using a stage-wise analysis to determine the optimal sequence of technologies to process the material input and return a purified product suitable for other uses. Figure 7 illustrates the steps used in this study to computationally determine the most optimal set of technologies to extract isoflavones from soybean meal. We first specified the material properties of soybean meal, determined a basis, and then identified the appropriate steps required to achieve the desired extraction. A superstructure-based optimization framework has identified and analyzed multiple separation techniques. Each technology was represented by mathematical equations, formulated, and solved as a mixed-integer non-linear programming problem. This method eliminates many pathways that cannot achieve the desired product recovery and are more expensive to operate.

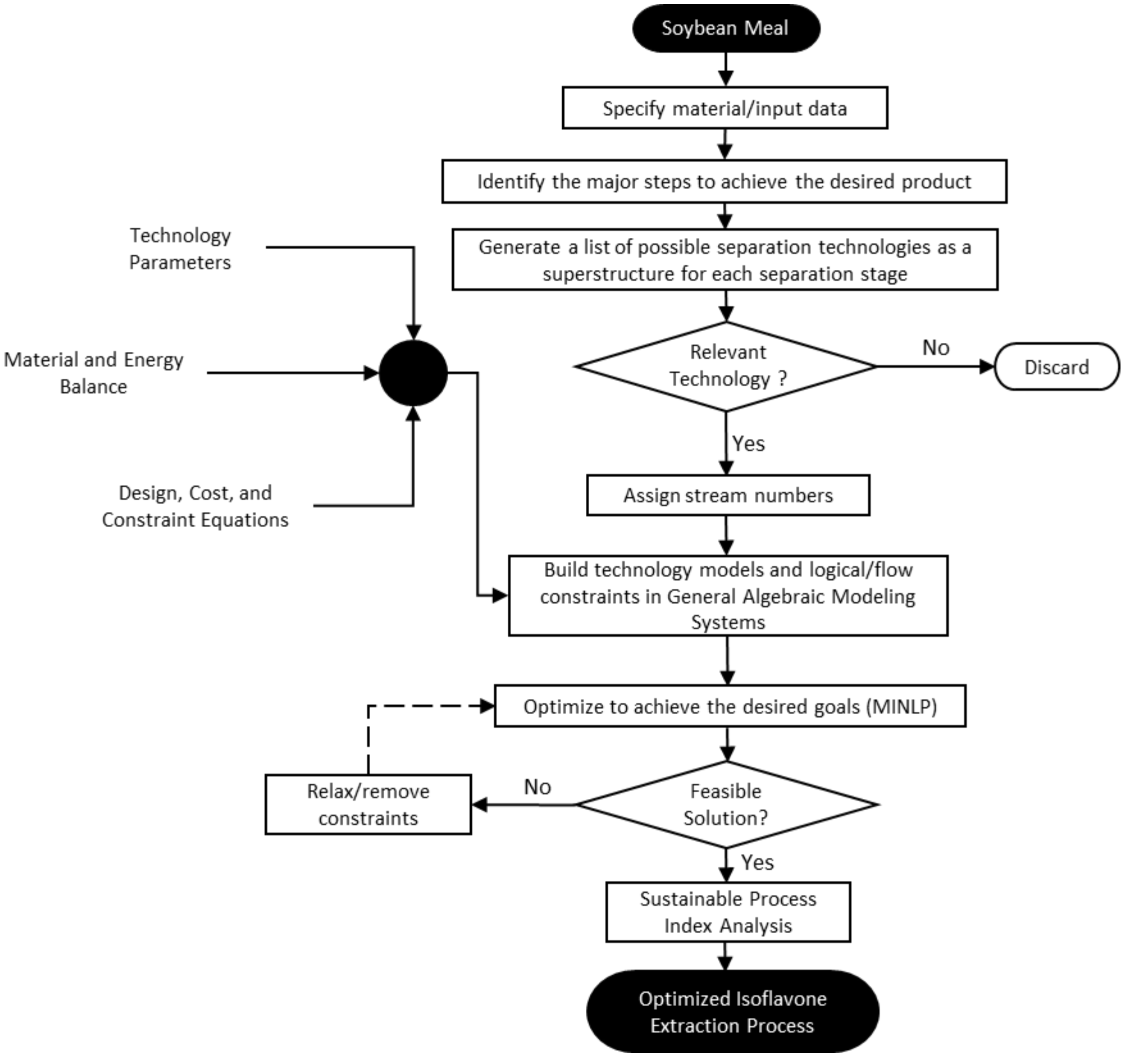


Figure 7. The overall analysis flow diagram used to optimize the isoflavone extraction process from soybean meal

Isoflavone extraction and purification from soybean meal is inherently a multi-step process resulting from extraction methods with impurities, or less desired components, that must be separated before the extracted chemicals are suitable for other uses. Therefore, we selected a stage-wise scheme to design an optimized isoflavone extraction process on a large scale. The extraction and purification technologies presented herein are categorized into four main stages: (1) pre-processing, (2) extraction, (3) acid hydrolysis, and (4) purification. Each stage may contain multiple technology options to perform a similar function. In addition, specific stages may be skipped through a bypass if the requirement has been met due to the inherent nature of the product or process. Figure 8 illustrates our proposed stages of typical isoflavone extractions and purifications based on past lab-scale extraction studies [287], [288], [292], [294], [295].

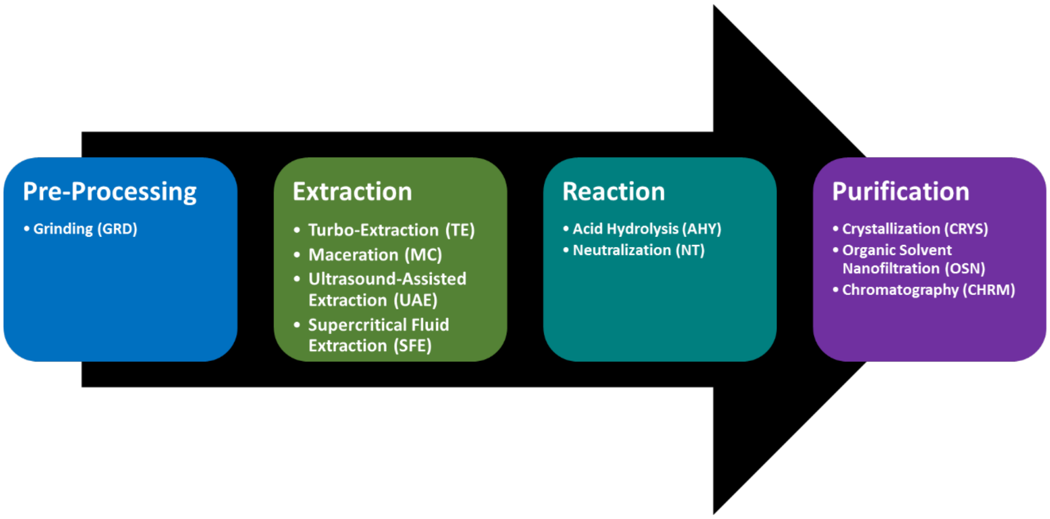


Figure 8. Possible technology options in major stages of isoflavone extraction from soybean meal

In this analysis, we assumed a scenario in which a fraction of the domestic defatted soybean meal in the United States is sent for extraction before being sold as animal feed or for other purposes. Before the extraction stage, a pre-processing step is typically employed to enhance extraction efficiency and remove unwanted components. In the case of isoflavone extraction from soybean meal, we considered only particle size reduction to improve the extraction efficiency without compromising the nutrient composition. Soybean oil was assumed to be removed before the isoflavone extraction process. Therefore, this separation was excluded from the scope of this study. As demonstrated in the literature, typical solvents used for direct extraction of isoflavone glucosides from soybean meal include acetone, methanol, ethanol, propan-2-ol, 1-butanol, ethyl acetate, and water [296]. If the soybean meal is returned to the animal feed supply chain containing residual amounts of some of these solvents, it has been suggested by Wu *et al.* (2010) that there exists a low risk to livestock health [296]. For example, selecting water or ethanol as an extraction solvent is more promising than acetone because of their low toxicity [296]–[298].

Given that isoflavones exist naturally as a glucoside, water is used to help solubilize the natural isoflavones [132]. The conventional isoflavone extraction method employed at the lab scale, Soxhlet extraction, possesses clear disadvantages at an industrial scale as this method requires constant heating and cooling over an extended operation time [299]. Therefore, Soxhlet extraction was excluded from consideration. Four extraction methods have been considered in this work: Turbo-Extraction (TE), Maceration (MC), Ultrasound-Assisted Extraction (UAE), and Supercritical Fluid Extraction (SFE). Despite the differences in operation, the fundamental mechanism of extraction remains similar among the methods. First, the solvent penetrates through the solid surface of the material to solubilize compatible chemical components. Next, the solute-rich solution diffuses toward the solid particle surface, where either natural or forced convection transfers the solute to the bulk solvent [132]. The naturally extracted isoflavone is then subjected to a reaction stage, which utilizes acid to hydrolyze the glucoside into glucose and isoflavone aglycones [300]. Purification is generally used in the final stage to isolate the product and remove unwanted impurities obtained during the extraction process [132]. It can involve technologies such as crystallization (CRYS), organic solvent nanofiltration (OSN), and/or chromatography (CHRM) to remove the remaining impurities from the desired product. A final drying (DRY) step can remove traces of solvent from the final isoflavone aglycone product.

Many of these technologies can be used to extract other natural chemicals from renewable resources, such as betulin from birch bark [52], [53], [132], [301], capsaicinoids from chili peppers [302], and *d*-limonene from citrus peels [132], [303]. Therefore, this approach can naturally be extended to other bio-based value-added chemicals and materials sources.

3.2.2 Technologies for Isoflavone Extraction

The isoflavone extraction is divided into four stages, as shown in Figure 8. The driving forces and crucial specifications required for each of the technologies are summarized in Table 5. In addition, detailed technology information and equations are available in Appendix A [129], [132], [159], [169], [294], [304]–[325].

Table 5

List of Potential Technologies for Extracting Isoflavones from Soybean Meal, the Main Driving Forces, and Important Specifications

Technology	Principle/ Driving Force	Specifications and Important Conditions	Literature Sources
Grinding (GRD)	Grindability, hardness	Particle size, bond work index, throughput	[159], [321]
Turbo-Extraction (TE)	Diffusion, concentration gradient	Residence time, power requirement, solvent ratio, temperature	[132], [305], [326]
Maceration (MC)	Diffusion, concentration gradient	Residence time, solvent ratio, temperature	[132], [326]
Ultrasonic-Assisted Extraction (UAE)	Cavitation	Power input, exposure time	[132], [307]
Supercritical Fluid Extraction (SFE)	Diffusion	Temperature, pressure	[289], [317], [327], [328]
Gravity Sedimentation (SDM)	Density gradient, Settling velocity	Size, density, tank depth, residence time	[159], [164]
Filtration (FLT)	Particle/molecular size/permeability Sorption/Diffusion Pressure	Pore size, Mol. Wt. Cut-off, average flux, Pressure gradient, type of membranes – M.F., U.F., NF, and RO	[159], [172]–[174]
Centrifugation (CNF)	Settling velocity Centrifugal force	Size, density, angular speed, the ratio of centrifugal to gravitational force, and settling distance	[159], [166], [167]
Acid Hydrolysis (AHY)	Acid concentration	Acid requirement, reaction temperature, hydrolysis time	[319], [329]
Neutralization (NT)	pH	Desired pH	[330]
Crystallization (CRYS)	Concentration gradient	Antisolvent availability and requirements, temperature, pH change	[159], [162]
Drying (DRY)	Convection, Sublimation	Temperature, Pressure	[129], [159], [166], [167], [331]
Organic Solvent Nanofiltration (OSN)	Particle/molecular size	Pore size, molecular weight cut-off, average flux, pressure gradient	[172]–[174]
Chromatography (CHRM)	Size, charge, binding capacity, polarity	Type of chromatography required, consumable cost	[314], [332]

3.2.3 Optimization Model Construction

This study examines the feasibility of extracting isoflavones from soybean meals commercially. Alternative options at various extraction and purification stages were considered simultaneously using a superstructure-based approach, as described in Chapter 2, Section 2.2.2.2. Figure 9 presents a superstructure to simultaneously analyze multiple pre-processing, extraction, separation, and purification options. This superstructure representation is then modeled mathematically into an optimization problem to obtain the ideal path based on the desired objective(s) [252], [255], [324], [333]–[335].

Extracting isoflavones from soybean meal may involve a grinding operation to increase the surface area for mass transfer before the extraction stage. Four possibilities for isoflavone glucoside extraction were considered: turbo-extraction (TE), maceration (MC), ultrasound-assisted extraction (UAE), and supercritical fluid extraction (SFE). TE involves vigorous agitation of soybean meal in the extractive solvent to accelerate mass transfer at the expense of high energy requirements. Conversely, MC relies on the diffusion of the isoflavone glucosides into the extractive solvent as a function of time. Such a process requires less energy than TE since no agitation is necessary. UAE subjects the soybean meal and solvent mixture to ultrasound waves, which supplies the energy needed and enhances mass transfer [322]. SFE is a green separation technology that operates at a condition above the critical temperature and pressure of the solvent to increase the solubility and mass transfer rate of nonpolar organic substances [289]. Polar cosolvents have been implemented with supercritical carbon dioxide to extract isoflavone glucosides, which are inherently polar [327]. The soybean meal can be recovered and sold as animal feed following TE, MC, UAE, and SFE through sedimentation (SDM), filtration (FLT,1), or centrifugation (CNF). Although not shown in the superstructure, additional drying stages can be implemented to remove process solvents from soybean meal. The extractive solvent containing isoflavone glucoside can be evaporated and condensed to be reused within the process. Acid Hydrolysis (AHY) is the third primary stage in obtaining isoflavone aglycones. The glucoside bond in isoflavone glucoside can be removed by adding acid [300]. A neutralization step (N.T.) is then employed to eliminate the presence of unreacted acid. A filtration (FLT,2) step removes the precipitated solids. Isoflavone aglycones with high purity can be obtained through three distinct possibilities, such as crystallization (CRYS), organic solvent nanofiltration (OSN), and chromatography (CHRM). Crystallization of isoflavone aglycones requires an antisolvent that is miscible with the carrier solvent but immiscible with isoflavone aglycones [310]. Following CRYS, a filtration step (FLT,3) is used to recover the crystallized isoflavone aglycones. Following a specific technology, the number notation represents the unit in the order of appearance in the superstructure (Figure 9). Alternatively, a membrane process such as organic solvent nanofiltration (OSN) can selectively recover solvents and separate solutes within a molecular weight range of 200-1000 g/mol [336]. This molecular weight range is applicable for daidzein (254.23 g/mol), genistein (270.24 g/mol), and glycitein (284.26 g/mol), which are the final desired products [337]–[339]. Chromatography (CHRM) is a purification process that can separate the three isoflavone aglycones based on polarity [332], [340]. A final drying step (DRY,2) can be employed following FLT,3, OSN, or CHRM to obtain the desired products, solid isoflavone aglycones.

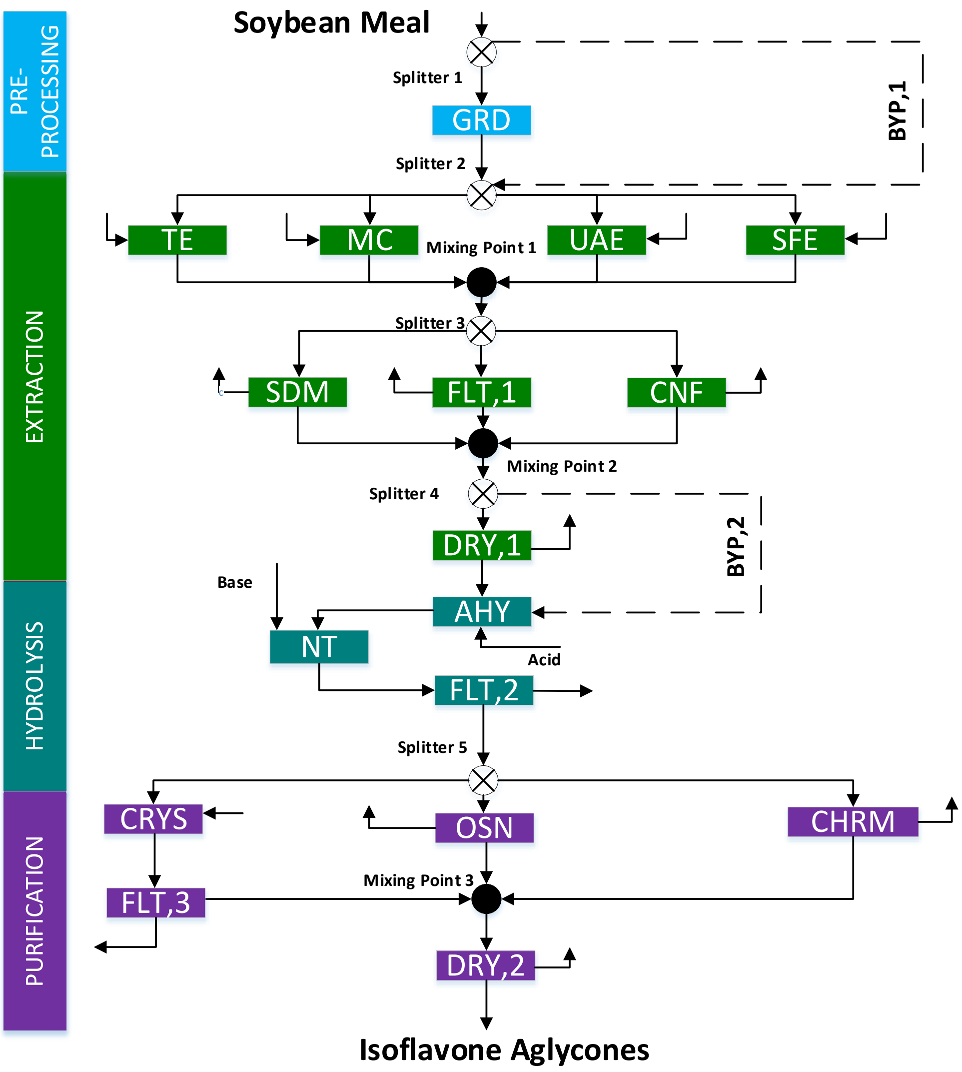


Figure 9. A superstructure of the conventional isoflavone extraction and purification pathways from soybean meal. Bypass streams skip optional stages that do not appreciably impact the outcome of the overall process. The unit processes considered include grinding (GRD), Turbo-Extraction (TE), Maceration (MC), Ultrasound-Assisted Extraction (UAE), Supercritical Fluid Extraction (SFE), Sedimentation (SDM), Filtration (FLT), Centrifugation (CNF), Thin-Film Evaporation (TFE), Acid Hydrolysis (AHY), Neutralization (NT), Crystallization (CRYS), Drying (DRY), Organic Solvent Nanofiltration (OSN), Bypass (BYP), and Chromatography (CHRM).

3.2.3.1 Economic Evaluation. The isoflavone extraction process evaluation was completed by modeling the proposed superstructure as a mixed-integer non-linear programming problem and solving it in the General Algebraic Modeling System (GAMS) language version 32.0. Material and energy balances, design, and operating constraints represent each technology. The technology costs were split into annualized capital, materials, utility, consumables, labor, and overhead (other). The capital cost was annualized using a capital recovery factor (CRF) of 0.11, assuming a plant life of 25 years. The material costs were estimated based on the average bulk pricing between 2010-2020 and using the materials database from SuperPro [341]. Consumable costs cover all expenses related to the periodic replacement of parts for a given process. Labor cost calculations were completed assuming the plant operates for 7,920 hours (330 days) annually. The amount of labor required per equipment can vary depending on the intensity of a specific process. For instance, in a mixing tank operation, at least one operator is assigned to monitor the process at all times. In contrast, a sedimentation process has fewer moving parts and strongly relies on gravity. Therefore, this technology requires a minimal workforce. The overhead cost includes research and development, sales and marketing, and general administration expenses [321], [333], [342]. All parameters relating to each extraction and purification technology are listed in Table A.4.1. Branch and Reduce Optimization Navigator (BARON) was selected as the global solver for this optimization problem, which uses lower and upper bounds of variables to create convex feasible regions that lead to a solution converging towards a global optimum [257], [343]–[345]. This solver algorithm has been used to solve MINLP problems ranging from heat integration, process selection, process sequencing, equipment design, and any other unique problems with multiple options and non-linear model behavior [324], [346]–[348].

3.2.3.2 Process Conditions and Specifications. The general parameter specifications for the isoflavone extraction model are presented in Table 6. The soybean meal used in this model is assumed to have been subjected to the defatting process. Most soybean meal mass contains protein, ash, starch, and fiber, representing insoluble solids in the extraction stage. The impurities component represents fat and moisture that remained after the defatting process. The remaining mass contains isoflavone percentages based on experimental studies [349].

Table 6

Isoflavone Extraction Model General Parameter Specifications

Parameters	**Values**
Feed rate (kg/hr)	1,000
Insoluble solids (wt%)	97.85
Impurities (wt%)	2
Isoflavone glucosides (wt%)	0.15
Operating time (hrs)	7,920
Number of workdays	330

The soybean meal was first subjected to a grinding operation for particle size reduction from 650 μm to 250 μm. The grinding model efficiency was assumed to be 75%. Cooling air was introduced to minimize soybean meal thermal degradation. We considered four common options in the extraction stage: TE, MC, UAE, and SFE. A solvent-to-feed ratio (S/F) of 10 L solvent/1 kg soybean meal was chosen in TE, MC, and UAE to minimize solvent removal costs in downstream processing [132]. The mixture contained 80% ethanol and 20% water by volume. In TE, an agitator power of 1.75 kW/m^3 was used based on the average fluid properties [321]. Cooling water was required to offset the temperature increase resulting from the high shear produced by this mixing process. In MC, time was the major parameter that strongly dictated the extraction efficiency. Agitation was not required because the solid soybean meal residence time in the extracting solution was much longer than TE. In UAE, an 80% efficiency and residence time of 20 minutes were chosen based on Rostagno *et al.* (2003) [295]. Rostagno also completed the optimization of isoflavone extraction through SFE, in which a ratio of 86.3 mg isoflavone/kg CO_2 was required to establish the ideal extraction conditions [327].

Three solid separation choices, sedimentation, filtration, and centrifugation, were considered following the solvent-based extraction steps. In sedimentation, 75% efficiency was assumed with liquid purity of 99% and a residence time of 30 minutes. For filtration, the flux of the membrane was specified as 0.2 kg/m^2-s. The retention factor condition was set to recover 99% of the isoflavone glucoside and solvent while removing unwanted solids from the product stream. In centrifugation, the solid-liquid separation efficiency was set to 95%. After the solid separation stage, a freeze-dryer model was implemented to remove 99% of the solvent, assuming an average heat transfer coefficient of 180 kJ/(m^2-K-hr) [324].

The dried isoflavone glucoside was hydrolyzed through acid hydrolysis to obtain isoflavone aglycones. The amount of acid (hydrochloric acid) required was specified as 0.791 kg HCl/kg solution to reach the ideal concentration of 4 M based on a study done by da Costa César *et al.* (2006) [340]. Steam at 120°C was selected as the heating agent to provide sufficient energy for hydrolysis. Sodium hydroxide was chosen as the base at the theoretical molar equivalent to hydrochloric acid for neutralizing excess acid after the hydrolysis reaction. Following the neutralization reaction, a filtration unit (FLT,2) was used to remove the excess salt precipitated from the acid-base reaction.

We considered three alternative technologies for removing any remaining impurities from the product stream in the purification stage. We specified an antisolvent addition at a 4:1 mass ratio of water to isoflavone aglycones [350]. The equilibrium can be shifted to force the nonpolar isoflavones to precipitate from the solution by adding water. A filtration unit can be used to recover the purified powder. Organic solvent nanofiltration can also efficiently separate the solvent from the valuable product. The third purification option requires chromatography. Several design variables of a chromatography column have been specified as parameters to reduce the overall complexity. These parameters included the chromatography column width of 0.05 m, the theoretical plate height of 0.0035 m, and the ratio between the column length and diameter of 0.14 [324].

3.2.4 Environmental Impacts Analysis

The sustainability of the proposed process has been evaluated using the E-factor and Sustainable Process Index (SPI). E-factor is a metric that allows direct quantification of resource efficiency [351], [352]. It accounts for non-product substances that are wasted. As demonstrated in Equation (7), a high E-factor value indicates that the process produces more waste than valuable products. A low E-factor is desired in process design and implementation, as it generally requires lower manufacturing costs and less waste [352].

The E-factor, however, does not account for the differences in wasted substances. Each material is counted based on the total mass. Therefore, an additional metric is required to help assess process sustainability.

$$\text{E-factor} = \frac{\text{Total Mass of Waste Produced}}{\text{Total Mass of Products Produced}} \tag{7}$$

The Sustainable Process Index (SPI) was chosen to examine the environmental impact analysis of the optimal solution. This concept coincides with the idea that a sustainable economy relies on the ability to responsibly use natural income, such as solar radiation and geothermal energy, for performing services and producing goods while minimizing the area required to sustain these tasks. Through this method, all material flows are crucial to assess the sustainability of the process. SPI measures the area needed to retain the carbon and water cycles and sustain and dissipate all potential emissions [353]. The water cycle begins with water being released into the atmosphere and returned to land as precipitation. The ecological footprint of the water cycle is determined based on the amount of precipitated water that returns to land after the natural rainfall and evaporation. The carbon cycle treats renewable (bio-based) and fossil resources as short-term and long-term cycles, respectively. Bio-based resources release carbon into the atmosphere as CO_2 at the end of their life. Bio-based resources would consume the CO_2 released over time. The area required to close the short-term carbon cycle represents the ecological footprint of bio-based resources. The ecological footprint of fossil-based resources is quantified by the seabed area, which is required to store the carbon from a process for an extended period of sedimentation. The impacts of natural material acquisitions are summed to calculate the total environmental footprint for a given process [353].

The ecological footprints calculated through SPI include the following categories: (1) direct area use and installations (Area), (2) non-renewable resources use (non-renewable), (3) renewable resources use (Renewable), (4) fossil carbon use (Fossil-C), (5) emissions to water (Water), (6) emissions to soil (Soil), and (7) emissions to air (Air). Direct area uses and installations consider all mass and energy movement throughout construction and installation and the emissions from the life cycle of the equipment. Non-renewable resources cover the impact from the extraction of metal ores and minerals to the end-of-life stage, where the materials are regarded as waste. The renewable resources category considers the production of renewable bio-based materials and the area required to grow these resources. Fossil carbon use analyzes the rate of carbon taken from the carbon cycle and stored for long-term usage. Over time, these carbons may end up in the seabed and form crude oil and natural gas. Emissions to water result accounts for the area required for pure water to dilute the emitted substance to a negligible concentration. Emissions to soil considers the area of green biomass required to generate the amount of compost to dilute the emission to a concentration of natural soil. Finally, the emissions to air are the area of natural forest that emits the same amount of substance released to the air as the amount released by the process. The SPI results provided the ecological footprints of these categories as the area per service unit (m^2a./unit) [354].

3.3 Results and Discussions

Bio-based chemicals acquisition at a commercial scale for applications to produce nutraceuticals, and other value-added materials, is composed of many challenges due to the unique properties associated with the chemicals of interest. The sources from which these chemicals are derived dictate the extraction steps. Particularly with isoflavone extraction from soybean meal, our superstructure-based optimization approach has determined that an initial particle size reduction is required to enhance the extraction efficiency. A high turbulence mixing tank with green solvents such as ethanol and water can extract isoflavone glucosides from the soybean meal. The remaining soybean meal can be recovered, dried, and used in the animal feed industry as this extraction process does not affect the protein content and other essential nutrients. Acid hydrolysis and subsequent neutralization can cleave the glucoside link and obtain the final product in the solution phase. A crystallization process can improve the purity of the final isoflavone aglycone concentrate. A final drying step removes traces of liquid solvent from the product to a negligible level.

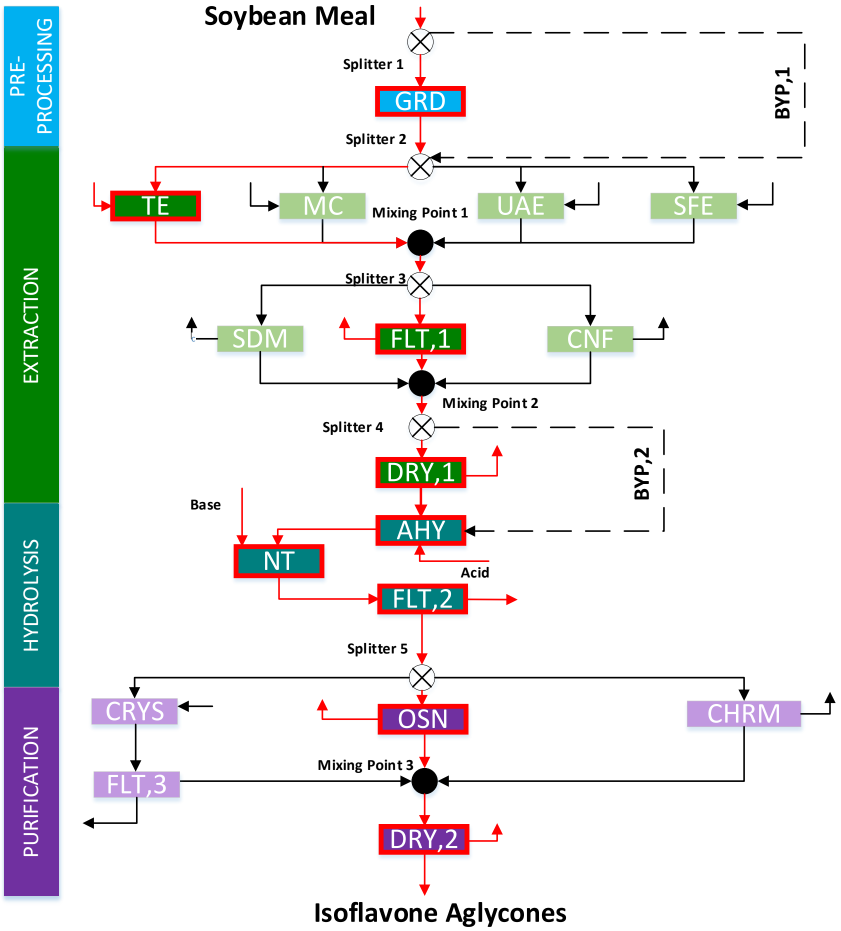


Figure 10. A superstructure of the conventional isoflavone extraction and purification pathways from soybean meal with optimal pathway selected. Bypass streams skip optional separation stages that do not appreciably impact the outcome of the overall process. The unit processes considered include: Grinding (GRD), Turbo-Extraction (TE), Maceration (MC), Ultrasound-Assisted Extraction (UAE), Supercritical Fluid Extraction (SFE), Sedimentation (SDM), Filtration (FLT), Centrifugation (CNF), Acid Hydrolysis (AHY), Neutralization (NT), Crystallization (CRYS), Organic Solvent Nanofiltration (OSN), Chromatography (CHRM), Bypass (BYP), and Drying (DRY).

Figure 10 illustrates the pathway selection, whereby the optimal pathway includes process units outlined boldly in red and indicated by red arrows. This process is economically feasible at a 1000 kg/hr soybean meal feed rate as long as internal material recovery and reuse are implemented. The GAMS model consists of 3,044 equations, 562 variables, and 10 discrete variables. The solution converged within 3.63 seconds with a relative optimality gap of 1.00×10^{-9}. Two separate versions containing (1) a method that utilizes material recovery and (2) ignores recovery options are included in sections G.1 and G.2, respectively. Additional economic and sustainability improvements to the optimized extraction process can be completed by implementing in-process material recovery and heat integration [347], [355]–[359].

3.3.1 Economic Analysis

We have considered two extreme scenarios for the isoflavone extraction process with and without internal material recovery. The total cost breakdown is summarized in Table 7. The first scenario is treated as a "base case" and assumes that internal material recovery is factored into the extraction process to reduce the required yearly expenditure and minimize material waste. Internal material recovery is handled by a simple equation that gets activated to subtract from the raw material cost based on the amount recovered. We calculated the cost of solvents and soybean meal recovered from the process and subtracted them from the raw material cost in the extraction stage. The equation for internal material recovery is shown in Equation (8).

$$\text{Raw Material Cost} = \text{Cost}_{\text{ethanol}} + \text{Cost}_{\text{water}} + \text{Cost}_{\text{CO2}} - \text{Cost}_{\text{solvent recovered}} - \text{Cost}_{\text{feed recovered}} \qquad (8)$$

$\text{Cost}_{\text{ethanol}}$ and $\text{Cost}_{\text{water}}$ represents the purchasing cost of solvents required for the extraction. Cost_{CO2} represents the supercritical fluid carbon dioxide required for supercritical fluid extraction. $\text{Cost}_{\text{solvent recovered}}$ represents the credit gained for recovering solvents, which offsets the raw material cost. $\text{Cost}_{\text{feed recovered}}$ also counts as credit toward the recovered soybean meal. Unlike solvents, this material cannot be reused in the extraction process because the isoflavone molecules have already been removed.

If internal material is not considered, represented by Equation (9), raw material costs only include the cost of purchasing the solvents. $\text{Cost}_{\text{solvent recovered}}$ and $\text{Cost}_{\text{feed recovered}}$ are excluded, leading to a higher overall cost.

$$\text{Raw Material Cost}=\text{Cost}_{\text{ethanol}}+\text{Cost}_{\text{water}}+\text{Cost}_{\text{CO2}} \tag{9}$$

The base case scenario also accounts for the processed soybean meal returned to the animal feed industry or repurposed for another application after the extraction stage. We assumed that 100% of the soybean meal would be recovered and sold for the same value of \$0.45/kg, based on the soybean meal commodity price average between 2010-2020 [360]. The solvents used in the extraction stage are recovered with a 5% purge to reduce impurity accumulation.

The total cost of operating this scenario equates to \$12.25 million/yr, assuming the plant operates for 7,920 hours (330 workdays) annually. Overhead cost (Other) accounts for 37% of the total annual process cost, followed by material (33%), labor (21%), capital cost (8%), consumables (0%), and utilities (1%). It should be noted that the consumables cost value is shown as zero percent based on rounding because it is considerably lower than the remaining cost categories. The solvent and consumables prices were taken from

SuperPro Designer databanks [341]. The minimum isoflavone aglycones sale price required to achieve a profit with this process is \$1,548/kg. An illustration of the total cost breakdown, with consideration for material recovery, is shown in Figure 11a.

Table 7

Process Cost Breakdowns of the Optimal Solution Under Two Extreme Scenarios that Factor in Internal Material Recovery and Lack of Material Recovery

	Material Recovery (\$ million/yr)	No Material Recovery (\$ million/yr)
Annualized capital cost	1.00	1.00
Material cost	4.00	55.99
Consumables	0.06	0.06
Labor	2.53	2.53
Utility	0.16	0.16
Other	4.50	4.50
Total process cost	12.25	64.24

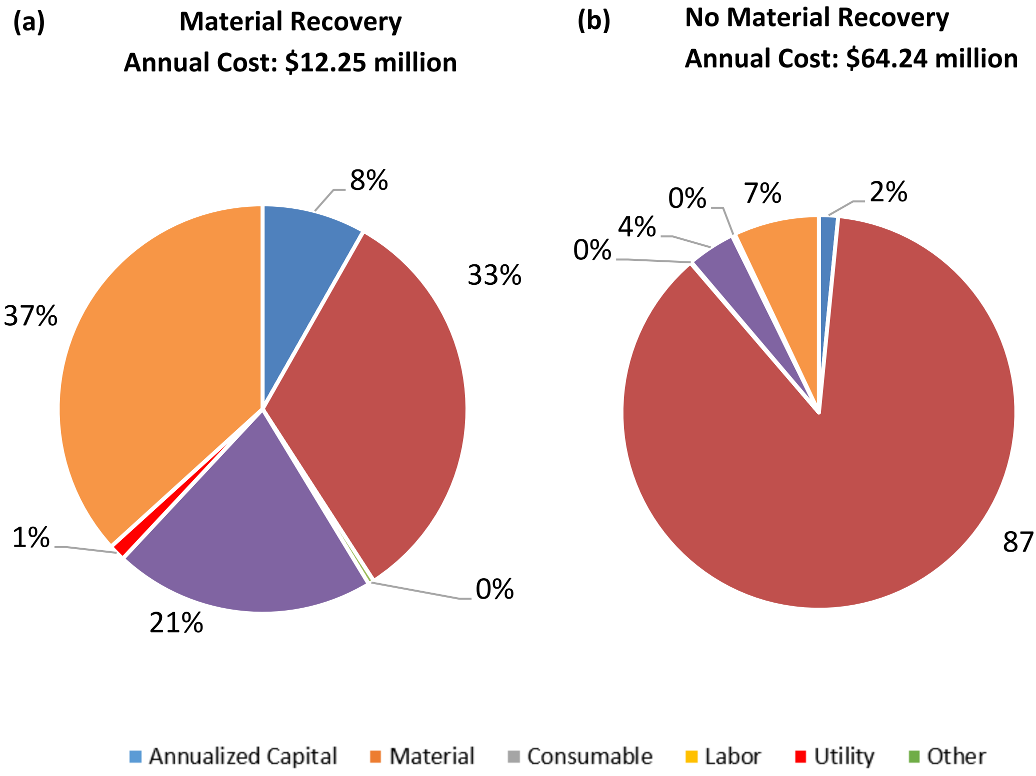


Figure 11. (a) Cost distribution of the optimal solution with material recovery and (b) without material recovery. The total annual cost associated with material recovery is $12.25 million, while the lack of material recovery requires $64.24 million annually.

The second scenario assumes that the extraction process does not include material recovery. Solvents, such as ethanol and water used for the isoflavone extraction process, would be considered waste and unrecoverable. In this scenario, new materials must continuously be purchased to maintain the process. The total cost of operating this scenario equates to $64.24 million/yr, assuming the plant operates for 7,920 hours (330 workdays) annually. Unlike the scenario with internal material recovery, an isoflavone aglycone sale price of $1,548/kg is insufficient. The minimum isoflavone aglycone sale price required to achieve a profit with this process is $8,113/kg. An illustration of the total cost breakdown, without consideration for material recovery, is shown in Figure 11b. The material cost accounts for up to 87% of the annual operating costs as these materials are discarded and replaced after the initial throughput. This action greatly increases the total material waste, reducing the process viability. The lack of material recovery reduces the economic viability of this process because the product must be sold for a higher cost.

A stage-wise cost analysis was performed to identify the largest cost contributor. In the base-case extraction with resource recovery, the extraction stage (2) contributed 65%, pre-processing (1) at 29%, hydrolysis (3) at 5%, and purification (4) at 1% to the total annual process cost of $12.25 million. Without resource recovery, the extraction stage (2) contributed 93%, pre-processing (1) at 6%, hydrolysis (3) at 1%, and purification (4) at 0% to the total annual process cost of $64.24 million. A large contribution from stage 2 is expected because the extraction is solvent intensive (10 L solvent to 1 kg soybean meal ratio), contributing greatly to the material cost. A solvent recovery system can reduce the need to constantly purchase fresh solvents for extraction. The exiting stream of the Dryer 1 unit in the extraction stage contains most of the extracting solvents in the vapor phase. Therefore, a preliminary solvent recovery step was included, which utilizes a total condenser to recover the evaporated solvents for reuse in the extraction stage. The approximate annual cost of recovering the evaporated solvent is $73,000/yr. Compared to the total annualized cost of isoflavone extraction, solvent recovery costs are relatively insignificant. The total condenser fully converts the evaporated solvent into the liquid with the same composition as the original solvent mixture. The impurities from the extraction stage are not likely to escape to the vapor phase following Dryer 1. Therefore, minimal processing of the recovered solvent is required before reuse. However, purging the recovered solvent and adding fresh solvent may prove beneficial in reducing the overall solvent impurity accumulation. Additional information about the temperature of the exiting streams of Dryer 1 was determined through additional thermodynamic calculations in A.5 and A.6, which contain the equations and methods used to estimate the price of the solvent recovery and standard cost analyses related to the condenser unit.

In the subsequent stages, various components such as solvent, soybean meal, and isoflavones are separated, leading to a lower mass intensity. Given that the technology cost is scaled based on standard capacity and cost, stage 3 (hydrolysis) and stage 4 (purification) are not expected to contribute much toward the total annualized process cost in both extraction scenarios. In addition, the successful recovery of materials used can considerably reduce the need to purchase solvent.

We observed from the two extreme extraction scenarios that material recovery and product sale price strongly influence the profitability of the entire process. However, the product sale price is a finite number that must remain competitive with the existing supply in the current market. This goal can be realistically met by employing the optimal isoflavone extraction from the soybean meal process instead of synthetically deriving them. Alternatively, synthetic routes can obtain the same isoflavone aglycones [361]. However, synthetic isoflavones require multiple reaction and purification steps, resulting in high operating costs and reduced yields from process inefficiencies. In addition, depending on the nature of the process, the final product may have traces of toxic chemicals. Extracting these natural chemicals allows multi-stage chemical syntheses and subsequent purification processes to be avoided entirely. We have also chosen green solvents for the extraction stage to reduce soybean meal exposure to toxic chemicals.

3.3.2 Environmental Impacts Assessment

3.3.2.1 E-Factor Calculations. An E-factor calculation was performed to assess the resource efficiency of the isoflavone extraction process. Table 8 summarizes the E-factor results for the extraction cases with and without internal material recovery. The material flows within this process include soybean meal, ethanol, water, hydrochloric acid, and sodium hydroxide. For the scenario with internal material recovery, the E-factor equates to 836 kg waste/kg product. This waste is attributed to the extraction solvent being purged to remove the excess impurities with every reuse cycle. In addition, hydrochloric acid and sodium hydroxide are consumed during hydrolysis and neutralization reactions. Conversely, the E-factor of the extraction process without material recovery is 13,293 kg waste/kg product. This value includes the entire soybean meal feed, ethanol, water, hydrochloric acid, and sodium hydroxide used with no mass recovery.

The E-factor reported is subject to change based on various assumptions. In the first scenario with material recovery, we assumed that 100% of the soybean meal is recoverable and reusable in the animal feed industry. The solvent (ethanol and water) is fully recovered using a total condenser with a 5% purge and 5% make-up during steady-state operation. Sheldon 2017 tabulated an approximation of the E-factor for various industries. The E-factor of the process with material recovery is within the same magnitude as that of the pharmaceutical sector, which has 25 – 100 kg waste/kg product [352]. Although the case presented in this study appears to generate considerable waste, we must note that the amount of natural product present in the original source dictates the process efficiency. Soy isoflavones make up approximately 0.15% of soybean meal by mass. The extraction of bio-based chemicals from other sources, following a similar approach, can likely result in a lower E-factor value if the material of interest is present in a considerable quantity. Based on a 1000 kg/hr flow rate, up to 1.5 kg can be extracted per hour. However, the purification and efficiency challenge realistically reduce the recovered amount to 1 kg/hr. Suppose the concentration of isoflavone doubles to 0.30% of soybean meal; then 3 kg/hr is available for extraction. By following the trend of the expected product amount, 2 kg/hr of isoflavone aglycones can be obtained. Doubling the products obtained effectively halved the E-factor value to 418 kg waste/kg product. Therefore, it is crucial to note that the optimization solution obtained is specific for isoflavone extraction from soybean meal. Nevertheless, natural chemical extraction remains a favorable option over the synthesis route, provided that the process is designed with considerations for waste minimization. Biegasiewicz *et al.* (2010) have demonstrated a four-step daidzein synthesis scheme from 2,4-dihydroxyacetophenone, a commercially available plant metabolite [281]. The product yield is reduced after each reaction step, increasing the amount of waste in the overall process. The estimated E-factor in the synthesis process has been approximated to 13,733 kg waste/kg product, based on the reported product and materials used within the lab-scale synthesis of daidzein [281]. This value is similar to the E-factor of isoflavone extraction without material recovery (13,293 kg waste/kg product). In the case of isoflavone extraction, internal resource recovery may reduce the process waste by up to 94%, further emphasizing the need to implement internal material recovery where possible.

Table 8

E-factor Calculation of the Optimized Isoflavone Extraction Process

	E-Factor Values	
	With Internal Material Recovery	**No Internal Material Recovery**
Soybean Meal (kg/hr)	0.00	1,000.00
Ethanol (kg/hr)	438.48	8,769.61
Water (kg/hr)	138.93	2,778.61
Acid (kg/hr)	107.87	107.87
Base (kg/hr)	118.32	118.32
Total Mass Waste (kg/hr)	803.60	12,774.00
Mass Product (kg/hr)	0.96	0.96
E-factor (kg waste/kg product)	836.00	13,293.00

Note. Two distinct scenarios were considered: material recovery and lack of material recovery. The flow rates shown signify the rate of loss per hour of materials.

3.3.3 Sustainable Process Index Calculations

An environmental impact assessment was completed using the Sustainability Process Index (SPI) to assess the ecological footprint of the optimal process. The material inputs include ethanol, water, soybean meal, hydrochloric acid, and sodium hydroxide to extract and purify isoflavones from soybean meal. The SPI database shows the potential emissions to water, soil, and air and the impacts on the Earth's resources as m^2 of arable land area. Figure 12 compares the two isoflavone extraction cases: (i) internal material recovery and (ii) without internal material recovery. The ecological footprint of the isoflavone extraction process equates to 87,204 m^2.a/kg product. Based on a yearly operation time of 7,920 hrs, the theoretical annual arable land area required to maintain process sustainability equates to 690 million m^2.a/yr. Without internal material recovery, the total ecological footprint equals 1.38 million m^2.a/kg-product. We observed a 93.7%

decrease in environmental footprint could occur by choosing to implement internal material recovery. The land surface area of Earth equates to 149 trillion m^2 (57.51 million mi^2). As of 2016, the arable land was estimated to be 11.06% of the total land surface area (16.5 trillion m^2). The environmental footprint of the optimized isoflavone extraction process accounts for 0.004% of the total arable area on Earth annually. Although the percentage reported from this process appears insignificant concerning the total possible land surface area of Earth, the combined ecological footprints from other processes across all industries worldwide can likely add up to a significantly higher arable area required. This theoretical required arable area value can add up higher than the available land surface area on Earth. Therefore, recovery is crucial to ensure that finite resource consumption is minimized. It should be noted that the arable land area required is a theoretical representation of the process sustainability. It does not reflect the actual land area needed to operate the process. Ideally, the arable area required should be minimal. The area estimated through SPI is more closely related to the pressure that a specific activity is expected to inflict on the environment while competing with other activities and processes.

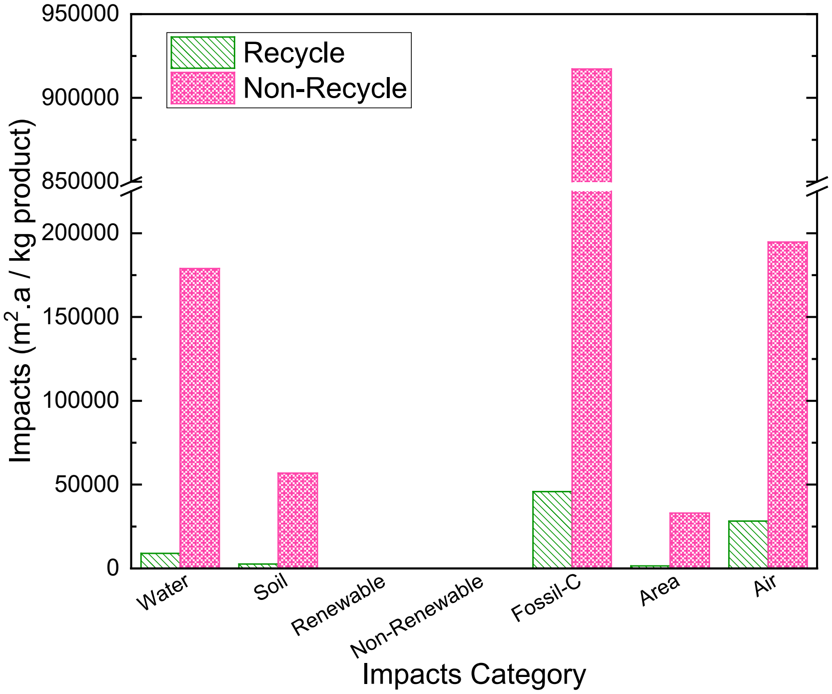


*Figure 12***.** Environmental impacts comparison between internal material recovery route (optimal) and without internal material recovery method

3.3.4 Transforming the Superstructure into a Process Flow Diagram

Thus far, we have demonstrated an optimization model that our proposed isoflavone extraction pathway is economically feasible with minimal environmental impacts based on 1000 kg/hr feed of soybean meal. SuperPro Designer Version 12 was used to determine feasible operating conditions for major processes involved in the extraction and purification of isoflavone molecules from soybean meal. The block flow diagram created in SuperPro Designer was done to suggest the minimum requirement for normal operation. Table A.8 describes the function, operating condition, and the input and output streams connecting to their respective units. Based on the optimal result determined using GAMS and SuperPro Designer, A process flow diagram (PFD) was subsequently generated and displayed in Appendix A.8, detailing the selected process pathway in greater detail. This PFD can be further subjected to detailed designs before the implementation can be considered.

3.4 Conclusions

The superstructure-based approach applied for the study of isoflavone extraction considers alternative technology options in all the major stages of separation, recovery, and purification. The simultaneous analysis of multiple potential options is more efficient than single-pathway or flowsheet analyses because this method actively selects the most cost-effective and feasible option at every stage until the final product is recovered. Given the desired specification, the optimal pathway can thus be obtained in a respectable timeframe to obtain a high-level estimation of the total process economics and capabilities. Our analysis indicated technologies such as grinding (GRD), turbo-extraction (TE), filtration 1 (FLT,1), drying (DRY,1), acid hydrolysis (AHY), neutralization (N.T.), filtration 2 (FLT,2), organic solvent nanofiltration (OSN), and drying 2 (DRY,2), should be used in sequential order to extract and purify isoflavones at the commercial scale. However, internal material recovery is required to reduce process costs and increase environmental sustainability. Process cost reduction can ultimately increase the profit margin. Furthermore, minimized environmental impacts correlate with waste reduction. Although the E-factor calculation suggested that the optimal isoflavone extraction process generates over 800 times more waste than products, this case highly depends on the concentration of products in the natural material. A high concentration of extractable natural materials is expected to correlate to a lower E-factor and higher revenue. By applying the same principles, optimizing bio-based chemical extraction from other natural sources may present starkly different solutions and E-factor results, depending on the processing requirements and characteristics of the original material. Through a detailed analysis of the selected pathway, the accuracy of the prediction can be further refined by considering alternative chemicals, heat integration, material recovery, and process intensification.

The commercial-scale extraction of natural chemicals from renewable resources can prove advantageous as more renewable chemicals become available for existing applications and the design of novel materials with unique properties and reduced toxicity. Bio-based chemical extraction can minimize or eliminate the reaction steps that would have otherwise been required. With over 125 million metric tons of soybeans produced annually in the United States, there is potential to obtain approximately 187,500 metric tons of soy isoflavones. The extracted isoflavone aglycones can be used in the polymers, nutraceuticals, beverage, food, and cosmetics industries. This work presents a method to increase bio-based chemical supply in the existing market without compromising the supply chain. The successful commercialization of bio-based chemical extractions can add tremendous value to the existing underutilized renewable resources by increasing accessibility, paving the way to produce promising materials reliably, and shifting the reliance away from conventional petroleum-derived chemicals. Similar approaches can be applied to other sources containing promising natural substances to increase renewable chemical feedstock supply. However, the generalization of bio-based extraction processes remains challenging because the extracted materials differ greatly in characteristics. This work presents one possible extraction case out of many to demonstrate an approach to estimate a screening-level process design, cost, and environmental impact of the extraction process before committing to one specific pathway. Additional chemical extraction scale-up studies from other renewable resources can provide more alternative technology possibilities in the superstructure approach and help create a generalized extraction framework.

Chapter 4

Adding Values to Naturally Extracted Materials

Texts and figures are publication pending.

Modern polymeric materials are often derived from petroleum, a long-term non-sustainable resource. Conversely, bio-based alternatives can be produced from naturally grown sources with inherent attributes. For example, birch tree bark has been considered waste in the papermaking industry [362], [363]. However, this substance contains many valuable chemicals that can be functionalized and polymerized into bio-based materials, such as triterpenoids, consisting of betulin, betulinic acid, and lupeol, as well as lignin, polysaccharides, and suberin. These substances offer additional hydrophobicity that could benefit birch bark extract (BBE)-based polymeric materials in many applications, such as coatings and adhesives. Research has shown that betulin-based thermoplastics have good mechanical and thermal properties; however, obtaining pure betulin requires many costly purification steps [23], [364]. In Chapter 4, we proposed using BBE as raw materials to synthesize polymers to minimize the number of steps in material acquisition. For comparison, the BBE was obtained through lab-scale Soxhlet extraction using selected solvents such as chloroform and ethanol. Molecular characterization of the extract was completed using proton NMR, advanced polymer chromatography (APC), high-performance liquid chromatography (HPLC), and hydroxyl value titration to confirm and characterize the presence of the chemicals of interest. Bio-based polyester thermosets were synthesized from the obtained BBEs with high viability for coating applications. Birch bark-derived epoxy was also synthesized for coating applications, but this material is better suited as an additive in a coating resin formulation. We believe that strategically combining the characteristics of molecules present in the BBEs with other bio-based molecules presents a viable solution that minimizes manufacturing costs and affords more environmentally friendly and sustainable polymers.

4.1 Transforming Birch Bark Extracts into Polymeric Materials

Petroleum is often the resource of choice responsible for creating many modern polymers, which can cause several negative impacts on human health and the environment [12], [13]. Most of the precursors to manufacturing thermoset polymers are the derivatives of toxic and volatile organic compounds such as bisphenol A (BPA), ammonia, styrene, and acyl chlorides, and thus their use in plastics is tightly regulated by several government agencies [43], [365]. Bio-based precursors can offer more sustainable, less toxic, and annually renewable alternatives to petroleum upon proper processing and modifications [22]–[27]. Utilizing bio-derived sources is not only crucial to achieving less toxic and more sustainable manufacturing principles, but they can also embed several unique and valuable features in polymers. Within this context, Hu *et al.* (2014) previously demonstrated the effectiveness of furan-based precursors, a hemicellulose-derived biomass, on the improved char yield and modulus of the epoxy-amine thermoset networks [366]. Similarly, Bassett *et al.* (2019) effectively utilized lignin and distilled cashew nutshell liquid (CNSL) derivatives in epoxy thermoset applications as phenol replacements achieving impressive thermo-physical properties comparable to BPA and improved corrosion performance [25]. La Scala *et al.* (2004) similarly developed a series of methacrylated fatty acid-based reactive diluents as partial styrene replacements in vinyl ester formulations, achieving improved toughness and flexibility without adversely affecting the overall polymer performance significantly [367].

Among the bio-derived feedstocks, birch bark represents an outstanding opportunity to supply readily accessible and non-toxic building blocks into various plastic formulations since the birch tree is abundant and the bark is easy to peel and process via well-established conventional methods [362]. Birch is a versatile tree that can grow in diverse types of soil and has one of the widest ranges of any tree, spanning the entire northern hemisphere. Birch bark has been regarded as waste in the papermaking industry and is typically discarded or burned as a low-grade fuel [363]. However, recent advances have discovered uses for birch bark and its extracts in medical applications, including antioxidant, anticancer, anti-HIV, anti-inflammatory, antimicrobial, antifungal, anti-pigmentation, and antiseptic applications [368]–[370]. Birch bark contains many unique bio-chemicals, including pentacyclic triterpenoids (betulin, lupeol, and betulinic acid) and other lignocellulosics such as tannins, lignin, and suberin that are highly qualified for various types of synthetic modifications for plastic processing. Components of the birch bark have been previously studied in detail [54], [371].

A couple of studies focused on the extraction of the birch bark using various methods such as reflux boiling and microwave-assisted extraction to maximize the betulin extraction efficiency, the most value-added component of the bark [52], [301], [372]–[375]. So far, various solvents such as chloroform, ethyl acetate, ethanol, alkaline hydrocarbons, and various bio-derived saturated monoterpenes such as limonene, pinane, and hydrogenated turpentine oil have been used for the extraction of birch bark up to 80%

betulin recovery [301], [376], [377]. Using green solvents as a selective extraction medium of betulin from the birch bark under the action of microwave-assisted extraction enabled the significant solubility of triterpenoids at high temperatures, good betulin crystallization on cooling, and poor extraction of polar impurities. The contents of the birch bark extract tightly depend on the location, age, and season of the bark collected. These extracts can contain up to 50-70% pentacyclic triterpenoids based on dry weight, namely, betulin, lupeol, and betulinic acid that are hydrophobic and contain highly reactive functional groups such as primary and secondary alcohols, carboxylic acids, and allyl groups that are very prone to further chemical modifications to yield functional polymeric networks [378]–[380].

Birch bark extracts (BBE) are widely used as a nutritional supplement and accepted as a safe additive in many countries due to their antioxidant, anticancer, anti-HIV, and anti-inflammatory properties [54], [368], [381]. Various BBE products with betulin content ranging between 80-99% are available in small quantities (<100 mL) at grocery and drug stores in the US. More recently; high purity betulin (>99%), the main component of the processed BBE, has been successfully functionalized for the production of thermoset and thermoplastic polyesters in combination with various petroleum and bio-derived di- and poly- acids and their acyl chlorides [23], [382]. In a study by Okada *et al.* (2019), betulin was reacted with various aliphatic acid chlorides changing in methylene units (2-10) to obtain thermoplastics with glass transition temperature (T_g) values ranging between 115-165°C based on the methylene length [364]. Curia *et al.* (2019) also employed pure betulin in the production of thermoplastic and thermoset polyesters synergized with bio-derived di-acids such as adipic and succinic acid and glycerol using a “greener” approach to synthesize various polyesters with impressive dimensional stability and T_g values ranging between 70-205°C based on the chain length of the di-acid [23]. In a series of studies, Huang *et al*. (2019) also demonstrated the effectiveness of betulin-based polyesters in water-repelling textile applications owing to their hydrophobic fused cycloaliphatic backbone [382]. In a recent study, Kumar *et al.* (2022) functionalized the suberin-based fatty acid content of the BBE via maleic anhydride and octadecyltrichlorosilane and applied it on wood substrates as protective surface coatings [383]. As determined by xenon light aging and contact angle studies, suberin-derived coatings demonstrated impressive color stability and hydrophobicity. These studies prove that betulin and other components of BBE can be effectively modified to manufacture plastics for a wide range of applications. However, isolating pure betulin from BBE requires many costly purification steps, increasing its price exponentially and making it impossible to develop materials at commercial scales and competitive prices for CASE (coatings, adhesives, sealants, and elastomers) applications.

This work investigates the viability of utilizing BBE as a precursor with minimal processing as a feedstock to synthesize value-added thermosets. BBE contains the unique benefit of having a mixture of pentacyclic triterpenoids and other hydroxyl-containing aromatic/aliphatic substances capable of providing inherent reactivity. We investigated the epoxidation of BBE and implemented this material as a polyester thermoset precursor without isolating any specific chemicals. Barks are collected from the same location through different seasons of the year and designated as spring (March-June), summer

(June-September), fall (September-December), and winter (December-March) based on the time of the year they were collected. Processed barks were subjected to Soxhlet extraction using chloroform, and their triterpenoid contents were identified via a combination of HPLC, APC, and hydroxyl value titrations to explore the seasonal effects on the chemical composition of BBE. Barks collected at different seasons were individually used for polyester production in the presence of glycerol and 1,12-dodecanedioic acid to achieve a fully biobased thermoset polyester. The effect of the chemical composition (e.g., seasonal variations) of the BBE on the thermophysical properties of the polyester thermoset networks, such as T_g and initial degradation temperature (IDT), was demonstrated to be negligible via DSC and TGA studies, respectively. As an alternative reaction, BBE from different seasons was combined to synthesize diglycidyl ether of birch bark extract (DGEBBE) in the presence of excess epichlorohydrin along with diglycidyl ether of betulin (DGEBet) to explore the viability of BBE in epoxy thermosets.

Bimodal resin blends of DGEBet and DGEBBE were prepared with diglycidyl ether of hydrogenated bisphenol A (Eponex 1510). Eponex 1510 was chosen as a control for property comparison because of its better compatibility and similar structure to betulin and BBE epoxies. The blends were thermally cured with various amine hardeners such as Epikure W. We further investigated the blends of DGEBBE by increasing the DGEBBE content in Eponex 1510 up to 100% DGEBBE by weight. Other curing agents from bio-based sources, such as Cardolite® NC-558, a CNSL-derived phenalkamine, and DFDA, a furan-based diamine, were used for comparison with petroleum-derived Epikure W curing agent. Thermophysical performance and structure-property relations of the epoxy-amine blends were investigated via DMA, DSC, and TGA, and compared with the ones derived from DGEBet. Various coating tests, such as shore hardness, cross-hatch adhesion, and mandrel bend, were performed per related ASTM standards to explore the potential of BBE-based thermoset polyesters and epoxies as a sustainable and renewable alternative for CASE applications. Nevertheless, birch bark can be a promising underutilized source for developing value-added polymeric materials.

4.2 Materials and Methods

4.2.1 Materials

Birch barks were peeled monthly from river birch trees (Betula Nigra) found at the Jean and Ric Edelman Fossil Park of Rowan University, NJ, USA. The extraction stage utilizes chemical solvents such as chloroform (Reagent ACS grade 99.8+% from VWR Chemicals) and ethanol (200 proof from Pharmco Products Inc.). For analytical methods such as high-performance liquid chromatography (HPLC) and Advanced Polymer Chromatography (APC), methanol at >99.8% HiPerSolv CHROMANORM®, acetonitrile at >99.9% HiPerSolv CHROMANORM®, and tetrahydrofuran (THF) at >99.7% HiPerSolv CHROMANORM® were purchased from VWR Chemicals BDH®. Ultrapure deionized (DI) water for general purposes, reactions, and washes was generated from a Sartorius Arium Mini Water Purification System. Other extract characterization, such as hydroxyl value titration, used pyridine ACS grade suitable for Karl Fischer Reagent purchased from Fisher Chemical, and acetic anhydride >99.0% purity purchased from Fluka Analytical. In the synthesis of BBE polyester thermoset, 1,12-dodecanedioic acid (C_{12} diacid) >99.0% purity was purchased from TCI Chemicals, glycerol with >99% purity was purchased from Acros Organics, and the required dibutyltin (IV) oxide (DBTO) catalyst 98% purity was purchased from Acros Organics. For the epoxidation reaction, epichlorohydrin at 99% purity was purchased from Acros Organics, sodium hydroxide (50% w/w) was purchased from VWR Chemicals BDH®, and tetrabutylammonium hydrogensulfate (TBAHS) at 97% purity was purchased from Sigma-Aldrich. The reaction workup uses ACS grade sodium chloride purchased from Fisher Chemical, magnesium sulfate anhydrous at >99.5% purity purchased from Thermo Fisher Scientific, and ACS grade dichloromethane (DCM) purchased from VWR Chemicals BDH®. For baseline comparison with BBE, betulin at 98% purity was purchased from BOC Sciences®. For characterizing the epoxy equivalent weight (EEW) of the synthesized epoxies, 0.1N perchloric acid in acetic acid standardized solution was purchased from Alfa Aesar.

4.2.2 Triterpenoid Extraction from Birch Barks

An industrial lab-grade blender was used to process the barks before Soxhlet extraction. Approximately 600 mL of solvent (chloroform and ethanol) was consumed per 120 g extract. The final product was filtered to separate solid particles, and the extract solution was dried using a rotary evaporator. HPLC was used to separate and quantify different chemicals in the powdered BBE. Based on a previous study by Maji *et al.* (2014), the mobile phase composition was selected as 94% acetonitrile (ACN) with 0.1% acetic acid and 6% water at a 1 mL/min isotactic flow [240]. The XTerra MS C18 Column, a reversed-phase silica-packed column, was chosen as the stationary phase. All samples were dissolved in HPLC grade methanol at a 10 mg sample/50 mL solvent ratio and then analyzed at a column temperature of 25°C over 20 minutes at 210 nm wavelength. The resulting chromatogram was analyzed for the concentration of betulin, betulinic acid, and lupeol, with the remaining peaks classified as unknown. Waters ACQUITY APC was used with a refractive index detector (calibrated with polystyrene standards with a molecular weight range between 474 – 2,500,000 g/mol and dispersity of 1.15) to determine the molecular weight distributions of materials extracted and synthesized. The samples were run in tetrahydrofuran (THF) at a flow rate of 0.6 mL/min using a series of ACQUITY APC columns (XT 450, 2.5µm, XT 125 µm, and XT 45 1.7 µm). Bruker Avance Core NMR Spectrometer was used to obtain ^{1}H-NMR spectra analysis of each extract and synthesized monomer to confirm the chemical structure and presence of key functional groups necessary for specific reactions. Samples were dissolved in deuterated chloroform, and 16 scans were collected at 25° Cat 400 MHz. Hydroxyl number titrations were also performed to determine the total number of free hydroxyl groups as per ASTM E222-17.

4.2.3 Synthesis Procedures

4.2.3.1 Processing BBE for Thermoset Polyester Synthesis and Subsequent Characterization. High-purity betulin molecule contains two hydroxyl groups available for polyesterification with dicarboxylic acids; thus, the stoichiometric ratio is easily determined. BBEs obtained through extraction, on the other hand, contain a combination of many different chemicals, including phenolics and hydroxyl groups. Therefore, the average hydroxyl values for each extract from all seasons were calculated before the esterification reaction to determine the stoichiometric amount of 1,12-dodecanedioic acid, glycerol crosslinker, and the required DBTO catalyst for the complete reaction. The hydroxyl value and molecular weight of BBEs (obtained using Chloroform solvent) used in this synthesis process generally ranged between 112 – 142 g/eq OH (124.5 g/eq OH average) and 477 – 538 g/mol (510 g/mol average), respectively. Therefore, based on a one-gram BBE reaction, 1.96 g of C_{12} diacid, 0.46 g of glycerol, and 12.20 mg DBTO catalyst are required to reach the approximate stoichiometry. This reaction scale can be changed by multiplying the desired value by the one-gram scale basis. The appropriate amounts of raw materials were homogenized in a round bottom flask through heating and stirring in an oil bath at 200°C for 1 hour and transferred to aluminum dishes. The mixture was cured at 200°C for 24 hours in a thermal oven to ensure complete crosslinking. The reaction scheme is illustrated in Figure 13.

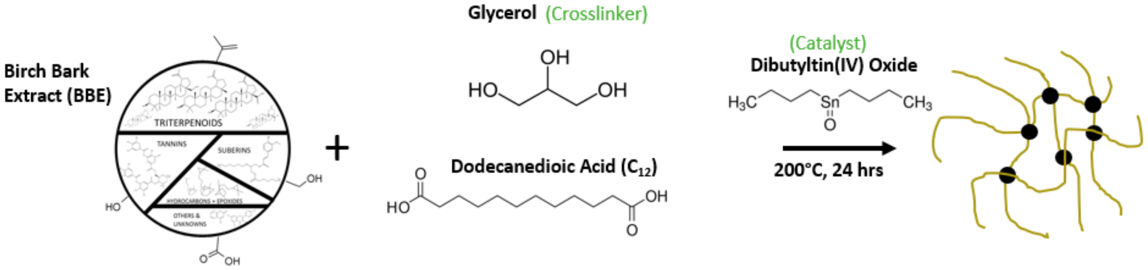


Figure 13. Reaction scheme for the synthesis of birch bark extract polyester thermoset

The swelling studies of the polyester thermoset were performed by placing approximately 30 mg of each sample in 2 mL of THF, DCM, chloroform, ethanol, and ethyl acetate. Each sample was agitated continuously on a shaker plate for 7 days and dried in a conventional oven for several hours above the boiling point of the solvents used.

The viability of BBE polyester thermoset as surface coating materials was tested by applying them on the 3×6 in^2 QD-36 rectangular mild steel panels via a Bird thin film applicator (1 mil). The reaction mixture was mixed for 1.5 hrs in an oil bath at 200°C before applying to the panels and cured in a thermal oven at 200°C for 24 hrs.

The finished coatings were tested for shore hardness, mandrel flexibility, cross-hatch adhesion, and direct impact resistance according to ASTM D2240, D552, D3359, and D2794, respectively [384, p. 01], [385], [386], [387, p. 01]. In addition, the weather resistance of the coated panels was tested after they were cut with an X shape from the middle via a razor blade and exposed to outside conditions for over a month to simulate exposure to environmental effects.

4.2.3.2 Birch Bark Extract Epoxidation, Polymerization, and Characterization. The conventional glycidyl epoxidation process typically involves hydroxyl-containing reactant mixing with excess epichlorohydrin (EpCl) in the presence of a phase transfer catalyst and eventual dehydrochlorination via concentrated sodium hydroxide solution [22]. Processing pure triterpenoid molecules such as betulin presents a challenge at low temperatures because betulin absorbs epichlorohydrin, creating compatibility issues for an adequate reaction. Therefore, N,N-Dimethylformamide (DMF) was chosen to aid and maintain betulin solubility and a homogeneous reaction media through the epoxidation process. Figure 14 depicts the proposed reaction scheme for synthesizing DGEBet through an epoxidation reaction in 30 molar excess epichlorohydrin (EpCl) to ensure sufficient contact in excess DMF and to improve the inherited lower reactivity of the primary and secondary alcohols located on the betulin molecule concerning phenols. Tetrabutylammonium hydrogensulfate (TBAH) was selected as a phase transfer catalyst at a 0.16 molar ratio to betulin or BBE. The reaction temperature was maintained at 90°C with continuous stirring for 72 hours, followed by a dropwise addition of 50% sodium hydroxide (NaOH). The color of the reaction changed from light yellow to dark brown after 72 hours of reaction at 90°C. The final product was dissolved in dichloromethane (DCM) and washed with deionized water once and with brine ten times at a 1:1 volume ratio to minimize the concentration of DMF. The final organic phase was dried using anhydrous magnesium sulfate. Vacuum distillation was used to remove DCM, the excess epichlorohydrin, and trace amounts of DMF (only in the betulin case) for several hours (>3 hours) to obtain a hard solid resin with brown color depicted as diglycidyl ether of betulin (DGEBet).

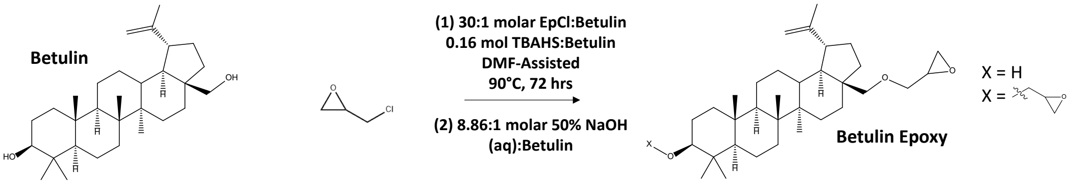


Figure 14. The general synthesis scheme of diglycidyl ether of betulin (DGEBet)

A similar approach was applied to BBE, in which it was used as a raw material for epoxidation with 30 moles of excess epichlorohydrin at 90ºC for 72 hours. However, the solubility of BBE in epichlorohydrin is not an issue because the extracts dissolve easily in epichlorohydrin at relatively lower temperatures. At 90°C, all solid BBE in the reaction flask completely dissolved into one phase. Thus, DMF and excessive brine washes to remove DMF were eliminated from BBEepoxy synthesis entirely. The final material was vacuum distilled to remove DCM and excess epichlorohydrin to yield a soft solid material with brown color. The final structure of DGEBet and DGEBBE was estimated through ^{1}H-NMR and APC, similar to thermoset systems, as explained in the previous section. In addition, the EEW was also determined through titrations using ASTM D1652 [243].

A bimodal resin blend of DGEBet and DGEBBE with Eponex 1510 were compared. The epoxy-amine blends were thermally cured with various amine hardeners, such as aromatic Epikure W, CNSL-based phenalkamine NC-558, and furan-based di-amine DFDA. In addition, we further investigated the blends of DGEBBE by increasing the DGEBBE content in Eponex 1510 blend up to 100% DGEBBE by weight. All blended epoxy and amine mixtures were cast into rectangular rubber molds and cured at 125°C for 18 hours, then post-cured at 150°C for another 3 hours to ensure full conversion upon mixing and degassing via a centrifugal planetary mixer.

The conversion of epoxy and amine groups was confirmed via transmission near-IR in the 4000-8000 cm^{-1} range with an 8 cm^{-1} resolution and 32 scans per spectrum at 25°C. Samples were analyzed before the cure and after the post-cure. The extent of cure was calculated using Equation (10), where A represents the reduced absorbance of the epoxy, primary, and primary and secondary amine peaks observed around 4540, 4940, and 6570 cm^{-1}, respectively, before cure A(0) and after post-cure A(t).

$$\alpha = 1 - \frac{A(t)}{A(0)} \qquad (10)$$

The thermal stabilities of the fully reacted polyester and epoxy thermosets were measured using a TA Instruments Discovery Series TGA 550. The samples were placed in aluminum pans and equilibrated to 30°C, then heated to 700°C at a rate of 10°C/min under an inert and oxidative atmosphere.

A TA Instrument Discovery Series DSC 2500 was used to observe any primary and secondary transitions within the thermoset network as a function of temperature. For this purpose, 10-15 mg of cured sample was placed into hermetic aluminum DSC pans and thermally scanned from -50 ºC to 120 ºC using a heating rate of 10 ºC/min under nitrogen purge.

Dynamic mechanical analysis was performed via TA Instruments Discovery Series DMA 850 on rectangular specimens with approximate dimensions of $17.5 \times 12.5 \times 3.0$ mm^3 to verify the T_g and elastic moduli of post-cured thermosets. All samples were thermally scanned from -50 ºC to well above their T_gs at a frequency of 1 Hz, an amplitude of 10 µm, and a heating rate of 2°C/min. T_gs of the cured resins were obtained from the peak positions of both loss modulus (E'') and tan δ curves. The crosslink densities (v) were also obtained from storage modulus curves at 60°C above the loss modulus T_g according to the theory of rubber elasticity using Equation (11), where R is the ideal gas constant and T is the absolute temperature.

$$v = E'/_{3RT} \tag{11}$$

4.3 Results and Discussions

4.3.1 Material Properties Comparison

Birch bark extracts were obtained using two different solvents: chloroform and ethanol. The extraction yields generally ranged between 10 – 15% for the chosen birch tree barks described in Section 4.2.1 of this Chapter. Due to climate variation, other species of birch trees may possess different triterpenoid content. The molecular weight distribution of the extracts was confirmed using APC, and the weight percentages of each component were determined using HPLC. As shown in Table 9, there is a change in composition and reactive sites of the extract based on the season of the year and different extracting solvents. The percentages of unknown impurities and hydroxyl values are generally higher in the ethanol extract than in the chloroform extract. This trend is expected because the hydroxyl from the ethanol can form hydrogen bonds with the hydroxyl groups from other substances within the birch bark, leading to a higher concentration of hydroxyl compounds in the final extract. Although the composition of betulin, betulinic acid, and lupeol varies between seasons, the total triterpenoid concentration within BBE ranges between 23% and 39% on a dry mass basis. The identities of impurities (Other %) have been determined in literature, including betulinic aldehyde, methyl betulinate, lupenone, aromatics, and lignin [362]. The molecular weight of the extract and chemical composition data were used to determine the hydroxyl values of the extracted materials and estimate the number of reactive groups present for functionalization and polymerization. These molecular weights have been relatively consistent throughout different seasons, regardless of solvent choices.

Table 9

Birch Bark Extracts Composition as a Function of the Time of Year

Birch Bark Extracts (BBE)	Betulin %	Betulinic Acid %	Lupeol %	Total %	Other %	M_n (g/mol)	Hydroxyl Value (mg OH/g sample)
Chloroform (Summer)	13.7 ± 1.5	15.8 ± 2.0	7.4 ± 0.8	36.9	63.1	501 ± 1.3	125.7 ± 33
Chloroform (Fall)	8.8 ± 1.3	19.8 ± 2.3	5.5 ± 0.8	34.1	65.9	525 ± 5.2	117.7 ± 9.1
Chloroform (Winter)	9.5 ± 0.68	20.4 ± 0.84	5.9 ± 0.45	35.7	64.3	538 ± 5.2	112.2 ± 19
Chloroform (Spring)	17.5 ± 1.0	16.6 ± 0.3	7.3 ± 0.7	41.4	58.6	477 ± 12	142.4 ± 39
Ethanol (Summer)	10.1 ± 1.3	13.9 ± 3.6	6.3 ± 3.1	30.3	69.7	575 ± 5.2	100.0 ± 17
Ethanol (Fall)	6.2 ± 0.8	9.9 ± 1.3	4.1 ± 0.9	20.2	79.8	596 ± 6.6	197.9 ± 33
Ethanol (Winter)	15.9 ± 1.3	15.8 ± 1.7	7.6 ± 0.98	39.3	60.7	598 ± 3.8	188.9 ± 17
Ethanol (Spring)	6.3 ± 2.7	11.1 ± 4.0	5.5 ± 1.5	22.9	77.1	542 ± 6.3	134.3 ± 32

Note. All samples shown were extracted from river birch trees found at the Jean and Ric Edelman Fossil Park of Rowan University. The summer season includes June, July, and August; the fall season includes September, October, and November; the winter season includes December, January, and February; the spring season includes March, April, and May.

4.3.2 Birch Bark Extract-Based Thermoset Synthesis and Characterization

The combination of BBE, glycerol, 1,12-dodecanedioic acid, and DBTO catalyst resulted in a crosslinked, dark brown, flexible thermoset after curing at 24 hours at 200°C.

The initial blending process via a magnetic stirrer in an oil bath at 200°C for 1 hour is critical to ensure the complete homogenization of the reactants before transferring them into a thermal oven at the same temperature. The 200°C curing step in the thermal oven induces further crosslinking and locks the polymer chains into one solid, infusible, and flexible material. It has been shown that the hydroxyl values and chemical composition do fluctuate depending on the season and solvent used for extraction. This behavior is expected because the natural material has been subjected to different weather conditions throughout the year. However, these variables do not alter the success of this reaction because the measured hydroxyl values are within the 95% confidence interval range from the BBE obtained from the appropriate season. The potential deviation from the average hydroxyl value may cause the ideal stoichiometry to change. However, this change is insignificant to the success of the reaction because the average hydroxyl value has been used to create new samples with similar thermal properties. Other bark sources from different regions, climates, and species types may have starkly different results from the River Birch chosen for this study because the trees can alter their bark composition to fulfill their immediate needs. Regardless, the hydroxyl value can approximate the reactive group (-OH) available for reaction.

DSC result has shown high consistency with T_g of BBE obtained from different seasons, ranging between -12 to -9°C. This characterization method thus confirms the reason for the flexible property at room temperature. Curia *et al.* (2019) have previously synthesized betulin-C_{12} polyester thermoset and determined that their T_g is approximately 3°C [23]. The T_gs from the peak of the tan δ obtained by DMA followed a similar trend.

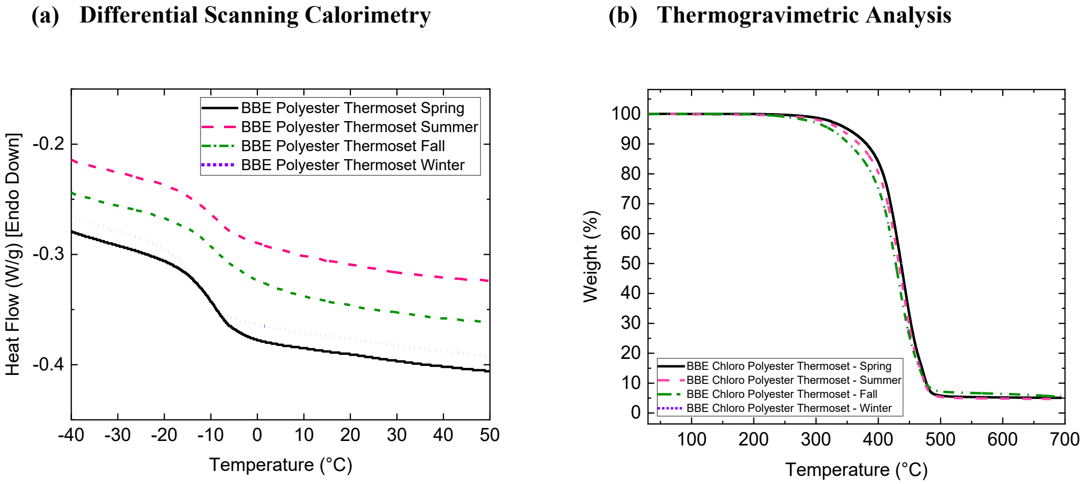
The BBE polyester thermoset has a T_g at 8°C compared to the betulin-C_{12} polyester thermoset at 26°C. This difference is expected because BBE is a mixture of various components, including phenolic and aliphatic species, that are not reactive toward polycondensations, unlike betulin and triterpenoids. The slightly higher T_g of the betulin-based thermosets is attributed to its bulky cyclo-aliphatic nature, fused tricyclic ring structure, and the lack of unreactive phenolic/aliphatic species, unlike the BBE.

Our thermal degradation study obtained from the TGA showed a negligible difference for various BBE polyesters obtained through different seasons, including the betulin-based polyester thermoset. BBE polyester thermosets can withstand high temperatures (up to 320°C under a nitrogen-rich atmosphere) before losing their structural integrity, similar to betulin-based polyester thermosets. Indeed, BBE-based thermoset polyesters demonstrated quite compatible thermophysical properties with the betulin regardless of the season the bark was collected and thus represent a more cost-effective alternative to betulin as a polyester precursor. DSC and TGA experimental trends are shown in Table 10, Figure 13, and Figure 15.

Table 10

A Comparison of Thermophysical Properties of Birch Bark Extract Polyester Thermoset to Betulin-Based Polyester Thermoset

Sample Type	T_g (°C) - DSC	$T_{95\%}$ or IDT (°C)	$T_{50\%}$ (°C)	$T_{max,1}$ (°C)	$T_{max,2}$ (°C)	Char (%) at 700°C
Spring BBE Polyester Thermoset	-9 ± 1	348 ± 6	434 ± 6	435 ± 8	471 ± 4	4.8 ± 0.5
Summer BBE Polyester Thermoset	-11 ± 1	337 ± 8	432 ± 3	434 ± 13	470 ± 4	3.9 ± 1.9
Fall BBE Polyester Thermoset	-10 ± 5	325 ± 4	429 ± 1	432 ± 3	467 ± 1	5.8 ± 1.5
Winter BBE Polyester Thermoset	-12 ± 3	328 ± 1	429 ± 4	433 ± 9	467 ± 6	5.6 ± 0.6
Betulin-C_{12} Polyester Thermoset [23]	3 ± 1	323	409	N/A	N/A	N/A

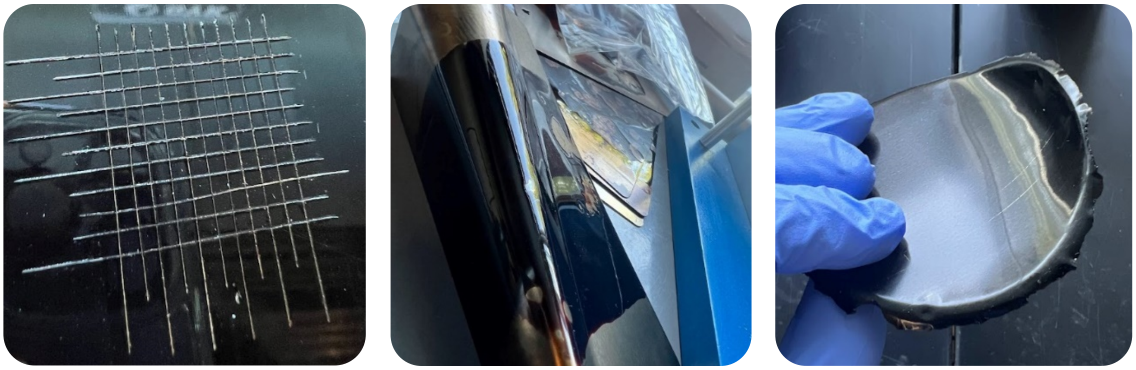


(a) Differential Scanning Calorimetry

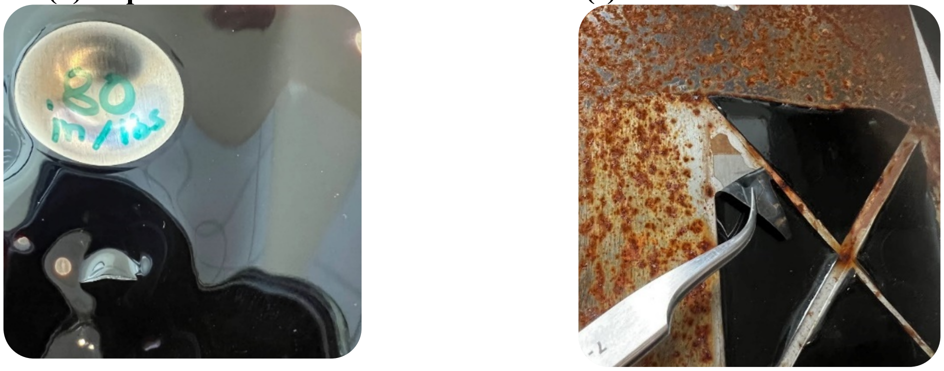
(b) Thermogravimetric Analysis

Figure 15. Thermal analysis of BBE polyester thermoset. (a) Represents the DSC curve comparison between the polyester thermoset derived from each major United States season using a 10°C/min heating rate to 120°C. No observable endo or exotherm is seen between 50 to 120°C. (b) Represents the TGA curves in nitrogen-rich conditions using a 10°C/min heating rate of 700°C.

4.3.2.1 BBE Polyester Thermoset Coating. After 40 min of mixing, the BBE polyester thermoset resin provided strong adhesion to the substrate even when the plate had been cooled to room temperature. The test result shows that this material has strong adhesion and displayed 0% mass loss due to cuts. This material easily passed the mandrel bend test because it is highly elastic at room temperature and can be manipulated similarly to the metal substrate. The maximum allowable impact force that this material could withstand is between 75 – 80 lbs/in. As a thin film, this material can be torn with sufficient force. Increasing the coating thickness can increase the maximum allowable impact force and, thus, its durability. The Shore, A hardness of this material, is 76, which is considered a medium hardness with a characteristic similar to the soft wheels of roller skates. Following one month of weather resistance test, substrate surfaces exposed to the weather have rusts formed. However, surfaces coated by the polyester thermoset were fully protected and showed no sign of corrosion. Therefore, BBE polyester thermoset can be a competitive material for high-temperature bio-based coating considering the thermal stability and coating properties. Figure 16 displays the results of various coating tests performed.



(a) Crosshatch Adhesion Test **(b) Mandrel Bend Test** **(c) Hardness Test**



(d) Impact Force Test **(e) Weather Resistance Test**

Figure 16. Qualitative results of coating test for BBE polyester thermoset

4.3.3 Betulin and Birch Bark Extract Epoxidation and Characterization

The epoxidation reaction of betulin and BBE were carried out in excess epichlorohydrin, with relatively higher synthesis temperatures and time to effectively modify the less reactive and hindered secondary and primary hydroxyl groups presented on the triterpenoids. The ring-opening reaction between epichlorohydrin and BBE was confirmed by a visible color change from light yellow to dark brown after 72 hrs of reaction time at 90°C. In addition, the ring-closing reaction with 50% NaOH (aq) generated visible salt solids, indicating the formation of oxirane moieties. The reaction mixture was extracted with equal volume DCM and washed with DI water once to remove sodium chloride salt and poly-epichlorohydrin formed during the reaction, followed by multiple brine washes.

The DGEBet synthesis required a minimum of ten brine washes to remove DMF to a negligible concentration. For DGEBBE, three additional brine washes were done to remove polyepichlorohydrin traces. Excluding DMF from DGEBBE synthesis eliminated one solvent choice that generally proved difficult to separate with vacuum distillation. Both DGEBet and DGEBBE are clear dark orange solids at room temperature. The EEW of the epoxidized products is shown in Table 11. The high reaction temperature and extended synthesis time can force oligomerization during the epoxidation reaction. NMR analysis confirmed the attached epoxy groups (3.0 – 4.5 ppm) combined with the triterpenoid region (0.5 – 2.5 ppm). All NMR spectra are shown in Appendix B.1.

Table 11

Epoxy Equivalent Weight and Number Average Molecular Weight of Eponex 1510, DGEBet, and DGEBBE

Material	EEW (g/eq)	M_n (g/mol)	Đ
Eponex 1510	210	437 ± 1.4	1.09 ± 0.004
DGEBet	1997 ± 13	342 ± 6.6	1.52 ± 0.01
DGEBBE	523 ± 52	530 ± 1.4	1.54 ± 0.01

Table 12

Thermophysical and Thermomechanical Characterization of Birch Bark Epoxy (DGEBBE) and Betulin Epoxy (DGEBet) Bimodal Blend with Eponex 1510

Sample Type	Extent of Cure(%) via FT-IR	T_g (°C) - DSC	T_g(°C) – tan δ	T_g(°C) – Loss Modulus	E′ (GPa) @ 25°C	T_{95}% or IDT (°C)	Char (%) at 700°C
Eponex 1510 - Epikure W (Baseline)	99.9	116 ± 3	130 ±3	128 ± 3	1.97 ± 0.75	334 ± 11	0.0 ± 0.1
DGEBet and Eponex1510 Blend – EpikureW	99.9	79 ± 4	91 ± 1	76 ± 2	2.60 ± 0.25	282 ± 5.2	3.0 ± 0.4
DGEBBE and Eponex1510 Blend – EpikureW	99.9	107 ± 2	115 ± 5	105 ± 7	2.52 ± 0.03	284 ± 5	3.1 ± 0.9
DGEBBE and Eponex1510 Blend – NC-558	99.9	67 ± 2	79 ± 4	66 ± 4	2.10 ± 0.52	288 ± 1	4.4 ± 0.8
DGEBBE and Eponex1510 Blend – DFDA	82.8	78 ± 5	86 ± 1	77 ± 3	2.76 ± 0.20	283 ± 3	12.2 ± 0.7

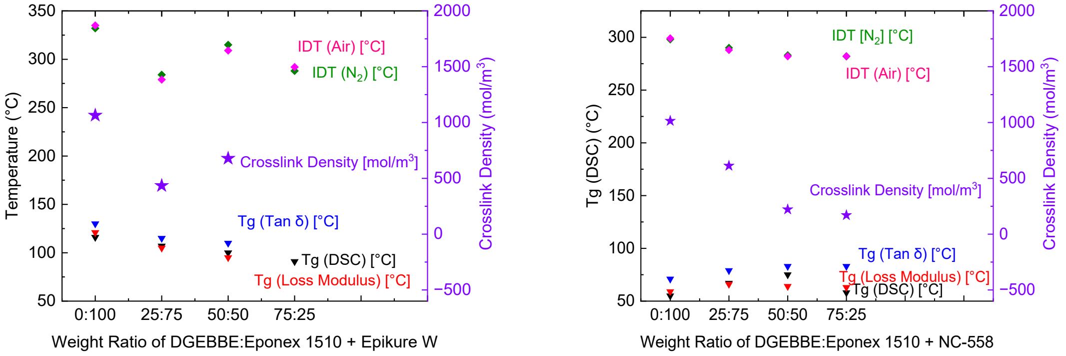
Note. All blended samples, excluding the baseline sample, are done at a 25:75 wt% ratio and cured with a select group of curing agents (Epikure W, NC-558, And DFDA)

The merit of utilizing DGEBBE and DGEBet in commercial epoxy resin systems and alternative curing agents was evaluated and shown in Table 12**.** In addition, the extent of cure was confirmed using near FT-IR using the primary epoxy region 4540 cm^{-1} and carbonyl reference peaks between 5300 – 5610 cm^{-1}. The FT-IR plots are available in Appendix B. There is a minimal difference in the T_g between the baseline Eponex 1510 and samples with DGEBBE implemented at 25 wt. %. However, the glass transition and the initial decomposition temperature of the resin system with DGEBet incorporated decreased significantly. The T_g, according to the peak of the tan δ, follows a similar trend.

By incorporating 25 wt% DGEBBE into Eponex 1510 resin system, the storage modulus (E′) at 25°C improved from 2.02 GPa to 2.5 GPa. DGEBet also increased E′ at 25°C of the Eponex 1510 resin system to a high value (2.60 GPa). Thus, the introduction of DGEBBE and DGEBet into the existing resin system made the final products more resistant to deformation.

The effects of curing agents from various sources were determined under similar conditions. Eponex 1510 cured with Epikure W continues to have the highest T_g. Additionally, increasing DGEBBE content, when cured with Epikure W, decreased the T_g by approximately 16°C. This difference establishes a new temperature limit when the epoxy is operated below the T_g. For example, the operating condition of the cured Eponex 1510 is no longer advisable at 110°C, assuming DGEBBE is implemented into the resin system at a 25% weight ratio. This change is attributed to the epoxy thermoset becoming softer and more rubbery at approximately 107°C.

Further observations showed that NC-558 and DFDA curing agents decreased the T_g further. The curing agent choices do not significantly affect the initial decomposition temperature at 25:75 DGEBBE:Eponex 1510 ratio. However, resins cured with DFDA possessed the highest storage modulus at 25°C (2.76 GPa) and char % (12.2%) at 700°C. In all instances, including BBE epoxy in the resin mixture improved the room temperature (25°C) storage modulus of the final material.



(a) Epikure W

(b) NC-558

(c) DFDA

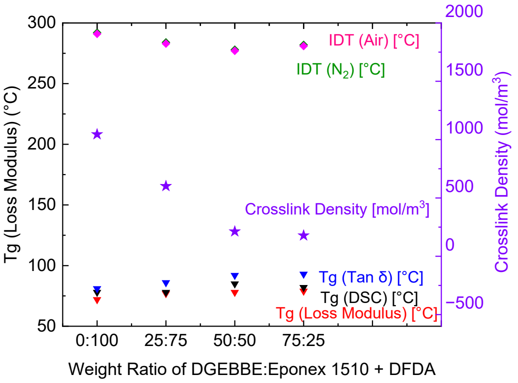
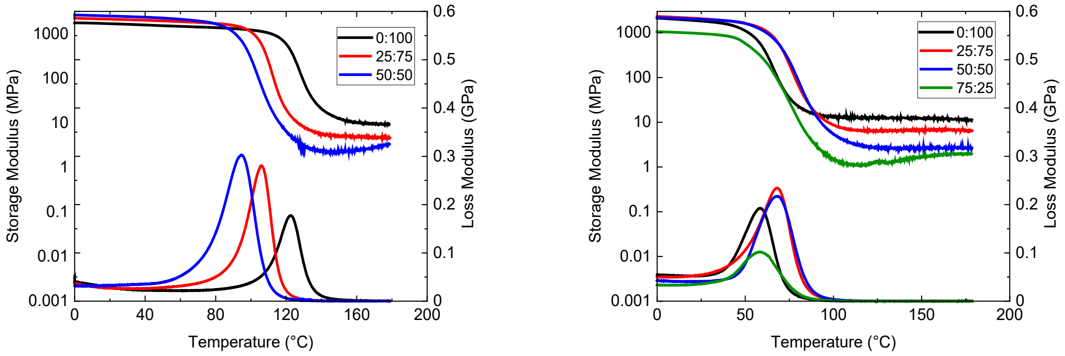


Figure 17. General DSC, TGA, and DMA trends of the bimodal blend of birch bark extract epoxy and Eponex 1510. All samples were cured with (A) Epikure W, (B) NC-558, and (C) DFDA

The general trends of the thermophysical and thermomechanical analyses are shown in Figure 17. DGEBBE is too brittle to be used for thermomechanical analysis, such as DMA. Therefore, we collected DMA results up to 75:25 DGEBBE:Eponex 1510 weight ratio. The IDT generally follows a consistent trend in both air and nitrogen-rich condition. However, the 25:75 DGEBBE:Eponex 1510 ratio, in Figure 17a, drastically reduced the IDT instead of following a steady decreasing trend like samples cured with NC-558 and

DFDA. The IDT trend corresponds to the crosslink density, despite the extent of cure being over 99%. It is possible that additional hydrogen bonding occurred at the curing temperature and higher DGEBBE ratio. The T_g generally decreases with Epikure W as a function of DGEBBE content. Conversely, NC-558 and DFDA increase the T_g as a function of DGEBBE content.

(a) Epikure W **(b) NC-558**



(c) DFDA

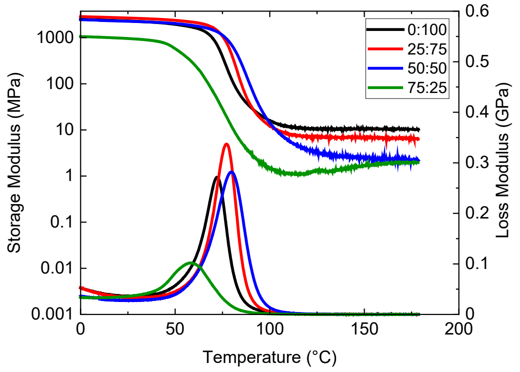


Figure 18. Storage and loss modulus curves of DGEBBE and Eponex 1510 blend

Figure 18 displays the general DMA trends observed with the epoxy thermoset systems cured with (a) Epikure W, (b) NC-558, and (c) DFDA. The storage and loss moduli increase at 25:75 and 50:50 DGEBBE:Eponex 1510 blends cured with NC-558 and DFDA. At a 75:25 wt % ratio, both loss and storage modulus decreased below the cured Eponex 1510 system. At this weight ratio, all samples are challenging to degas because the epoxy blend is an amorphous solid. The presence of microbubbles within the DMA bar can greatly decrease the resistance to deformation and toughness of the sample. Epoxy blends cured with Epikure W followed an opposite trend to NC-558 and DFDA, where the storage and loss moduli decreased as a function of DGEBBE content. This trend is attributed to the post-curing condition of the epoxy blends with Epikure W being different from NC-558 and DFDA. A higher temperature is needed to cure the resin system with Epikure W fully.

4.3.3.1 Utilizing Birch Bark Extract Epoxy as a Coating Material. The viability of DGEBBE as a coating material was tested against Eponex 1510 for various curing agents, as shown in Figure 19 and Table 13. All 100% Eponex 1510 samples cured by Epikure W, NC-558, and DFDA passed the cross-hatch adhesion test with no material removal. However, implementing DGEBBE at a 25 wt% ratio made the cured coating more brittle. The triterpenoid molecules within BBE are bulky with cyclo-aliphatic rings, reducing the flexibility of the cured coating. Conversely, this characteristic, at 25:75 wt. % ratio allowed DGEBBE to withstand direct impact twice as Eponex 1510 when Epikure W was selected as the curing agent. The bio-based curing agents, NC-558 and DFDA, enhanced the adhesion strength of the 25:75 wt. % resin mixture to 5B (0% removal rate). However, both samples observed major delamination in the mandrel bend test and low impact force resistances (10 – 15 lbs/in). The major failure in the mandrel bend test for flexibility is attributed to the increased stiffness in the sample caused by the interaction between the resin blends. NC-558 and DFDA curing agents do not specifically affect the results of the mandrel test because 100% Eponex 1510 was able to pass the bend test with no delamination. Impact force resistance has shown a minimal correlation between the curing agent choice, suggesting that the compatibility between the resin formulation can negatively affect the impact force resistance. The hardness test indicated no significant difference between the 0:100 and 25:75 mixture, regardless of the curing agent choice. Therefore, in coating applications, this bimodal blend of DGEBBE and Eponex 1510 is not viable because the mixture becomes more brittle with increasing DGEBBE content. However, this study specifically used Eponex 1510 as a basis for comparison between bio- and petroleum-derived epoxies. The ideal formulation for DGEBBE may be drastically different from the combination chosen for this study.

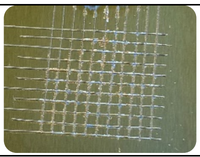
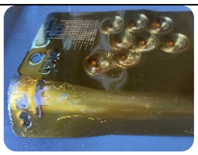
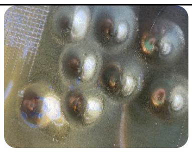
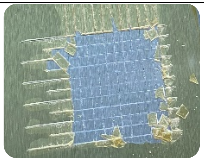
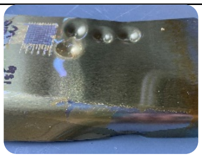
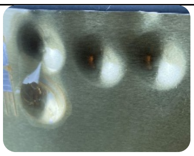
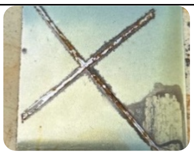
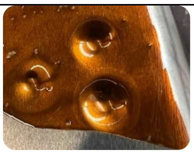
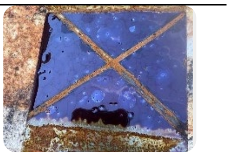
Sample	Crosshatch Adhesion	Mandrel Bend Test	Impact Resistance	Weather Resistance
Eponex 1510 & Epikure W				
25:75 BBE Epoxy: Eponex 1510 & Epikure W				
25:75 BBE Epoxy: Eponex 1510 & NC-558				
25:75 BBE Epoxy: Eponex 1510 & DFDA				

Figure 19. Epoxy coating application qualitative test results

Table 13

Coating Test Application Quantitative Results

Sample Composition % (DGEBBE/Eponex 1510)	Curing Agent	Crosshatch Adhesion Test	Mandrel Bend Test	Impact Test (lbs/in)	Shore D Hardness Test
0:100	**Epikure W**	5B → 0% area removed	Failed → minor delamination	15 – 20	77.0 ± 7.5
	NC-558	5B → 0% area removed	Passed	35 – 40	63.6 ± 5.2
	DFDA	5B → 0% area removed	Passed	20 – 25	81.6 ± 1.4
25:75	**Epikure W**	0B → greater than 65% area removed	Failed → minor delamination	40 – 45	80.6 ± 3.8
	NC-558	5B → 0% area removed	Failed → major delamination	10 – 15	74.0 ± 4.3
	DFDA	5B → 0% area removed	Failed → major delamination	10 – 15	80.7 ± 1.4

4.4 Conclusions

The capability of an underutilized resource was demonstrated through the synthesis of BBE polyester thermoset and epoxidation reactions. The birch bark specimens for this work were taken from one location to minimize property variability due to climate and species. The change in triterpenoid composition, molecular weight, and reactive group throughout different seasons was observed. However, the success of each reaction remained unaffected because the mass ratio was adjusted to match the desired stoichiometry. BBE polyester thermoset possessed comparable glass transition temperature and thermal stability values to a betulin-based polyester thermoset. This material is proven viable for coating based on its strong adhesion, resistance to deformation, high impact force resistance, and weather resistance. However, this material requires a high temperature (200°C) curing for several hours before it solidifies; thus, the resin must be placed on a flat and horizontal surface during curing.

Conversely, DGEBBE improved the impact force resistance of coating materials but failed the cross-hatch adhesion and mandrel bend test. Higher adhesion strength is observed when the bimodal blend of DGEBBE and Eponex 1510 is cured with NC-558 and DFDA. Before DGEBBE can be used as a coating material, additional optimization to the synthesis stage is needed to improve resin characterization such as EEW and overall molecular weight. DGEBBE, synthesized through the conditions chosen for this work, can realistically be used as part of a formulation rather than as a standalone coating material. As a solid epoxy, there is an inherent processing challenge that requires mixing at a temperature above the melting point of the epoxy. However, DGEBBE may be dissolved and blended with a liquid resin system, such as Eponex 1510, and still exhibit high mixture stability. Although this bimodal blend study did not yield convincing results in favor of DGEBBE, future studies may consider using DGEBBE as part of a separate formulation to develop a different coating material with high adhesion, flexibility, impact force resistance, weather resistance, and storage modulus.

BBE is relatively inexpensive compared to obtaining and purifying individual triterpenoid components (betulin, betulinic acid, and lupeol). BBE-derived polymers do not possess superior properties to petroleum-derived polymers when used as epoxy. However, this underutilized resource served as an essential step in demonstrating the potential use of biomass commonly treated as waste, increasing the overall resource sustainability.

Chapter 5

A Systems Approach to Enhancing Solvent Recovery

Texts and figures are reproduced and adapted with permission from J. D. Chea, A. L. Lehr, J. P. Stengel, M. J. Savelski, C. S. Slater, and K. M. Yenkie, "Evaluation of Solvent Recovery Options for Economic Feasibility through a Superstructure-Based Optimization Framework," Industrial & Engineering Chemistry Research, vol. 59, no. 13, pp. 5931–5944, Apr. 2020, DOI: 10.1021/acs.iecr.9b06725. and E. A. Aboagye, J. D. Chea, A. L Lehr, J. P. Stengel, K. L. Heider, M. J. Savelski, C. S. Slater, and K. M. Yenkie., "Systematic Design of Solvent Recovery Pathways: Integrating Economics and Environmental Metrics," ACS Sustainable Chem. Eng., vol. 10, no. 33, pp. 10879–10887, Aug. 2022, DOI: 10.1021/acssuschemeng.2c02497.

As the chemical market continues to expand, environmental concerns have increased due to the excessive disposal of organic solvents. To date, there is no comprehensive mitigation plan to completely handle the 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 into the environment. This chapter presents a systematic framework for solvent recovery 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. The capability of our solvent recovery framework to obtain economically viable solvent recovery pathways is demonstrated.

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

In 2017, the chemical industry was the world's second-largest manufacturing industry and was projected to double between 2017 and 2030 [388]. 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 [388]. The United States Environmental Protection Agency (US EPA) has estimated that solvent emissions from the chemical market growth can reach up to 10 million metric tons of carbon dioxide equivalent, accounting for up to 62% of the total emission in 2017 [389]. This amount of chemical emission can substantially increase the Global Warming Potential (GWP), a metric developed to measure the amount of energy that emissions can absorb for a given period [390]. 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 is often disposed of after one cycle because of purity concerns, which is not a sustainable practice [136], [391]–[393]. 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 [152], [391]. 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 [388], [394]–[398]. Additional work is in progress by several researchers to address environmental management [399], [400], sustainability indicators [401]–[404], controllability [405], [406], multi-stakeholder decision-making [6] for the greater benefit of society and thus supporting the global environmental initiative and the United Nations Sustainable Development Goals of responsible consumption and production as well as climate action [407], [408]. This study proposes an optimization framework to address the economic challenges in implementing waste recovery in chemical processes.

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 [75], [76]. Industrial scrubbers are used to reduce pollution when disposing of solvent vapor into the air. 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 [152]. Incineration can be used to dispose of wastes, either on-site or off-site. 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 [232], [409], [410]. 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 [398], [411]. 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 [412]. Incineration produces approximately 6.7 kg CO_2/kg organic carbon, which along with other solvent disposal methods, contributes negatively to the emission statistics and consequently increases environmental risks and concerns [412], [413]. Recovery methods are being considered to improve the greenness and overall sustainability of processes in the pharmaceutical and fine chemical industries [398]. Multiple unique greenness analysis methods were developed in the past decade by [5], [141], [414]–[417] 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 [7], [398], safety, and economics [253], [254], [418], [419]. Nationwide data from the United States EPA’s Toxic Release Inventory (TRI) database were analyzed between 2007 and 2017 to observe the cumulative solvent waste from the past decade from solvent-consuming industries [38]. As shown in Figure 20, the general chemical waste trend for the top ten most wasted solvents has been relatively consistent, with minor fluctuations between values. The TRI database only reports solvent wastes considered detrimental to the environment and human health, which excludes more benign solvents such as acetone and ethanol.

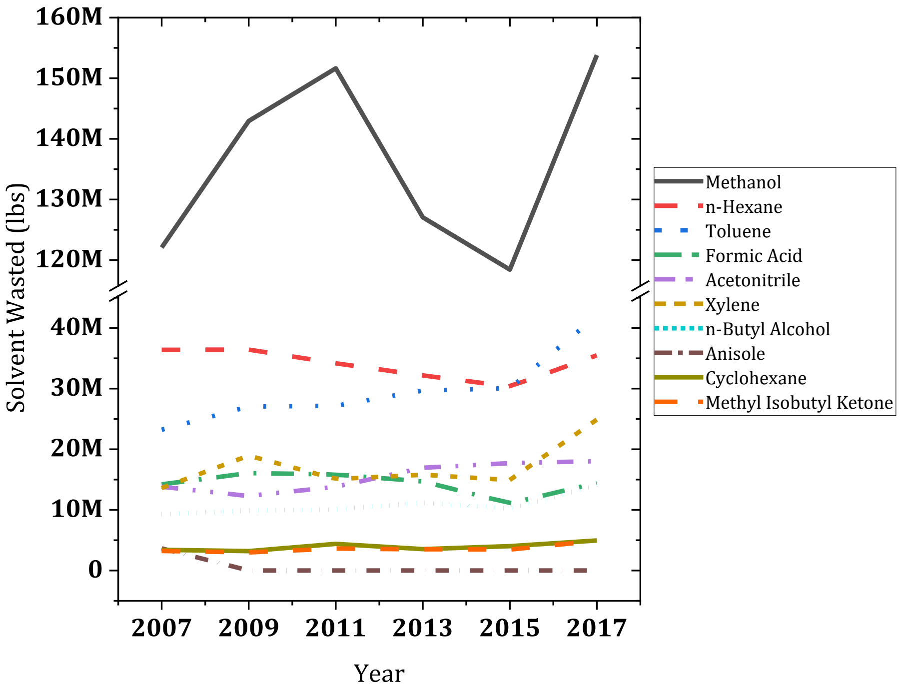


Figure 20. Top ten US EPA TRI (Toxic Release Inventory) waste solvents in the United States between 2007 and 2017

In 2015, the US EPA published a revision for solvent waste recycling under Subtitle C of the Resource Conservation and Recovery Act (RCRA), which redefines 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 [420]. This act does provide strong encouragement for solvent recovery. However, the chemical waste trend following 2015 continues to rise despite the revision because a higher quantity of solvent waste is generated from the increasing chemical demand.

The rising trend is expected to raise global toxic chemical waste and emissions 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 [413]. Hence, incineration can account for one-third of the original price of purchase. Although incineration can recover energy, the emissions cannot be controlled and are released into the environment [421].

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 timeframe. A practical solvent recovery framework can help design sustainable processes by recycling materials, reducing emissions, and enhancing the economics of chemical processes [422]–[425]. The framework proposed in this chapter applies to a multitude of solvent-utilizing industries because it starts from the basics, such as the physical properties of the components involved, driving forces of the recovery, and purification technologies, and then extends to broader metrics, such as process economics and environmental impacts. Therefore, this chapter explores the sustainability assessment gap for the solvent recovery framework and presents a comparative evaluation approach using multi-objective superstructure-based optimization techniques.

5.2 Materials and Methods

5.2.1 Designing a Framework for Process Evaluation

As an initial step in designing the solvent recovery framework, we collected information on common solvent 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 [426], [427]. These results were compared to the waste stream incineration model to demonstrate the feasibility of solvent recovery from an economic and environmental standpoint. All separation technologies were modeled according to mathematical equations found in typical engineering textbooks and research articles [129], [159], [172], [180], [185], [253], [254], [321], [418], [428]–[430].

5.2.2 Annualized Cost Evaluation

The analysis of each separation technology was divided into material and energy balances, design, constraints, capital cost, and operating cost [428], [431]. 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 include added chemicals required for 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 replacement periodically. Finally, 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 non-linear programming (NLP) problems, where cost minimization is the objective [333], [334]. Appendix C contains all equations used for relevant technologies in this study.

5.2.3 Constructing an Optimization Model

Designing a solvent recovery process is a complex task because multiple stages of separation are required, with several technologies applicable at each stage. Figure 21 depicts this complexity in decision-making. The solvent recovery process 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 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 similar technology as the recovery stage, but the majority of the impurity associated with the original waste stream has been eliminated from the recovery stage. Solvents with higher purity are anticipated. A refinement stage may be used further meet the standards set forth by the user. The selection of solvent recovery technology depends on factors such as process efficiency, chemical waste characteristics, capital and operating cost, and environmental impacts. Suppose a process cannot achieve the desired specification and operates at a cost that significantly exceeds the disposal price. In that case, 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.

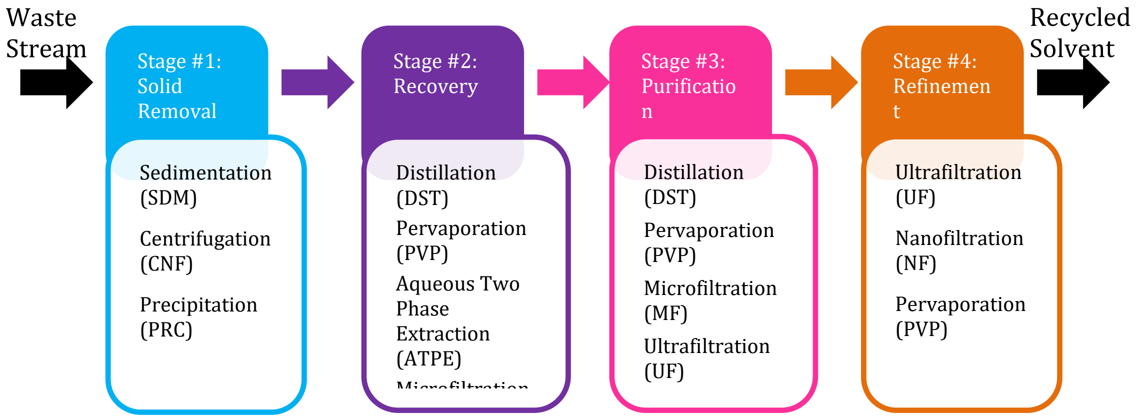


Figure 21. General steps for recovery and purification of solvents

A superstructure optimization approach was used to develop the framework for solvent recovery, as previously described in Chapter 2, Section 2.2.2.2 [253], [254], [333], [418], [419], [432], [433]. Figure 4 illustrates a proposed solvent recovery superstructure with logical equations for single pathway selection. This method begins with waste stream specification and desired purity for solvent recovery. 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 requires 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 separate other components within the waste stream. For example, the purification stage may consider distillation, pervaporation, microfiltration, and ultrafiltration. A bypass may be used in all major steps if the technology options are not applicable to reach the desired purity.

We combined the NLP technology models in GAMS as Mixed-Integer Non-Linear Programming (MINLP) problems to model and assess 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 [333], [434]. The linear and nonlinear equations consist of material and energy balance, design equations specific to a given technology, and constraints. The developed mathematical models for each technology are in the supporting document. Binary variables are either active (1) or inactive (0). In the case of using an MINLP approach to select a process path, the chosen technology is assigned "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 helps 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, reduce waste). Therefore, solvent recovery is inherently a multi-stakeholder 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 [257], [343], [435]. The combined modeling, multi-stakeholder formulation, and superstructure optimization approach can 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.

5.2.4 Modeling Selective Superstructure for Case-Studies Evaluation

The viability of the generalized solvent recovery superstructure, as shown in Figure 4, was determined through case studies of waste accumulation in the major sector of the chemical industry. We fully defined the flow rate and physical properties of the waste stream components before applying the solvent recovery framework. Based on 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, the solid removal stage is not considered if no solid or dissolved solid is present in the original waste stream. The reduced case-specific superstructure was then modeled in GAMS using equations from Appendix C. In GAMS, we first defined "sets," which contain relevant separation technology assignments, stream numbers, and components. The necessary parameters, colored in red text in Appendix C, were specified according to property estimations and thermodynamics data. Next, 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 Equation (12). The binary variable "y" represents the selection of a specific pathway in a superstructure. The subscript "j" refers to the stream number.

$$\sum y_j = 1, \forall\, y_j \in \{0,1\}, j \in \{1,2,3,..\} \tag{12}$$

5.2.5 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 5.3.

5.2.5.1 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 (flocculate), effectively enhancing the rate of sedimentation [436]. However, solid particles are generally too far apart at a low concentration of solids to settle at a constant rate [159]. Decantation (DCT) is similar to gravity sedimentation, but the terminology applies to liquid-liquid separation. For a feed stream containing a dispersion of immiscible fluids at different densities, a decanter acts as a tank to give sufficient time for the immiscible fluids to either settle or rise to their respective phases. Three layers can be observed as the fluid travels through the decanter: 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 [321].

Centrifugation (CNF) is a form of forced sedimentation that subjects materials (liquids or solids) of different densities to centrifugal force. This operation can be carried out continuously and have a short retention time, meaning that heavier material will settle relatively fast and leave the centrifugation unit within a matter of seconds [159]. 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 [166], [321],

[437], 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 power required to force particle sedimentation. Therefore, if the density difference between the substances of interest is high, simple gravity sedimentation or decantation is preferred due to the low energy requirement.

Precipitation (PRC) is typically used as an initial purification step to remove the product, impurities, and contaminations by adding solvents, salts, or polymers, temperature modification, or pH adjustment. This event occurs because of a shift in phase equilibrium. A solvent is added to a liquid mixture containing the dissolved substance in antisolvent precipitation. 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 removes the precipitate from the liquid [159], [162]. The antisolvent can be recovered using other liquid-liquid separation, such as distillation or membrane, depending on thermodynamic properties.

5.2.5.2 High-Temperature Separation. Distillation (DST) is a technique that separates chemical compounds based on relative volatility at a given temperature and pressure. Multi-component 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 contacting 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 (heavy key-rich phase) is removed from the distillation unit as the bottom product. This partial reboiler provides a major driving force that separates the 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 (light key-rich phase). 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 mainly contains light key components [159], [170], [171], [334].

5.2.5.3 Membrane Processes. Membrane processes are a separation technique that relies on semi-permeable 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 allowed to flow through the membrane freely, while the retentate stream flows through the unit and becomes more concentrated with the rejected component [159]. Diffusion is the leading factor in molecular transport through a porous membrane, which means that the size of the material of interest will greatly affect its permeability through the membrane [129], [438]. The selection of membrane processes, 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 [129], [172]–[174]. The nominal pore sizes of the membranes are as follows: microfiltration (0.1 to 10 μm), ultrafiltration (10 to 100 nm), and nanofiltration (1 to 10 nm) [439]. Despite the differences in naming, the inherent nature of these separations is the same, which requires some external pressure to drive the permeate stream through a semi-permeable 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 [311]. Depending on the nature of the process, the efficiency of membrane separation is characterized by flux, solute rejection, recovery, or perm-selectivity of the solute [159], [311].

Pervaporation (PVP), one of the major membrane processes, separates 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 effectively separating the desired component. By lowering the permeate partial pressure through either vacuum or sweep gas, the permeate solubilizes in the membrane and 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 with a strong affinity for water. This type of membrane is selected to remove water from the organic phase. The 'hydrophobic membrane' has a stronger affinity for organic compounds and is used to remove organic compounds from water [159].

5.2.5.4 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 more soluble impurities 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 water-rich phase (raffinate), is employed according to density difference [159], [321]. 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 [321]. LLE has been applied to processing petrochemicals, biomolecules, wastewater, coal and wood-derived chemicals, pharmaceuticals, food, and agricultural products [159]. Compared to distillation, LLE is generally a cheaper approach to separation as long as the desired result can be accomplished with low energy consumption and the relative volatility of the two components is less than 1.05 [321]. 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, and 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 separating and recovering biomolecules, such as proteins, to prevent denaturation [440]. ATPE system typically consists of liquid polymers, salts, low molecular weight alcohols, surfactants, and ionic liquids [182], [183], [185], [441]. This method relies on the molecular weight, miscibility of each component, and the concentration of hydrocarbon and inorganic salt added. As a result, ATPE can handle high liquid capacity, be low in cost and processing time, and achieve the desired purification and concentration specification without additional steps [186]. 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 [182], [185], [440], and for biological molecules, the partition coefficient can be as high as 30-45 [442], [443].

5.2.5.5 Incineration (INCN). Incineration is a process employed to eliminate waste through combustion reactions, typically to recover energy. A waste stream enters the incinerator along with air and fuel gas. Other incinerators may utilize steam. Elevated temperatures drive a chemical reaction 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 various disposal needs, such as solvents, plastics, and municipal waste. 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 [20], [232], [411], [421]. The driving forces and crucial specifications required for each of the technologies are summarized in Table 4. Detailed equations and parameters specified are available in Appendix C.8.

5.3 Results and Discussions

Despite the efforts to encourage sustainable solvent waste management, the rapid expansion of the chemical market caused the total chemical waste to increase and exceed the reported waste values from 2007 – 2017 [38], [420]. 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 various chemical industries. Our results demonstrated that solvent recovery is more economically viable than incinerating chemical wastes (See Table 14 and Table 15). In addition, two illustrative cases from the pharmaceutical and specialty chemical industries were studied using the proposed solvent recovery framework to describe the process economics regarding resource recovery and reuse.

5.3.1 Case Study 1: Pharmaceutical Waste Stream

Our previous work examined a case of isopropanol (IPA) recovery from the celecoxib waste stream [335]. The celecoxib process produces the API for an arthritic medication known as Celebrex® [413, p. 20]. Since the study was published in 2012, the process chemistry, flow rates, and concentrations have 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 purification steps following synthesis. Figure 22 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 up to 2.19 kg total emissions/kg IPA used can be released. These emissions include 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.

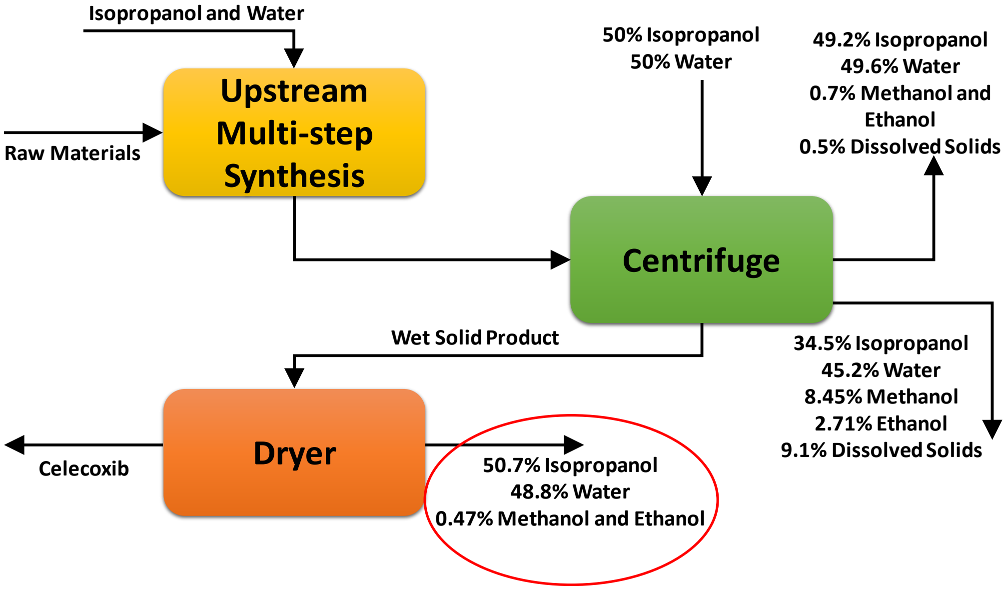


Figure 22. Celecoxib synthesis, purification, and possible waste streams [444]. The circled stream is used as the entering waste in our recovery superstructure

5.3.1.1 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 may not achieve the desired purity [445]. Before modeling the IPA recovery case study, we assumed a waste stream feed basis of 1000 kg/hr, 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, precipitation may be used. In the case of the dryer distillates, the impurities are methanol and ethanol. Both components do form an azeotrope with water. Once the organic is fully separated from water, a membrane process can 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 23 illustrates a proposed selective superstructure for recovering 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 three separate pathways containing five unique processing units and 23 streams. Aqueous two-phase extraction, pervaporation, and distillation were considered part of the recovery stage, followed by other 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. Ultrafiltration (UF1) can separate and recycle hexane from the IPA/hexane mixture. Separating solid salt and water is possible through decantation, which allows salt recycling for reuse in ATPE technology. Water has a higher affinity for salt, while the IPA separates into the hexane layer. The second IPA recovery path utilizes membrane technology, such as pervaporation and ultrafiltration, with relatively low energy requirements. The third, more energy-intensive method 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 the light key with a normal boiling point of 82.5°C. Pervaporation was implemented to effectively separate the distillate stream since there is an azeotropic point at 87.7 wt% and 80.37°C.

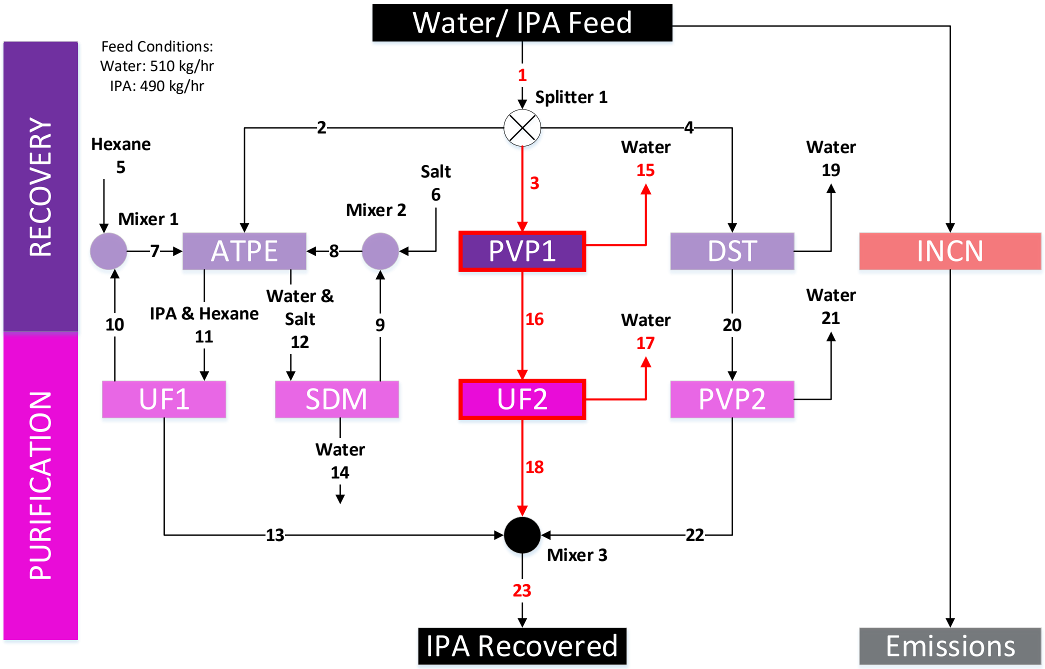


Figure 23. The superstructure of possible solvent recovery methods to separate IPA from a pharmaceutical waste stream containing a mixture of IPA and water. ATPE, UF, SDM, PVP, DST, and INCN represents Aqueous Two-Phase Extraction, Ultrafiltration, Sedimentation, Pervaporation, Distillation, and Incineration, respectively. Recycle streams are also included. The optimal pathway has been selected through GAMS.

5.3.1.2 Economic Evaluation. Table 14 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 seconds with an optimality gap of $1.00*10^{-9}$. The optimized solvent recovery pathway is selected as PVP1-UF2, which meets the purity requirement, has the lowest annualized cost of $524,000, and requires $0.14 per kg solvent recovered. Figure 24 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. ATPE-UF1-SDM pathway could not meet the desired recovery and purity requirement, and thus the solution became infeasible. However, it is possible to relax the constraint on purity to allow the solution to converge to a 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 a low-purity solvent can reduce the API quality in pharmaceutical applications. The feasible solvent recovery pathway cost is considerably cheaper than the cost of incineration, which is $8.1 million/yr for a flow rate of 1000 kg/hr of IPA/water waste. The energy requirements to break the chemical bonds of organic compounds are the highest contributor to the estimated cost of incineration. This operation typically requires the incinerator temperature to be maintained above the ignition temperature, ranging between 590 to 1200°C [446]. Conversely, distillation is regarded as one of the most energy-intensive separation methods. However, the price of choosing the distillation pathway is minor compared to incineration because the operation temperature only requires the boiling point of the organic compound of interest. Therefore, incineration is the least economical choice for solvent waste processing.

Table 14

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

Solvent Recovery Pathways	Annualized Cost ($ million/yr)	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

a. This 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%

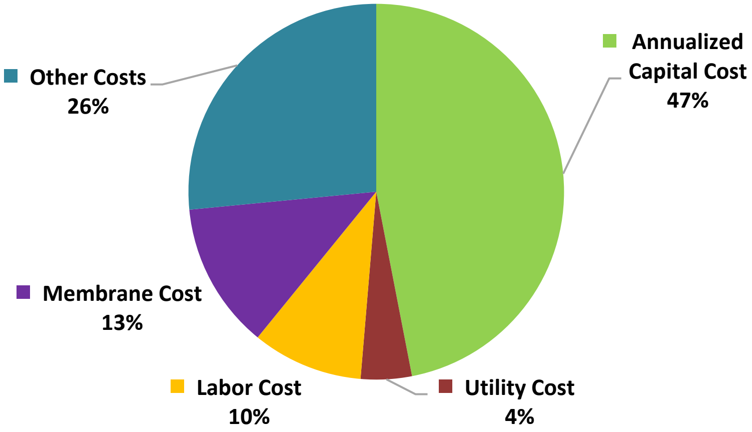


Figure 24. Cost distribution of the optimal solvent recovery pathway (PVP-UF1) for recovering IPA from Case Study 1

As a multi-stakeholder problem, the environmental factor was also considered. Through stoichiometry, the complete combustion of 1 kg of IPA through incineration equates to 2.2 kg CO_2 released into the atmosphere. For this case study, the assumed 1,000 kg/hr waste stream basis contains 510 kg/hr of IPA. For 330 workdays, this flow rate equates to 4,039 metric tons/yr of IPA. Therefore, the complete combustion of this amount of IPA is expected to result in 8,886 metric tons/yr of CO_2 released into the atmosphere. Such release is equivalent to greenhouse gas emissions from 21.7 million miles driven by an average passenger vehicle [447]. As of 2017, the annual vehicle miles in the US has reached 3.2 trillion [448], meaning that the carbon dioxide emission from the combustion of one single pharmaceutical waste stream is equivalent to approximately 0.0007% of annual vehicular emission in the US alone. Although such a number may appear insignificant, consistent practice of incineration in the chemical industry will stack and consequently impact the environment significantly. Therefore, the selection of solvent recovery has higher economic viability and lower environmental impact than the incineration pathway.

5.3.2 Case Study 2: Specialty Chemical Waste Stream

Seyler *et al.* (2006) have reported an annual solvent waste accumulation of 135,000 kg (~17 kg/hr for an annual operating hour of 7920) at Lonza Group Ltd., which is an international chemical and biotechnology company based in Visp, Switzerland that, operates as a manufacturer of specialty chemical for pharmaceutical and agrochemical industries [421]. Approximately 25,000 kg/yr of dimethoxyethane have been recovered via distillation. However, distillation is energy intensive, requiring continuous boiling and condensation of the liquid components of interest.

5.3.2.1 Process Conditions. This solvent waste stream typically contains 21.3% dimethoxyethane (DME), 35.3% water, 41.3% toluene, 1.3% 1-ethoxy-1-methoxy ethane (EME), and 0.7% impurities by weight. Alternative processes have been explored to provide similar results to minimize operating expenses without sacrificing process efficiency. Given that the identities of the waste stream impurities were unspecified, we assumed that the 0.7% impurity value is a part of the water phase. The targeted purities of DME, EME, and toluene were set to 95%.

Figure 25 illustrates a proposed selective superstructure, with 12 possible pathways to consider for recovering dimethoxyethane from a mixture of solvent waste. The initial step involves feeding the chemical waste stream into a mixer where anhydrous salt comes in contact with the liquid mixture of aqueous (water) and organic compounds (DME, EME, and 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 [449]. This phenomenon increases the miscibility of DME and EME in the aqueous phase. Therefore, using decantation to separate the combined aqueous and organic layers is invalid and, thus, not considered for this case study. Anhydrous salt consists entirely of cation (positively charged ion) and anion (negatively charged ion). It 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 depends on the settling velocity of the salt particles after mixing. For instance, gravity sedimentation is infeasible if the solid present in a liquid mixture is classified as a colloidal particle. Centrifugation, although capable of enhancing sedimentation rate, is impractical in cases where solid particles are considerably denser than the fluid medium. The recovered hydrated salt can be dried to become anhydrous and reused in the solvent recovery because water is loosely held to the salt molecules. Following removing the aqueous phase, we considered four unique processing paths for organic separation. Although distillation in a sequence was reported to be successful [421], our relative volatility calculation indicated that the relative volatility of DME to EME is 1.06. This number is close to 1.05, the minimum recommended relative volatility threshold for distillation [450]. Therefore, the distillation pathway was compared against less energy-intensive processes such as pervaporation, 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/hr. Toluene has the highest boiling point of the three components, with 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 exits 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°C and 87°C, respectively [421]. In DST2, DME is the light key with relative volatility of 1.017, while the bottom product is EME. The top stream comprises 95% DME and 0.03% EME at 3.16 kg/hr, while the bottom stream is composed of pure EME at 1.26 kg/hr. The second major recovery pathway utilizes a pervaporation system followed by ultrafiltration. The waste stream enters the pervaporation system at 11.36 kg/hr. 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/hr. 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).

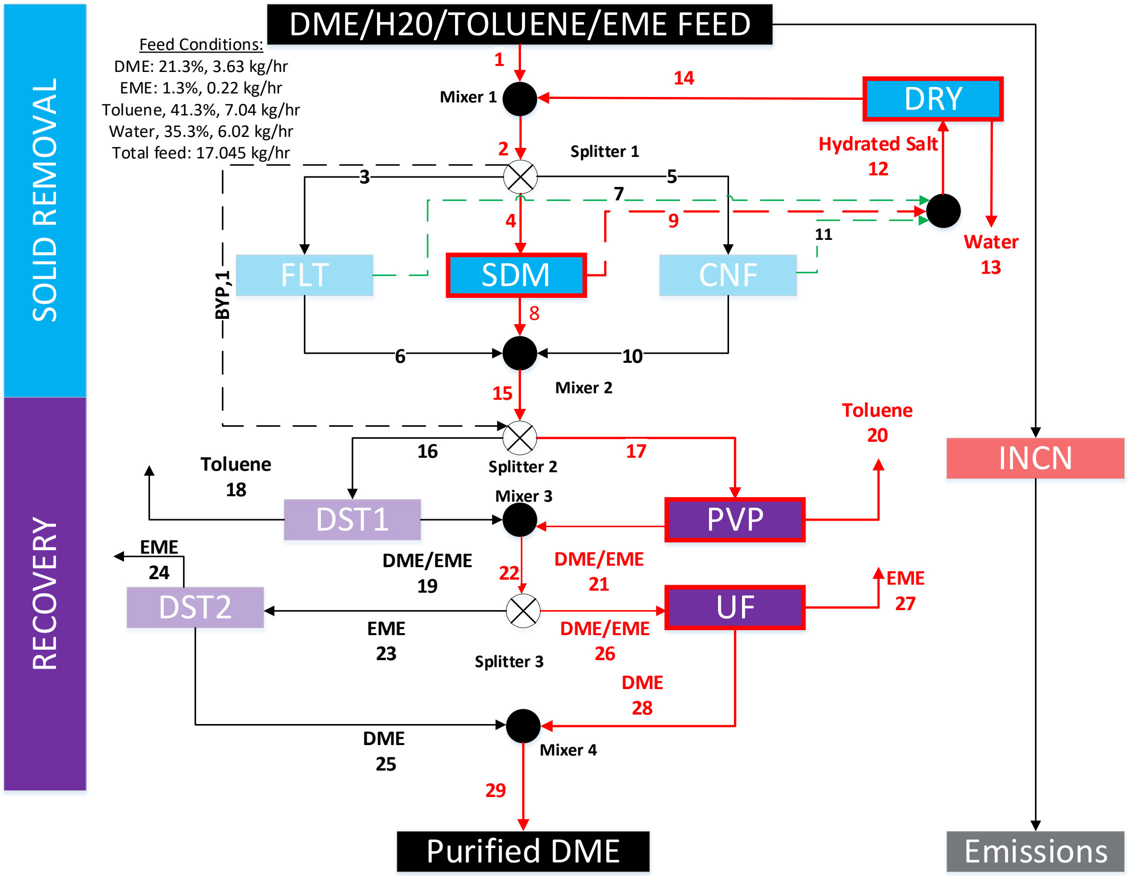


Figure 25. Recovery pathways to purify Dimethoxyethane. DRY, FLT, SDM, CNF, DST, PVP, and UF represent Drying, Filtration, Sedimentation, Centrifugation, Distillation, Pervaporation, and Ultrafiltration, respectively. The red dashed line represents the ideal recycle stream for recovering anhydrous salt. INCN represents incineration, which results in emissions.

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.

5.3.2.2 Economic Evaluation. Table 15 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 seconds 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 requires water removal through anhydrous salt, solid separation, pervaporation, and ultrafiltration. These operations require a cost of \$330,000/yr at an annual solvent recovery rate of 53.9 metric tons/yr of water, 55.5 metric tons/yr of toluene, 1.6 metric tons/yr of EME, 25.8 metric tons/yr of DME. 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/hr), which scales to a lower cost. The price of incinerating the DME waste stream is \$14.6 million/yr, a considerable increase from the three feasible recovery pathways.

Table 15

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

Solvent Recovery Pathways	**Annualized Cost ($ million/yr)**	**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

Figure 26 displays the total cost distribution for the feasible pathways in GAMS. The overhead (other) cost contributes to most of the total cost, followed by the labor costs. The annualized capital, consumable, and utility costs are attributed to reduced equipment capacity 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. Therefore, continuous solvent recovery at a low flow rate is not viable 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 metric tons/yr of CO_2 released into the atmosphere. Such release is equivalent to greenhouse gas emissions from 584,000 miles driven by an average passenger vehicle [447].

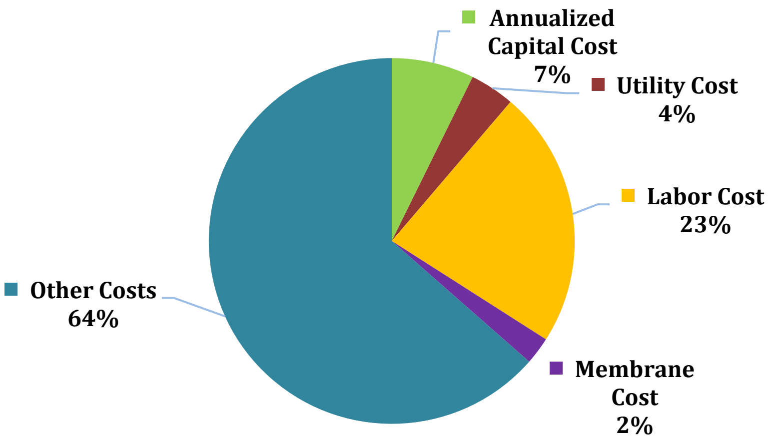


Figure 26. Cost distribution for the optimal recovery pathway to recover DME in Case Study 2

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 27 demonstrates the reduction 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 capital cost calculations. Given that we used unique systems of non-linear 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. Therefore, in comparison to the market price of \$0.39/kg solvent, solvent recovery can appear less favorable in the chosen condition. However, the multi-stakeholder 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 can negatively impact the overall environmental sustainability.

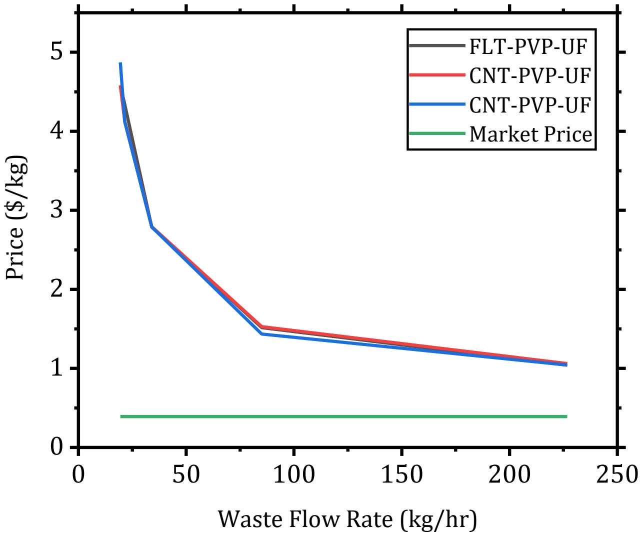


Figure 27. Sensitivity analysis of prices as a function of waste feed for Case Study 2 (DME Recovery)

Both case studies observed a similar trend between optimal solvent recovery and incineration for organic solvent recovery from a waste stream, where it is more economically viable to recover solvent than to incinerate. The pharmaceutical case study demonstrated a simple case in which one solvent recovery option, aqueous two-phase extraction, is more expensive than incineration. However, implementing solvent recovery can recover solvents for reuse in the process instead of the degradation option associated with incineration. Such a trade-off between economics and environmental impact should be considered, given that solvent recovery is a multi-stakeholder problem. In the recovery of the DME case study, we observed an instance when solvent recovery was more expensive than purchasing the fresh solvent. Depending on the values of the decisionmaker, 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 to 5%) of the overall waste stream mass, recovery will be costlier than disposal 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, and extraction cannot 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 recovery price. If the flow rate of the waste stream is too low, then the cost to recover the solvents can be larger. The design equations used for our mathematical models are based on industrial-scaled equipment. Therefore, 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 to the solvent waste being stored at a satellite accumulation area and later sent to a recovery process.

There is approximately ±30% uncertainty 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 typical process design. The result and uncertainty from one process unit would transfer to the next unit and continues until the desired product is obtained.

While commercial simulation software, such as Aspen, can provide detailed analyses of a specific flowsheet, it cannot compare multiple options at once simultaneously. Using GAMS, we can simultaneously evaluate multiple solvent separations and recovery technologies through its optimization capability. Users can write their own equations, introduce limits on crucial process variables, and integrate 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 can help narrow down the possible options and give a reasonable cost estimate for implementing solvent recovery. The uncertainty of the solutions resulting from this work can be reduced further during the detailed design phase.

5.4 Conclusions

The existing research in waste solvent disposal has a narrow focus on cost minimization or profit maximization without much consideration of the sustainability assessment. As global consumption and production continue to grow, waste and emission generation are inevitable. Methods to reduce solvent waste and emissions need to be evaluated further, considering the often-conflicting objectives of economic and environmental impacts. 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. As evidenced by the Specialty Chemical Waste Stream case study, selecting solvent recovery as the primary waste handling practice will not always yield economically favorable results. 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, the incineration process is a costly approach in solvent waste handling that can also release unwanted substances into the environment. Solvent recovery is preferable since 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 multi-stakeholder problem. Based on our environmental impact analysis, we observed that emissions are highly dependent on the flow rate of the waste stream processed, as depicted by the two case studies. We observed that solvent recovery is less preferred at lower flow rates than incineration in capital and operating costs. We do realize that achieving sustainability is not an isolated problem but a confluence of several factors. Hence our choice of two metrics that give different perspectives about the process can lead to further improvements. This framework benefits businesses, academia, policymakers, and institutions that generate waste solvents from their operations. Other constraints, such as social and political, can be integrated into this framework to solve the multi-stakeholder problems.

Chapter 6

Transforming Waste Management Paradigm to a Circular Economy

Texts and figures are reproduced and adapted with permission from Chea, J.D., Yenkie, K.M., Stanzione, III, J.F., Ruiz-Mercado, G.J., 2022. A Generic Scenario Analysis of End-of-Life Plastic Management: Chemical Additives. Journal of Hazardous Materials 129902. https://doi.org/10.1016/j.jhazmat.2022.129902.

This chapter shifts focus beyond the sustainable process design and examines the challenges in the waste handling sector. The possible movement of plastics was chosen for analysis to capture the effects of the considerable demand for plastics on the environment, health, and carbon and energy footprints. This chapter also examines the potential chemical additives released from plastics during use and post-consumer processes, contaminating their surroundings and creating unwanted hazards. A novel generic analysis of the current US EoL stage of plastic additives is described to track and estimate their potential migration, releases, and occupational exposure throughout the plastic EoL stage and activities (recycling, waste-to-energy, and landfilling). The potential hazards and risks identified in this research create an opportunity to design a safer closed-loop plastic recycling infrastructure to handle chemical additives strategically and support sustainable materials management efforts to transform the US plastic economy from linear to circular.

6.1 A Generic Scenario Analysis of End-of-Life Plastic Management: Chemical Additives

Plastics have proven their use as an essential material in applications ranging from packaging, storage, vehicles, and insulation because of their low cost, versatility, durability, and low weight [15]. However, the current plastic end-of-life (EoL) management pathways are not sustainable and are prone to releasing toxic chemical additives into the surrounding environment [209], [210]. Without a dramatic shift in the current state of plastics production, usage, and EoL, by the year 2050, the ocean is expected to contain more plastics than fish, while the plastics industry alone will consume 20% of the total oil produced and 15% of the annual carbon budget [451]. Moreover, the presence of plastics in the environment and consumer products may, over time, generate microplastics and nanoplastics that may end up in the digestive tracts of animals and humans [452]. Therefore, the increasing reliance on plastics, in conjunction with the chances of additive migration, requires modification of the existing EoL management pathways to reduce plastic and toxic chemical releases and achieve a circular economy.

Chemical additives release problems are originated from the plastic production stage. Plastics generally require the compounding of polymer resin with various chemicals to achieve the desired properties for a specific application or use [453]. The compounding of chemical additives into polymer resins is a physical process in which the additive molecules are not chemically transformed or bound to the polymer matrix. The chemical additives for plastic products include, but are not limited to, antioxidants, antistatic agents, blowing agents, colorants, coupling agents, curing agents, fillers, flame retardants, heat/ultraviolet stabilizers, impact modifiers, lubricants, plasticizers, preservatives, reinforcements, and slip agents. The intended application of plastics determines the combination and amount of chemical additives in the formulation. In most cases, chemical additives are solid powders, flakes, granulates, spheres, and emulsions. These materials can be incorporated into the polymer matrix at various production steps, including polymer production, pelletization, and surface modification [454]. The plastic resins can then be converted to finished products for consumer usage [455].

As shown in Figure 28, the plastic wastes found in municipal solid waste (MSW) are capable of releasing chemicals into the surrounding environment based on the following mechanisms: (1) diffusion through the polymer matrix to the surface, (2) desorption from the polymer surface, (3) sorption at the plastic-food interface, and (4) absorption into the surrounding medium (e.g., bulk food phase) [209]. The chemical diffusion through a polymer is governed by parameters such as pore size, temperature, and external medium (extractant). In some instances, residual monomers and solvents from the manufacturing stage may be present in the polymer matrix. These substances are likely to migrate and evaporate, creating a strong odor. Additives generally have higher molecular weights than solvents and monomers, ranging between 200 – 2000 g/mol [456]. High molecular weight substances are generally large molecules that are not expected to diffuse quickly through the polymer matrix. However, utilizing large additive molecules cannot entirely prevent diffusion because of factors relating to operating temperature and various stimulants serving as the driving force for mass transfer [209]. The molecular weight of the substance and the pore size of the plastics governs the rate of this diffusion. High molecular weight additives can diffuse more slowly than smaller molecules because it has to travel through the pores. Once the additives diffuse to the surface of the polymer, the solubility and compatibility between the two phases may further determine the dispersion of chemical additives throughout the solution. The surrounding medium can influence the migration of chemical additives because of the additive concentration difference between the phases. Chemical additives can slowly diffuse toward the surface of the polymer to reach an equilibrium with the surrounding medium. Generally, higher chemical additive migration is observed when plastics are in contact with high temperatures for a long duration and with non-polar substances such as fat and oil [209], [457]–[465].

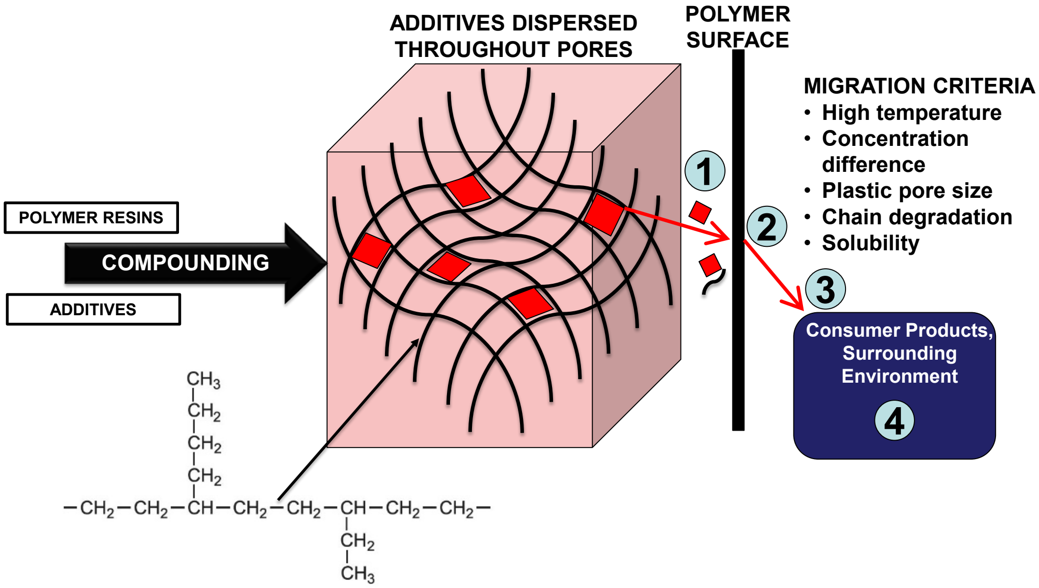


Figure 28. Additive release mechanism of plastics in a medium (food, water supply, landfill). The red object represents chemical additives residing inside the pore of the polymer matrix. The mechanism of additive releases includes (1) Diffusion, (2) Desorption, (3) Sorption, and (4) Absorption

EoL plastic management pathways, such as recycling, incineration, and landfilling, can aid the release of compounded additives into the environment because normal operation only considers the treatment of the plastics rather than the separation between chemical additives and plastics. Mechanical recycling is the most common recycling practice because of its low operational costs and high reliability [214]–[218]. The recycling process begins with the separation and sorting of the collected materials. Alternatively, incineration can be used with a large amount of energy to thermally decompose MSW (e.g., plastics), releasing energy, greenhouse gases, and other pollutants into the environment [219], [220]. MSW incineration may produce other byproducts, such as soot particles (e.g., PM2.5) and bottom ash residues that may act as carrier agents to transfer toxic chemicals to the environment. Although pollution control technologies reduce environmental impacts, incineration irreversibly converts plastics into other forms that are no longer usable from a closed-loop system standpoint [74], [221], [232]. Landfilling plastic EoL pathway has been debated as both an impediment to further improvement in recycling and a necessity for storing nonrecoverable materials. Also, plastics may persist within landfills for many years, creating an accumulation of solid waste and occupying land space [233].

Chemical additive migration during the EoL plastic stage presents a concern for workers in the EoL plastic pathways, ecosystems, and the public. Regardless of the EoL pathway, the adverse impacts warrant a closer analysis of chemical additive movement to identify areas for improvement. Thus, this work aims to (1) complete a material flow analysis of plastics and chemical additives, (2) develop a generic scenario analysis to estimate environmental releases and occupational exposure for risk assessment in day-to-day operation, and (3) analyze the environmental burden, and (4) perform sensitivity analysis under different scenarios to justify changes to the existing EoL plastic management infrastructure. These analyses estimate the possible additive migration, greenhouse gas emissions, and other releases within the plastic life cycle and provide foundational knowledge to assist risk assessment efforts as mandated under the Toxic Substances Control Act (TSCA) and amended by the Frank R. Lautenberg Chemical Safety for the 21st Century Act [466], [467]. Thus, stakeholders can evaluate potential risks and address any unreasonable risks chemicals may have on human health and the environment. Plastic management within the EoL pathways can also be optimized using the knowledge of chemical additive flow and potential chemical releases to design and alter the traditional linear production paradigm into a circular economy structure. In addition, identifying EoL pathways with high mass flow intensity can help prioritize the development of legislation and guidelines for improving existing and future EoL stages.

6.2 Materials and Methods

Creating a generic scenario for plastic management in the EoL stage requires a starting point for analysis. The United States MSW data published in 2018 was chosen to characterize material waste flow [211]. Our analysis considers plastic movement and major types of discarded material collected. The mass flow intensity was then determined based on the magnitude of material movement. The chemical additive values reported in this work contain uncertainties because of the variation in product types. Plastic products require different amounts of chemical additives based on their intended application or condition of use.

The possible release and additive migration routes identified in this work are generally specific to collection, sorting, mechanical recycling, incineration, and landfilling stages. In each major EoL pathway, general information, such as the number of companies, facilities, and employees, was defined. However, there are inherent differences between the EoL pathways, which require separate analyses. Issues relating to plastics, chemical additive contamination, and material degradation ultimately affect the quality of the recycled products and create unwanted exposure to workers in the facility [230].

The environmental impact and sustainability of the current EoL plastics management were measured using the Sustainable Process Index (SPI). An SPI calculation for a given process provides a land area required to close the material loop and dissipate all emissions and wastes sustainably. The total calculated area comprises the area required to produce the raw material, provide energy, install the process, hire the required staff for the process, and accommodate products and byproducts [468]. SPIonWeb, a web tool, was used to calculate the arable areas required for a given process [469]. The user defines the material inputs required to manufacture a particular product. This tool considers the history of the materials, releases, and impacts information in a database, then sums the contribution from all material inputs. The possible impact on the air, water, and soil can be estimated as an arable area. A low arable area correlates to a more sustainable process.

The numerical estimation associated with this work was completed with published data from the US EPA and key research articles [209], [225], [455], [470]–[474]. Our chemical additive tracking analysis occurs during the EoL pathways, from plastic waste collection to mechanical recycling, incineration, and landfilling. Also, all datasets and spreadsheets used to generate our results are available at https://github.com/USEPA/GS_End-of-Life_Plastic_Additives [209], [472], [475]–[482].

6.3 Results and Discussions

This section presents a material flow analysis of plastics and additives with an emphasis on the EoL stage to assess the state of plastic management efforts within the United States. We then examined each major EoL stage in greater detail through the generic scenario analysis. This analysis estimated the releases of chemical additives and occupational exposure in day-to-day EoL plastic management operations within the United States. An environmental impact assessment was performed to estimate the theoretical burden that the existing EoL practice has on the environment and natural resources. Following the discussions on the state of EoL practices and hazardous releases in the United States, we performed sensitivity analyses under different scenarios to determine the effects of (1) altering the plastic recycling rate, (2) using chemical recycling, and (3) including additive extraction post-mechanical recycling to the existing EoL plastic management infrastructure.

6.3.1 Material Flow Analysis of Plastic Life Cycle

EoL plastic management was assessed using the MSW data in the United States in 2018. The composition of MSW in 2018 is shown in Figure 2a, and the EoL plastic composition is shown in Figure 2b. Papers, metals, glasses, and plastics are the primary components considered for recycling. The US EPA has estimated that over 35.7 million tons (32.4 billion kg) of plastic waste were generated in the United States in 2018. The municipal plastic waste is composed of 14.8% polyethylene terephthalate (PET), 17.7% high-density polyethylene (HDPE), 2.4% polyvinyl chloride (PVC), 24.1% low-density polyethylene (LDPE), 0.3% polylactic acid (PLA), 22.8% polypropylene (PP), 6.3%

polystyrene (PS), and 11.7% other plastics. The EoL plastic categories coincide with polymer resin identification codes 1 through 7, with the addition of polylactic acid (PLA). Most of the recycling efforts have been allocated toward recovering PET, HDPE, LDPE, and a select group of uncategorized plastics. Up to 3 million tons (2.7 billion kg) (~8.4%) of the waste plastics were successfully recycled, 75.8% were landfilled, and 15.8% were incinerated [211]. Recycled plastics are generally reprocessed into pellets to be used as raw materials for new plastics. Similar EoL pathways were reported by the United Nations, in which 9% of the global plastics were recycled, 79% were landfilled, and 12% were incinerated [225]. This concerning fact suggests improving the existing plastics processing infrastructure to minimize excess environmental accumulation and toxic exposure. This information was used as the MSW stream composition for the material flow analysis.

Consumer plastics are commonly produced from a blend of polymer resins and chemical additives to achieve the desired characteristic for a particular application. The chemical additives may include but are not limited to plasticizers (10–70 wt.%), flame retardants (3–25 wt.%), antioxidants (0.05–3 wt.%), UV stabilizers (0.05–3 wt.%), heat stabilizers (0.05–3 wt.%), slip agents (0.1–3 wt.%), lubricants (0.1–3 wt.%), antistatics (0.1–1 wt.%), curing agents (0.1–2 wt.%), blowing agents (0.5–20.5 wt.%), biocides (0.001–1 wt.%), colorants (0.25–5 wt.%), pigments (0.001–10 wt.%), fillers (0–50 wt.%), and reinforcements (15–30 wt.%) [209], [210], [483], [484]. These composition ranges were included as part of the generic post-consumer plastic stream. An abbreviated list of chemical additives can be found through a Github link in Appendix D.7. A more comprehensive additive list is available from Wiesinger *et al.* (2021), which identified over 2,400 substances of concern used in plastics [485].

The 2018 MSW plastic waste stream was subjected to a material flow analysis under the existing EoL infrastructure to assess the possible chemical additive migration, greenhouse gas emissions, leaching, degradation, and release of substances into the surrounding environment. Our analysis scope is limited to collection, sorting, and EoL pathways (mechanical recycling, incineration, and landfilling). Figure 29 presents a high-level screening estimation of the chemical release within the Production, Use, and EoL stages of plastics using 2018 MSW data as the basis for calculation. The calculations done in this analysis were completed using assumptions tabulated in Table D.1., supported by published research [209], [233], [486]–[491]. Table D.4. provides the calculation results from the material flow analysis.

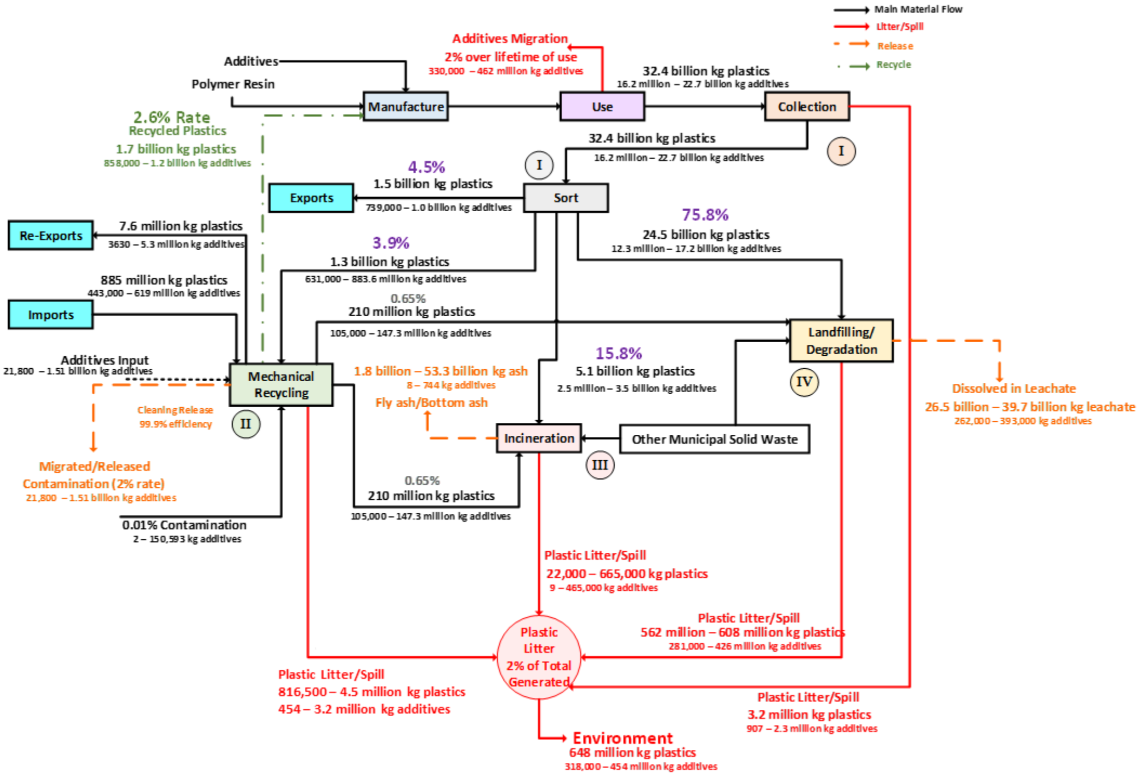


Figure 29. Material flow analysis of the plastic and additive mass flow using the 2018 municipal solid waste data as a basis. The black arrow indicates the main material movement, the red arrow indicates release as litter and spillage, the orange dashed line indicates migration and contamination, and the green arrow indicates recycling.

Plastic products are typically manufactured to possess high stability for long-term use, regardless of the actual application. Single-use plastics, for instance, persisted in the environment for several decades despite being made for one use. Following plastic disposal, the plastics are collected with other recyclable products like metals, glass, and paper. These recyclable materials are sent to a sorting facility. The US EPA waste characterization study determined the allocation of plastic recycled, incinerated, and landfilled plastic [211]. The plastic flow from the manufacturing stage through the EoL stage is not considered steady because plastic products can be reused and accumulate at various stages. However, tracking generic plastics throughout their life cycle requires a steady-state assumption. In addition, time is not factored into the calculation because this analysis aims to identify areas of concern during the plastic life cycle. Thus, the calculated values reported material inflow and outflow irrespective of the actual process duration.

A circular economy is not observed, given that only ~8.4% of plastic waste has been recycled. However, the reported recycling percentage combines international plastic export intended for recycling (4.5%) and domestic recycling (3.9%) [476], [489], [492]. The values associated with EoL plastic export and domestic recycling do not reflect the actual mass that was successfully recycled. Instead, the reported recycling values are mass sent from the sorting facilities to domestic and overseas recycling facilities. State-of-the-art recycling techniques are not expected to achieve a 100% recovery rate. Law *et al.* (2020) also reported that 25 – 75% of US EoL plastic exports are mismanaged in the receiving country [489]. The plastic wastes exported indirectly lead to additional additive releases into the environment because some receiving countries are not equipped to process the wastes and scraps.

Table 16

Life Cycle Inventory of Plastics and Additives at Various Stages of the Plastic Life-Cycle

End-of-Life Plastic Waste Management LCI

Materials	Input (kg/total kg input)	Output (kg/total kg input)	Releases to Land (kg/total kg input)	Releases to Air (kg/total kg input)	Releases to Water (kg/total kg input)	Greenhouse Gas Emissions (kg CO2-eq/kg input)
Collection and Sorting						
PET	1.5E-01	1.4E-01	1.3E-02	Negligible	3.8E-04	4.1E-01
HDPE	1.7E-01	1.7E-01	8.0E-03	Negligible	2.3E-04	4.1E-01
PVC	2.3E-02	2.3E-02	0.0E+00	Negligible	0.0E+00	4.1E-01
LDPE	2.3E-01	2.3E-01	5.0E-03	Negligible	1.5E-04	4.1E-01
PLA	2.0E-03	2.0E-03	0.0E+00	Negligible	0.0E+00	4.1E-01
PP	2.2E-01	2.1E-01	0.0E+00	Negligible	1.0E-05	4.1E-01
PS	6.0E-02	6.0E-02	0.0E+00	Negligible	1.0E-05	4.1E-01
Other (Mixed)	9.0E-02	7.9E-02	1.1E-02	Negligible	3.4E-04	4.1E-01
Additives	5.6E-02	5.2E-02	4.0E-03	Negligible	1.2E-04	4.1E-01
Mechanical Recycling						
PET	1.8E-01	1.9E-01	1.8E-05	4.7E-08	5.3E-07	-1.2E+00
HDPE	1.2E-01	1.2E-01	1.2E-05	3.0E-08	3.4E-07	-9.7E-01
PVC	1.3E-02	1.4E-02	1.3E-06	3.0E-09	4.0E-08	Negligible
LDPE	8.4E-02	8.7E-02	8.2E-06	2.1E-08	2.4E-07	Negligible
PLA	Negligible	Negligible	Negligible	Negligible	Negligible	Negligible
PP	9.0E-03	9.0E-03	8.7E-07	2.0E-09	3.0E-08	Negligible
PS	1.1E-02	1.2E-02	1.1E-06	3.0E-09	3.0E-08	Negligible
Other (Mixed)	3.7E-01	3.8E-01	3.6E-05	9.4E-08	1.1E-06	-1.1E+00
Additives	2.1E-01	1.8E-01	2.1E-05	5.4E-08	6.1E-07	-5.4E-01
Incineration						
PET	1.4E-01	Negligible	1.4E-05	0.0E+00	4.0E-07	1.4E+00
HDPE	1.7E-01	Negligible	1.7E-05	0.0E+00	5.0E-07	1.4E+00
PVC	2.2E-02	Negligible	2.1E-06	0.0E+00	6.3E-08	7.4E-01
LDPE	2.4E-01	Negligible	2.3E-05	0.0E+00	7.0E-07	1.4E+00
PLA	2.0E-03	Negligible	2.0E-07	0.0E+00	6.0E-09	1.4E+00
PP	2.4E-01	Negligible	2.3E-05	0.0E+00	6.8E-07	1.4E+00
PS	6.5E-02	Negligible	6.3E-06	0.0E+00	1.9E-07	1.8E+00
Other (Mixed)	7.5E-02	Negligible	7.2E-06	0.0E+00	2.2E-07	2.6E+00
Additives	5.1E-02	Negligible	5.0E-06	1.5E-12	1.5E-07	1.1E+00
Landfilling						
PET	1.3E-01	Negligible	1.9E-02	Negligible	5.6E-04	4.4E-02
HDPE	1.7E-01	Negligible	2.2E-02	Negligible	6.5E-04	4.4E-02
PVC	2.3E-02	Negligible	2.7E-03	Negligible	7.9E-05	4.4E-02
LDPE	2.4E-01	Negligible	3.0E-02	Negligible	8.9E-04	4.4E-02
PLA	2.0E-03	Negligible	2.4E-04	Negligible	7.1E-06	4.4E-02
PP	2.4E-01	Negligible	2.8E-02	Negligible	8.5E-04	4.4E-02
PS	6.7E-02	Negligible	7.9E-03	Negligible	2.4E-04	4.4E-02
Other (Mixed)	6.9E-02	Negligible	1.1E-02	Negligible	3.2E-04	4.4E-02
Additives	4.9E-02	Negligible	6.9E-03	Negligible	2.1E-04	4.4E-02

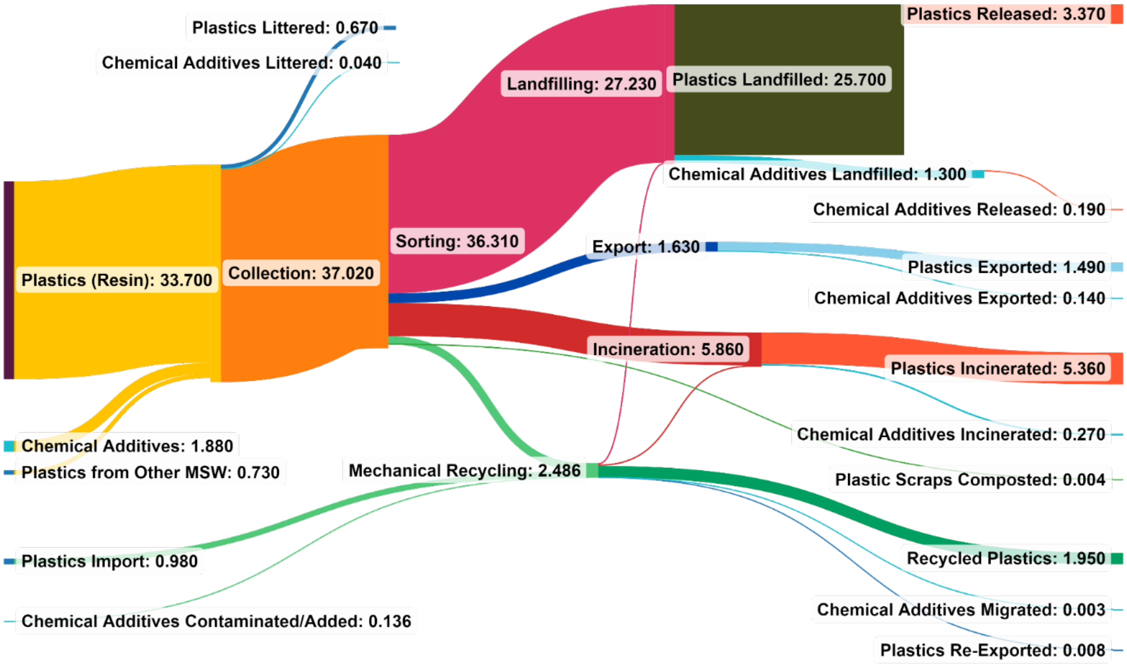


Figure 30. Sankey diagram to illustrate the mass flow intensity of the 2018 EoL plastic waste management in the US. All numbers should be multiplied by 10^6 tons (US)

Overall, the material flow analysis describes a high-level overview of plastic and additive mass movement throughout the plastic life cycle using the 2018 MSW data reported by the US EPA. The case-specific values of calculated releases shown in Figure 29 were transformed into a life cycle inventory, as summarized in Table 16, for estimating plastic and additive releases for any given mass flow basis [209], [211], [477], [493]–[495]. Although the release values are relatively small for a given mass unit input, processing billions of kg of plastic waste can raise the releases to an alarming level. Incineration and landfilling provide negligible mass output because these operations are designed to degrade thermally and contain solid waste, respectively. However, they do not solve the issue regarding resource circularity because the wastes are no longer recoverable.

On the other hand, mechanical recycling does provide a positive mass output toward the manufacturing stage if we combine the treatment of plastic waste import and plastics sent for recycling from the sorting stage. Figure 30 summarizes the relative mass flow intensity of plastics and additives by considering the standard MSW management practices, efficiency issues, and plastic waste imports and exports. As expected, we observed a heavy shift toward landfilling and incineration instead of mechanical recycling. More importantly, every EoL process that contains plastics has the potential to release chemical additives over time in less controlled environments (land, air, water, general contamination). In addition, the theoretical additive release routes can expand further to specific cases that include but are not limited to drinking water quality, hazardous substances in aquatic life, and recycling of other plastics. Thus far, the results are nationwide estimations based on the US 2018 MSW management. The uncertainty is further reduced in Sections 6.3.2 – 6.3.5, the generic scenario analysis of plastic waste and chemical additives. This analysis contains the numerical estimations of facility-level releases, contamination, and exposures under normal EoL operation.

6.3.2 Generic Scenario of Plastic Collection and Sorting (I)

The current collection methods employed to gather post-consumer plastics are not expected to alter the quality of the substance considerably due to the short residence time between disposal collection and sorting [496]. Therefore, chemical additive transfer between materials can be neglected at the collection stage. However, plastic littering into the environment is a likely occurrence during material transfer and transport. For instance, a collection truck utilizing automation to lift and dump the content of the curbside blue recycling bin will not always successfully collect every material. In addition, low-density materials may be swept out of the falling trajectory into the surrounding environment by wind or incorrect bin positioning before the collection process. Given the lack of spillage data during curbside collection, the US EPA recommends a spillage release rate of 0.01% [455]. Equation (13) estimates approximately 3,570 tons (3.2 million kg) of plastics/yr. $(R_{total,collection,spill})$can be spilled as litter during the collection stage. $M_{plastic,collection}$ represents the mass rate of post-consumer plastics collected yearly and $L_{collection,spill}$ is the loss fraction during collection due to spillage. The spilled plastics remain in the environment until they are manually removed. In some cases, the wind may sweep the plastics to a nearby wood, pond, or river, where the materials would reside for many decades and centuries. The chemical additives within the littered plastics are prone to migration to the environment over time due to partial degradation from UV and interactions with the surrounding medium [497]. Wildlife may confuse the materials with food and consume the plastics unknowingly. Research has suggested that the digestive fluid within animals may act as an organic solvent to promote the leaching of chemical additives from plastics because traces of chemical additives accumulating within the tissues of the affected animals have been detected [498].

The US EPA has approximated that the fraction of chemical additives is 0.0005 – 0.70 kg/kg of plastic and 0.55 kg/kg of plastic on average [455]. The expected range of chemical additive release during the entire lifetime of spilled plastics may thus range between 0.0005 – 0.70 kg/kg spilled. However, this estimation is time-dependent, which means the mass basis of 3,570 tons (3.2 million kg) of plastics spilled per year can release between 1 – 2,500 tons (907 – 2.3 million kg) of chemical additives to different sources during the plastic lifetime.

$$R_{total,collection,spill}=M_{plastic,collection} \cdot L_{collection,spill} \tag{13}$$

It should be noted that the litter generated during waste collection is a minor contribution to the current total litter fraction. Jambeck *et al.* (2015) have estimated that approximately 2% of all plastic waste generated globally becomes litter [477]. Thus, the 35.7 million tons (32.4 billion kg) of plastics collected in 2018 may release up to 714,000 tons (648 million kg) of plastic, i.e., 350 – 500,000 tons (318,000 - 454 million kg) of associated chemical additives, across the entire plastic life cycle. Sorting methods may introduce chemical hazards to workers because manual sorting is required in some steps. Impurities and material types may unintentionally be mixed in a specific pile, complicating downstream recycling processes. For example, in PET recycling, PVC has been a known contaminant capable of generating acids to degrade PET resin and subsequently degrade the mechanical and chemical properties of the polymer [499]. A concentration as low as 50 ppm PVC can cause considerable damage to the PET resins [499], [500]. Therefore, errors made during plastic sorting may lead to unintended complications during the reprocessing stage.

6.3.3 Generic Scenario of Plastic Mechanical Recycling (II)

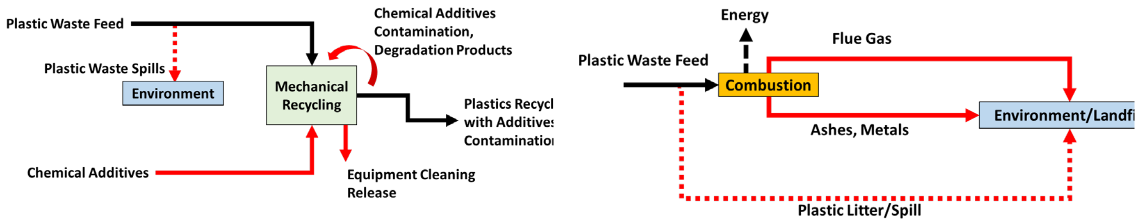
This generic scenario analysis identified the major release points and potential release quantities during mechanical recycling. A high-level description of the mechanical recycling material release route is shown in Figure 31a. Sorted plastics are typically sent to separate recycling facilities to process the specific material type. A typical practice of thermoplastic recovery includes particle size reduction, washing, rinsing, drying, and extrusion. Plastic wash has been reported to consume 2 – 3 m^3 of water per ton of material [501]. However, impurities from the consumer use stage and disposal can remain on the surface or within the plastic container even after a wash. Additionally, chemical additives are present in the plastic from the manufacturing stage. More additives can also be introduced into the recycling steps to ensure that the materials can be processed easily. The simplified illustrations, shown in Figure 31, highlight the environmental release points, a crucial step for performing occupational risk assessment, rather than demonstrating the technical detail of the process.

The generic scenario for mechanical recycling estimates the following:

- The number of mechanical recycling facilities in the US
- Releases to air, water, incineration, or landfill from material transport
- Releases during the extrusion process, including changing or cleaning of emission control filter (from dust and fugitive air emissions), equipment cleaning, and cooling water
- Number of workers that may come in contact with the chemical of interest during operation

- Inhalation and dermal exposures from material handling
- Release of chemical additives and volatile organic compounds to workers and nearby environment
- Chemical contamination incorporated into the reformed plastics after melt extrusion

(a) Mechanical Recycling (b) Incineration



(c) Landfilling

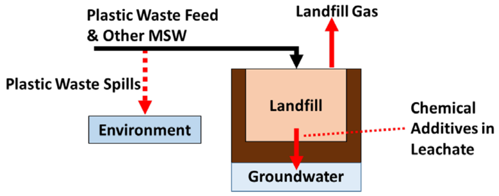


Figure 31. The major chemical additive release routes during (a) Mechanical recycling, (b) Incineration, and (c) Landfilling. Solid lines are releases generated as a result of the process. The dotted line indicates releases prior to the process.

6.3.3.1 General Facility Estimates. Material recycling facilities can be represented by NAICS Code 562920 [502]. There are 373 verified active companies in the United States with approximately 21,834 workers [502]. Each recycling facility across the

US typically processes between 100 to 500 tons (90,719 – 453,600 kg) of plastics per day [503]. The US EPA suggested a default estimate of an 8-hr workday and up to 250 days of operation per year for exposure estimation in the plastic converting industry [474]. Material recycling utilizes similar processes as plastic compounding and converting industries. Therefore, the operation hours during mechanical recycling are assumed to be the same as the plastic compounding and conversion. The mass of plastics may contain between 0.05 to 70% of chemical additives and impurities from the previous use [209]. The general estimates presented thus far were used to analyze occupational exposure, releases, and contamination of unwanted substances during mechanical recycling.

6.3.3.2 Chemical Additive Use in Mechanical Recycling. Chemical additives, e.g., plasticizers, stabilizers, chain extenders, compatibilizers, and fillers, may be added throughout the mechanical recycling process to increase polymer processability. The amount added may range between 0.05 – 70% by weight [230], [474]. For instance, PET and HDPE have been blended with 5 – 15% compatibilizer before extrusion blow molding [504]. A compatibilizer allows for the successful blending of two immiscible phases. Thus, the combined properties of the two polymers can overcome challenges related to recycling individual polymers if the waste materials would otherwise be discarded or considered acceptable for use in low-value applications [505]. During mechanical processing, such as extrusion, chemical bonds may break in the main polymer chain, causing free radical formation [230], [504]. This issue is generally mitigated using thermal, light, and antioxidant stabilizers. Such addition is necessary because the polymers produced are stabilized with considerations for the use phase. However, these polymers can be exposed to oxygenated species, high temperatures, and UV light during the mechanical recycling phase, requiring more additive stabilizers [230]. Stabilizers do not necessarily eliminate degradation and radical attack with 100% efficiency. Chain extenders have been reported as an inexpensive option to reverse the damage caused by degradation. Oligomers formed from polymer chain degradation would react with the chain extenders through its reactive site and effectively experience regrowth in the chain length. Fillers are an alternative to mitigate damages caused by chain degradation by increasing Young's modulus, elongation at break, and impact strength while decreasing processability. Starch, cellulose, chitin, glass fibers, wood, and lignin are generally used for fillers [230]. PVC recycling presents a challenge as the polymer becomes brittle in the EoL stage. Therefore, additional plasticizers are needed to increase the ductility during reprocessing. However, the most used plasticizers, phthalates, present a health safety hazard because they are susceptible to migration from within the polymer matrix to the surface over time. The differences in properties and structure between recycled and virgin plastics are governed by degradations that occur during conventional recycling processes. Additionally, while chemical additives are generally non-volatile solids and liquids, these substances may migrate to the polymer surface, contaminate equipment surfaces, and cause unintentional exposure.

6.3.3.3 Releases and Contamination in Mechanical Recycling of Plastics. Plastics transferred during the recycling process are susceptible to spillage, which can be treated as mass loss to the environment. Plastic material processing may generate dust caused by abrasion of the plastics in granulated, cut, and pelletized forms [506]. The dust released from plastic processing is an inhalation hazard for workers without proper personal protective equipment (PPE). It serves as another source of plastic released into the environment without recovery. The US EPA recommends a conservative estimate for spillage and dust release as approximately 0.01% [474]. Through Equation (14), the possible release to water and land due to material spillage $\left(R_{\mathrm{mech,spill}}\right)$ is approximately 9 – 45.4 kg/(day·site). $M_{\mathrm{plastic,mech}}$ represents the plastics processed daily and $L_{\mathrm{mech,spill}}$ is the loss fraction due to spillage. Suppose a similar mass loss rate applies to all verified recycling facilities within the US. In that case, the conservative plastic release from mechanical recycling facilities due to spillage is 900 – 5000 tons/yr (816,500 – 4.5 million kg/yr). The released plastics can be similar to landfilled plastics because they are not recovered.

$$R_{\mathrm{mech,spill}}=\frac{M_{\mathrm{plastic,mech}}}{N_{\mathrm{site,mech}}}\cdot L_{\mathrm{mech,spillage}} \tag{14}$$

The chemical additives used to improve recycled plastics processability have unintended consequences on human health and the environment. He *et al.* (2015) assessed volatile organic compounds (VOCs) from various plastic recycling workshops and identified the concentration of alkanes, alkenes, monoaromatics, oxygenated VOCs, chlorinated VOCs, and acrylonitrile emitted to the surrounding air during extrusion [507].

The total concentration of the emitted chemicals varies drastically between recycling facilities because of the difference in chemical composition and stability at the extrusion temperature (100 – 300°C). The total indoor VOC concentration was estimated at various recycling facilities with a mean concentration of 3.9 mg/m^3 for polystyrene, 2.1 mg/m^3 for polyamide, 1.9 mg/m^3 for polyvinyl chloride, 1.1 mg/m^3 for polyethylene, and 0.60 mg/m^3 for polycarbonates to the surrounding air. Monoaromatic compounds contributed 47.7 to 91.6% of the total VOC content across all recycling facilities. These hazardous compounds emitted from the extrusion processes may pose cancer risks to the lung, blood, brain, liver, kidney, and biliary tract. Non-cancer risks may include sensory, liver, kidney, and central nervous system damage. Exposure to chemical vapors such as benzene, toluene, ethylbenzene, styrene, methylene chloride, acrylonitrile, and trichloroethylene poses substantial cancer and non-cancer chemical risks [507]. The recycling facility data analyzed in this study is based on poor ventilation and can be considered a worst-case scenario.

The chemical additives are susceptible to migration from the polymer matrix to the surface as non-volatile substances because these chemicals were mixed with the polymer during manufacturing rather than through a chemical reaction. Therefore, the connections between the chemical additives and the polymer matrix can be broken with a sufficient driving force. Tang *et al.* (2014) assessed the concentration of polybrominated diphenyl ethers (PBDEs), a flame retardant released into soils, sediments, and human hair [508]. PBDE concentration around plastic mechanical recycling facilities was detected at 1.25 – 5504 ng/g (600 ng/g average) in soils, 18.2 – 9889 ng/g (1619 ng/g average) in sediments, and 1.50 – 861 ng/g (112 ng/g average) in human hair. PBDEs present a major environmental and health concern because these chemicals can persist in the environment and bioaccumulate upon exposure [508].

While polymer reprocessing is generally done in separate facilities to avoid plastic cross-contamination, this practice does not account for the unintentional transfer of chemicals to recycled plastics. Migrated chemical additives and degradation products formed during melt extrusion may adhere to the processing equipment [509]. Purging compounds are used to clean residual materials from the previous cycle. In addition, the equipment may be manually cleaned through brushing and scraping. The residual materials at the end of the equipment cleaning process present a possible source of chemical release to incineration or landfill. Equation (15) describes the chemical release estimation during the equipment cleaning. $m_{additive,mech}$ is the mass of chemicals added to improve plastic processability during recycling and $L_{mech,cleaning}$ is the fraction of chemical loss from processed plastics. The US EPA recommends a 2% conservative estimate for chemical release rates during processing [455]. For estimation purposes, the US EPA defaults the chemical additive fraction in plastic products ranges between 0.0005 – 0.70 kg chemical additive/kg plastic [455]. Based on the typical plastic material flow of 90,719 – 453,600 kg/(day·site), approximately 45.4 – 317,500 kg of chemical additives/(day·site) has been released from recycling equipment cleaning. Therefore, $m_{additive,mech}$ exists to compensate for the mechanical property loss resulting from reprocessing, and its value is assumed as 45.4 – 317,500 kg chemical additive/(day·site) added during the recycling process. The release was due to equipment cleaning ($R_{mech,cleaning}$) is, therefore, 816.5 – 5.8 million kg/(day·site).

$$R_{mech,cleaning}=m_{additive,mech}\cdot L_{mech,cleaning} \tag{15}$$

The equipment cleaning operation is not expected to have 100% efficiency in removing the released chemical additives. Traces of contamination between batches have been reported from an analysis of recycled HDPE and LDPE [478]. These plastics contain approximately 30-100 µg contaminants/g plastic, 330-700 µg chemical additive degradation product/g plastic, and 30-800 µg chemical additives/g plastic [478]. These substances may accumulate through every iteration of plastic recycling and cause unwanted exposure and release during the plastic use stage. Based on the level of unintentional substances found in recycled HPDE and LDPE plastics, we approximated the cleaning operation may possess an efficiency of up to 99.9% [510].

6.3.3.4 Occupational Exposure in Mechanical Recycling. Workers in the EoL material management sector have experienced a higher illness rate relating to the respiratory system, including bronchitis and decreased lung function [511]. Handling plastics may generate airborne substances containing a mixture of dust, plastics, and volatile organic compounds released from material degradation. Our general facility estimate has shown that there are currently 373 verified active companies in the United States with approximately 21,834 employees [502]. An average of 58.5 workers per recycling facility can thus be assumed for calculation. This information does not account for the division of labor among the total workers in a given recycling facility. Not all workers can be exposed to the same level of inhalation hazard due to the variation in job function. However, workers at a recycling facility remain at a higher risk than the common public and should be included in a conservative estimate.

Inhalation exposure $(EXP_{inhalation,mech})$ can be represented by Equation (16), where $C_{particulate,mech}$ is the concentration of the particles of concern (15 mg/m^3 for unregulated particulates based on TWA PEL)[512], [513], $r_{breathing}$ is the rate of breathing (1.25 m^3/hr)[514], $t_{exposure}$ is the duration of exposure (8 hrs/day), and $F_{additive,plastic}$ is the fraction of additives in plastic (0.0005 – 0.70 kg/kg plastic and 0.55 kg additives/kg plastic average) [455]. The inhalation exposure rate $(EXP_{inhalation,mech})$ for workers handling mechanical recycling can range between 0.075 – 105 mg particles/day. This estimation assumes insufficient PPE use; thus, the reported value is likely higher than the actual daily exposure. We assumed a low PPE usage to provide a conservative estimate for designing a ventilation system for reducing the concentration of solid particles in the air.

$$EXP_{inhalation,mech}=C_{particulate,mech} \cdot r_{breathing} \cdot t_{exposure} \cdot F_{additive,plastic} \tag{16}$$

Direct contact of chemical additives with the skin during mechanical recycling is plausible because additives are typically added to ensure the materials can be processed efficiently. Given that chemical additives are generally solids, the potential dermal exposure was estimated using the EPA/OPPT Direct 2-Hand Dermal Contact with Solids Model [455]. In Equation (17), $EXP_{dermal,mech}$ represents the potential dermal exposure to chemical additives per day, $a_{incd,additive}$ is the mass of chemical additives in contact for a given incident (up to 3,100 mg chemical additive/incident), $N_{exp,incd,incn}$ is the number of exposure incidents per day (1 incident/day), and $F_{additive,plastic}$ is the fraction of chemical additives in plastic (0.0005 – 0.70 kg/kg plastic and 0.55 kg chemical/kg plastic average).

The dermal exposure rate for workers handling mechanical recycling can range between 1.6 – 2,170 mg particles/day.

$$EXP_{dermal,mech}=a_{incd,additive} \cdot N_{exp,incd,mech} \cdot F_{additive,plastic} \qquad (17)$$

6.3.4 Generic Scenario of Plastic Incineration (III)

Incineration is generally used to reduce the volume of waste materials while simultaneously recovering energy [515], [516]. Plastic waste incineration involves the destruction of MSW through combustion and may reduce the methane gas generation from landfills [471]. However, this process may negatively impact the environment if the pollutants from combustion are not controlled [487]. For example, open burning of plastics may release vaporized dioxins, furans, mercury, and polychlorinated biphenyls into the atmosphere, creating persistent and unintentional hazards to human and animal health and the environment [232], [487], [501], [517].

The plastic incineration process begins with collected plastics unloading from the collection truck and storing them in a bunker [471]. The plastics are then sent to combustion using a choice between a fluidized bed, grate technology, and rotary kiln [471]. A fluidized bed combustor contains an emission control system, a small boiler size, and generates no ash content. One possible configuration of a fluidized bed combustor includes using the operating temperature conditions at 450 - 550°C, 64 bars, and 0.4 – 1.0 m/s of air or superheated steam. The polymer becomes volatile, leaving fibers, fillers, metals, and other non-volatile elements in the fluidized bed. A secondary combustion chamber is used at a higher temperature to ensure the complete oxidation of the plastics [515]. Grate incineration is a one-stage combustion process operating at a temperature greater than 850°C in the presence of oxygen. Bottom ash can be generated with this method [213]. Rotary kiln combustion operates between 900 – 1200°C to incinerate waste, forming CO_2 and H_2O. A rotary kiln is advantageous over other incinerators because solid, liquid, and gas can be processed. The heat from the exhaust gas generated by the combustion of plastics gets transferred through a steam turbine to produce energy. Ash generated at the end of incineration is collected and transported to an enclosed building by leak-proof trucks for landfilling [471]. The thermal destruction route of plastics is expected to release many substances that are not necessarily similar to the initial chemicals. Figure 31b illustrates the major additive release routes described during incineration.

The generic scenario for plastic incineration aims to estimate the following:

- The number of MSW combustion facilities in the U.S (NAICS 562213)[518]
- Releases to air, water, or landfill from material transport
- Releases during the incineration process, including changing or cleaning of emission control filter (from dust and fugitive air emissions), equipment cleaning, and cooling water
- Number of workers that may encounter the chemicals of concern during normal operation
- Inhalation and dermal exposures from gases generated during operation

  Release of chemical additives and volatile organic compounds to workers and nearby environment

6.3.4.1 General Facility Estimates. Waste incineration facilities can be represented by NAICS Code 562213 [518]. In 2018, 61 verified active companies in the United States and approximately 2,246 employees [515]. A waste incineration unit may process between 50 – 1000 tons/day (45,360 – 907,185 kg/day) of materials. A typical incineration facility may include between two to three incinerators, leading to an approximate process flow rate between 100 – 3000 tons/day (90,719 – 2.7 million kg/day) for a given facility [212], [503], [519]. Based on the MSW data in 2018, approximately 12 – 360 tons of plastics/day (10,900 – 327,000 kg) are incinerated per facility. These facilities can operate continuously for up to 8000 hrs. (334 days) within a year.

6.3.4.2 Releases from Incineration. Like the previous cases, such as mechanical recycling, materials transported to incineration facilities are susceptible to spillage and thus can be treated as mass loss to the environment. The US EPA recommends a conservative estimate for spillage release of approximately 0.01% [474]. Through Equation (18), the possible release to water and land due to waste spillage $\left(R_{\text{incn,spill}}\right)$ is approximately 1 – 33 kg plastics/(day·site). $M_{\text{plastic,incn}}$ represents the total plastics processed by incineration in 2018. Incineration facilities are expected to handle a combination of different substances and plastics. Given that plastics account for approximately 12% of MSW, $R_{\text{incn,spill}}$ only reflects the MSW plastic fraction. $F_{\text{incn,spillage}}$ is the loss fraction due to spillage. If a similar mass loss rate applies for all incineration facilities within the US, the conservative yearly release from incineration facilities due to spillage is 24 – 733 tons (21,800 – 665,000 kg) of plastics/yr. The released plastics can be regarded similarly to landfilled plastics because they are not recovered.

$$R_{incn,spill} = \frac{M_{plastic,incn}}{N_{site,incn}} \cdot L_{incn,spill} \tag{18}$$

The incineration process releases carbon dioxide and water vapor while producing byproducts such as nitrogen oxide, dioxins, furans, metals, acid gases, volatile chlorinated organic compounds, polycyclic aromatic compounds, and incombustible ashes. This process generally reduces the waste to 10 – 15% of the original volume and 20 – 35% of the initial mass as ash [520]. Emission control technologies such as electrostatic precipitators, fabric filters, wet scrubbers, and spray-dry absorbers can remove and control airborne particles, hydrochloric acid, sulfur dioxide, dioxins, and heavy metals. Under the normal operating condition, the amount of pollutants released can be expected to be minimal because all emission control technologies are present to mitigate the hazards. However, a spike in pollutant release to the atmosphere may deviate beyond normal during incinerator startup and shutdown after a change in waste composition, equipment malfunctioning, operator error, and poor incinerator maintenance [231]. Therefore, the incineration release estimates from this study utilize data during steady-state operations. Additional accuracy can be obtained with more emission data throughout the waste incineration process.

One ton (907 kg) of MSW incineration may generate up to 0.033 tons (30 kg) of air pollution control (APC) residues, 0.33 tons (300 kg) of bottom ash, and flue gas at a flow rate of 4500 – 6000 Nm^3. Air pollution control (APC) residues are hazardous solid waste with high pH, volatile heavy metals, soluble salts, dioxins, and furans [221]. In the absence of control devices, incineration may release flue gas up to 1 – 3% of the total ash content, containing inorganic ash, soot, and organic compounds deposited on fine particles [231], [520]. The general composition of the pollutants and the permissible release concentration are shown in Table D.2. The pollutants exit a typical incineration furnace at high concentrations. Thus, a gas cleaning system is generally implemented under normal conditions to remove fly ash, acids, dioxins, and furans before the gas exits the flue-gas stack [221]. The desired concentration can be achieved using a combination of wet scrubbers, dry multi-cyclone, semi-dry scrubbers, selective catalytic reduction, electrostatic precipitator, fabric hose filter, and activated carbon [521].

Given that plastic wastes are commonly incinerated with other MSWs, the release contribution from plastic incineration must be estimated separately to assess the environmental impacts of the thermal destruction of plastics. PVC, PTFE, and plastics containing brominated flame retardants have been reported to release flue gas containing a considerable level of halogens, acid gases, and persistent organic pollutants such as dioxins and furans compared to the remaining plastics [209], [522]. In 2018, over 5.6 million tons (5.1 billion kg) of plastics (15.8% of total MSW) were sent to incineration facilities, with 2.6% (1.7 billion kg) of the incinerated plastic being PVC [213], [471], [522]. Weber and Kuch have shown that considerable formation of dioxins, furans, and other potentially toxic substances can occur due to the incomplete combustion of plastics [523]. PVC is considered the highest contributor to toxic substance release because it provides up to 38 – 66% chlorine content in MSW. Brominated aromatic flame retardants may contribute to brominated compounds concentration in flue gas and ultimately support the synthesis of dioxins and furans [523]. Incineration experiments have shown that brominated-chlorinated dibenzodioxins and dibenzofurans concentration in uncontrolled waste burning can range between 1 – 9000 μg/g solid combustion residue and 0.8 – 1700 μg/m^3 flue gas [523]. Many of these chemical formations are influenced by the incomplete combustion of brominated flame retardants (BFRs) in plastics. Controlled combustion (temperature >850°C) may be used to thermally degrade between 90 – 99.9% of the brominated flame retardants, thus inhibiting the formation of furans and dioxins [523], [524]. The Clean Air Act of 1970 has prohibited incineration facilities from practicing uncontrolled burning to ensure that emission regulations are met [471]. A conservative estimate can be made by treating the release factor of BFR to be representative of other chemical additive release from incinerating MSW plastics.

Based on the reported mass of incinerated plastic in 2018 [211], the estimated chemical additive release from incineration may range between 4,546 – 408,200 kg/(yr·site) that end up in the incinerator ash as a result of incomplete combustion. Incinerator bottom ash may include the remaining MSW that can no longer be burned. Additional treatment can remove valuable metals from the bulk ash. The remaining ash can be used in construction [520]. The chemical additives released as fly ash are subjected to air pollution control technologies to ensure that emission regulations are met according to the requirements listed in Table D.2. Unmitigated fly ash may release chemical additives into the atmosphere at a rate of 136 – 12,250 kg/(yr·facility) [221]. The removal efficiency of 99.9% may reduce this release rate to 0.14 – 12.2 kg/(yr·facility).

Dispersion modeling was used to estimate the potential exposure from incineration flue gas. The scenario of release from an incineration facility can be represented by the Pasquill-Gifford model for a plume with a continuous steady-state source at height above ground level with wind moving in the x-direction at constant velocity [473]. Equation (19) displays the model for predicting the average flue gas concentration ($\overline{C}$) at a specified coordinate from the source. The x-direction represents the direction of the wind, y is the crosswind, and z is the vertical direction. The concentration is a function of the gas flow rate (Q_m), average gas velocity ($\overline{u}$), dispersion coefficient (σ) in the x, y, and z directions, and the stack height (H_r) [473].

$$\overline{C}(x,y,z)=\frac{Q_m}{2\pi\sigma_y\sigma_z\overline{u}}\exp\left[-\frac{1}{2}\left(\frac{y}{\sigma_y}\right)^2\right]\cdot\left\{\exp\left[-\frac{1}{2}\left(\frac{z-H_r}{\sigma_z}\right)^2\right]+\exp\left[-\frac{1}{2}\left(\frac{z+H_r}{\sigma_z}\right)^2\right]\right\} \tag{19}$$

The daytime maximum ground-level concentration in the wind direction is 0.39 – 0.69 ppm at approximately 23 – 322 m (0.014 – 0.200 mi) from the source for an urban environment. Alternatively, the daytime maximum ground-level concentration in the wind direction in rural settings is 0.12 – 0.28 ppm at approximately 55.5 – 1203 m (0.034 – 0.748 mi) from the source for an urban environment. Table D.3. summarizes the parameters used for estimating the flue gas dispersion [473], [525]–[527]**.** Dow Chemical and the US EPA have tested the effect of transient combustion and established that particulate matter concentration increases by 100% from steady-state combustion [231]. Transient state combustion is likely to occur during startup and shutdown. However, such an operation is not common throughout a given year because incineration can be continuously operated with minimal downtime.

Pollutants released from the incinerator may be dispersed into the environment, exposing the population to potentially toxic substances through inhalation. The pollutants may contaminate and persist in the nearby waters and food supply. If the pollutant concentrations exceed the permissible exposure limits, humans and animals consuming the contaminated substance may be subjected to short- and long-term side effects. Workers at an incineration facility are at a higher risk for exposure to toxic chemicals than the general public living in the surrounding area [231]. Without proper PPE, toxic chemical exposure through inhalation and skin contact may become possible during solid waste feed handling and incinerator cleaning [71]. Chemical additives and other degradation products may contaminate solid ash post-incineration. Maintenance workers entering the incinerator to clean, inspect, or repair are highly susceptible to exposure to residual solid waste. These wastes result from incomplete combustion products, including polychlorinated biphenyls (PCB), polychlorinated dibenzofurans (PCDF), dioxins, and carbon monoxide [528]. Daily cleaning is generally performed around the incinerator grate and ash pit to prevent clogging.

6.3.4.3 Occupational Exposure in Mechanical Recycling. Inhalation exposure in incineration can be represented by Equation (20), where $C_{particulate,incn}$ is the concentration of the particles of concern (15 mg/m^3 for unregulated particulates based on TWA PEL) [512], [513], $R_{breathing}$ is the rate of breathing (1.25 m^3/hr) [514], $t_{exposure}$ is the duration of exposure (8 hrs/day), and $F_{additive,ash}$ is the fraction of chemical additives in incinerator ash

(0.000015 – 0.0014 kg chemical additives/kg ash, as estimated from additive released and ash generated in incineration). Thus, the inhalation exposure rate ($EXP_{inhalation,incn}$) for workers in an incineration facility can range between 0.0023 – 0.21 mg chemical additives/day.

$$EXP_{inhalation,incn} = C_{particulate,\ incn} \cdot R_{breathing} \cdot t_{exposure} \cdot F_{additive,ash} \tag{20}$$

The EPA/OPPT Direct 2-Hand Dermal Contact with Solids Model was used to estimate potential dermal exposure in mechanical recycling [455]. In Equation (21), $EXP_{dermal,incn}$ represents the potential dermal exposure to chemical additives during the incineration process (cleaning ashes from the incinerator) per day, $a_{incd,ash}$ is the mass of ash in contact for a given incident (assumed 5000 mg ash/incident)[529], $N_{exp,incd,incn}$ is the number of exposure incidents per day (1 incident/day), and $F_{additive,ash}$ is the fraction of chemical additives in ash (0.000015 – 0.0014 kg chemical additives/kg ash, as estimated from chemical additives released and plastics processed in incineration). The dermal exposure rate ($EXP_{dermal,incn}$) for workers handling incinerator ashes can range between 0.075 – 7 mg chemical additives/day.

$$EXP_{dermal,incn} = a_{incd,ash} \cdot N_{exp,incd,incn} \cdot F_{additive,ash} \tag{21}$$

6.3.5 Generic Scenario of Plastic Landfilling (IV)

Landfills are designed as solid waste containments, as an option regulated under the Resource Conservation and Recovery Act (RCRA), subtitle D (solid waste), and subtitle C (hazardous waste) [530]. The types of landfills may include those intended for municipal solid waste (MSWLFs), industrial waste (construction and demolition (C&D) debris and coal combustion residual), hazardous waste, and polychlorinated biphenyl (PCB). MSW landfills, specifically, can generate and release an excess of methane gas, capable of trapping heat in the atmosphere with 28 – 36 times more potency than carbon dioxide. A gas collection system generally collects methane gas with 38 – 88% efficiency. This action reduces the carbon emissions from landfills, air pollution, and energy cost [516].

Landfills are built with several protective measures to prevent unwanted substances from leaching into groundwater. The content of groundwater is regularly monitored to ensure that waste materials do not leach into the groundwater supply. A composite liner establishes the capacity of a landfill and blocks unwanted substances from leaching into the groundwater supply using a combination of clay and plastic liner. A collection pipe is used on the plastic liner to collect leachates for treatment. A crushed rock layer is placed around the collection pipe to prevent waste materials from clogging the pipe. A gas collection system is implemented to collect and store landfill gas (50% methane and 50% carbon dioxide) for future use. Solid wastes are dumped above the crushed rock layer and then covered using soil to reduce the odor. Landfills that have reached the maximum capacity for trash must have a final cap consisting of synthetic plastic and a layer of dirt over the landfill. Plants are grown above the plastic cap to reduce the chance of erosion [531]. Fencing is used as a last line of defense against wind-blown waste litter. However, landfilling operation is a source of unintentional chemical releases, as shown in Figure 31c.

The generic scenario for plastic landfilling aims to estimate the following:

- The number of landfills in the US
- Number of workers that may come in contact with potential toxins
- Releases to air and water (methane gas, plastic leak)
- Release from waste transport
- Inhalation and dermal exposures

6.3.5.1 General Landfill Estimates. Solid waste landfills can be represented by NAICS Code 562212 [532]. There are currently 651 verified active companies in the United States with 20,786 employees. The US EPA has an estimated 2,627 active landfills in the United States as of March 2021 [532]. A landfill site may follow different hours of operation. Once enough waste has been stored, landfills continue to generate leachate and gas to the surrounding environment regardless of the operation status. Therefore, a simplification was made, which assumes 365 days of operation to calculate releases. Based on the inflow of waste in 2018, an average landfill may receive over 55,000 tons of waste/day (50 million kg/day). However, landfill sites are not equivalent in capacity across the United States. The actual values associated with this vary greatly depending on the population density and geographic location.

6.3.5.2 Releases in Landfilling. Despite the multitude of safeguards incorporated into landfills, littering is a common problem that can release waste to unexpected areas, including homes, roads, water supplies, and the ocean. Waste may be blown out of the vehicle during waste transport to the landfill and create litter in the street. The wind remains an essential factor during the waste dumping process. A semi-permanent litter fencing can mitigate a portion of the plastic litter swept by daily unloading operations. In addition, landfill gas may escape the gas collection system and into the atmosphere through cracks and leaks around the containment [531].

We have previously estimated that 714,000 tons (648 million kg) $(R_{total,litter})$ of plastic waste generated became litter throughout the EoL processing for a given year. To maintain the material balance, the releases of plastic mass have been compiled and used to calculate the rate of plastic release from landfills as litter. $R_{mech,spill}$ may range between 900 – 5000 tons/yr (816,500 – 4.5 million kg/yr), $R_{collection,spill}$ equates to 3,570 tons/yr (3.2 million kg/yr)., and $R_{incn,spill}$ is 24 – 733 tons/yr (22,000 – 665,000 kg/yr).

Equation (22) estimates approximately 620,000 – 670,000 tons of plastics/yr (562 million – 608 million kg). $(R_{total,landfill,spill})$ can be spilled as litter during the landfilling operation based on a 35.7 million tons (32.4 billion kg) plastics basis. The landfill contribution toward chemical additives release can thus reach 310 – 470,000 tons (281,200 – 426.4 million kg) over the lifetime of plastics, based on the typical mass fraction of chemical additives in plastics (0.0005 – 0.70).

$$R_{total,landfill,spill}=R_{total,litter}-R_{total,collection,spill}-R_{total,mech,spill}-R_{total,incn,spill} \quad (22)$$

Rainwater and groundwater may penetrate through the containment and into the landfill containing mixed MSW, presenting a complex environment that may cause chemical additives to be released from the polymer matrix [470]. The contaminated rainwater acts as leachate, containing organic compounds resulting from plastics and bacteria activity throughout the degradation process. Landfill sites in industrialized countries have been known to perform leachate treatment, such as using aerobic and membrane bioreactors to reduce the BPA concentration to 0.11 – 30 μg/L [472], [533]. Without proper leachate treatment, chemical additives and BPA could be released into the environment and contaminate the nearby water supply. The rate of leachate release has been estimated to vary between 20 – 30% of the waste in the landfill [534]. Our generic scenario analysis holds that over 146 million tons (132.4 billion kg) of waste have been sent for landfilling in 2018, with each landfill receiving, on average, 55,000 tons (50 million kg) of MSW/day. The potential leachate generated from landfills may approach 10 million – 15 million kg/(yr·site). For a given site, the estimated yearly chemical additive release through leachate equates to 100 – 150 kg/(yr·site) (0.001% additive in leachate) [472].

6.3.5.3 Occupational Exposure in Landfilling. The transmission of chemical additives to humans due to landfill activity is not straightforward. Plastics, chemical additives, and the corresponding degradation byproducts leave the containment as leachate or litter. Animal species such as birds, fish, and other marine mammals are likely to ingest these materials by mistake because of their similarity to food. The contaminants have been shown to desorb from plastics in gastric conditions and expose the organism to unintended toxicity [472]. Humans or other animals that consume the affected organisms can indirectly expose themselves to the contaminants. The concentration varies depending on geographic location and the rate of leachate and litter release into the environment. The resultant hazardous effects of chemical additives can vary depending on the organism type, duration of exposure, and chemical interaction within the biological system [452]. Additionally, the chemical additive desorption rate from plastic depends on the size, type, and state of the plastic. For example, rubbery plastic items do not have many adsorption sites for chemicals; however, glassy plastic items possess high rigidity and tiny pores that serve as adsorption sites.

Workers at landfill sites can be directly exposed to potentially hazardous substances primarily through dermal contact. Sharp objects may temporarily injure workers and expose them to toxins that cause severe health complications, including disease, infection, and cuts. Liquid leachate may also be absorbed through the skin, posing more potentially hazardous issues. Like other EoL processing methods, not all workers are exposed to the same level of dermal hazard because their job function varies. However, the likelihood of exposure for workers in the waste management industry is much higher than for the common public.

Chemical additives in leachate are present at approximately 0.00001 kg of chemical additives/kg of leachate. Landfill workers are not expected to be exposed to chemical additives through the inhalation route under normal conditions. However, other volatile substances, such as methane gas generated from MSW degradation, remain constant. Direct contact with chemical additives may occur during landfilling operations because workers may be required to handle waste materials directly. Accumulated leachate in landfill sites may contain a small fraction containing dissolved chemical additives. The potential dermal exposure was estimated using the EPA/OPPT Direct 2-Hand Dermal Contact with Liquid Model [455]. $EXP_{dermal\_landfill}$ represents the potential dermal exposure to chemical additives in landfilling per day, $b_{liq,skin,landfill}$ is the amount of liquid remaining on the skin (0.7 - 2.1 mg chemical/($cm^2 \cdot$incident), $A_{surface}$ is the surface area of contact (1,070 cm^2 for two hands), $N_{exp,incd,landfill}$ is the number of exposure incidents per day (1 incident/day), and $F_{additive,leachate}$ is the fraction of chemical additives in leachate (0.00001 kg chemical additives/kg leachate). Through Equation (23), dermal exposure rate ($EXP_{dermal,landfill}$) for landfill workers can range between 0.007 – 0.02 mg additives/day.

$$R_{total,landfill,spill}=R_{total,litter}-R_{total,collection,spill}-R_{total,mech,spill}-R_{total,incn,spill} \tag{23}$$

The generic scenario calculations were categorized as the following: plastic wastes processed, plastic spilled/released, chemical additives released, inhalation exposure, and dermal exposure. There is limited data on chemical additive release in the collection and sorting stages. Therefore, the estimation for this stage was made from a holistic standpoint. Recycling, incineration, and landfilling EoL routes were estimated on a mass per facility per given year. It is expected that the number of EoL facilities, workers, recycling, incineration, and landfilling rates may change as a function of time. However, these generic scenario values can assist with identifying challenges regarding plastic recycling and the danger of toxic chemical release in typical operations.

6.3.6 Environmental Impact Assessment

The current methods of plastic waste management release materials into the environment and expose workers in the EoL stages, creating unintended and long-lasting consequences to health and the ecosystem. In Sections 6.3.1 – 6.3.5, we have quantified the potential plastics and additives mass flow throughout the EoL stages and estimated generic facility-level releases to highlight additive exposure risks. This section estimates the environmental consequences of the existing EoL practices by assessing energy footprints, greenhouse gas (GHG) releases, and ecological footprints to identify the environmental burden and motivate the shift toward a circular economy approach with minimal releases.

6.3.6.1 Releases. The GHG releases associated with plastics throughout the plastic life cycle have been calculated using the EPA Waste Reduction Model (WARM) [535]. The calculated mass flow and composition of the generic plastic waste stream were multiplied by the GHG emission factors shown in Table D.1 [535]. Through incineration, up to 8.6 million tons (7.8 billion kg) of CO_2-eq in 2018 were generated from plastic components. Up to 1.2 million tons (1.1 billion kg) of CO_2-eq can be generated annually from landfilling plastics. By choosing mechanical recycling for 8.4% of the wasted plastic, up to 2.9 million tons (2.6 billion kg) of CO_2-eq emission can be prevented. If the United States can double the recycling rate to 16.8%, over 5.8 million tons (5.3 billion kg) of CO_2-eq emissions can be prevented. As shown in Figure 29, up to 648 million kg (2%) of plastic waste generated can be released into the environment for a given year because of littering in the EoL stage. Most littering comes from landfilling operations because it is designed to store material waste. A greater volume of materials is expected to enter landfill sites than a recycling or incineration facility. The released plastics from littering equate to approximately 31,500 tons (28.6 million kg) CO_2-eq of emissions. While the magnitude of overall plastic litter is far lower than direct landfilling, littering presents a source of uncontrolled release. Each year, more materials may become litter and increase the impacts accordingly.

The world produces more than 360 million tons (326.6 billion kg) of plastics annually from a global perspective [493]. Assuming the cumulative plastic waste generated is subjected to the United States plastic recycling infrastructure, there is a potential annual chemical additive release of 1.25 million tons (1.1 billion kg) and a GHG release of 111 million tons (100 billion kg) of CO_2-eq. However, many countries worldwide do not necessarily possess state-of-the-art recycling technologies to minimize toxic chemical releases, creating large uncertainties in the release estimations. Although analyzing the global EoL plastic management is beyond the scope of our work, efforts to improve EoL management processes are needed to achieve a circular economy.

6.3.6.2 Sustainable Process Index. The Sustainable Process Index analysis was used to assess the ecological footprint of EoL plastic management for 2018. SPI calculates the total arable area required to sustainably achieve one unit of the desired product for a given process. In EoL plastic management, the successful recycling of 1 kg of waste plastics equates to 371 m^2.a, where 'a' signifies arable [468]. The processes and the required arable areas to obtain 1 kg of recycled plastic have been listed in Table 17.

Table 17

Arable Area Contribution Required to Obtain 1 kg of Plastic from Post-Consumer Plastic Waste

Processes	Inventory	Arable Area (m^2.a/kg)	% Total Area
Main Product			
Recycled Plastics	1 kg	371	100
Sub-Processes			
Waste plastics mixture	11.8 kg	0.261	0.1
Municipal waste collection by 21 metric ton lorry	1 tkm	0.297	0.1
Treatment of waste plastic, a mixture	2.17 kg	187	50.3
Extrusion (Final processing)	1 kg	144	38.9
Treatment of MSW, incineration	4.03 kg	39.8	10.7
Waste in a landfill for inert matter	19.4 kg	0.0230	0.0

The required area for recycling 1 kg of plastic ultimately impacts fossil carbon, water, air, soil, renewable, land area, and non-renewable resources. Based on the material flow in 2018, the management of plastics consumed water equivalent to 226 m^2.a/kg, fossil carbon equivalent to 116 m^2.a/kg, soil equivalent to 16 m^2.a/kg, and air equivalent to 13 m^2.a/kg. Figure D.6. illustrates this distribution of the resource impacts. The footprint impacts on renewable, non-renewable resources and land area are negligible and thus were excluded.

The current land surface area of Earth equates to 149 trillion m^2 (57.51 million mi^2) [536]. The arable land was estimated to be 10.83% of the total land surface area (16.1 trillion m^2) in 2018 [537]. The United States could recycle up to 3.02 million tons (2.7

billion kg) of post-consumer plastics. The SPI analysis from disposal to recovery indicated that 1.02 trillion m^2.a is required to embed this process sustainably. The plastic management impact on the land is equivalent to 7% of the total arable land area on Earth. It is crucial to note that SPI serves as a theoretical representation of sustainability and is standardized as an arable land area. Over time, the arable land area on Earth may change depending on land use, pollution, and erosion. In the present state, the United States EoL plastic management process is not sustainable if we include other post-consumer wastes such as food, glasses, metals, papers, and more in the analysis. Although the Earth does replenish resources over time due to material cycles, the rate of resource gain is drastically lower than the resource loss. Responsible allocation of spent resources ensures that annual carbon consumption is minimized.

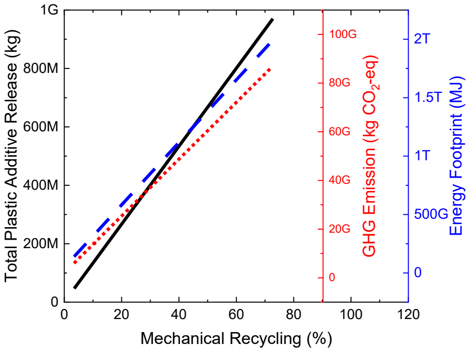
The environmental footprint and release rates calculated in this work were based on the US EPA 2018 data on plastic waste management. Although the parameters used to estimate plastics and chemical additives releases are expected to change between years, a sensitivity analysis study can estimate the trend of releases and impacts.

6.3.7 Sensitivity Analysis

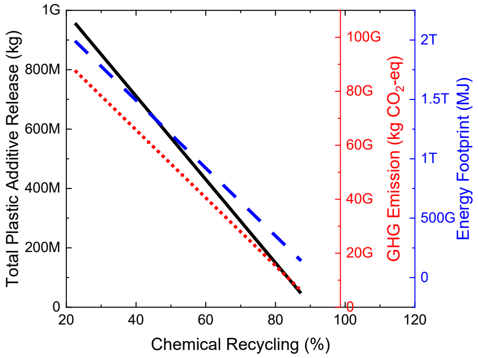
We analyzed three distinct scenarios to predict the impacts of (1) altering the efficiency of existing EoL plastic management, (2) incorporating chemical recycling techniques as a primary plastic management route, and (3) extracting chemical additives from bulk recycled plastics before reuse, on chemical additive release, GHG emissions, and energy footprints. The emission factors and energy footprints used in this study are summarized in Table D.5 [220], [535], [538]–[541].

6.3.7.1 Scenario 1: Recycling Efficiency is Increased Beyond the Current Rate to a Maximum Technical Feasibility Point. This hypothetical scenario predicts the effects of increasing the mechanical recycling rate on the global warming potentials, chemical additive releases, and energy footprint [538]. The maximum technical feasibility of plastic recovery from the collection, sorting, and mechanical recycling methods can theoretically reach a maximum recovery of 72% [542]. Therefore, the recovery rate of the plastics sent for recycling could theoretically be between 0 – 72%. Plastic waste export value was held constant at 4.5% regardless of the increase in recycling efficiency [543]. Incineration and landfilling are selected as the secondary method for processing non-recyclable plastic and were held at a constant ratio of 17.2:82.8. Figure 32a shows that the increase in mechanical recycling rate effectively increases the total chemical additive release, greenhouse gas emissions, and energy footprint.

(a) Scenario 1



(b) Scenario 2



(c) Scenario 3

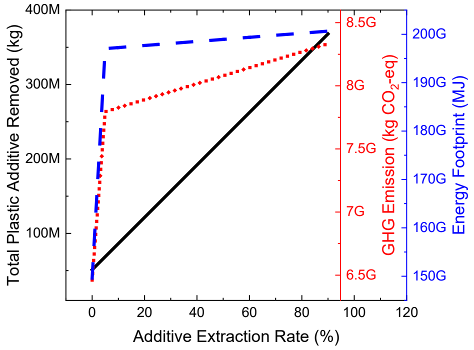


Figure 32. Sensitivity analyses of three hypothetical scenarios and their impacts on the total plastic additive released (black solid), greenhouse gas emissions (red dot), and energy footprint (blue dash). (a) Scenario 1 examines the effect of increasing the rate of plastic recycling to the maximum technical feasibility limit; (b) Scenario 2 implements pyrolysis as a secondary plastic waste processing method in addition to mechanical recycling; (c) Scenario 3 includes a chemical additive extraction stage before recycled plastics are sent to the manufacturing stage. The total plastic additive release has been redefined as total plastic additive removed to reflect the purpose of the additive extraction process.

The increase in the chemical additive release is proportional to the chemical additive contamination in recycled plastics. Unrecyclable plastics are sent to incineration and landfilling, creating opportunities to release harmful gas-phase emissions and accumulation of plastic mass, respectively [71], [74], [212], [533]. These estimations were highlighted in our generic scenario analysis. Chemical additives may be released slowly into the surrounding area as leachate over time. Mechanical recycling is expected to release chemical additives faster than other plastic waste processing methods within a given period. However, this statement should not detract from the merit of increasing the plastic recycling rate. The successful recovery of EoL plastic reduces the potential release and accumulation of plastics in the environment. The chemical additives would be accumulated in a more controlled environment within the recycled plastics. Additional processing may be implemented to reduce harmful chemicals from recycled plastics. Conversely, non-recycled plastics that accumulate in the environment can release harmful chemical additives to the ecosystem without control. Figure D.4.1. summarizes scenario 1 by illustrating the overall movement of plastics, chemical additives, and other MSW at the EoL stages based on 2018 MSW data on plastics.

6.3.7.2 Scenario 2: Chemical Recycling is Used in Conjunction with Mechanical Recycling. This hypothetical scenario examines the effects of implementing pyrolysis to treat all plastics that were not successfully recycled through the mechanical route and the associated global warming potentials, chemical additive releases, and energy footprint. Mechanical recycling remains the primary chosen method for plastic recycling. All untreatable plastic waste and solid residues resulting from mechanical and chemical recycling are sent to incineration and landfilling at a constant ratio of 17.2:82.8. International plastic waste export remains constant at 4.5%.

Pyrolysis was chosen to represent chemical recycling because it has been used commercially with a conversion efficiency range between 60 - 95% [544]. Alternative other chemical recycling techniques may include catalytic cracking, conventional gasification, plasma gasification, depolymerization, and hydrocracking. The life cycle inventory for the pyrolysis process was estimated based on the values reported by [539]. The mechanical recycling efficiency was constant at 66.7% [542]. The pyrolysis conversion efficiency was held at 95% [544]. Figure 32b shows the increase in chemical recycling (pyrolysis) rate decreases the total chemical additive release, GHG emissions, and energy footprint. This reduction is expected because pyrolysis chemically converts plastics into energy, gas, oil, and solid residues [539], [544], [545]. Other techniques, such as depolymerization, can recover the original monomer and thus provide opportunities for upcycling [546]. Harmful chemicals are converted into new products without damaging the identity of the materials. Therefore, the combination of mechanical and chemical recycling is a feasible approach to processing and minimizing the release of plastic waste. Figure D.4.2. summarizes scenario 2 by illustrating the overall movement of plastics, chemical additives, and other MSW at the EoL stages with considerations for chemical recycling.

6.3.7.3 Scenario 3: Chemical Additives are Extracted from Mechanically Recycled Plastics. This hypothetical scenario examines the effects of implementing an extraction technique post-mechanical recycling on global warming potentials, chemical additive releases, and energy footprint. Chemical additive extraction is promising when performed as a solid-liquid extraction with dissolution-precipitation [488]. Common extraction types may include shake-flask extraction, Soxhlet extraction, ultrasonic extraction, microwave-assisted extraction, supercritical fluid extraction, accelerated solvent extraction, and dissolution-precipitation [488]. The success rate of these methods is highly dependent on the additives, plastics, and extraction conditions. The authors identified that dissolution-precipitation is preferable in the case of a broad range of chemical additives. However, chemical additives may degrade because of the high-temperature operation. Chemical additive degradation is not essential for this scenario because the extracted chemicals are present as a mixture in small quantities. Additionally, the separation and purification of the individual chemical additive components are not expected to be economically viable because of the large variety of substances present. Therefore, the extracted chemical additives were treated as process waste. While there may be economic value to the chemical additives extracted because these chemicals are generally organic compounds, this analysis is beyond the scope of our work.

Dissolution-precipitation showed that CO_2 savings equate to 65-75 wt.%, as opposed to incineration and landfilling, because there is no chemical bond destruction [540]. Therefore, the global warming potential for this process has been estimated to be approximately 30% of the incineration of individual plastics. The energy footprint of the dissolution-precipitation process of various plastic types was estimated based on carbon content [540], [541]. The efficiency of the chemical additive extraction technique is varied between 0% - 90%, where 0% signifies a complete bypass of processing the recycled materials. The domestic plastic recycling and international export rates were held constant at 3.9% and 4.5%, respectively. The mechanical recycling efficiency was held constant at 66.7%. Incineration and landfilling remained at a 17.2:82.8 ratio. A plastic loss rate of 10% was assumed post-dissolution-precipitation process.

Figure 32c demonstrates that increasing the chemical additive extraction rate could effectively prevent over 350,000 tons (317.5 million kg) (95%) of the chemical additives in the recycled plastics from contaminating materials in the subsequent life cycle. The GHG and energy footprint scale steadily with the number of chemical additives removed because of the additional management of the extracted materials as waste. The mixture of extracted chemical additives cannot be separated into individual components economically at a large scale. However, the extraction solvent in the dissolution-precipitation step can be recovered and reused [547], [548]. The amount of additives released from plastics has been defined as the total plastic additives removed, which scales with the amount of mass of plastics processed. The abrupt jump in GHG releases and energy footprint beyond the 0% chemical additive extraction rate is attributed to subjecting the recovered plastics to dissolution-precipitation, an additional process with scalable GHG emission and energy footprint. Both categories were observed to increase, a necessary trade-off because potentially harmful chemical additives are removed from the recovered plastics. The quality of these materials would approach 95% of the virgin polymer in the best-case scenario. Figure D.4.3. summarizes scenario 3. It illustrates the overall movement of plastics, chemical additives, and other MSW at the EoL stages resulting from implementing chemical additive extraction in the post-mechanical recycling stage.

Based on the maximum technical feasibility, these sensitivity analyses have highlighted the merits of improving the existing plastic recycling rate if chemical recycling and additive extraction are implemented before plastic reuse. Incineration is effective at thermally degrading plastics and additives, but these materials are transformed into a non-usable state. Alternatively, landfilling contains plastics and additives with a barrier. However, there are chances of additives being released from the containment in leachates. Although this release is not as high as mechanical recycling, landfilling is not a sustainable solution because these materials take decades and centuries to degrade.

6.3.8 Potential Improvement

Modifications to the current plastic life cycle can be made to minimize resource consumption, environmental impacts, and adverse health effects on humans and animals. The manufacturing, use, collection, and sorting stages would remain consistent with the existing plastic processing methods. However, incentives and policies can be implemented to minimize chemical release. Manufacturers should design plastics with consideration for the possible release of toxic chemical additives during use and EoL stages. For instance, single-use plastics may not necessarily require the same concentration of chemical additives as plastics that play a longer-term role in our daily lives, such as electronics, storage, and automobile parts. Manufacturers may choose to be accountable for the materials produced by designing the materials to be degradable in the presence of a specific substance. Consumers should be informed of the potential danger of subjecting plastics to conditions that favor chemical additive migration during the use stage. In addition, only 8.4% of the plastics collected in the EoL stage were reported as recycled (4.5% exported overseas and 3.9% recycled domestically). Although EoL plastic export is beyond the scope of our study, modifications to domestic and international plastic waste management remain crucial.

Heavy reliance on incineration and landfilling presents the largest obstacle to achieving a circular economy in the plastic life cycle. A circular economy can be achieved if plastic manufacturers design plastics with recycling in mind. Prioritizing plastic recycling practices at the end-of-life stages by reducing incineration, landfilling, and littering may keep plastics in the loop. However, such a condition is unrealistic until technological efficiencies, operation costs, incentives, and legislative support associated with the current plastic recycling efforts are improved [209], [223], [224]. Smith *et al.* (2022) performed a separate material flow analysis, specifically on PET, throughout the end-of-life processes and further highlighted processing challenges regarding contaminants and additives present during mechanical recycling [549]. One solution to addressing this issue is implementing a chemical additive removal stage to eliminate the primary contamination source. This method may use solvent extraction and dissolution-precipitation to separate the polymer from the chemical additives loosely held in the polymer matrix. The solvent utilized in this process can be recycled and reused [550]. In addition to mechanical recycling, chemical recycling, such as pyrolysis, may depolymerize the plastics and recover the original monomer and other pyrolysis-derived products such as aromatics, fuels, and waxes [551]. This processing route provides opportunities for upcycling, transforming the material into new products with minimal waste [488], [552]–[555]. The judicious use of chemical additives during the plastic manufacturing stage and the standardization of material collection, sorting, and recycling (mechanical, chemical, and chemical additive extraction) in EoL plastic processing is expected to address current concerns.

6.4 Conclusions

Post-consumer plastics are prone to negatively impacting the environment through many forms of unintentional releases. Although highly beneficial for enhancing the properties of the materials, the chemical additives are not linked to the plastics network, allowing the molecules to migrate and contaminate the surrounding environment. The material flow analysis performed in this work has shown that the current plastic economy is linear because most plastic waste has been incinerated and landfilled. Non-recyclable plastics are sent to incinerators and landfills in large quantities due to sorting and reprocessing challenges. Furthermore, the generic scenario analysis highlighted that incineration and landfilling could adversely affect the environment due to the potential release and exposure of toxic substances to workers and the surrounding areas. The current mechanical recycling methods are not immune to these releases either, which created the need for an improvement in the plastic waste management infrastructure. An environmental impact assessment was completed to predict the environmental consequences of the existing EoL practices by assessing energy footprints, greenhouse gas (GHG) releases, and ecological footprints. This result can help identify the environmental burden and motivate the shift toward a circular economy approach with minimal releases. We provided a theoretical representation of the area required to sustainably achieve one unit of product (recycled plastics). The plastic waste processing in MSW requires up to 7%

of the total arable land area on Earth. This theoretical area should be minimized because land is a limited resource, and it is not sustainable to consume resources faster than the generation rate. In this case, the treatment of plastic waste and mechanical recycling are hot spots that cost the greatest theoretical ecological footprint. Thus, we further emphasized the need to optimize the plastic waste treatment process and minimize the chemical additive releases and contamination that were identified from the material flow analysis and generic scenario analysis.

We have also demonstrated from our sensitivity analyses that mechanical recycling may assist with closing the material loop, despite the large ecological footprints. Poor recycling efficiency caused by chemical additive contamination and migration can further create the opportunity for toxic substances to release into the surrounding environment. However, the recycling rate can realistically be improved, reducing the reliance on incineration and landfilling, if initiatives are taken to enhance EoL plastic management. More importantly, plastic recycling should not be the sole focus. Chemical recycling should be used to process waste plastics that cannot be recycled mechanically. Additionally, chemical additive extraction should be used with conventional mechanical recycling to minimize unintentional chemical releases and contamination in the future life cycle. Ultimately, the effective separation of plastics and additives without compromising the structural and mechanical properties of the original product is the key to making plastic recycling safer and more sustainable.

Therefore, analysis regarding chemical additive releases during chemical recycling should be investigated to determine a mitigation strategy before a standard chemical recycling practice is used. We aim to create a tool that performs all the calculations done in this work while providing the users with crucial data and plots. This tool can simulate the effects of altering key parameters (recycling, incineration, landfilling rate, MSW composition, import and export rate, and efficiency at various stages) on chemical releases, greenhouse gas emissions, and energy footprint. Although the data used in this work is primarily from 2018, this tool is also set to contain data from previous years, allowing users to generate a custom dataset to test their own scenarios. This contribution may be used to support the United Nations Sustainable Development Goals for ensuring sustainable consumption and production patterns with plastic waste.

Chapter 7

Automating Decision-Making Processes through Software Tool Designs

Texts and figures used in this Chapter are publication-pending.

The largest barrier to implementing some of the computational techniques shown in this dissertation is the difficulty in making the solution practical for industrial and everyday use. This chapter addresses the most up-to-date progress toward overcoming these hurdles. Herein, an alpha version of a solvent recovery tool was developed through MATLAB with the solvent recovery analysis framework from Chapter 5. A hazardous chemical tracking tool was also developed using Python GUI to guide policy-makers and researchers through a simpler yet interactive platform.

7.1 Development of Graphic User Interface-Based Tools to Lower the Knowledge Barrier for Process System Engineering

7.1.1 MATLAB-Based Solvent Recovery Tool

We have seen from Chapter 5 that solvent recovery is an ideal alternative to incineration and landfilling because it can improve the sustainability and greenness of chemical processes [556], [557]. In addition, solvent recovery poses economic benefits since fresh solvents will not need to be purchased in high quantities anymore, as much of these recovered solvents can be reused. However, while many unique recovery methods have been researched, no standard solvent recovery method has been implemented [558]–[560].

To this end, a solvent recovery tool can be a viable and quick solution to identifying solvent waste mitigation strategies to reduce the total amount of hazardous waste released into the environment. However, solvent recovery design is very complex, requiring engineers to design a new system to implement in their facility. In addition, the engineer needs to collect, process, and analyze large amounts of information to get a feasible recovery option which can be very time-consuming. Many engineers do not have the time to analyze all available options within a limited timeframe due to the fast-paced nature of design projects. We have previously developed, in Chapter 5, a superstructure-based solvent recovery framework capable of suggesting an optimal recovery pathway with minimal cost and environmental impacts [557]. This work can analyze multiple recovery options simultaneously within a short timeframe. However, the approach is not user-friendly and requires the user to have prior knowledge of chemical engineering and coding experience. This work aims to provide a user-friendly approach to solvent recovery that can eliminate the need for high-level programming knowledge. By building this GUI around the solvent recovery framework, industries can start to explore and implement new solvent waste handling, recovery, and recycling methods. It is crucial to note that collaborator, Jake Stengel, has led this part of the work effort with other collaborators (myself, Austin Lehr, and Emmanuel Aboagye). The full description of the results can be found in Jake Stengel's Master's Thesis [561].

7.1.2 Python-Based Hazardous Chemical Tracker

Chapter 6 discusses a material flow analysis of the plastic life cycle while highlighting chemical additive release opportunities at every major stage in the EoL plastic waste management process. This analysis uses the latest data published by the US EPA (2018) to monitor the high-level process efficiency, environmental impacts, and unintentional environmental releases. Various scenarios were analyzed in Section 6.3.7 to predict the effects of altering the plastic waste management infrastructure. As shown in Figure 30, the connections between the plastic waste management stages and the various processes employed are not intuitive. The actual fate of material is more complex than the general values displayed in public databases and reports. The generic scenario analysis from Section 6.3.2 – 6.3.5 has further estimated the potential releases and occupational exposure to a typical worker at a generic facility within the United States.

The primary drawback of these results is their relevance to the existing plastic waste management trend. At the time of this dissertation, the US EPA published the fate of plastics collected in the MSW up to 2018 [211]. The analysis is static, meaning that the results do not consider the potential changes in plastics recycling, incineration, landfilling, export, and import rates between different years. Policymakers and researchers may wish to compare the release differences or study the fate of plastics under different conditions. The sensitivity analysis shown in Chapter 6 is only a theoretical result based on a compilation of data and assumptions. We previously built an Excel-based tool to perform the material flow analysis on over 30 separate streams, representing the plastics life cycle with up to 36 components (pure plastic resins, additive types, other MSW, and contaminations). Although it is easy to repeat the study and replace all 2018 data with the other years (2016, 2017, etc.), the effort can be tedious and confusing because too many data and spreadsheet tabs are available to the user simultaneously. Therefore, we generated a python-based tool that can function independently from the spreadsheet. It can contain pre-made datasets from other years, as well as able to accept custom datasets for the programmed calculations.

7.2 Tool Architecture

7.2.1 The Functionality of the Solvent Recovery Tool

The solvent recovery framework introduced in Chapter 5 used a superstructure-based approach to determine the most economical solvent recovery route through GAMS [557]. However, this algorithm-requires knowledge of Excel, GAMS, and database management, creating a large knowledge barrier for new users. Therefore, a GUI-based tool was developed to provide a user-friendly option for optimizing solvent recovery. This GUI was built using MATLAB app designer, which can connect with Excel and GAMS to solve user-specified problems. GAMS may communicate with this Excel spreadsheet through GDXXRW (GAMS Data Exchange Excel Read and Write) command. A GDX (GAMS Data Exchange) file is generated, which contains user-input parameters in GAMS format. Following a successful optimization, the data is translated back into Excel. MATLAB then interprets the data and returns values to the users through the GUI. This tool can thus be used to quickly estimate feasible high-level waste recovery schemes based on the solvent recovery framework proposed in Chapter 5. As stated in Section 7.1.1, the full description of this tool development effort can be found in Jake Stengel's Master's Thesis [561].

7.2.2 Building the Python-Based GUI for Tracking Hazardous Materials

Process waste management impact estimation challenges exist at the process design level and in the EoL stages. The Generic Scenario analysis of EoL plastic waste management presented in Chapter 6 uses an Excel-based calculator and database, which can be difficult to navigate for new users. A python-based GUI chemical additive tracker tool was created to streamline the calculations and simulate the effects of altering key parameters (recycling, incineration, landfilling rate, MSW composition, import and export rate, and efficiency at various stages) on chemical releases, greenhouse gas emissions, and energy footprint. Figure 33 displays the major operations contained within the python-based tool. A graphic user interface (GUI) was created through the Tkinter package, allowing all users to input specific information. In addition, algorithms are implemented to check and correct proportion errors related to instances where the total percentage must be 100%.

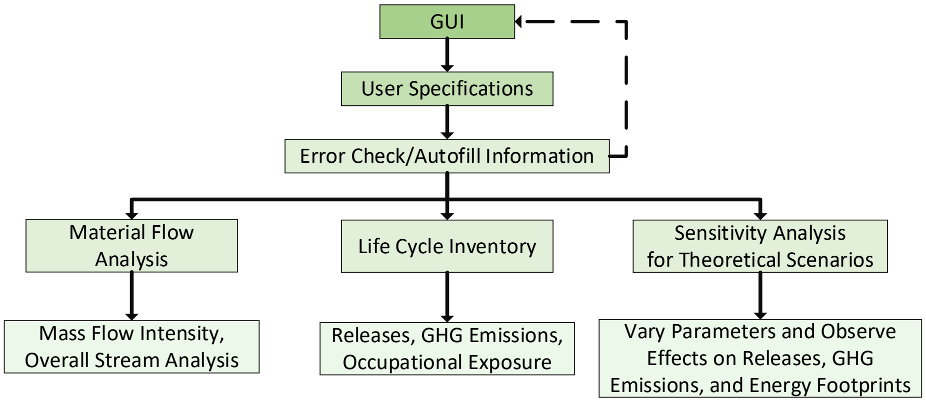
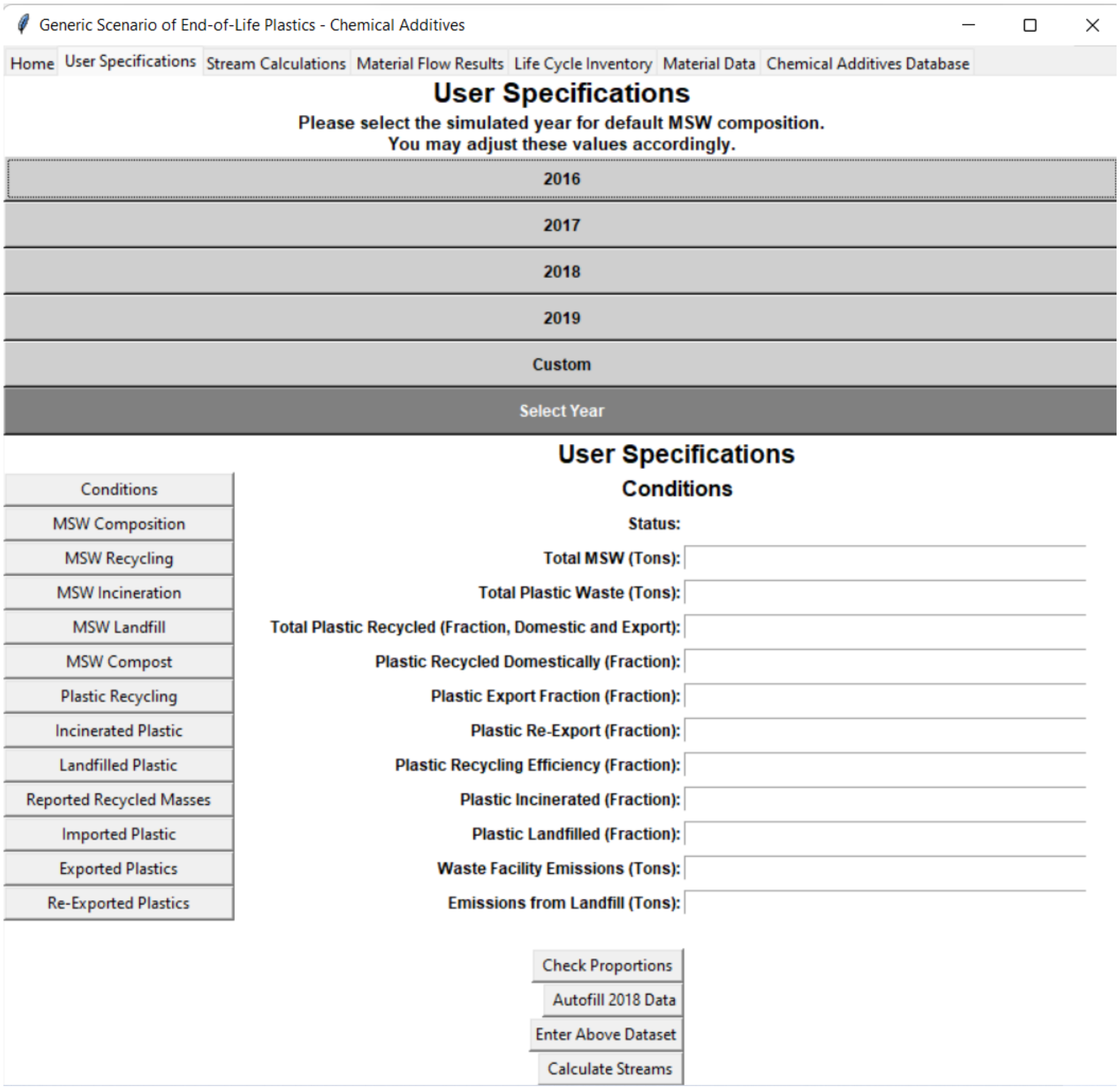


Figure 33. Python-based GUI tool main features

The data used in this work thus far is specifically from 2018. However, this tool also contained 2016 and 2017 data, allowing users to generate a custom dataset representative of a given year. Figure 34 displays a screenshot of the plastic EoL estimation tool input tab, in which the users may use default values reported by the US EPA or enter custom data to simulate a specific waste plastic waste stream.



Generic Scenario of End-of-Life Plastics - Chemical Additives

User Specifications

Please select the simulated year for default MSW composition.
You may adjust these values accordingly.

User Specifications

Conditions

Status:

Figure 34. A preview of the plastics EoL chemical release estimation tool

Three major results can be obtained from this each iteration of specification submission. First, a material flow analysis, similar to Figure 29, is shown and updated according to the values inputted by the users. Relevant plots and mass flow intensity diagrams are created to illustrate the state of plastic waste management and potential chemical additive releases in the EoL stages. Life cycle inventory presents the second major result, which contains information regarding plastics and chemical additives releases, greenhouse gas emissions, and occupational exposure. This tool can also perform sensitivity analysis by varying specific parameters to the maximum technical feasibility limit as part of the third major result. Furthermore, custom scenarios regarding the usage of chemical recycling, in addition to the conventional MSW plastics EoL processes, were added to assist with comparative studies.

The development of this python-based tool thus ensured that releases and harmful effects from the current EoL plastic stage are estimated with the necessary plots and valuable information for preliminary studies. Diagrams and plots like Figure 29 and Figure 32 are available as results and can change according to the parameters inputted by the users. We compiled data from multiple sources and stored them in this tool for quicker and more convenient estimation. Additionally, this tool is modular, and new scenarios can be created to predict the outcome of various methods and identify concerning steps in the EoL stages that demand immediate attention.

7.3 Summary

The solvent recovery tools and the python-based chemical tracker served as proofs-of-concept that can reduce the barrier to implementing the solutions described in Chapters

3 – 6. The solvent recovery tool can take user inputs through a GUI and apply the superstructure approach to determine the most economical pathway to recover target solvents. However, environmental metrics have not been implemented. This complexity can be implemented in future updates of the tool. Regarding the chemical additive tracker tool, the mathematical background behind the tool has been completed. This tool can take custom inputs, perform a material flow analysis, and provide the relevant releases, emissions, and energy footprints. Plots and figures can be generated to illustrate the major results. However, the GUI and representation of the results need, at present, both tools are in alpha version and thus are not yet ready for industrial or nationwide usage. Significant improvement to the GUI is required before both tools can transition toward the Beta phase.

Chapter 8

Concluding Remarks on Achieving Sustainable Process Designs

8.1 Conclusions

This dissertation has proven the overarching hypothesis that the strategic optimization of practices and resource allocation in process engineering can enhance global environmental and resource sustainability. Testing the effects of the strategic optimization aspect of this hypothesis requires that challenges are solved and solutions are proposed at various stages of the life cycle of a material to transform the existing material flow paradigm toward the state of a circular economy.

8.1.1 Summary of Sustainable Feedstock Acquisition Progress

Decisions made in the manufacturing stage greatly dictate the fate of all materials used in a product formulation because this stage is an origin point that later dictates the recyclability, global warming potential, and environmental impacts. Manufacturers generally seek to maximize profits while using the most accessible raw materials that meet the consumers' needs. Petroleum is often chosen because the synthesized products offer better properties at lower prices than their bio-based counterparts. However, petroleum is not a sustainable solution because the materials require millions of years to regenerate. Conversely, the sources used to create bio-based materials can be regenerated in a shorter timeframe. These reasons raise the question regarding the merit of using bio-based materials as a replacement. Our first sub-hypothesis stated that bio-based resource availability and cost challenges could be solved using minimally processed renewable resources with fast replenishment time. As it stands, the conventional synthesis scheme of bio-based chemicals and products starts with extraction. It ends with multi-step purification to a purer component before the reaction or the product manufacturing process. On the surface level, this sequence of steps can be costly, especially when the resultant product may not achieve competitive thermal or mechanical properties against petroleum-based products for the same application. It is possible to optimize this process to reduce costs, as demonstrated in Chapter 3. Generally, the initial capital investment may vary according to the raw material source because substances grown or found in nature have different characteristics and processing requirements. Thus, performing an individual study to determine unique challenges is crucial before scaling the process. In some cases, the cost of isolating a specific chemical can greatly exceed the cost of purchasing the petroleum-based counterpart. This issue can be solved with a modification to the conventional bio-based material processing and synthesis schemes by using impure extracts instead of targeting the isolation of a specific chemical. For example, we have seen in Chapter 4 that birch bark extract-based polyester has exhibited similar properties to the purer and component-specific (betulin-based) counterpart. However, the materials synthesized from the impure birch-derived extract could not compete against a commercial petroleum-derived resin such as Eponex 1510. This limitation does not necessarily mean that bio-based resources are not worth pursuing because the resin formulation can be adjusted with different chemicals to compensate for the property differences.

8.1.2 Summary of Solvent Recycling Progress

The synthesis and manufacturing stages often generate a large amount of waste that is mainly incinerated or landfilled. Process waste management is equally as important as the initial design decision and material selection because many opportunities exist to recover and reuse substances that may demand high raw material costs. In Chapter 5, we examined two separate case studies of solvent being discarded in existing practices because the quality of the spent solvent does not meet the requirement for reuse. We proposed a solvent recovery framework that considers multiple pathways to systematically treat solvents to obtain solvents at the desired purity and recovery rate for reuse. Minimizing cost to maximize profit is the most crucial objective to stakeholders in all instances of process design because it is not practical to build a process with a consistent negative profit for the sake of only minimizing the environmental impacts. We thus extended our waste recovery research scope by treating sustainability and economics as a multi-objective problem. We observed that a large waste generation rate creates a sizeable environmental burden that scales proportionally with waste quantity increase. The sustainability of chemical processes is thus reduced with increasing waste generation. From an economic standpoint, solvent recovery has consistently provided favorable savings for most cases during a process. However, material recovery becomes unfavorable at low flow rates because the process investment and operational cost cannot be offset by the materials recovered. It is recommended that the waste recovery process be performed once sufficient waste has accumulated to a feasibly large batch to maximize the potential recovery and minimize cost. Also, minimizing environmental impacts can be a realistic goal if the waste generation rate is minimized. The solvent recovery framework may be adapted to handle other types of process waste.

The main hurdle of altering many existing processes is evidenced by processes designed without a waste recovery system because the wastes are expected to be handled either externally or through offsite processes (incineration and landfilling). Furthermore, modifying the existing process to include recovery can be time-consuming because many options exist, and the process design sequence is traditionally completed through a one-by-one comparison. To streamline the waste recovery process design, we further advanced the superstructure-based solvent recovery framework with the development of a basic computational software tool. The GUI interface allowed process designers to input a customized waste stream without being required to understand an unfamiliar coding language. Our second hypothesis, which states that The sustainability of manufacturing processes can be improved with a comparative assessment framework that can significantly reduce the time from process design to implementation, has thus been proven.

8.1.3 Summary of Plastics EoL Management Progress

Designing a sustainably sourced material with minimal waste is a strong guideline to consider. However, the sustainable process design must also ensure that the materials created remain in a circular economy after consumer use. As previously mentioned, the raw material acquisition and product manufacturing stages determine the level of an environmental, economic, or social burden later in the life cycle of a material, particularly the EoL stages. In Chapter 6, we performed a material flow analysis of the current state of plastic waste management to quantify releases that manufacturers, policymakers, and consumers often overlook. The current plastic economy is linear because most plastic waste has been incinerated and landfilled due to sorting and reprocessing challenges.

Furthermore, the generic scenario analysis indicated that these EoL processes, including mechanical recycling, can release toxic substances to workers and the environment. Thus, an improvement in the plastic waste management infrastructure is warranted. The energy footprints, greenhouse gas (GHG) releases, and ecological footprints scale with the mass of plastic waste process, suggesting that waste minimization should be considered a high priority at all stages. At the current state, mechanical recycling, the most common plastic recovery method, needs to be optimized to recover enough of the post-consumer plastic waste to yield a circular economy. We observed poor recycling efficiency caused by chemical additive contamination and migration. This efficiency can be improved if we consider both physical and chemical recycling while using technologies that provide a more considerable margin of error to account for the possible variation in waste composition, properties, and contamination level. The successful recovery of post-consumer waste with minimal downcycling and unintentional mass releases can make EoL processes more sustainable and alter the existing linear paradigm toward circular, as shown by the sensitivity analyses in Chapter 6. Thus, the third hypothesis has been proven, which states that better material management can be achieved by preventive actions and mitigation strategies that lead to higher recovery rates. This dissertation explicitly targeted plastic because this material type is abundant, complex, and constantly manufactured with many chemical additives for many applications. The EoL treatment of other products made from other materials (metals, woods, stones, etc.) is characteristically different from that of plastic EoL. However, the fundamental ideas behind EoL processing and recycling criteria are similar. A generic material may or may not be used with a formulation, chemical additive, or as a composite to fulfill the demands. All three conditions are observed more frequently with synthetic plastics manufactured than natural-occurring materials with set properties, such as metals and stones. Modifying the chemistry and synthesis conditions in plastic manufacturing can change the properties drastically, making plastics possess a higher complexity than other material types at all stages.

8.2 Recommendations and Future Works

The state of a circular economy can be achieved using sustainable process design practices, from selecting viable raw materials to their end-of-life. This dissertation demonstrates that having access to a sustainable raw material source can streamline the production of chemicals or materials for specific demands. However, bio-based resources have limitations and cannot rival petroleum-based resources regarding availability and cost. The commercialization of bio-based materials for solving the “availability” issue is highly dependent on the source. Presently, a framework for the general extraction and purification of bio-based materials has yet to be developed. A comprehensive bio-based extraction framework, similar to the solvent recovery framework from Chapter 5, can prove helpful for determining the ideal processing routes from any source. We demonstrated the viability of bio-based chemical extraction from Chapter 3. Even so, petroleum acquisition has been a well-established practice, and it is used to synthesize many products used in everyday life. Conversely, a specific bio-based resource cannot be assumed to meet all the needs of the consumer for a specific application. Many different viable bio-based chemical sources have yet to be studied comprehensively. This superstructure approach presented in this work accounted for many variations in pre-processing, extraction, purification, and refinement while also containing the logic to eliminate irrelevant technologies from consideration. The superstructure used to extract and purify soy isoflavone can be adapted to other bio-based extraction processes to aid the commercialization of other renewable resources. Identifying potentially promising renewable resources is one of the largest obstacles to the implementation changes proposed in this research. Extensive research is required to identify the promising chemicals in existing resources, provided that it has never been done before. Process system engineering approaches such as machine learning (ML) may be used for the initial feedstock identification [562]–[566]. Key characteristics such as location, resource types, chemical species, solubilities, and their physical and chemical properties can help identify potential resources with targeted chemical groups. The initial training set may be built using existing bio-based research and expanded as more discoveries are made. The accuracy of the resources and types of chemicals present can be tested using conventional extraction and analytical techniques.

We selected birch bark extract for material synthesis to demonstrate the potential shortcut to accessing viable starting materials without extraneous purification or refinement to a specific chemical. In exchange for cheaper costs, we sacrificed the predictability of the raw material by using impure extract as a raw material for synthesis. Throughout this study, we have used birch bark from a single source to minimize variability and understand the effects of seasonal changes on the chemistry of the bark. Future studies should focus on synthesizing similar products from birch trees of the same and different species found in other geographical locations. The triterpenoid composition is expected to vary considerably because of the climate and soil conditions. The potential correlation between species, location, season, and climate can shed further insight into the necessity of standardizing the extraction process for property consistency. Even so, the properties of the birch-derived product, such as epoxy, could not perform on an equal footing with the petroleum-based substance. Future studies should use birch bark extract-derived chemicals as part of a formulation with the appropriate additives until the desired property is reached. Methacrylation of BBE is also a feasible route to explore for additive manufacturing applications because of the hydroxyl content present within the extract. However, the potential solubility issue with the other reactants may require a deviation from conventional methacrylation reaction schemes [567]. For example, solvents may aid with homogenizing the reaction when solubility is not observed at the reaction condition. Considerations should also be made regarding the level of quality of the plastics synthesized because creating the perfect plastic that can withstand damage and persist in the environment for centuries post-use can negatively impact material circularity and pollute the environment. Depending on the chemistry of the synthesis process, bio-based materials may be biodegradable and inexpensive if the raw material is subjected to minimal processing. However, environmental degradability is not guaranteed because of the variation between the interactions and bonds between various chemicals. Instead, introducing certain chemical functionalities may allow controlled degradation in the EoL management stage when the material is subjected to specific substances such as base, acid, or alcohol.

Process waste generation is a constant problem that should be mitigated through sustainable means. However, its implementation in an industrial setting may be challenging because this optimization method requires chemical engineering and coding knowledge.

Therefore, the solvent recovery framework and a GUI-based optimization software tool developed in this study can recommend a sustainable approach for waste handling and recovery in the manufacturing industry. Sustainability analyses, such as SPI, emergy, life cycle assessments, may be introduced into the analysis further to explore the trade-off relationships between cost and environmental consequences. Additionally, the current function of this tool is relatively basic and requires a connection to licensed GAMS software. Future development of this tool can be refined further into standalone software or a web-based application that can be used in all processes that generate excessive solvent waste. Additional technologies to purify and refine solvent waste can be added as needed based on new research findings. Although this tool is specifically used for solvent waste reduction, a similar material recovery framework and GUI tool creation can be applied to other material types used in a process. However, the robustness of these products should be tested vigorously in industrial settings by varying waste stream composition. Potential challenges such as azeotropes, chemical interactions, and multi-phase separation can thus be addressed. ML has been used for the physicochemical properties of organic solvents and the solubility of organic solvents in water under variable conditions such as temperature, molar volume, enthalpies of fusion, and vaporizations [562], [568]. Additionally, membrane selection for processes such as ultra-, micro-, nano-filtrations, and reverse osmosis can be improved using ML methodologies, which can predict optimal membrane properties and help select efficient membrane technologies for solvent recovery [569]–[571]. Further adaptation can be made to consider energy-efficient technologies during the design phase of the recovery process [572].

Decisions made during every stage of the life cycle of a material can directly affect the fate of the material in the EoL stages. Plastic was selected as the material of interest to demonstrate that a circular economy can be achieved if the conventional recycling paradigm is adjusted to include chemical treatment and optimize the existing EoL treatments. EoL waste management solutions should not solely consider increasing recycling because other factors, such as estimating releases in the EoL stages, are often overlooked or not publicly known, as shown in this dissertation. These releases are stemmed from decisions made during product manufacturing, throughout the usage phase, and through waste management infrastructure. The EoL generic scenario analysis should be used to develop safety protocols to minimize unwanted migration, emission, leaching, degradation, and exposure for workers handling EoL substances. With this information, recycling facilities should work with the manufacturer to ensure that the EoL of plastics or any materials is considered before a product is made. This collaboration and the chemical release tracker tool can ensure that the necessary risks and recycling difficulties are considered. Consequently, the material exchange process between each stage (manufacturing, use, and EoL management) can be streamlined. Future work should consider analyzing the generic scenario of chemical recycling. Mechanical recycling is incapable of such chemical separation and transformation. Mechanically recycled plastics, for example, has considerably lower quality and contamination than virgin plastic. In the US, mechanical recycling is used nationwide, but the government does not commonly use or mandate chemical recycling. This method is necessary to successfully upcycle materials that are fated to be incinerated and landfilled. However, chemical recycling requires further improvement because of the potentially high energy requirement, and some contamination (e.g., PVC) can be detrimental to the final product yield and quality. Additionally, the potential impacts on the health and safety of the workers and the environment should be estimated and implemented into the Python-based GUI chemical release tracker tool before policies or recommendations are made to support the nationwide use of chemical recycling. Providing this additional scenario can allow policymakers to decide on the safest and most sustainable regulations quickly. Similar work to EoL plastic management can be applied to other recyclable materials such as paper, cardboard, glass, and metal. The fundamental issues regarding low recycling rates depend on contamination, material types, sorting, and releases. These factors can negatively affect the recyclability of the spent materials. The successful tracking of EoL materials can provide insight into the challenges with post-consumer waste management, which can be optimized to maximize material recovery and minimize releases.

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Appendix A

Supporting Information for Chapter 3

A.1 Potential Technologies for Isoflavone Extraction from Soybean Meal

Pre-processing

Grinding (GRD) is a particle size reduction process that consumes energy to impose mechanical stress on large particles to induce brittle fracture, shearing, and surface abrasion. A variety of mills and crushers may be used based on the hardness of the material to accomplish this grinding operation [321]. This process is generally used as the precursor step in extraction processes to enhance efficiency by increasing the surface area for mass transfer [294], [316]. The ease of particle size reduction is governed by the Bond work index, defined as the amount of energy required to reduce one short ton of solid from large particle size to 80% smaller than 100 µm. Particle size reduction has been reported to increase the diffusivity of chemicals from natural materials [294]. Grinding can be performed under wet or dry conditions. Wet grinding produces less dust and requires approximately 25% less Bond work index when compared to the dry grinding process. However, wet grinding can impose additional wear and tear and lead to equipment corrosion [321].

Extraction

Turbo-Extraction (TE) is a high shear solid-liquid mixing process that facilitates the diffusion of specific solutes into the liquid phase. The material of interest and extracting solvent are mixed at high intensity with the aid of an impeller. Extraction time, temperature, solid particle size, and impeller stirring speed are crucial in designing a turbo-extraction unit. The high shearing force in this unit can reduce the entering solid particle size [305]. The particle size reduction is expected to increase the extraction efficiency due to the increased surface area for mass transfer [326]. However, the high shear resulting from TE can generate considerable heat that may cause protein denaturation, reducing the soy protein quality and preventing soybean meal from being reused in the animal feed industry [312]. Cooling can be implemented to avoid overheating of heat-sensitive materials. **Maceration (MC)** is a soaking method that relies on the diffusion of solute into the solution. The material of interest is mixed with a solvent in a holding tank for an extended time. A typical maceration extraction can last for several days as this process is diffusion limiting. However, this extraction can be completed at room temperature and atmospheric pressure with no agitation [132], [309]. Key factors to consider in the design of a maceration unit include the choice of the extraction solvent and the residence time. The choice of extracting solvent can influence the final extract mixture composition due to the interaction between different chemicals present and the solvent [132]. **Ultrasonic-Assisted Extraction (UAE)** is an alternative extraction method that applies sound energy to agitate a solution containing solvent and particles. During this process, microbubbles are formed and collapsed repeatedly, which creates a change in pressure and temperature [307], [313]. Compared to conventional extraction methods that involve mixing, UAE has been shown to improve mass transfer and requires less solvent [322]. UAE is also favorable for biomass handling processes because the increased agitation facilitates the breakdown of the cell wall, further enhancing mass transfer [132], [323]. The frequency of the ultrasonic waves, the shape of the probe or vessel, solvent choice, operating temperature, and the solvent feed ratio are integral factors in designing an ultrasonic-assisted extraction unit [132]. **Supercritical Fluid Extraction (SFE)** is used to remove the organic solute of interest from a bulk mass by dissolution through a supercritical solvent (at critical temperature and pressure). In this state, the supercritical fluid possesses a density similar to a liquid, while its viscosity and diffusivity are similar to a gas. Carbon dioxide is commonly chosen as a supercritical fluid for extraction because of its nonpolar behavior. Ethanol has been commonly employed as an entrainer, which holds the dissolved solutes in solution after extraction from the solid particles by the supercritical fluid. Diffusion dominates the initial transport mechanism after the supercritical fluid has made contact with the surface of the particle. The desired solute dissolves into the supercritical fluid phase and diffuses outward to the particle surface [317]. The solute separation from the supercritical solvent can be done by adjusting the thermodynamic conditions or using adsorption. The operating temperature and pressure, solvent to feed ratio, particle size, porosity, and moisture content are crucial in designing supercritical fluid extraction units [132].

Solid Separation

Gravity sedimentation (SDM) is a process that is designed to remove settleable solids using gravity. This solid-liquid separation method is typically employed for water treatment applications to remove clay, silts, and other dense particulates [318]. The particle settling velocity plays an essential role in designing a gravity sedimentation process because it dictates the required residence times and, in turn, equipment sizes. [159]. **Filtration (FLT)** is a solid-liquid separation process that relies on a driving force such as vacuum or pressure to allow the liquid to pass through the insoluble solid collected on a filter medium. Filtration design is dependent on the required throughput, solid concentration in the feed, and properties of the liquid. Depending on the application, the products can be either the solid collected or liquid filtrate that passed through the filter media [321]. **Centrifugation (CNF)** is a mechanical process that applies centrifugal force by rotation to assist the settling of colloidal particles or particles with similar specific gravities to the liquid phase. This method is more efficient than a conventional gravity sedimentation unit as it can separate particles within a reasonable time. A slurry feed containing liquid and solid particles enters at the center of the centrifuge in a typical centrifugation operation. The lighter components are sent outwards, causing the material (solid particles or liquid) with higher density to occupy the centrifuge center. CNF may be performed either as a batch or continuous process [129], [169].

Solvent Removal

Freeze Drying (DRY) is an energy-intensive moisture removal process that requires freezing of both the solutes and solvent, followed by a sublimation step, typically carried out at high vacuum. This method reduces pressure to convert the solvent into the vapor phase allowing for operation at reduced temperatures instead of heating like conventional evaporation techniques. Freeze drying is preferable in applications that involve thermally sensitive materials as it avoids high temperatures. DRY may be operated in a batch or continuous mode. The crucial parameters surrounding the design of a freeze dryer include selecting the refrigerant, operating pressure, and operating temperature [132].

Reaction

Acid Hydrolysis (AHY) is a reaction process that typically employs acid to cleave a molecule into smaller components [319]. For instance, adding 20% sulfuric acid at high temperatures to polysaccharides can convert them to monosaccharides [304]. AHY is also used to treat cellulosic and hemicellulosic material [315], [324]. AHY process efficiency depends on the type of acid chosen, amount, pH, reaction temperature, and time. This process is highly exothermic as chemical bonds are broken and formed in the presence of an acid (proton donator). **Neutralization (NT)** is used to neutralize the pH of the solution by reacting hydroxide ions with the hydrogen ions from the acid hydrolysis reaction. Following acid hydrolysis, this process can be used to neutralize the excess acid and form salt and water as products. This process is also necessary as isoflavones possess increased degradation at acidic pH values and elevated temperatures [320].

Purification

Crystallization (CRYS) is a purification process that takes advantage of the limited solubility of a substance in a solvent for a given state to produce crystalline materials. Purified products can be obtained using this method because of the highly-ordered arrangement of molecules. Crystallization may be performed through (1) evaporation, (2) controlled cooling to reduce substance solubility, and (3) adding liquid antisolvent to shift the solid-liquid equilibrium and alter the solubility of the solute in the solution [132], [325]. Antisolvent crystallization was chosen for the isoflavone purification method as this technique does not require heating or cooling to produce crystalline products. This method introduces a secondary solvent (antisolvent) to force the solution to reach supersaturation and reduce the solubility of the solute in the original solvent [310]. For heat-sensitive products, antisolvent crystallization may be used to avoid product degradation [310], [321]. **Organic solvent nanofiltration (OSN)** is a pressure-driven separation process capable of selective transport of solvent through a nonporous membrane [306]. An OSN membrane may be created from a composite of polymeric and inorganic materials with high thermal, chemical, and mechanical stability [308]. The principle behind this purification technique is the same as conventional membrane processes. The presence of the membrane serves as a semipermeable barrier that selectively controls the transport of molecules of a specific size range. The efficiency of this separation process is determined by flux, solute rejection, recovery, and perm-selectivity of the component of interest [159], [311]. **Chromatography (CHRM)** is a purification process that utilizes the affinity of the solute to the stationary phase [132]. Column chromatography is the most commonly used chromatographic method in the industry. In column chromatography, the solvent and solute mixture is treated as the mobile phase, while the packing material, such as silica, is treated as the stationary phase. The mobile phase flows through the stationary phase. The solvent and solute components exit the column individually at separate times based on their distribution coefficient. Chromatography is favorable for processes that involve biological material as it operates at moderate temperatures [314].

A.2 Isoflavone Extraction Model Equations

Applicable to all technologies

A.2.1 Indices and Sets

i ∈ ***I*** – technologies (used as subscript to variables)

{split1-5 – Splitters 1-5

mix1-3 – Mixers 1-3

GRD - Grinder,

TE – Turbo-Extraction,

MC - Maceration,

UAE – Ultrasound Assisted Extraction

SFE – Supercritical Fluid Extraction,

CNF- Centrifugation,

FLT1- Filtration 1,

SDM – Sedimentation

DRY1 – Dryer 1,

AHY- Acid Hydrolysis,

NT – Neutralization

FLT2 – Filtration 2

CRYS – Crystallization

FLT3 – Filtration 3

NF – Organic Solvent Nanofiltration (OSN)

CHRM – Chromatography

DRY2 – Dryer 2}

j ∈ ***J*** – stream (used as subscript to variables)

{1, 2, 3, 4 …}

$k \in \boldsymbol{K}$ – components (used as subscript to variables)

{largesoy – soybean meal before particle size reduction,
soy – soybean meal post grinder,
i-glucoside – isoflavone glucoside
i-aglycone – isoflavone aglycone
ethanol – ethanol,
water – water,
CO2 – carbon dioxide
Base – sodium hydroxide
HCl – hydrochloric acid
Impurity –impurity}

A.2.2 Subsets

Subsets for Technologies

I^{CST} – technologies with costs

{GRD, TE, MC, UAE, SFE, CNF, FLT1, SDM, DRY1, AHY, NT, FLT2, CRYS, FLT3, NF, CHRM, DRY2}

I^{AE} – technologies after extraction

{CNF, FLT1, SDM, DRY1, AHY, NT, FLT2, CRYS, FLT3, NF, CHRM, DRY2}

I^{CF} – technologies with concentration factor

{SDM, FLT1, CNF, FLT2, FLT3}

I^{CONS} – technologies with consumables

{FLT1, FLT2, FLT3, NF}

I^{BV} – technologies with binary selection constraints

{TE, MC, UAE, SFE, CNF, FLT1, SDM, CRYS, FLT3, NF, CHRM}

Subsets for Components

J_{split1} – splitter 1 streams

$J_{split1, F}$ – splitter 1 feed streams

$J_{split1, E}$ – splitter 1 effluent streams

J_{GRD} – grinder streams

$J_{GRD, F}$ – grinder feed streams

$J_{GRD, E}$ – grinder effluent streams

J_{split2} – splitter 2 streams

$J_{split2, F}$ – splitter 2 feed streams

$J_{split2, E}$ – splitter 2 effluent streams

J_{TE} – turbo-extraction streams

$J_{TE, F}$ – turbo-extraction feed stream

$J_{TE, S}$ – turbo-extraction solvent stream

$J_{TE, E}$ – turbo-extraction effluent stream

J_{MC} – maceration streams

$J_{MC, F}$ – maceration feed stream

$J_{MC, S}$ – maceration solvent stream

$J_{MC, E}$ – maceration effluent stream

J_{UAE} – ultrasound-assisted extraction streams

$J_{MC, F}$ – ultrasound-assisted extraction feed stream

$J_{MC, S}$ – ultrasound-assisted extraction solvent stream

$J_{MC, E}$ – ultrasound-assisted extraction effluent stream

J_{SFE} – supercritical fluid extraction streams

$J_{SFE, F}$ – supercritical fluid extraction feed stream

$J_{SFE, S}$ – supercritical fluid extraction solvent stream

$J_{SFE, E}$ – supercritical fluid extraction effluent stream

J_{mix1} – mixer streams 1

$J_{mix1, F}$ – mixer 1 feed streams

$J_{mix1, E}$ – mixer 1 effluent streams

J_{split3} – splitter 3 streams

$J_{split3, F}$ – splitter 3 feed streams

$J_{split3, E}$ – splitter 3 effluent streams

J_{SDM} – sedimentation streams

$J_{SDM, F}$ – sedimentation feed stream

$J_{SDM, S}$ – sedimentation solid phase stream

$J_{SDM, E}$ – sedimentation effluent stream

J_{FLT1} – filtration 1 streams

$J_{FLT1, F}$ – filtration 1 feed stream

$J_{FLT1, S}$ – filtration 1 cake stream

$J_{FLT1, E}$ – filtration 1 effluent stream

J_{CNF} – centrifugation streams

$J_{CNF, F}$ – centrifugation feed stream

$J_{CNF, S}$ – centrifugation solid stream

$J_{CNF, E}$ – centrifugation effluent stream

J_{mix2} – mixer streams 2

$J_{mix2, F}$ – mixer 2 feed streams

$J_{mix2, E}$ – mixer 2 effluent streams

J_{split4} – splitter 4 streams

$J_{split4, F}$ – splitter 4 feed streams

$J_{split4, E}$ – splitter 4 effluent streams

J_{DRY1} – dryer 1 streams

$J_{DRY1, F}$ – dryer 1 feed stream

$J_{DRY1, S}$ – – dryer 1 solid stream

$J_{DRY1, E}$ – – dryer 1 effluent stream

J_{AHY} – acid hydrolysis streams

$J_{AHY, F}$ –acid-hydrolysis feed stream

$J_{AHY, A}$ – acid feed stream

$J_{AHY, E}$ – – acid hydrolysis effluent stream

J_{NT} – neutralization streams

$J_{NT, F}$ – neutralization feed stream

$J_{NT, Base}$– neutralization base added stream

$J_{NT, E}$– neutralization effluent stream

J_{FLT2} – filtration 2 streams

$J_{FLT2, F}$ – filtration 2 feed stream

$J_{FLT2, S}$ – filtration 2 cake stream

$J_{FLT2, E}$ – filtration 2 effluent stream

J_{split5} – splitter 5 streams

$J_{split5, F}$ – splitter 5 feed streams

$J_{split5, E}$ – splitter 5 effluent streams

J_{CRYS} – crystallization streams

$J_{CRYS, F}$ –crystallization feed stream

$J_{CRYS, A}$ – antisolvent feed stream

$J_{CRYS, E}$ – crystallization effluent stream

J_{FLT3} – filtration 3 streams

$J_{FLT3, F}$ – filtration 3 feed stream

$J_{FLT3, S}$ – filtration 3 cake stream

$J_{FLT3, E}$ – filtration 3 effluent stream

$J_{NF\,–}$ filtration 3 streams

- $J_{NF,\,F\,–}$ nanofiltration feed stream
- $J_{NF,\,E–}$ nanofiltration effluent stream
- $J_{NF,\,R\,–}$ nanofiltration rejected stream

$J_{CHRM\,–}$ chromatography streams

- $J_{CHRM,\,F\,–}$ chromatography feed stream
- $J_{CHRM,\,R–}$ chromatography unwanted component stream (components that exits the column at a different time is treated as a different stream)
- $J_{CHRM,\,E\,–}$ chromatography effluent stream (product)

$J_{mix3\,–}$ mixer streams 3

- $J_{mix3,\,F\,–}$ mixer 3 feed streams
- $J_{mix3,\,E\,–}$ mixer 3 effluent streams

$J_{DRY2\,–}$ dryer 2 streams

- $J_{DRY2,\,F\,–}$ dryer 2 feed stream
- $J_{DRY2,\,S\,–\,–}$ dryer 2 solid stream
- $J_{DRY2,\,E\,–\,–}$ dryer 2 effluent stream

Subsets for components

K – components *k*

{largesoy, soy, i-glucoside, i-aglycone, ethanol, water, CO2, HCl, Base, impurity}

K_1 – components *k* in stream flows

{largesoy,soy,i-glucoside,i-aglycone,ethanol,water,CO2,Base,HCl,impurity}

K_2 – non-soy components { i-glucoside, i-aglycone, ethanol, water, CO2, HCl, Base, impurity}

K_3 – solvent components {ethanol, water}

K_4 – SFE solvent components {ethanol, CO2}

K_P – pre-processing components {largesoy, soy, i-glucoside}

K_B – initial basic components {largesoy, i-glucoside}

K_C – extraction components {soy, i-glucoside, ethanol, water, largesoy}

K_{add} – externally added components {ethanol, water, HCl, Base}

K_{L4} – light components in dryer {ethanol, water}

K_{Sld} – added solvents {ethanol, water, CO2, i-glucoside, impurity}

K_{Sol} – solid components {largesoy, soy}

K_{NSDRY1} – non-solvent components in DRY1 {largesoy, soy, i-glucoside, i-aglycone}

K_{NS} – non-solvent components{ largesoy, soy, i-glucoside, i-aglycone, HCl, Base, impurity}

K_{FLT1} – relevant components in FLT1{largesoy, soy, i-glucoside, ethanol, water, impurity}

K_{NTSalt} – Components in Filtration 2 after Neutralization Reaction {i-aglycone, i-glucoside, ethanol, water}

A.2.3 Dynamic sets for connectivity

To denote connection between technologies, streams and components (*Yes* if connected, *No* if not)

$\boldsymbol{J_i}$ – streams of technology *i*
$\boldsymbol{Jin_i}$ – inlet streams of technology *i*
$\boldsymbol{Jout_i}$ – outlet streams of technology *i*
$\boldsymbol{K_i}$ – components *k* in technology *i*
$\boldsymbol{K_j}$ – components *k* in stream *j*

A.2.4 General Parameters

Qf (kg/hr) = initial feed flow

g (m/s^2) = acceleration due to gravity

C_{lbr} (\$/hr) = labor wage

T_{ann} (hrs) = annual hours of operation

BMC_mult = bare cost multiplier

Rep_time = membrane replacement time

ρ (kg/m^3) = density of component k

MW (g/mol) = molecular weight of component k

Cp (kJ/kg-°C) = Specific heat of component k

Tcw_{in} (°C) = Cooling water temperature in (25)

Tcw_{out} (°C) = Cooling water temperature out (30)

λ_{stm} (kJ/kg) = Latent heat of steam

$Q0_i$ (m^3 or m^2 or m^3/h) = Standard capacity of a technology for costing, labor and power required

$C0_i$ ($/capacity) = Cost of a technology with standard capacity

$Nlabr_i$ (#/h) = # of laborers required for technology *i* per hour

nc = cost scaling index (2/3 rule)

Wsp (kW/h) = power required by technology *i* per hour

A.2.5 General Variables

$M_{j,k}$ (kg/h) = Mass flowrate of component k in stream j

CF_i (m^3/m^3) = Concentration factor for technologies $i \in \boldsymbol{I^{CF}}$

Qc, (m^3 or m^2 or m^3/h) = Costing variable for technologies $i \in \boldsymbol{I}^{\mathbf{CST}}$

$Cc_{,i}$ ($) = Purchase cost of unit *i*

$M_{cw,i}$ (kg/h) = Mass flowrate of cooling water required for technology i

$M_{stm,i}$ (kg/h) = Mass flowrate of steam required for technology i

$N_{lbr,i}$ (kg/h) = Number of labors required for technology i

Cpr_k ($/h) = Purchase cost of added components (k ∈ $\mathbf{K^{ADD}}$)

$Cons_i$ ($/unit) = Consumable costs for technology i

U_i = Sigma factor for technology i

$Feed_C$ – Cost of entering feed stream

y_i – binary variables corresponding to a technology i

Obj – objective function

Costing variables

$CCAC_{Nstg}$ (\$) = annualized capital (fixed) cost in stages

$CCRM_{Nstg}$ (\$) = raw material costs in stages

$CCCS_{Nstg}$ (\$) = consumable costs in stages

$CCLB_{Nstg}$ (\$) = labor costs in stages

$CCUT_{Nstg}$ (\$) = utility costs in stages

$CCTC_{Nstg}$ (\$) = total cost in stages

$CCOT_{Nstg}$ (\$) = other costs (overheads and supervision) in stages

CFAC (\$) = annual feed costs

Notes:

- The ‘uppercase italic Latin fonts (not colored)’ are for variables (values determined through the solution of the optimization problem)
- The uppercase Latin font and lowercase Greek fonts in red are the specified input parameters
- The parameter or variable to be evaluated is always on the L.H.S of the equation

Component balances in all technologies:

$$\sum_{j \in Jin_i} \boldsymbol{M_{j,k}} = \sum_{j \in Jout_i} \boldsymbol{M_{j,k}} \; ; \; \forall \; \boldsymbol{k} \in \boldsymbol{K_i} \; \boldsymbol{and} \; \boldsymbol{i} \in \boldsymbol{I^{AE}}$$

Connectivity Matrix

For J_I =/= 0

$$J_{I,in} = 1$$

$$J_{I,out} = -1$$

Cost of entering feed:

$$C_{Feed} = \pi_{feed} M_{1,B}$$

Cost of technologies:

$$\left(\frac{Ce_i}{C0_i}\right) = \left(\frac{Qc_i}{Q0_i}\right)^{nc_i} \; ; \; \forall i \in \boldsymbol{I^{CST}}$$

Labor requirement in technologies:

$$Nlb_i Q0_i = Nlabr_i Qc_i \; ; \; \forall i \in \boldsymbol{I^{CST}}$$

Consumable costs in technologies:

$$Cons_i = \frac{\tau_{ann}}{\theta_i{}^{Rep}} \pi^{Rep}{}_i Qc_i \; ; \; \forall i \in \boldsymbol{I^{CST}}$$

Logical equations:

$$M_{j,k} - M1_k y_i \leq 0 \; ; \; \forall \; i \in \boldsymbol{I^{BV}}, j \in \boldsymbol{J}, k \in \; \boldsymbol{K_i} and \; \boldsymbol{K_j}$$

Grinder (GRD)

Parameters:

Y_{GRD} (%) = Release parameters

Frc_k (unitless) = Fraction of component k

θ_{GRD} (h) = Residence time in grinder

d_1 = original average particle diameter (μm)

d_2 = desired particle diameter (μm)

$T_{ca_{in}}$(°C) = Temperature of cooling air in

$T_{ca_{out}}$(°C) = Temperature of cooling air out

BWI (kWh/2000 lb) = Bond Work Index by Vishwanathan and Subramanian, 2014 (235 kJ/kg)

$\hat{E}_{GRD}$ (kJ/kg)= Energy per mass required **(**evaluated parameter**)**:

$$\hat{E}_{GRD} = \mathrm{BWI}\left(\frac{10}{\sqrt{\mathrm{d}_2}} - \frac{10}{\sqrt{\mathrm{d}_1}}\right)$$

d_1 – original particle diameter (m)

d_2 – desired particle diameter (m)

Equations:

Component Release Equation:

$$M_{jGRDE,k} = Y_{GRD} Frc_k M_{jGRDF,k}; \forall k \in \boldsymbol{K}$$

Residual large soy after release:

$$M_{jGRDE,largesoy} = M_{jGRDF,largesoy} - M_{jGRDE,soy}$$

Costing variables:

$$Qc_{GRD} = \theta_{GRD}\left[\sum\nolimits_{k\in\boldsymbol{K}}\left(\frac{M_{GRDF,k}}{\rho_k}\right)\right]$$

Power required in grinder (kW):

$$PW_{GRD} = \frac{\hat{E}_{GRD}\rho_k Q_{c_{GRD}}}{\theta_{GRD}}$$

Assuming 60% of power dissipates to heat, cooling air is required:

$$Mca_{GRD}Cp_{ca}(Tca_{out} - Tca_{in}) = (0.6PW_{GRD})$$

Turbo Extraction (TE) – Mixer Tank

Parameters:

$moist_{soy,TE}$ = moisture of soy

$Tcw_{in,TE}$ (°C) = Cooling water temperature in (25)

$Tcw_{out,TE}$ (°C) = Cooling water temperature out (30)

$P_{agit,TE}$ (W/m^3) = average power draw

$D_{soymeal}$ (m) = diameter of soybean meal particles

Δt_{TE} (hours) = time required for extraction (0.5 hrs)

Equations:

Ethanol requirement in TE:

$$M_{jTES,ethanol} = M_{jTEF,k} * 8.774\frac{kg}{hr}$$

Water requirement in TE:

$$M_{jTES,water} = M_{jTEF,k} * 2.780\frac{kg}{hr}$$

Volume of liquid (Continuous):

$$V_{liq,TE} = \sum\nolimits_{j\in Jin,i} \frac{M_{j,k}}{\rho_j}\Delta t_{TE}; \forall\, j \in J^{TE}, k \in K^{TE}$$

Height of liquid TE:

$$Z_{liq,TE} = \frac{4V_{liq,TE}}{\mathrm{\pi D}_{tank,TE}^2}$$

Rewritten as:

$$Z_{liq,TE}\mathrm{\pi D}_{tank,TE}^2 = 4V_{liq,TE}$$

Volume Tank TE:

$$V_{tank,TE} = 1.3 * V_{liq,TE}$$

Power requirement:

$$PW_{TE} = P_{agit,TE} * V_{tank,TE}$$

Heat Produced by agitator

$$QH_{TE} = 0.5 * PW_{TE}$$

Cooling Duty

$$QC_{TE} = QH_{TE}$$

Cooling water required:

$$Mcw_{TE}Cp_w(Tcw_{out} - Tcw_{in}) = QC_{TE}$$

Costing Variable:

Costing variable of Cone Tank without agitator

$$QS_{tank,TE} = V_{tank,TE}$$

Costing variable of agitator;

$$QS_{agit,TE} = P_{agit,TE}$$

Combined costing variable of tank

$$Qc_{TE} = QS_{tank,TE}$$

General Design and Constraints

Liquid height (H_L) to tank diameter (D_T). If the ratio is 1.4, use dual impellers

$$0.8 \leq \frac{Z_{liq,TE}}{D_{tank,TE}} \leq 1$$

Written as two constraints:

$$0.8D_{tank,TE} \leq Z_{liq,TE}$$

$$Z_{liq,TE} \leq D_{tank,TE}$$

Diameter ratio: Should be between 1/3 to ½ for impeller

$$0.33 < \frac{D_{agit,TE}}{D_{tank,TE}}$$

$$\frac{D_{agit,TE}}{D_{tank,TE}} < 0.50$$

Off bottom impeller clearance with respect to diameter of tank

$$0.17 < \frac{c_{agit,TE}}{D_{tank,TE}} < 0.33$$

$$\frac{c_{agit,TE}}{D_{tank,TE}} < 0.33$$

Maceration (MC) – Holding Tank

Parameters:

$moist_{soy,MC}$ = moisture of soy

$D_{soymeal}$ (m) = diameter of soybean meal particles

Δt_{MC} (hrs) = time required for extraction (24 hrs = 1 day)

Equations:

Ethanol requirement in MC:

$$M_{jMCS,ethanol} = M_{jMCF,k} * 8.774 \frac{kg}{hr}$$

Water requirement in MC:

$$M_{jMCS,water} = M_{jMCF,k} * 2.780 \frac{kg}{hr}$$

Volume of liquid (Batch):

$$V_{liq,MC} = \sum_{j \in Jin,i} \frac{M_{j,k}}{\rho_j} * \Delta t_{MC} \, ; \forall \, j \in J^{MC}, k \in K^{MC,Effluent}$$

Volume of Tank

$$V_{tank,MC} = 1.3 * V_{liq,MC}$$

Costing Variable:

Costing variable of Cone Tank

$$QS_{tank,MC} = V_{tank,MC}$$

Combined costing variable of tank

$$Qc_{MC} = QS_{tank,MC}$$

Sedimentation (SDM)

Parameters

θ_i^R (hr) = residence time in technology *i* (0.5 hrs)

η_{SDM} = efficiency of removal in typical sedimentation unit (75%)

Pur_{SDM} = purity of liquid

DpS (m) = diameter of the particles in sedimentation process

$\mu_{liq,SDM}$ (Pa*s) – viscosity of the liquid

Settling velocity (evaluated parameter**):**

$$U_{S,SDM} = \frac{gD_p^2(\rho_s - \rho_L)}{18\mu_{liq,SDM}}$$

$U_{S,SDM}$ – settling velocity (m/s)

D_p – particle diameter (m)

g – acceleration due to gravity (m/s^2)

ρ_s – density of solid (kg/m^3)

ρ_l – density of liquid (kg/m^3)

μ_{liq} – viscosity of fluid (N-s/m^2)

Equations

Efficiency:

$$\eta_{SDM} = \frac{M_{jSDMS,kSld}}{M_{jSDMF,kSld}}$$

Rewritten as:

$$\eta_{SDM} * M_{jSDMF,kSld} = M_{jSDMS,kSld}$$

Concentration factor: (volume concentration factor)

$$CF_{SDM} = \frac{\sum_{k\in K_j, j\in jSDMF}\left(\frac{M_{j,k}}{\rho_k}\right)}{\sum_{k\in K_j, j\in jSDME}\left(\frac{M_{j,k}}{\rho_k}\right)}$$

$$1.01 \leq CF_{SDM}$$

$$CF_{SDM} \leq 15$$

Surface overflow rate:

$$SOR_{SDM} = U_{S,SDM} * \eta_{SDM}$$

Area of sedimentation tank:

$$A_{SDM} = \frac{\sum_{k\in K_j\ j\in jSDMF}\left(\frac{M_{j,k}}{\rho_k}\right)}{SOR_{SDM}}$$

Rewritten as:

$$A_{SDM} * SOR_{SDM} = \sum_{k\in K_j\ \ j\in jSDMF}\left(\frac{M_{j,k}}{\rho_k}\right)$$

Filtration 1 (FLT,1)

Parameters

$\xi_{k,FLT1}$ - Retention factor of component k in FLT,1

ζ_{FLT1} - Flux through the membrane in FLT,1

CPM_{FLT1} – Cost per membrane in FLT,1

Equations

Retention factor:

$$\xi_{k,FLT1} = \frac{M_{jFLIT1E,k}}{M_{jFLIT1F,k}}; \forall k \in K_j$$

Concentration factor:

$$CF_{FLT} = \frac{\sum_{k\in K_j, j\in jFLIT1F}\left(\frac{M_{j,k}}{\rho_k}\right)}{\sum_{k\in K_j, j\in jFLIT1E}\left(\frac{M_{j,k}}{\rho_k}\right)}$$

$$2 \leq CF_{FLT1} \leq 30$$

Flux balance:

$$\zeta_{FLT1} Q_{C_{FLT_1}} = \sum_{k\in K_j, j\in jFLIT1F}\left(\frac{M_{j,k}}{\rho_k}\right)\left(1 - \frac{1}{CF_{FLT1}}\right)$$

Power required:

$$PW_{FLT1} = Wsp_{FLT1} Qc_{FLT1}$$

Centrifugation (CNF)

Parameters

$\eta_{CNF,soy}$ = efficiency of solid removal

$\eta_{CNF,solvent}$ = efficiency of solvent removal

U_{CNF} = sigma factor

Equations

Efficiency Equation:

$$\eta_{CNF,soy} = \frac{M_{jCNFE,kSld}}{M_{jCNFF,kSld}}$$

$$\eta_{CNF,solvent} = \frac{M_{jCNFE,kSol}}{M_{jCNFF,kSol}}$$

Concentration Factor:

$$CF_{CNF} = \frac{\left[\sum_{k\in K_j, j\in jCNFF}\left(\frac{M_{j,k}}{\rho_k}\right)\right]}{\left[\sum_{k\in K_j j\in jCNFE}\left(\frac{M_{j,k}}{\rho_k}\right)\right]}$$

$$2 \leq CF_{CNF} \leq 20$$

Sigma Factor Equation:

$$Qc_{CNF}U_{CNF} = \left[\sum_{k\in K_j j\in jCNFF}\left(\frac{M_{j,k}}{\rho_k}\right)\right]$$

Power Required:

$$PW_{CNF} = Wsp_{CNF}\left[\sum_{k\in K_j, j\in jCNFF}\left(\frac{M_{j,k}}{\rho_k}\right)\right]$$

Power dissipation to heat it about 40%, therefore cooling duty is required:

$$Mcw_{CNF}c_{pw}\left(T_{cw,out} - T_{cw,in}\right) = 0.4PW$$

Dryer 1 (DRY,1)

Parameters

η_{DRY1} = Dryer efficiency (99%)

$Cp_{rfg,DRY1}$ = Heat capacity of refrigerant (12 kJ/kg*K)

U_{DRY1} = Heat transfer coefficient (180 kJ/(m^2*K*hr))

Equations

Solvents removed by sublimation:

$$\sum\nolimits_{k\in K^{OTP}} M_{jDRY1S,k} = \eta_{DRY1} * \sum\nolimits_{k\in K^{OTP}} M_{jDRY1F,k} \,; \forall\, k \in K_j$$

Energy required for sublimation:

$$Q_{sub,DRY1} = \sum\nolimits_{k\in K^{OTP}} M_{jDRY1S,k} * [Cp_k * \left(T_{frz} - T_{amb}\right) + H_{sub,k}]; \forall k \in K_j$$

Refrigerant required for freezing:

$$Q_{sub,DRY1} = M_{rfg,DRY1} * Cp_{rfg,DRY1} * (T_{rfg,out} - T_{rfg,in})$$

Dryer Area:

$$Q_{sub,DRY1} = U_{DRY1} * A_{DRY1} * (T_{amb} - T_{rfg,out})$$

Capacity of the dryer:

$$Q_{c,DRY1} = \sum\nolimits_{k\in K} M_{jDRY1S,k}$$

Power required:

$$PW_{DRY1} = Wsp_{DRY1} * A_{DRY1}$$

Acid Hydrolysis (AHY)

Parameters

Y_{AHY} (%) = Release parameters

Frc_k (unitless) = Fraction of component k

$\phi_{add,Acid}$ (kg/kg) = Acid addition amounts for hydrolysis

π_{Acid} (\$/unit) = Unit price of acid

Wsp_{AHY} (kW) = Power required by acid hydrolysis

λ_{stm}(kJ/kg) = Latent heat of steam

T_{AHY}(°C) = Required temperature for acid hydrolysis

T_{amb}(°C) = Ambient temperature

Equations

Component Release Equation:

$$M_{jAHYE,k} = Y_{AHY} Frc_k M_{jAHYF,k}; \forall k \in \boldsymbol{K}$$

Acid added:

$$M_{jAHYA,Acid} = \phi_{add,Acid} \sum\nolimits_{k \in \boldsymbol{K}} M_{jAHYF,k}$$

Acid cost:

$$Cpr_{Acid} = \pi_{Acid} \, M_{jAHYA,Acid}$$

Costing variables

$$Qc_{ahy} = \sum\nolimits_{k \in \boldsymbol{K}} \left(\frac{M_{jAHYE,k}}{\rho_k} \right)$$

Power required:

$$PW_{AHY} = Wsp_{AHY} Qc_{AHY}$$

Steam required for heating to hydrolysis temperature:

$$Mstm_{ahy}\lambda_{stm} = \left[\sum_{k\in\boldsymbol{K}}(M_{jAHYF,k}Cp_k) + M_{jAHYA,Acid}Cp_{Acid}\right](T_{AHY} - T_{amb})$$

Neutralization (NT)

Parameters

θ_{NT} (h) = Residence time in neutralization (0.5 hrs)

Equations

Moles of acid in:

$$N_{in,HCl} = \frac{M_{jAHYA,HCl} * 1000\,\frac{mol}{kmol}}{MW_{HCl}}$$

Moles of base required (theoretical):

$$N_{base,req} = N_{in,HCl}$$

Mass of base required:

$$M_{jNTB,base} = \frac{N_{base,req} * MW_{base}}{1000\,\frac{g}{kg}}$$

Moles of Acid in:

$$N_{in,HCl} = \frac{M_{jNTF,HCl} * 1000\,\frac{mol}{kmol}}{MW_{HCl}}$$

Cost of Base:

$$C_{pr,Base} = C_{Base} * M_{26,Base}$$

Volume (costing variable) of bleaching:

$$Q_{c_{NTBL}} = \theta_{NT} * \sum\nolimits_{k \in k_j} \left(\frac{M_{jNTE,k}}{\rho_k}\right)$$

Power required in neutralization:

$$PW_{NT} = Wsp_{NT} * Q_{c_{NT}}$$

Filtration 2 (FLT,2)

Parameters

$\xi_{k,FLT2}$ - Retention factor of component k in FLT,2

ζ_{FLT2} - Flux through the membrane in FLT,2

CPM_{FLT2} – Cost per membrane in FLT,2

Equations

Retention factor:

$$\xi_{k,FLT2} = \frac{M_{jFLT2E,k}}{M_{jFLT2F,k}} ; \forall k \in K_j$$

Concentration factor:

$$CF_{FLT2} = \frac{\sum_{k\in K_j, j\in jFLT2F}\left(\frac{M_{j,k}}{\rho_k}\right)}{\sum_{k\in K_j, j\in jFLT2E}\left(\frac{M_{j,k}}{\rho_k}\right)}$$

$$2 \le CF_{FLT2} \le 30$$

Flux balance:

$$\zeta_{FLT2} Q_{C_{FLT_2}} = \sum_{k\in K_j, j\in jFLT2F}\left(\frac{M_{j,k}}{\rho_k}\right)\left(1 - \frac{1}{CF_{FLT2}}\right)$$

Power required:

$$PW_{FLT2} = Wsp_{FLT2} Qc_{FLT2}$$

Crystallization (CRYS)

Parameters

$\phi_{add,antisolv}$ (kg/kg) = Amount of antisolvent added with respect to feed

$\pi_{antisolv}$ (\$/unit) = Unit price of antisolvent

Wsp_{CRYS}= Power required by the technology (kWh)

T_{ann} (hr) = Hours of operation annually

$Q0_{CRYS}$ (m^3) = Standard capacity of a technology for costing, labor and power required– Source: SuperPro

$C0_{CRYS}$ (\$) = Standard cost

Equations

Antisolvent required for precipitation

$$M_{jCRYSA,antisolv} = \phi_{add,antisolv} * M_{jCRYSF,k}$$

Antisolvent cost:

$$C_{pur,antisolv} = \pi_{antisolv} M_{jCRYSA,antisolv}$$

Costing variables:

$$Qc_{CRYS} = \left[\sum_{k \in \boldsymbol{K}} \left(\frac{M_{jCRYSE,k}}{\rho_k}\right)\right]$$

Power required in crystallization (kW):

$$PW_{CRYS} = Wsp_{CRYS} Qc_{CRYS}$$

Filtration 3 (FLT,3)

Parameters

$\xi_{k,FLT3}$ - Retention factor of component k in FLT3

ζ_{FLT3} - Flux through the membrane in FLT3

CPM_{FLT3} – Cost per membrane in FLT3

Equations

Retention factor:

$$\xi_{k,FLT3} = \frac{M_{jFLT3E,k}}{M_{jFLT3F,k}}; \forall k \in K_j$$

Concentration factor:

$$CF_{FLT3} = \frac{\sum_{k\in K_j, j\in jFLT3F}\left(\frac{M_{j,k}}{\rho_k}\right)}{\sum_{k\in K_j, j\in jFLT3E}\left(\frac{M_{j,k}}{\rho_k}\right)}$$

$$2 \leq CF_{FLT3} \leq 30$$

Flux balance:

$$\zeta_{FLT3} Q_{C_{FLT3}} = \sum_{k\in K_j, j\in jFLT3F}\left(\frac{M_{j,k}}{\rho_k}\right)\left(1 - \frac{1}{CF_{FLT3}}\right)$$

Power required:

$$PW_{FLT3} = Wsp_{FLT3} Qc_{FLT3}$$

Organic Solvent Nanofiltration (OSN) / Nanofiltration (NF)

Parameters

$\xi_{k,NF}$ - Retention factor of component k in NF

ζ_{NF} - Flux through the membrane in NF

CPM_{NF} – Cost per membrane in NF

Equations

Retention factor:

$$\xi_{k,NF} = \frac{M_{jNFE,k}}{M_{jNFF,k}}; \forall k \in K_j$$

Concentration factor:

$$CF_{NF} = \frac{\sum_{k \in K_j, j \in jNFF} \left(\frac{M_{j,k}}{\rho_k}\right)}{\sum_{k \in K_j, j \in jNFR} \left(\frac{M_{j,k}}{\rho_k}\right)}$$

$$2 \leq CF_{NF} \leq 30$$

Flux balance:

$$\zeta_{NF} Q_{C_{NF}} = \sum_{k \in K_j, j \in jNFE} \left(\frac{M_{j,k}}{\rho_k}\right) \left(1 - \frac{1}{CF_{NF}}\right)$$

Power required:

$$PW_{NF} = Wsp_{NF} Qc_{NF}$$

Chromatography (CHRM)

Parameters

θ_{CHRM} (h) = Residence time in chromatography (0.5)

ρ_k (kg/m^3) = Density of component k

κc_{CHRM} = Capacity factor

w_{CHRM} (m) = Width of chromatogram (0.05)

$HETP_{CHRM}$ (m) = Height equivalent to theoretical plates (0.0035)

$R_{LD,CHRM}$ = Ratio of length to diameter (0.14)

Equations

Retention Time:

$$\tau R_{CHRM} = (1 + \kappa c_{CHRM})\theta_{CHRM}$$

Number of plates:

$$Np_{CHRM} = 16 * \left(\frac{\tau R_{CHRM}}{w_{CHRM}}\right)^2$$

Length of column:

$$L_{CHRM} = HETP_{CHRM} * Np_{CHRM}$$

Diameter of column:

$$R_{DL,CHRM} = \frac{D_{CHRM}}{L_{CHRM}}$$

Volume of column:

$$V_{CHRM} = \frac{\pi}{4} D_{CHRM}^2 L_{CHRM}$$

Solvents and other components removed by chromatography:

$$\sum\nolimits_{k \in K^{OTP}} M_{jCHRMR,k} = \kappa c_{CHRM} \sum\nolimits_{k \in K^{OTP}} M_{jCHRMF,k}$$

Product not retained by chromatography:

$M_{jCHRME,Prd} = M_{jCHRMF,Prd}$

Number of columns required:

$N_{col,CHRM} V_{CHRM} = \theta_{CHRM} * \sum_{k \in k_j} \left(\frac{M_{jCHRMF,k}}{\rho_k} \right)$

Total volume (costing variable) for chromatography:

$$Qc_{CHRM} = N_{col,CHRM} * V_{CHRM}$$

Power required:

$$PW_{CHRM} = Wsp_{CHRM} Qc_{CHRM}$$

Dryer 2 (DRY,2)

Parameters

η_{DRY2} = Dryer efficiency (99%)

$Cp_{rfg,DRY2}$ = Heat capacity of refrigerant (12 kJ/kg*K)

U_{DRY2} = Heat transfer coefficient (180 kJ/(m^2*K*hr))

Equations

Solvents removed by sublimation:

$$\sum\nolimits_{k \in K^{OTP}} M_{jDRY2S,k} = \eta_{DRY2} * \sum\nolimits_{k \in K^{OTP}} M_{jDRY2F,k} \, ; \forall \; k \in K_j$$

Energy required for sublimation:

$$Q_{sub,DRY2} = \sum\nolimits_{k \in K^{OTP}} M_{jDRY2E,k} * [Cp_k * \left(T_{frz} - T_{amb}\right) + H_{sub,k}]; \forall k \in K_j$$

Refrigerant required for freezing:

$$Q_{sub,DRY2} = M_{rfg,DRY2} * Cp_{rfg,DRY2} * (T_{rfg,out} - T_{rfg,in})$$

Dryer Area:

$$Q_{sub,DRY2} = U_{DRY2} * A_{DRY2} * (T_{amb} - T_{rfg,out})$$

Capacity of the dryer:

$$Q_{c,DRY2} = \sum\nolimits_{k \in K} M_{jDRY2S,k}$$

Power required:

$$PW_{DRY2} = Wsp_{DRY2} * A_{DRY2}$$

A.4 Model Specifications and Input Data (Standard Capacities and Costs, Parameters, Feed Compositions)

Table A.4.1.

Table for Standard Capacity, Costs, Scaling Factors, Labor Requirements for Technologies

Unit operation (costing capacity)	Standard capacity (units)	Base costs (million $)	Scaling exponent (n)	Laborers required (#/hr)	Power required (kW/capacity)	Consumable Costs ($/unit)
Grinder (Volume)	60,000 kg/hr	0.073	0.67	1	0	0
Turbo-Extraction (Volume)	80 m^3	0.185	0.67	1	0.1	0
Maceration (Volume)	80 m^3	0.185	0.67	1	0	0
Ultrasound-Assisted Extraction (Volume)	2000 m^3	0.2	0.67	1	17,280,000	0
Supercritical Fluid Extraction (Volume)	40 m^3	0.532	0.67	1	0.1	0
Centrifugation (Sigma factor)	60,000 m^2	0.66	0.67	1	19.2	0
Filtration 1 (Area)	80 m^2	0.082	0.67	1	0	400 ($/$m^2$)
Sedimentation (Area)	2500 m^2	0.0261	0.67	1	0.33	400 ($/$m^2$)[c]
Dryer 1	600 kg/cycle	0.107	0.67	1	0.3	0
Acid hydrolysis (Volume)	80 m^2	0.379	0.67	1	0.2	0.175
Neutralization (Volume)	0.27 m^3	0.1	0.67	1	0	0.35
Filtration 2 (Area)	80 m^2	0.082	0.67	0.5	0	400 ($/$m^2$)
Crystallization (Volume)	40 m^3	0.474	0.67	0.5	0.1	0.5
Filtration 3 (Area)	80 m^2	0.082	0.67	0.5	0	400 ($/$m^2$)
Nanofiltration (Area)	80 m^2	0.082	0.67	1	0	400 ($/$m^2$)
Chromatography (Volume)	0.633 m^3	0.775	0.67	1	0.33	0
Dryer 2	600 kg/cycle	0.107	0.67	1	0.3	0

A.5. Calculations for Solvent Recovery after DRY,1

Temperature of the vapor exiting Dryer 1

During the extraction stage in Dryer 1 (DRY,1) unit, the exiting stream contains a large amount of recoverable solvents (ethanol and water mixture) in vapor phase. The solid-vapor mixture in the freeze dryer was analyzed to find the equilibrium temperature.

In equilibrium condition, the fugacity of the vapor and solid phases are equivalent, as shown in Equation A.5.1.

$$\widehat{f_i}^{v} = \hat{f_i}^{s} \tag{A.5.1}$$

Equation A.5.2 displays the Poynting correction factor used to estimate the solid phase fugacity. The operating pressure was assumed to be low enough to allow the exponential term to be equivalent to 1. Therefore, the fugacity of the component can be assumed to be equal to its vapor pressure.

$$\hat{f_i}^{s} = \hat{f_i}^{sat} \exp\left\{\frac{\underline{V}(P - P^{sat})}{RT}\right\} \tag{A.5.2}$$

The vapor phase fugacity was calculated using the Peng-Robinson equation of state for a mixture, as shown in Equation A.5.3.

$$\begin{aligned} \ln\frac{\widehat{f_i}^{v}(T,P,\underline{y})}{y_iP} &= ln\widehat{\emptyset_i^v}\left(T,P,\underline{y}\right) \\ &= \frac{B_i}{B_{mix}}(Z_{mix}^v - 1) - \ln(Z_{mix}^v - B_{mix}) \\ &- \frac{A_{mix}}{2\sqrt{2}B_{mix}}\left[\frac{2\sum_j y_jA_{ij}}{A_{mix}} - \frac{B_i}{B_{mix}}\right]\ln\left[\frac{Z_{mix}^v + \left(1+\sqrt{2}\right)B_{mix}}{Z_{mix}^v + \left(1-\sqrt{2}\right)B_{mix}}\right] \end{aligned} \tag{A.5.3}$$

Where A_{ij} is the binary interaction coefficient of the mixture. This parameter was estimated used the critical volumes of the two components and using the following Equations A.5.4 and A.5.5.

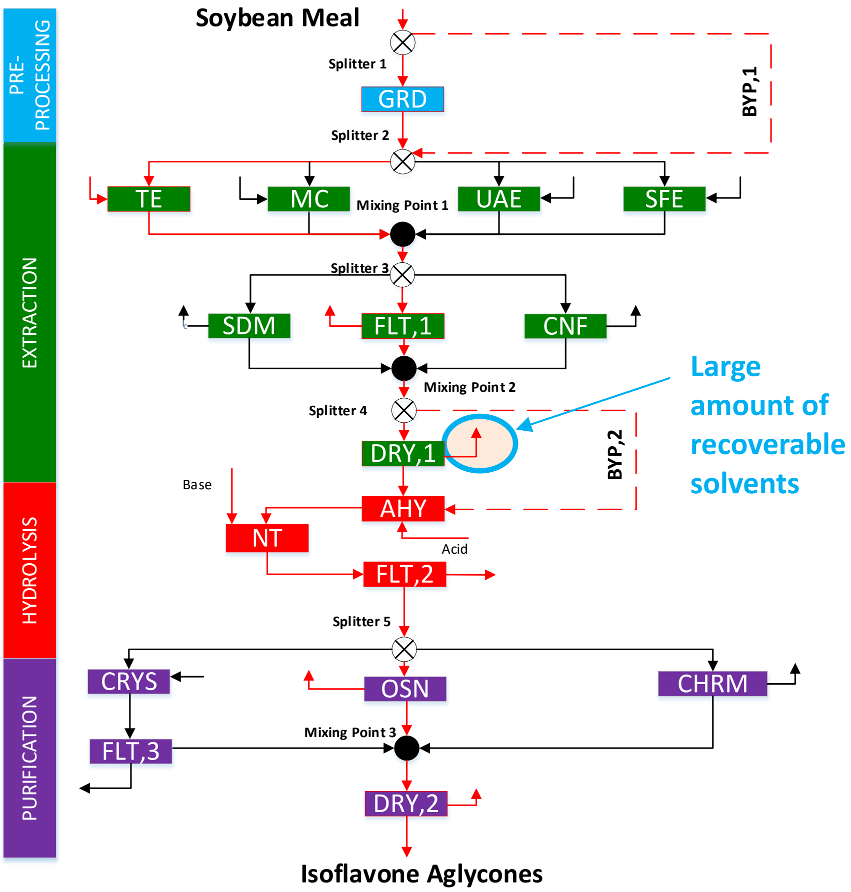
$$A_{ij} = \sum_i \sum_j x_ix_j\sqrt{A_iA_j}\left(1 - k_{ij}\right) \tag{A.5.4}$$

$$k_{ij} = 1 - \left[\frac{2\sqrt{v_{ci}^{\frac{1}{3}} v_{cj}^{\frac{1}{3}}}}{v_{ci}^{\frac{1}{3}} + v_{cj}^{\frac{1}{3}}} \right]^{n} \tag{A.5.5}$$

The value of n is set to 1.2. However, the exponent value can be changed to tune the results to data if available.

A.6. Solvent Recovery Cost Calculations

ASPEN Plus was used to obtain the heat duty for a total condenser. The design of the condenser was completed using the following modeling approach.



A shell and tube heat exchanger in the countercurrent configuration was modeled using the log-mean temperature difference approach. All process variables are outlined and defined in Appendix A.2. The heat transfer Q is modeled using Equation A.6.1, describing the heat transfer from the hot fluid, cold fluid, and exchanger design from left to right.

$$Q = \dot{m}_h C_{ph} \Delta T_h = \dot{m}_c C_{pc} \Delta T_c = U_o A \Delta T_{lm} \tag{A.6.1}$$

The exchanger area needed to affect the heat transfer specified by the temperature change of the hot and cold fluids is calculated as a function of the overall heat transfer coefficient U_o, the log-mean temperature difference ΔT_{LM}, and the correction factor F. The area calculation is shown in Equation A.6.2.2.

$$Minimize\ A = \frac{Q}{U_o \Delta T_{LM} F} \tag{A.6.2}$$

The ΔT_{lm} for the overall heat transfer is calculated using Equation A.6.3.

$$\Delta T_{lm} = \frac{(T_1 - t_2) - (T_2 - t_1)}{\ln(\frac{T_1 - t_2}{T_2 - t_1})} \tag{A.6.3}$$

To calculate the log-mean temperature correction factor, Equations A.6.4 and A.6.5 were evaluated.

$$R = \frac{(T_1 - T_2)}{(t_2 - t_1)} \tag{A.6.4}$$

$$S = \frac{(t_2 - t_1)}{(T_1 - t_1)} \tag{A.6.5}$$

With R and S, the log-mean temperature correction factor for a 1-shell 2-tube pass countercurrent heat exchanger is calculated using Equation A.6.6.

$$F = \frac{\sqrt{(R^2 + 1)}\, ln\frac{(1 - S)}{(1 - RS)}}{(R - 1) ln\left[\frac{2 - S[R + 1 - \sqrt{(R^2 + 1)}]}{2 - S[R + 1 + \sqrt{(R^2 + 1)}]}\right]} \tag{A.6.6}$$

The overall heat transfer coefficient U_o was calculated using the relationship between the heat exchanger geometry and the heat duty determined from ASPEN Plus. The total shell-side and tube-side areas were represented by Equations A.6.2.7 and A.6.2.8 respectively.

$$A_s = \frac{(P_t - d_o) D_s l_b}{P_t} \tag{A.6.7}$$

$$A_T = \frac{N_T}{n} \frac{\pi}{4} {d_i}^2 \tag{A.6.8}$$

The equivalent diameter of the shell side is needed to calculate heat transfer coefficients. The shell-side equivalent diameter for triangular pitch tube layouts is shown in Equation A.6.9.

$$d_e = \frac{1.1026\, {p_t}^2}{d_o} - d_o \tag{A.6.9}$$

GAMS was used to determine the minimum area needed to fulfill the required heat duties to convert the vaporized solvent into liquid phase for reuse. The cost of the condenser was done using the same set of equations as the other extraction and purification technologies.

A.6.1. Summary of Variables

Table A.6.1.

Overall Shell-and-Tube Heat Exchanger Variables

Overall Variables	Symbol	Unit
Log Mean Temperature	ΔT_{LM}	-
Ratio of Thermal Capacities	R	-
Temperature Efficiency	S	-
Correction Factor	F	-
Heat Transfer Rate	Q	W
Overall Heat Transfer Coefficient	U_o	W/m^{2}K
Length of Heat Exchanger	L	m
Baffle Spacing	l_B	in

Table A.6.2.

Shell-Side Shell-and-Tube Heat Exchanger Variables

Definition	Symbol	Unit
Equivalent Diameter	d_e	in
Shell Diameter	D_s	in
Flow Area	A_s	m^2
Shell Side Fluid Inlet Temperature	t_1	℃
Shell Side Fluid Outlet Temperature	t_2	℃

Table A.6.3.

Tube-Side Shell-and-Tube Heat Exchanger Variables

Tube-Side Variables	Symbol	Unit
Number of Tubes	N_T	-
Inner Diameter	d_i	in
Flow Area	A_T	m^2
Tube Side Fluid Inlet Temperature	T_1	℃
Tube Side Fluid Outlet Temperature	T_2	℃

A.7. General Algebraic Modeling Systems (GAMS) Codes

This section contains the information regarding the codes used to calculate the base case with a feed flow rate of 1000 kg/hr with and without material recovery.
A data repository containing all of the necessary files to run these codes is available at: https://github.com/jdchea95/isoflavoneextraction

A.8. Process Flow Diagram of Isoflavone Extraction

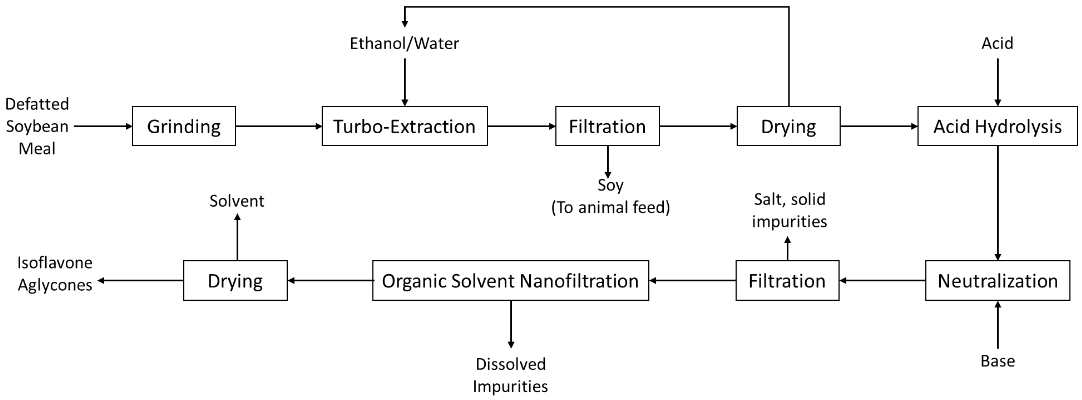
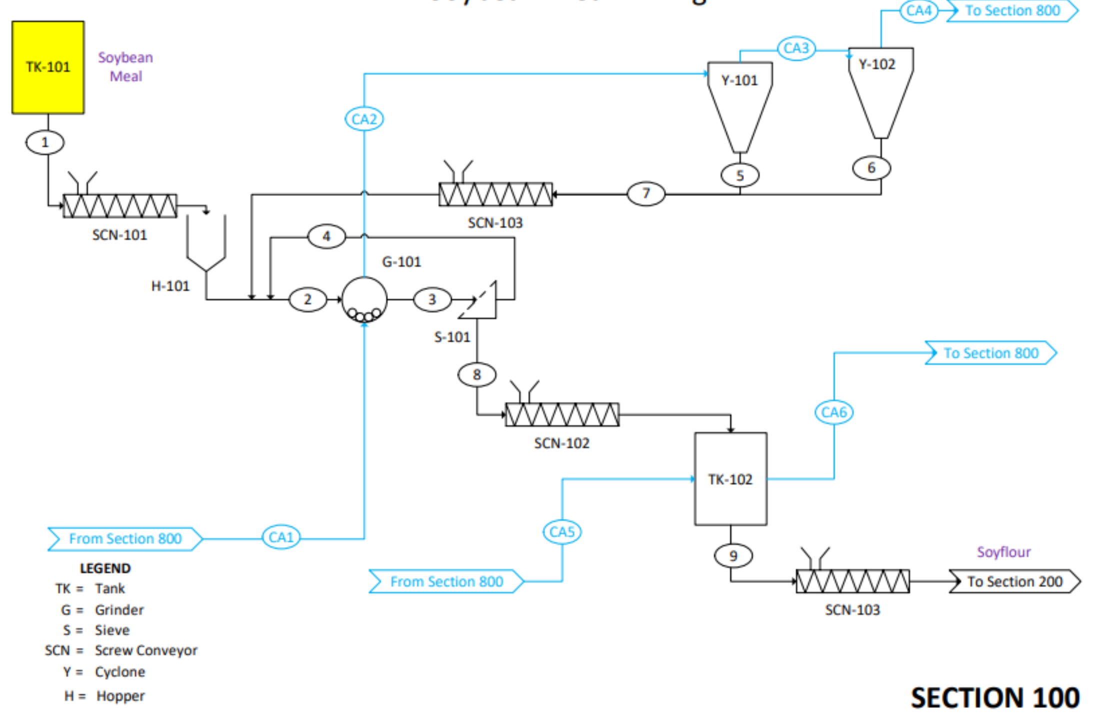


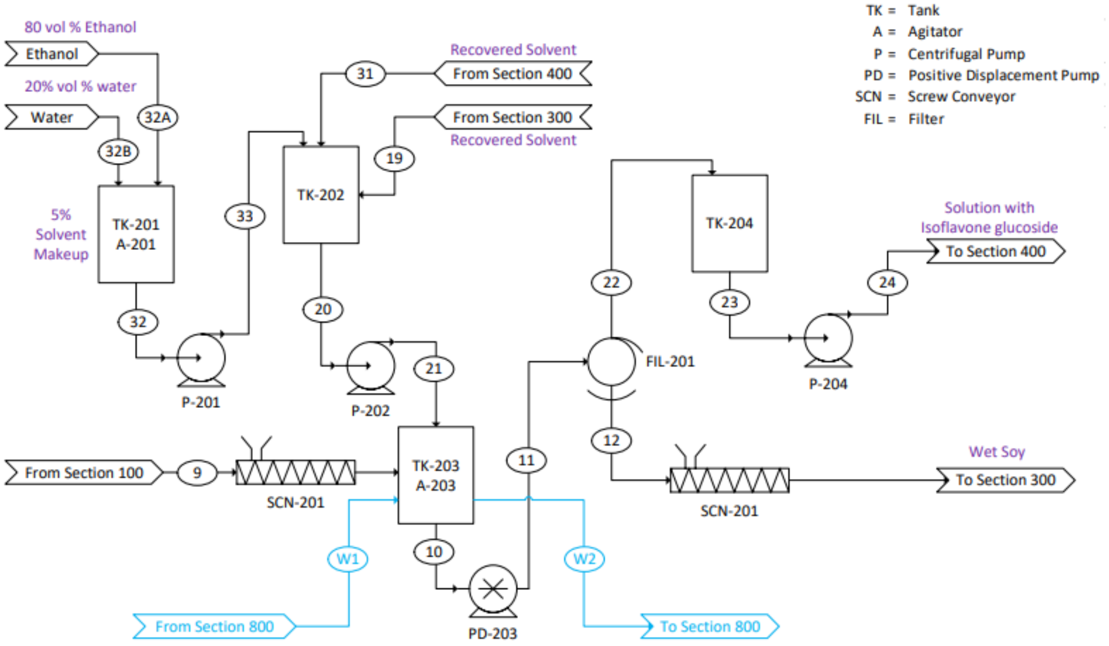
Figure A.8.1 Block flow diagram of commercial scale isoflavone extraction from defatted soybean meal, as determined from the superstructure approach in Chapter 3

The subsequent diagrams (Sections 100 – 800) transformed Figure A.8.1 to a process flow diagram with all the major streams required.

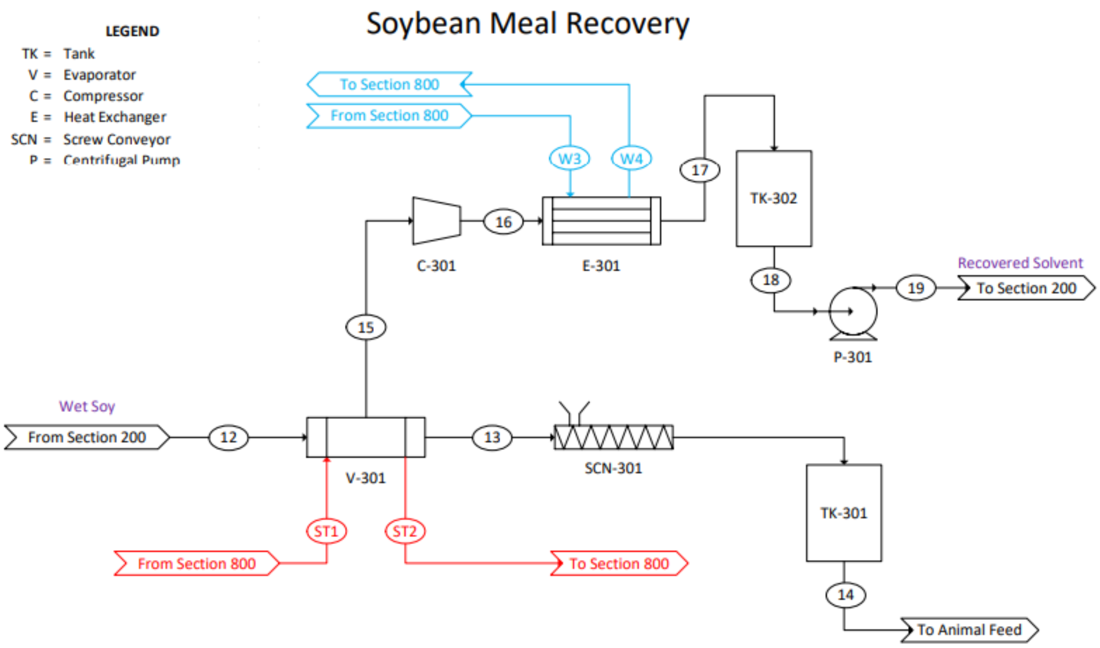
Soybean Meal Milling



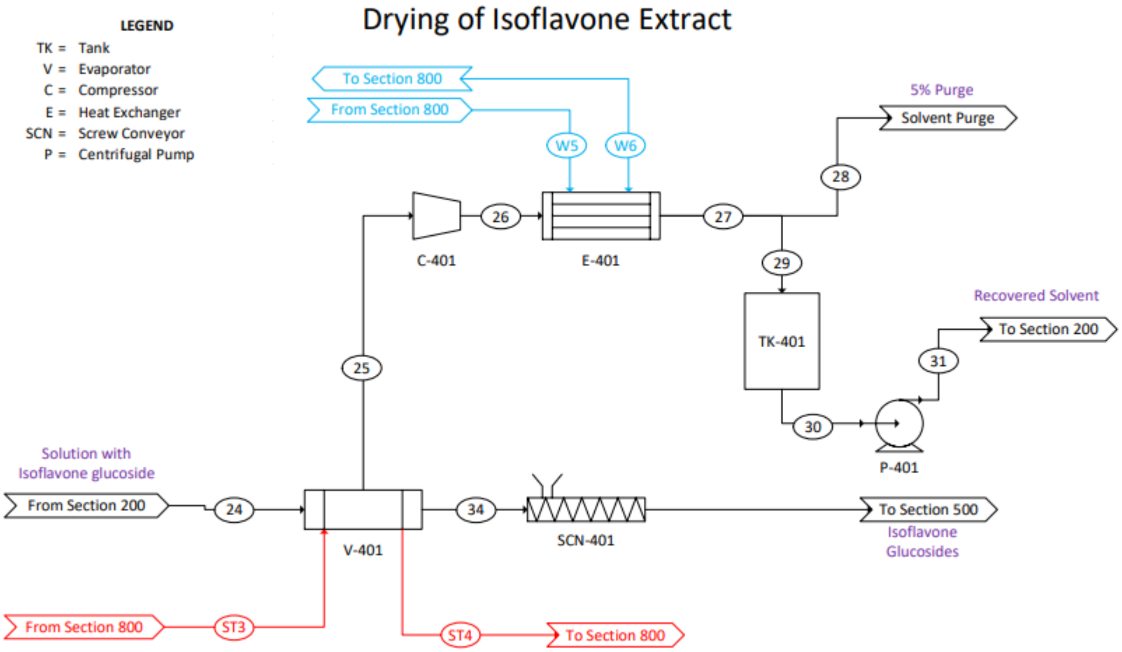
Extraction



SECTION 200

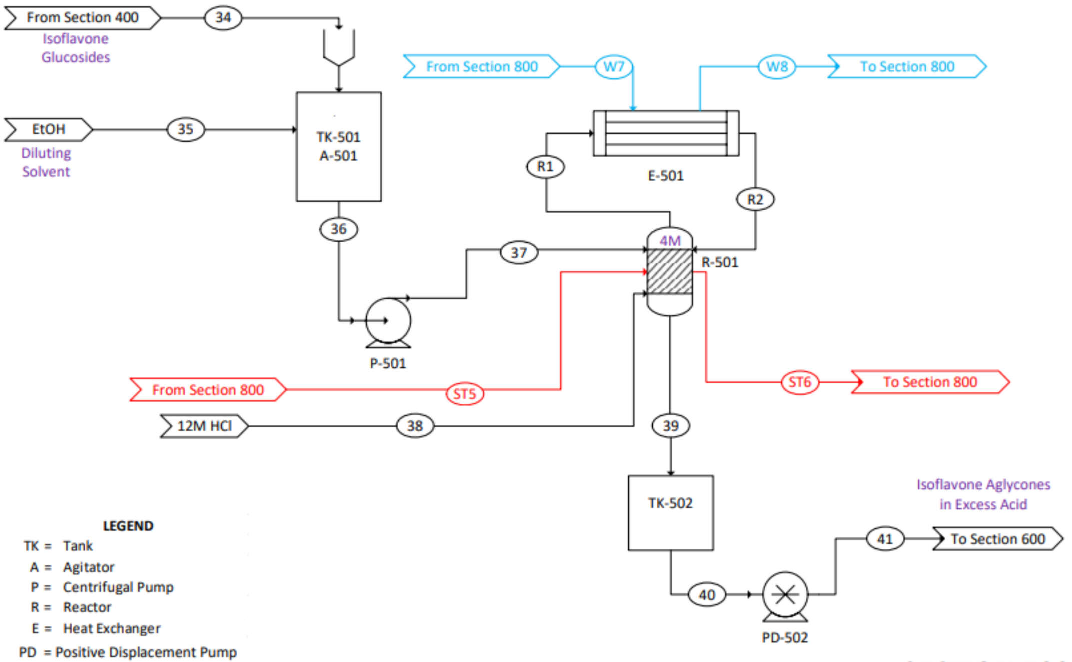


SECTION 300



SECTION 400

Acid Hydrolysis

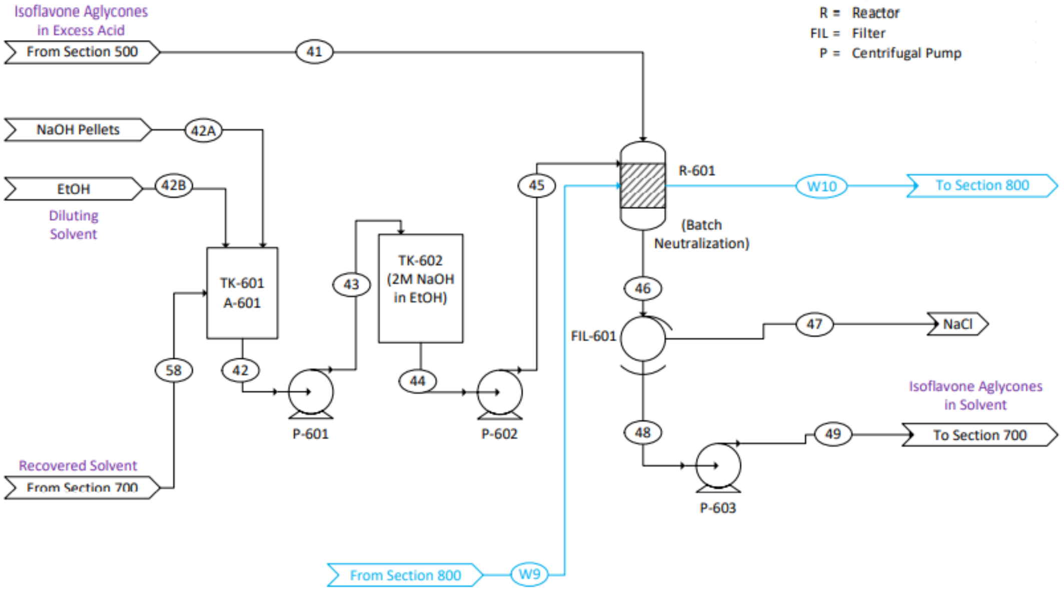


LEGEND
TK = Tank
A = Agitator
P = Centrifugal Pump
R = Reactor
E = Heat Exchanger
PD = Positive Displacement Pump

SECTION 500

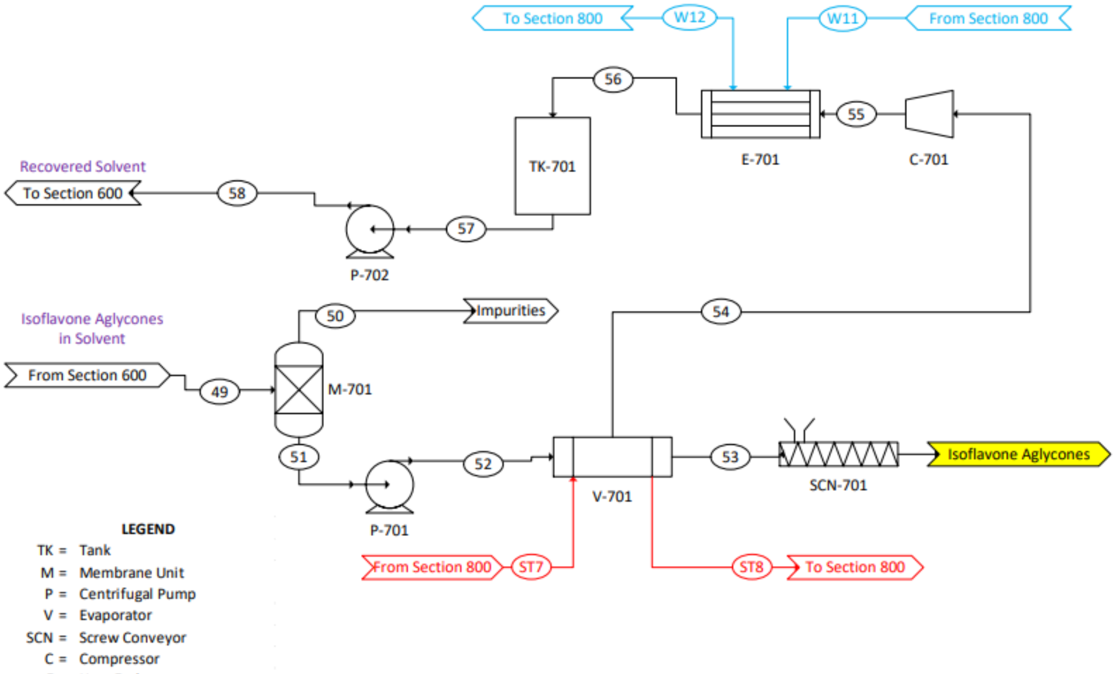
Post-Hydrolysis Neutralization

LEGEND
TK = Tank
A = Agitator
R = Reactor
FIL = Filter
P = Centrifugal Pump



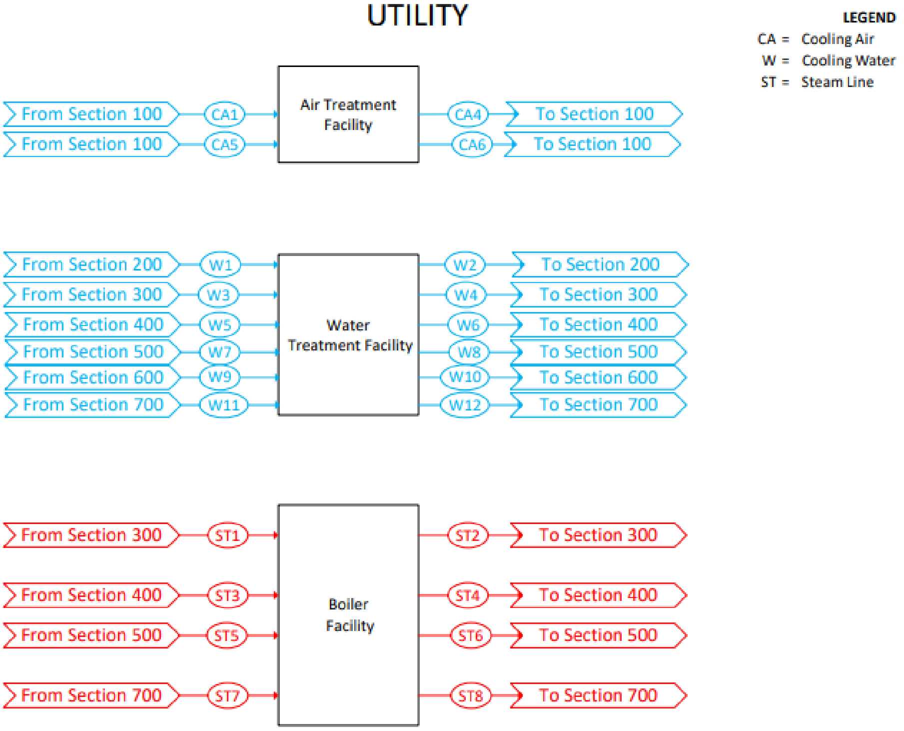
SECTION 600

Purification and Drying



SECTION 700

UTILITY



SECTION 800

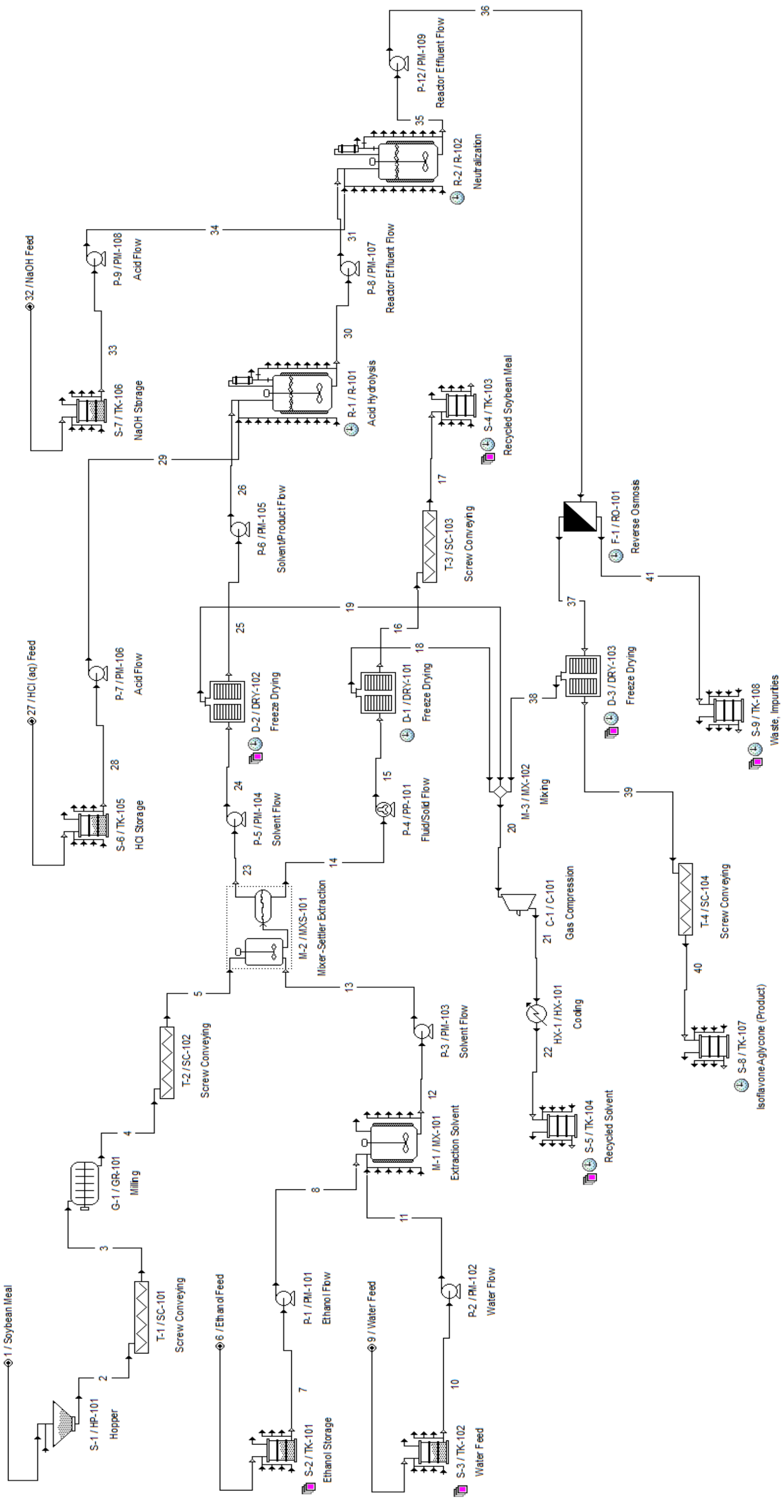


Figure A.8.2. Simulated process flow diagram of isoflavone extraction in SuperPro Designer v12

Table A.8.

A Summary of the Process Units and Operating Condition Illustrated in Figure A.8.2

Unit/Stream	**Function**	**Operating Temperature (°C)**	**Operating Pressure (bar)**	**Power (kW)**
HP-101 (Hopper)	Store and feed soybean meal to a screw conveyor (SC-101)	25	1.01	0
➢ Stream 1	Input of HP-101	25	1.01	
➢ Stream 2	Output of HP-101	25	1.01	
SC-101 (Screw Conveyor)	Transfer solid soybean meal to GR-101	25	1.01	0
➢ Stream 2	Input of SC-101	25	1.01	
➢ Stream 3	Output of SC-101	25	1.01	
GR-101 (Grinder)	Breaks down soybean meal to soyflour with cooling	25	1.01	0
➢ Stream 3	Input of GR-101	25	1.01	
➢ Stream 4	Output of GR-101	25	1.01	
SC-102 (Screw Conveyor)	Transfers solid soybean flour to MSX-101	25	1.01	0
➢ Stream 4	Input of SC-102	25	1.01	
➢ Stream 5	Output of SC-102	25	1.01	
TK-101 (Ethanol Storage)	Holding/Storage tank for pure ethanol feed, to be pumped to MX-101 via pump PM-101	25	1.01	0
➢ Stream 6	Input of TK-101	25	1.01	
➢ Stream 7	Output of TK-101	25	1.01	
PM-101 (Centrifugal Pump)	Pumps ethanol to MX-101	25	2.01	0.44
➢ Stream 7	Input of PM-101	25	1.01	
➢ Stream 8	Output of PM-101	25	2.01	
TK-102 (Water Storage)	Holding/Storage tank for pure water feed, to be pumped to MX-101 via pump PM-102	25	1.01	0
➢ Stream 9	Input of TK-102	25	1.01	
➢ Stream 10	Output of TK-102	25	1.01	

Unit/Stream	Function	Operating Temperature (°C)	Operating Pressure (bar)	Power (kW)
PM-102 (Centrifugal Pump)	Pumps water to MX-101	25	2.01	0.11
➢ Stream 10	Input of PM-102	25	1.01	
➢ Stream 11	Output of PM-102	25	2.01	
MX-101 (Extraction Solvent Mixing)	Mixes pure ethanol and water	25	2.01	0 (Based on Utility)
➢ Stream 8	Input of MX-101	25	2.01	
➢ Stream 11	Input of MX-101	25	2.01	
➢ Stream 12	Output of MX-101	25	2.01	
PM-103 (Centrifugal Pump)	Pumps extraction solvent to MX-101	25	3.01	0.55
➢ Stream 12	Input of PM-103	25	2.01	
➢ Stream 13	Output of PM-103	25	3.01	
MSX-101 (Mixer-Settler Extraction)	Extracts Isoflavone Glucoside	25	1.01	0 (Based on Utility)
➢ Stream 5	Input of MSX-101	25	1.01	
➢ Stream 13	Input of MSX-101	25	3.01	
➢ Stream 14	Output of MSX-101	25	1.01	
➢ Stream 23	Output of MSX-101	25	1.01	
PP-101 (Peristaltic Pump)	Pumps a slurry of solvent/soybean meal/flour to a DRY-101	25	2.01	0.04
➢ Stream 14	Input of PP-101	25	1.01	
➢ Stream 15	Output of PP-101	25	2.01	
DRY-101 (Freeze Dryer)	Separates solvent from wet soybean flour/meal	12	2.01	0 (Based on Utility)
➢ Stream 15	Input of DRY-101	25	2.01	
➢ Stream 16	Output of DRY-101	12	2.01	
➢ Stream 18	Output of DRY-101	12	2.01	
SC-103 (Screw Conveyor)	Transfers dried soybean flour to TK-103	12	2.01	0
➢ Stream 16	Input of SC-103	12	2.01	
➢ Stream 17	Output of SC-103	12	2.01	

Unit/Stream	**Function**	**Operating Temperature (°C)**	**Operating Pressure (bar)**	**Power (kW)**
TK-103 (Soybean flour Storage)	Stores soybean flour to be used in animal feed	12	2.01	0
➢ Stream 17	Input of TK-103	12	2.01	
PM-104 (Centrifugal Pump)	Pumps extractive solution to DRY-102	25	2.01	0.55
➢ Stream 23	Input of PM-104	25	1.01	
➢ Stream 24	Output of PM-104	25	2.01	
DRY-102 (Freeze Dryer)	Separates solvent from the extractive solution	12	2.01	0 (Based on Utility)
➢ Stream 24	Input of DRY-102	25	2.01	
➢ Stream 19	Output of DRY-102	12	2.01	
➢ Stream 25	Output of DRY-102	12	2.01	
MX-102 (Extraction Solvent Mixing)	Mixes recovered solvent	25	2.01	0 (Based on Utility)
➢ Stream 18	Input of MX-102	12	2.01	
➢ Stream 19	Input of MX-102	12	2.01	
➢ Stream 38	Input of MX-102	12	4.20	
➢ Stream 20	Output of MX-102	100	2.01	
C-101 (Gas Compressor)	Compresses solvent gas	25	4.20	515.4
➢ Stream 20	Input of C-101	100	2.01	
➢ Stream 21	Output of C-101	40	7.01	
HX-101 (Cooler)	Condenses solvent gas into liquid for reuse (Total condenser)	25	4.20	0 (Based on Utility)
➢ Stream 21	Input of HX-101	40	7.01	
➢ Stream 22	Output of HX-101	25	7.01	
TK-104 (Recycled Solvent Storage)	Stores recycled solvent for reuse	25	7.01	0
➢ Stream 22	Input of TK-104	25	7.01	
PM-105 (Centrifugal Pump)	Pumps isoflavone glucoside solution to acid hydrolysis (R-101)	12	3.01	0.01
➢ Stream 25	Input of PM-105	12	2.01	
➢ Stream 26	Output of PM-105	12	3.01	

Unit/Stream	**Function**	**Operating Temperature (°C)**	**Operating Pressure (bar)**	**Power (kW)**
TK-105 (Acid Storage)	Holding/Storage tank for Hydrochloric Acid (aq), to be pumped to R-101 via pump PM-106	25	1.01	0
➢ Stream 27	Input of TK-105	25	1.01	
➢ Stream 28	Output of TK-105	25	1.01	
PM-106 (Centrifugal Pump)	Pumps hydrochloric acid to acid hydrolysis (R-101)	12	2.01	0.01
➢ Stream 28	Input of PM-106	25	1.01	
➢ Stream 29	Output of PM-106	25	2.01	
R-101 (Acid Hydrolysis)	Cleaves glucoside link and convert isoflavone glucoside to isoflavone aglycone	70	11.63	0 (Based on Utility)
➢ Stream 26	Input of R-101	12	3.01	
➢ Stream 29	Input of R-101	25	2.01	
➢ Stream 30	Output of R-101	70	11.63	
PM-107 (Centrifugal Pump)	Pumps reactor effluent to neutralization (R-102)	70	12.63	0.01
➢ Stream 30	Input of PM-107	70	11.63	
➢ Stream 31	Output of PM-107	70	12.63	
TK-106 (Base Storage)	Holding/Storage tank for sodium hydroxide (aq), to be pumped to R-102 via pump PM-108	25	1.01	0
➢ Stream 32	Input of TK-106	25	1.01	
➢ Stream 33	Output of TK-106	25	1.01	
PM-108 (Centrifugal Pump)	Pumps reactor effluent to neutralization (R-102)	25	2.01	0.0025
➢ Stream 33	Input of PM-108	25	1.01	
➢ Stream 34	Output of PM-108	25	2.01	

Unit/Stream	**Function**	**Operating Temperature (°C)**	**Operating Pressure (bar)**	**Power (kW)**
R-102 (Neutralization)	Neutralizes excess acid from acid hydrolysis	70	3.20	0 (Based on Utility)
➢ Stream 31	Input of R-102	70	12.63	
➢ Stream 34	Input of R-102	25	2.01	
➢ Stream 35	Output of R-102	25	3.20	
PM-109 (Centrifugal Pump)	Pumps reactor effluent to neutralization (R-102)	25	4.20	0.01
➢ Stream 35	Input of PM-109	25	3.20	
➢ Stream 36	Output of PM-109	25	4.20	
RO-101 (Extraction Solvent Mixing)	Separates impurity and isolate isoflavone aglycones	25	4.20	0 (Based on Utility)
➢ Stream 36	Input of RO-101	25	4.20	
➢ Stream 37	Output/Permeate of RO-101	25	4.20	
➢ Stream 41	Output/Retentate of RO-101	25	4.20	
TK-108 (Waste Storage)	Stores waste/impurities	25	4.20	0
➢ Stream 41	Input of TK-108	25	4.20	
DRY-103 (Freeze Dryer)	Separates solvent from the final product	12	4.20	0 (Based on Utility)
➢ Stream 37	Input of DRY-103	25	4.20	
➢ Stream 38	Output of DRY-103	12	4.20	
➢ Stream 39	Output of DRY-103	12	4.20	
SC-104 (Screw Conveyor)	Transfers dried soybean flour to TK-107	12	4.20	0
➢ Stream 39	Input of SC-104	12	4.20	
➢ Stream 40	Output of SC-104	12	4.20	
TK-108 (Isoflavone Aglycone Storage)	Stores Product	12	4.20	0
➢ Stream 40	Input of TK-108	12	4.20	

Appendix B

Supporting Information for Chapter 4

B.1 NMR Comparison

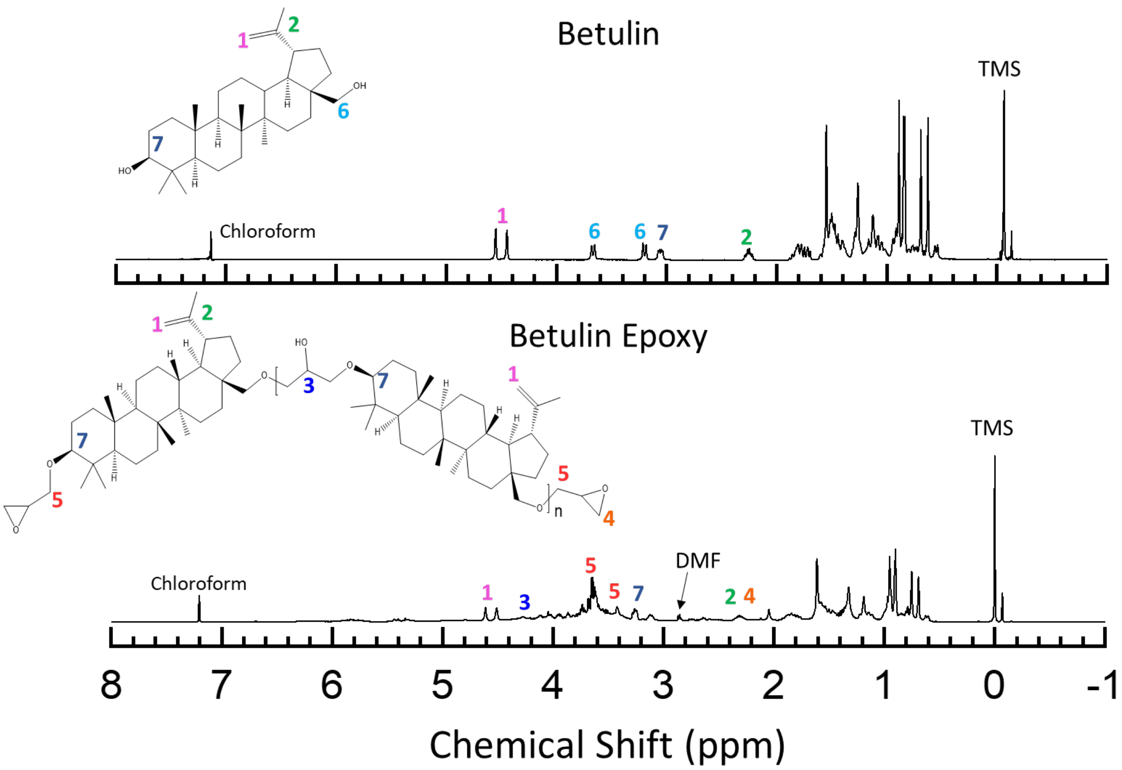


Figure B.1.1. NMR comparison between betulin and DGEBet

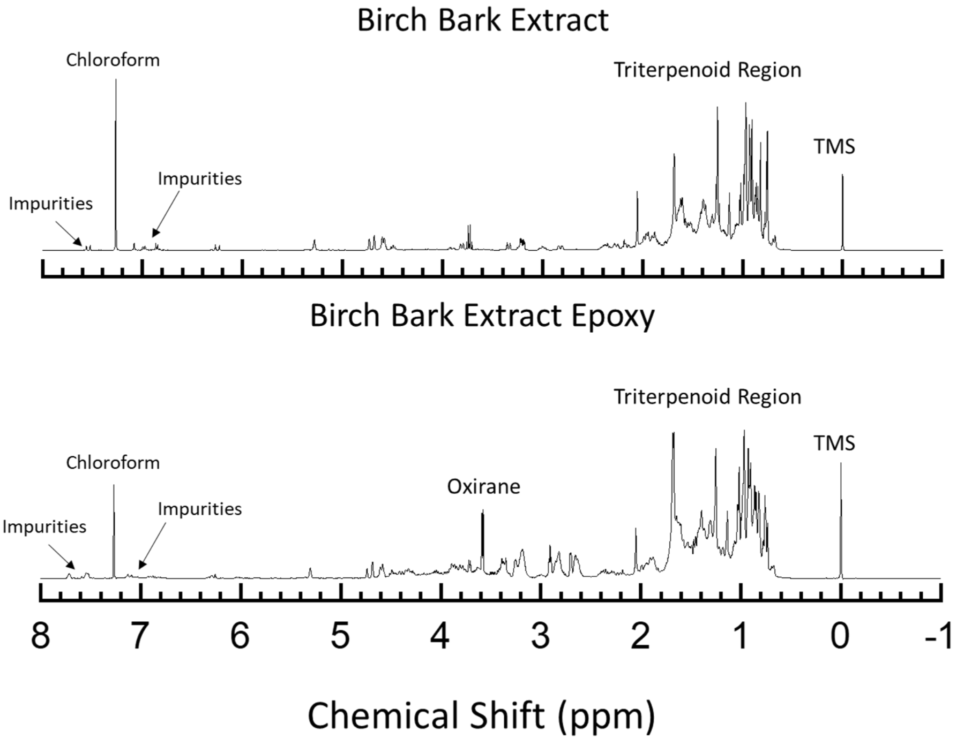


Figure B.1.2. NMR comparison between BBE and DGEBBE

B.2 Fourier Transform Infrared Spectroscopy

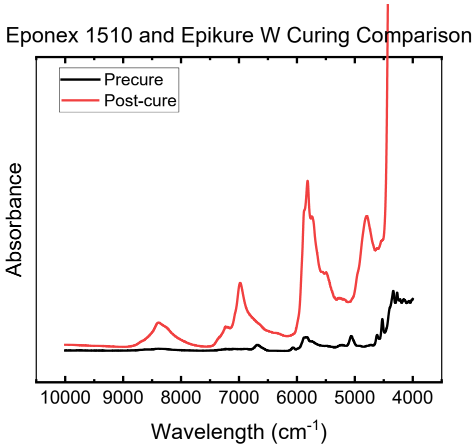


Figure B.2.1. FTIR comparison plots of Eponex 1510 cured with Epikure W

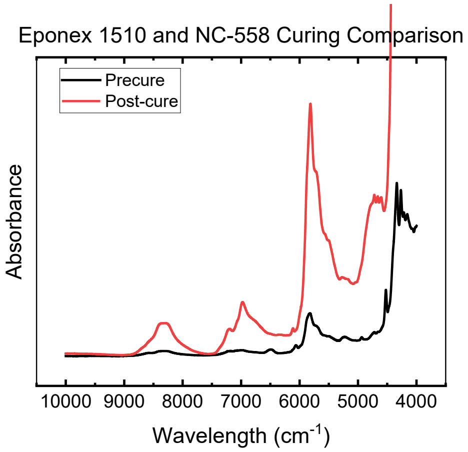


Figure B.2.2. FTIR comparison plots of Eponex 1510 cured with NC-558

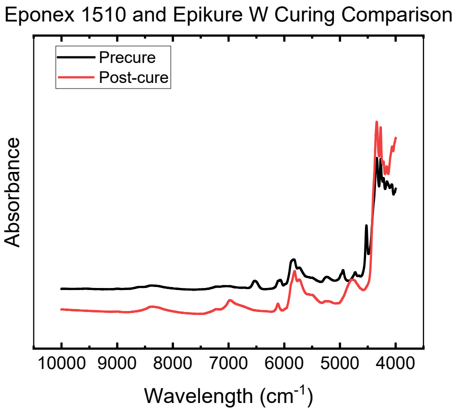


Figure B.2.3. FTIR comparison plots of Eponex 1510 cured with DFDA

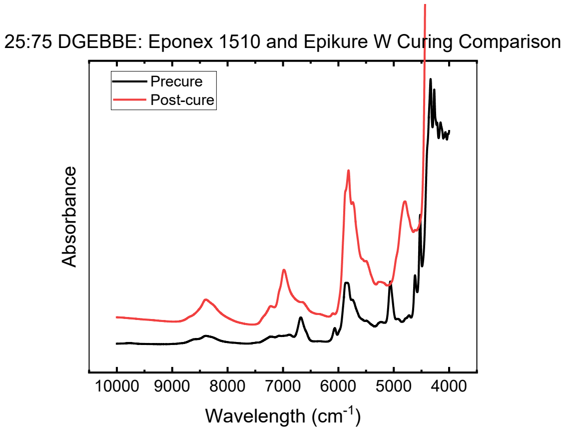


Figure B.2.4. FTIR comparison plots of 25:75 DGEBBE:Eponex 1510 cured with Epikure W

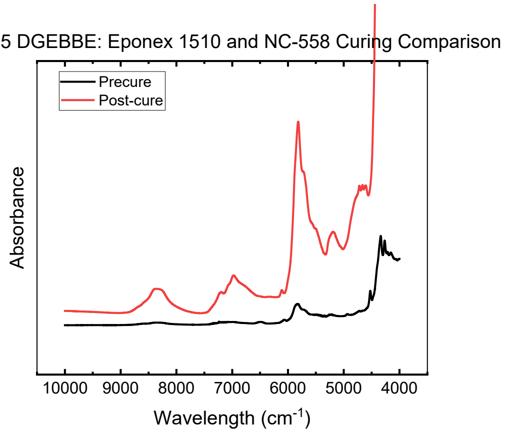


Figure B.2.5. FTIR comparison plots of 25:75 DGEBBE:Eponex 1510 cured with NC-558

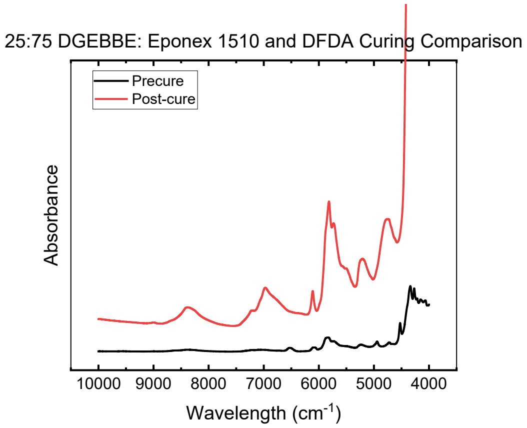


Figure B.2.6. FTIR comparison plots of 25:75 DGEBBE:Eponex 1510 cured with DFDA

B.3 Advanced Polymer Chromatography of Various Chemicals

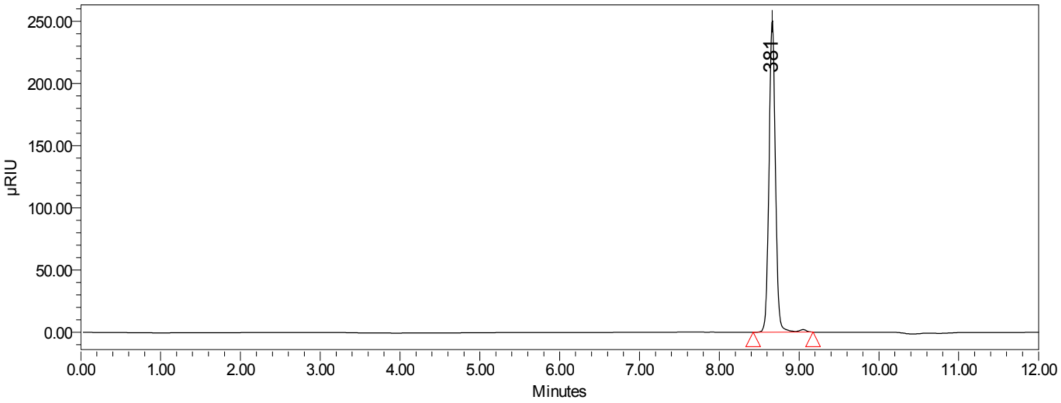


Figure B.3.1. APC of Betulin

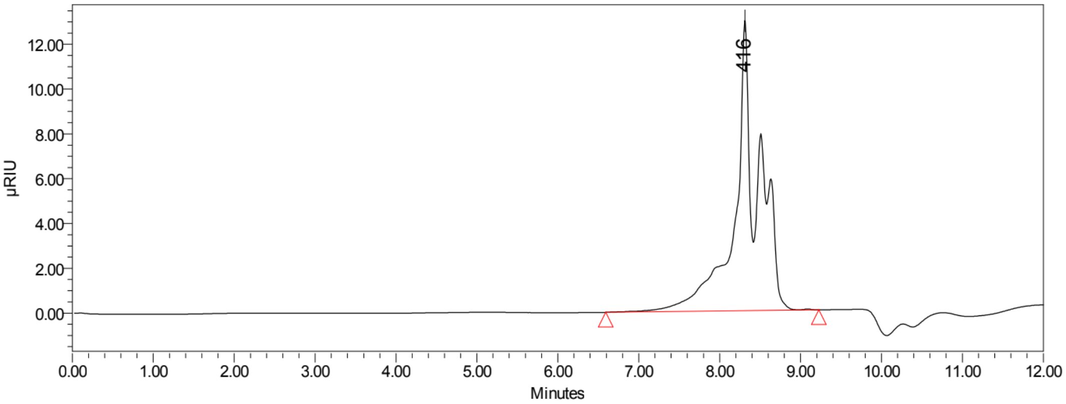


Figure B.3.2. APC of DGEBet

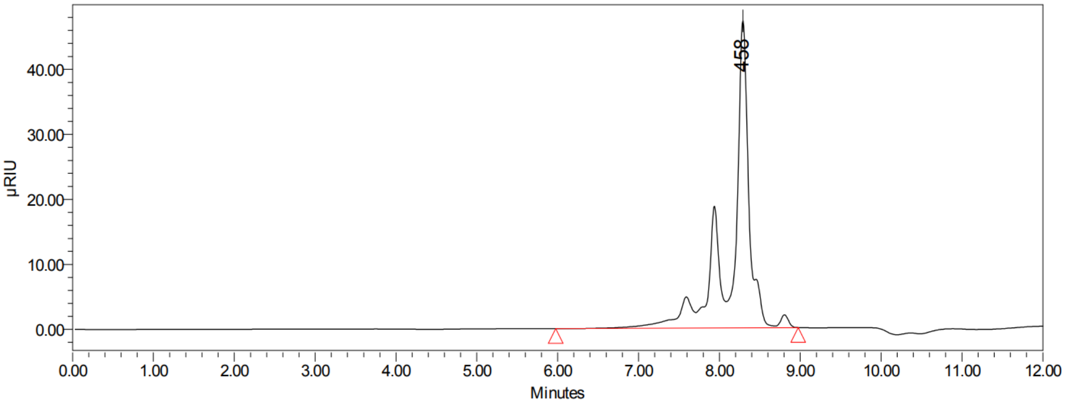


Figure B.3.3. APC of BBE extracted using chloroform solvent

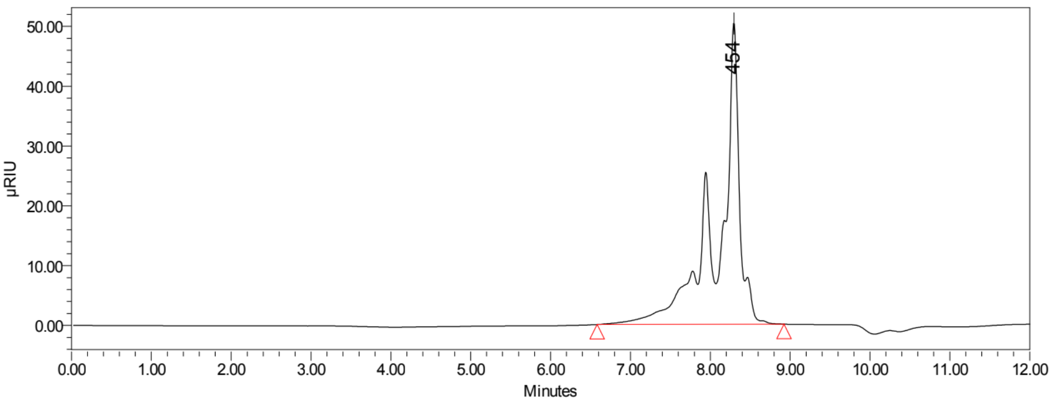


Figure B.3.4. APC of BBE extracted using ethanol solvent

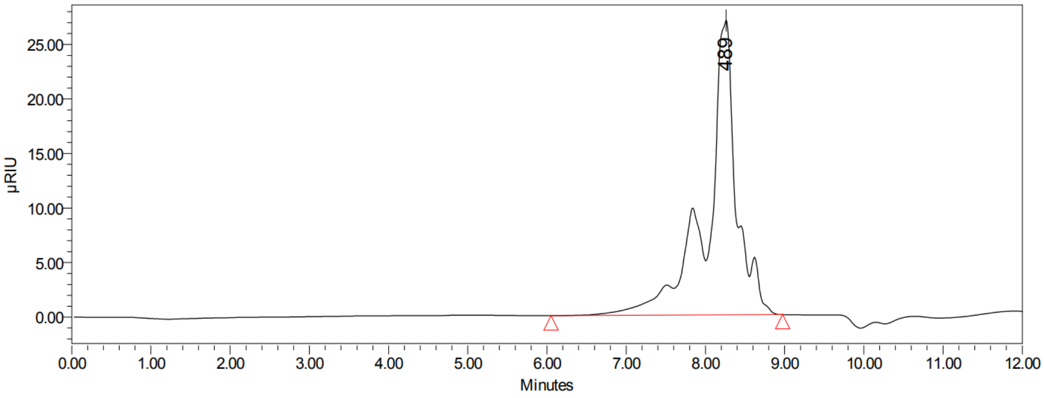


Figure B.3.5. APC of DGEBBE extracted using ethanol solvent

B.4 High-Performance Liquid Chromatography (HPLC) of Various Chemicals

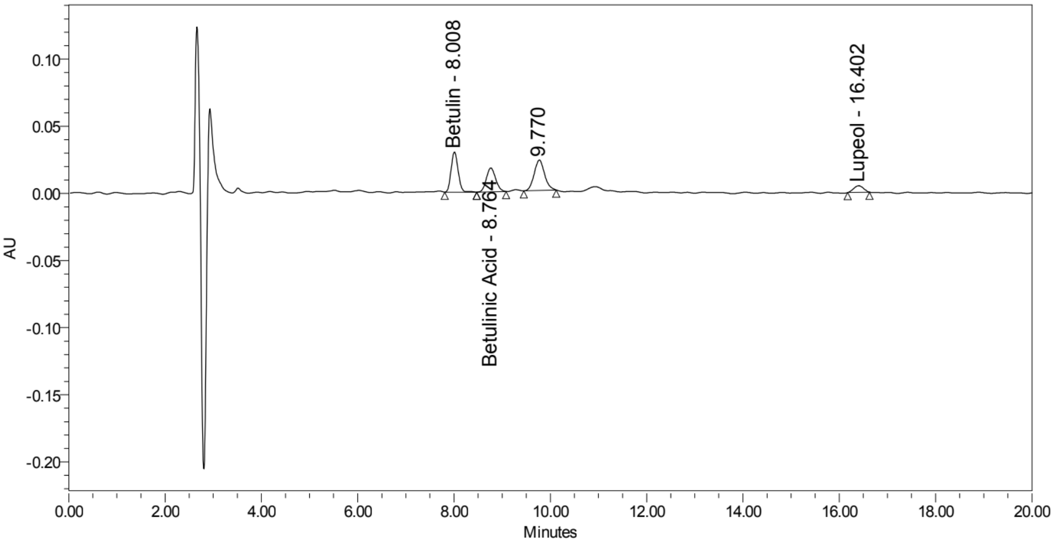


Figure B.4.1. HPLC of BBE extracted using chloroform solvent

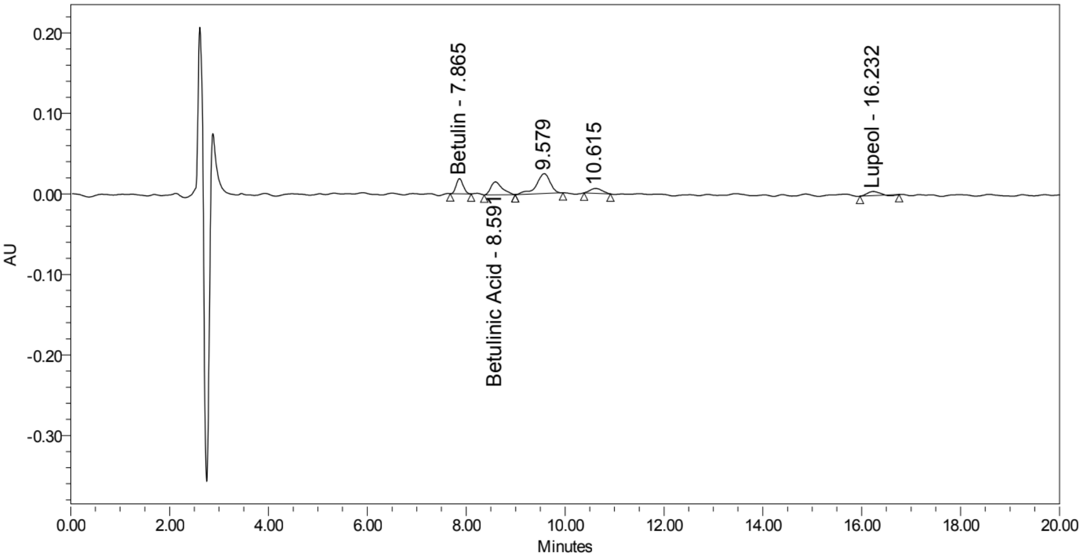


Figure B.4.2. HPLC of BBE extracted using ethanol solvent

B.5 Calibration Curve of Major Birch-Derived Triterpenoids for HPLC Analysis

The general procedure and equipment used for each run is described in Section 2.1.2 of Chapter 2.

Betulin

Absorbance = 8637.671*(Amount in ppm) + 6079.525
R^2: 0.9989

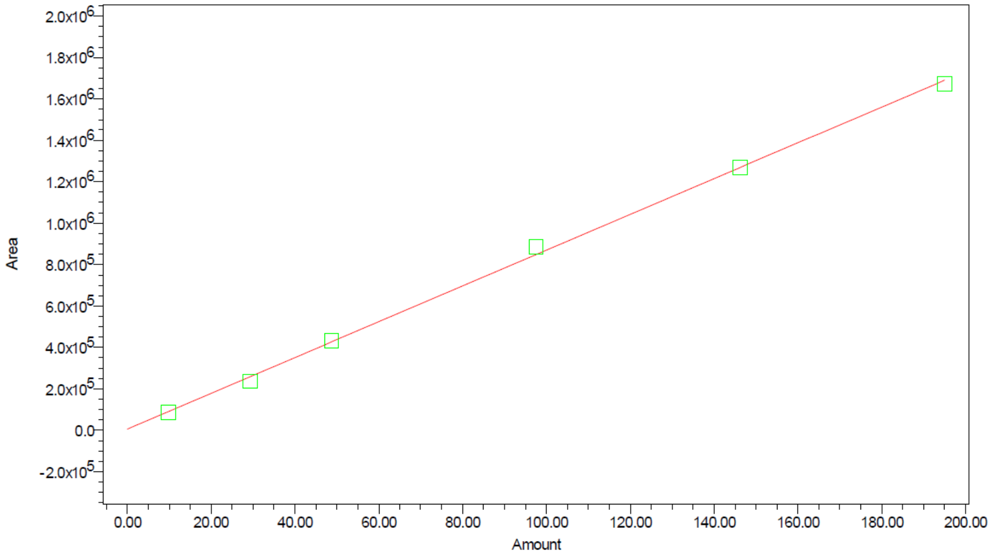


Figure B.5.1. HPLC calibration curves of (a) betulin

Betulinic Acid Absorbance = 7362.019*(Amount in ppm) + 32318.29
R^2: 0.9977

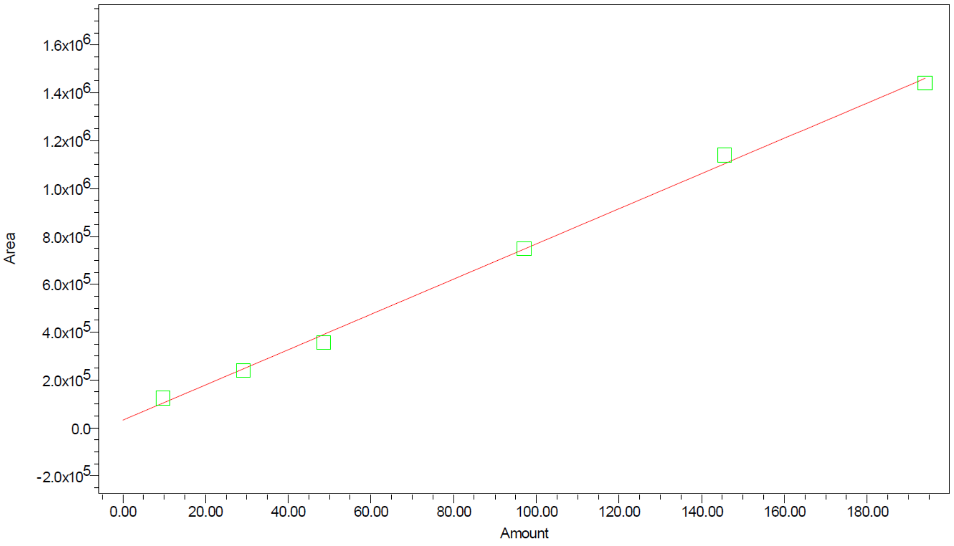


Figure B.5.2. HPLC calibration curves of betulinic acid

Lupeol Absorbance = 10710.03*(Amount in ppm) – 60371.59
R^2: 0.9988

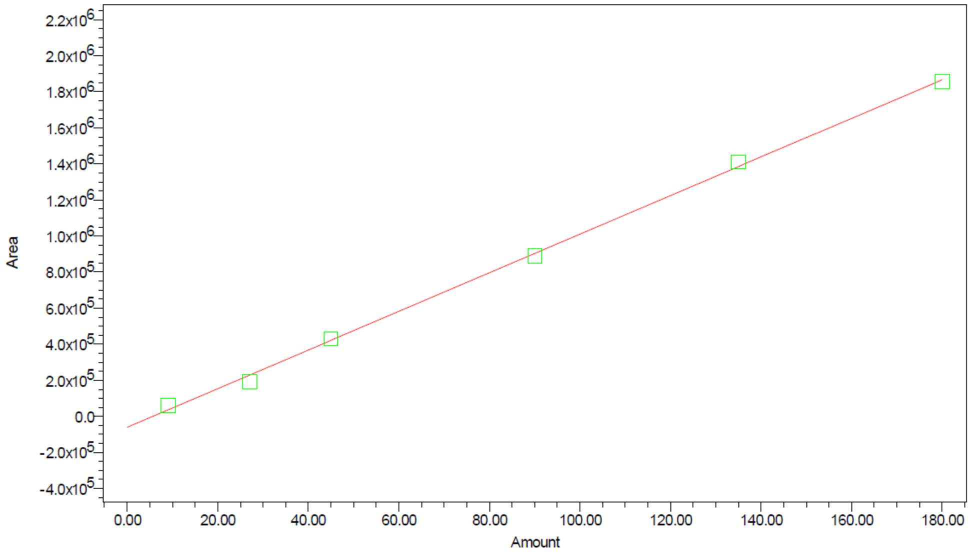


Figure B.5.3. HPLC calibration curves of lupeol

Appendix C

Supporting Information for Chapter 5

C. Model Equations

Applicable to all technologies

C.1 Indices and Sets

i ∈ $\boldsymbol{I}$ – technologies (used as subscript to variables)

{UF-Ultrafiltration,

PVP-Pervaporation,

DST-Distillation,

SDM-Sedimentation,

DRY- Dryer,

ATPE- Aqueous Two-Phase Extraction,

CNF- Centrifugation,

FLT- Filter,

INCN- Incineration}

$j \in \boldsymbol{J}$ – stream (used as subscript to variables)

{1, 2, 3, 4 …}

$k \in \boldsymbol{K}$ – components (used as subscript to variables)

{IPA – isopropyl alcohol,

Wtr – water,

Salt1 – sodium chloride

Salt2 – sodium sulfate anhydrous

Hex--Hexane – hexane,

DME – dimethoxyethane,

EME – 1-ethoxy-1-methoxyethane,

Tol – toluene}

C.2 Subsets

Subsets for Technologies

I^{CST} – technologies with costs

{UF, PVP, DST, SDM, DRY, ATPE, CNF, FLT, INCN}

I^{CF} – technologies with concentration factor

{PVP, UF, FLT, SDM, CNF}

I^{CONS} – technologies with consumables

{ATPE, PVP, FLT, UF}

Subsets for Components

Jbp_{ATPE} – bottom phase of ATPE

Jda_{DRY} – dry air inlet stream to DRY

$Jliq_{CNF}$ – stream containing no solids leaving CNF

Jin_i – inlet streams of technology *i*

$Jout_i$ – outlet streams of technology *i*

$Jpoly_{ATPE}$ – polymer feed stream to ATPE

$Jsalt_{ATPE}$ – salt feed stream to ATPE

$Jsld_{CNF}$ – stream containing solids leaving CNF

Jtp_{ATPE} – top phase of ATPE

K_i – components *k* in technology *i*

K_j – components *k* in stream *j*

K^{JP} – components in process streams

{IPA, Wtr, Salt1, Salt 2, Hex, DME, EME, Tol}

C.3 General Parameters

ρ (kg/m^3) = Density of component k

π_{feed} (\$/kg biomass) = Entering feed cost in terms of per kg waste

$\pi^{Rep}{}_i$ (\$/unit) = Replacement cost of consumables per unit capacity in technology i

λ_{stm} (kJ/kg) = Latent heat of steam

$\lambda_{vap,k}$ (kJ/kg) = Heat of vaporization of component k

α_k = Relative volatility of component k for technology i

μ (N-s/m^2) = viscosity of fluid

η_{stage} = stage efficiency

θ_i^R (hr) – residence time in technology i

θ_i^{Rep} (h/year) = Replacement time for consumables in technology i

τ_{ann} (h/annum) = (330 days x 24 h/day = 7920 hours)

$C0_i$ (\$/capacity) = Cost of a technology with standard capacity

Cp (KJ/kg-°C) = Specific heat of component k

$D_{p,SDM}$ = particle diameter in sedimentation unit

g (m/s^2) = gravitational constant

nc = cost scaling index (2/3 rule)

$Nlabr_i$ (#/h) = # of laborers required for technology i per hour

$Q0_i$ (m^3 or m^2 or m^3/h) = Standard capacity of a technology for costing, labor and power required

T_{amb} (°C) = ambient temperature

Tcw_i (°C) = Cooling water temperature in (25)

Tcw_o (°C) = Cooling water temperature out (30)

T_{sat} (°C) = saturation temp

C.4 Evaluated Parameters:

SOR_i (m/s) = surface overflow rate id sedimentation

U_i (m/s) = settling velocity of technology i

C.5 General Variables

B_i = volume ratio of equipment i

$Cc_{,i}$ (\$) = Purchase cost of unit i

CF_i (m^3/m^3) = Concentration factor for technologies $i \in \boldsymbol{I^{CF}}$

$Cpur_k$ (\$/h) = Purchase cost of added components ($k \in \mathbf{K^{ADD}}$)

D_i(m) = diameter of technology unit i

L_i(m) = length of technology unit i

Liq_{DST} = liquid molar flowrate in distillation column

$M_{j,k}$ (kg/h) = Mass flowrate of component k in stream j

N = actual number of stages

N_{min} = minimum number of stages

q = quality of mixture (for distillation, entering feed quality)

Qc, (m^3 or m^2 or m^3/h) = Costing variable for technologies $i \in \boldsymbol{I}^{\mathbf{CST}}$

QC_{DST} = cooling requirement for distillation unit

QH_{DST} = heat duty for distillation unit

Qs_{DST} = heat required to bring the feed to saturation

PW_i (kW/h) = Power required for technologies $i \in \boldsymbol{I}^{\mathrm{CST}}$

R_{min} = minimum reflux ratio

R = actual reflux ratio

U_v = Underwood variable

Vap_{DST} = vapor molar flowrate in distillation column

Wsp_i (kW/h) = Power required by technology i per hour

$X_{mj,k}$ = mole fraction of component k in stream j

Notes:

- The ‘uppercase italic Latin fonts (not colored)’ are for variables (values determined through the solution of the optimization problem)

- The uppercase Latin font and lowercase Greek fonts in red are the specified input parameters
- The parameter or variable to be evaluated is always on the L.H.S of the equation

C.6 General Equations

Component balances:

$$\sum_{j\in jin_i} M_{j,k} = \sum_{j\in jout_i} M_{j,k}\ ;\forall k \in K^{JP}\ and\ i \in I$$

Cost of technologies:

$$\left(\frac{C_{ci}}{C0_i}\right) = \left(\frac{Q_{ci}}{Q0_i}\right)^{nc}\ ;\forall i \in I^{CST}$$

Labor requirements of technologies:

$$Nlb_i Q0_i = Nlabr_i Qc_i;\forall i \in I^{CST}$$

Consumable costs:

$$Cons_i = \frac{\tau_{ann}}{\theta_i^{Rep}}\pi_i^{Rep} Qc_i;\forall i \in I^{CST}$$

Annualized Capital Cost (million$/year):

$$CCAC = \frac{(1.66 * CRF * BMC * \sum_i Cc_i)}{10^6}$$

Labor Cost (million$/year):

$$CCLB = \frac{(C_{lbr} * Tann * \sum_i Nlbr_i)}{10^6}$$

Utility Cost (million$/year):

$$CCUC = \frac{\left((\sum_i PW_i * C_{elec} + \sum_i Mstm_i * C_{stm}) * Tann\right)}{10^6}$$

Membrane Cost (million$/year):

$$CCMC = \frac{(Tann * \sum_{i1} CPM_{i1})}{Rep_{time} * 10^6}$$

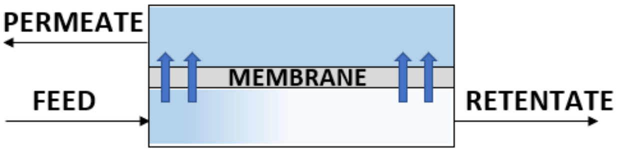
Other Cost (million$/year):

$$CCTC = 2.78 * CCLB$$

Total Cost (million$/year):

$$CCTC = CCAC + CCUC + CCMC + CCOC + CCLB$$

Ultrafiltration (UF)



Unit Specific Parameters

ζ_i (m^3 /m^2h) = Flux of technology *i*

ξk,(−−) = Retention factor of component k for technology *i*

Retention factor equations:

$$\xi_{k,UF} = \frac{M_{Jr_{uf},k}}{M_{Jin_{uf},k}}; \forall k \in K_j$$

Concentration factor:

$$CF_{UF} = \frac{\sum_{k \in K_j, j \in Jin_{UF}} \left(\frac{M_{j,k}}{\rho_k}\right)}{\sum_{k \in K_j, j \in Jretentate_{UF}} \left(\frac{M_{j,k}}{\rho_k}\right)}$$

$$1.01 \leq CF_{UF} \leq 35$$

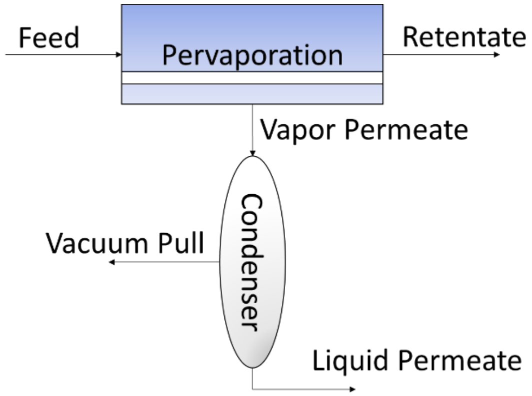
Flux balance:

$$\zeta_{UF} Qc_{UF} = [\sum_{k \in K_j, j \in Jin_{UF}} \left(\frac{M_{j,k}}{\rho_k}\right)] \left(1 - \frac{1}{CF_{UF}}\right)$$

Power required:

$$PW_{UF} = Wsp_{UF} Qc_{UF}$$

Pervaporation (PVP)



Unit specific parameters

λ_{stm} (KJ/kg) = Latent heat of steam

$\lambda_{vap,k}$ (KJ/kg) = Heat of vaporization of component k

Retention factor:

$$\xi_{k,PVP} = \frac{M_{Jr_{PVP},k}}{M_{Jin_{PVP},k}}; \forall k \in K_j$$

Concentration factor:

$$CF_{PVP} = \frac{\sum_{k\in K_j, j\in Jin_{PVP}} \left(\frac{M_{j,k}}{\rho_k}\right)}{\sum_{k\in K_j, j\in Jr_{PVP}} \left(\frac{M_{j,k}}{\rho_k}\right)}$$

Flux balance:

$$\zeta_{PVP} Q_{C_{PVP}} = \sum_{k\in K_j, j\in Jin_{PVP}} \left(\frac{M_{j,k}}{\rho_k}\right)] \left(1 - \frac{1}{CF_{PVP}}\right)$$

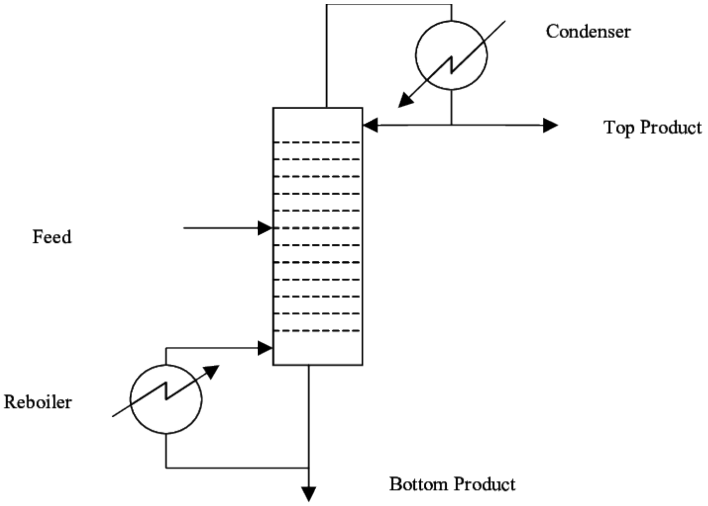
Power required:

$$PW_{PVP} = Wsp_{PVP} Qc_{PVP}$$

Heat required for vaporization:

$$Mstm_{PVP} \lambda_{stm} = \sum_{k\in K_j, j\in Jprm_{PVP}} M_{j,k} \lambda_k^{vap}$$

Distillation (DST)



Terms

LK = Light Key (Top Product)

HK = Heavy Key (Bottom Product)

λ_{stm} (kJ/kg) = Latent heat of steam

$\lambda_{vap,k}$ (kJ/kg) = Heat of vaporization of component k

T_{amb} (°C) = ambient temp

T_{sat} (°C) = saturation temp

α_k = Relative volatility of component k for technology i

η_{stage} = stage efficiency

Cp (KJ/kg-°C) = Specific heat of component k

Tcw_i (°C) = Cooling water temperature in (25)

Tcw_o (°C) = Cooling water temperature out (30)

$X_{mj,k}$ – mole fraction of component k in stream j

R_{min} – minimum reflux ratio

R – actual reflux ratio

N – the actual number of stages

Qs_{DST} – heat required to bring the feed to saturation

QH_{DST} - heat duty for the distillation unit

QC_{DST} – the cooling requirement for the distillation unit

Liq_{DST}- liquid molar flowrate in the distillation column

Vap_{DST} – vapor molar flowrate in the distillation column

U_v – Underwood variable

q – the quality of the mixture

Unit Specific Model Equations:

Molar flow rates in DST:

$$F_{j,k} = \frac{M_{j,k}}{MW_k}; \forall\, j \in J^{DST}, k \in K^{DST}$$

Component balance in DST:

$$\sum_{j \in Jin_i} F_{j,k} = \sum_{j \in Jout_i} F_{j,k}; \forall\, j \in J^{DST}, k \in K^{DST}$$

Mole fractions in DST:

$$X_{mj,k} = \frac{F_{j,k}}{\sum_{k \in K^{DST}} F_{j,k}}; \ \forall\, j \in J^{DST}, k \in K^{DST}$$

Constraints on recovery:

$$X_{m_{Jtop_{DST}},k} when(\alpha_k < \alpha_{HK}) = 0; \ \forall\, k \in K^{DST}$$

$$X_{m_{Jtop_{DST}},k} when(\alpha_k > \alpha_{LK}) = 0; \forall\, k \in K^{DST}$$

Distillate recovery constraints:

$$X_{m_{Jtop_{DST}},HK} = 0.08$$

$$X_{m_{Jtop_{DST}},LK} = 0.92$$

Minimum number of stages with Fenske's equation:

$$N_{min}\log(\alpha_i) = log\left[\frac{X_{m_{Jtop_{DST}},LK}}{X_{m_{Jtop_{DST}},HK}} \frac{X_{m_{Jbot_{DST}},HK}}{X_{m_{Jbot_{DST}},LK}}\right]$$

Underwood's variable:

$$(1-q) = \sum_{k \in K^{DST}, j \in Jin_{DST}} \frac{\alpha_k X_{m_{j,k}}}{\alpha_k - U_v}$$

Assume feed is a saturated liquid (q=1):

$$0 = \sum_{k \in K^{DST}, j \in Jin_{DST}} \frac{\alpha_k X_{m_{j,k}}}{\alpha_k - U_v}$$

Minimum reflux ratio:

$$R_{min} = \sum_{k \in K^{DST}, j \in Jtop_{DST}} \frac{\alpha_k X_{m_{j,k}}}{\alpha_k - U_v} - 1$$

Reflux ratio:

$$R = 1.3 R_{min} \ (assumption)$$

Number of stages:

$$0.6N = N_{min}$$

Number of actual stages:

$$N_{act} = \frac{N}{\eta_{stage}}$$

Height of column:

$$H_{DST} = H_{stage} N_{act}$$

Liquid and vapor flowrates:

$$Liq_{DST} = R \sum_{k \in K^{DST}, j \in Jtop_{DST}} M_{j,k}$$

$$Vap_{DST} = Liq_{DST} + R \sum_{k \in K^{DST}, j \in Jtop_{DST}} M_{j,k}$$

Column diameter:

$$D_{DST} = \sqrt{\frac{4 Vap_{DST}}{\pi u_{vap}}}$$

$$u_{vap} = vapor\ linear\ velocity$$

Costing variable of column:

$$Qc_{DST} = \frac{\pi}{4} D_{DST}^2 H$$

Initial heating of feed to reach saturation:

$$QS_{DST} = \sum_{k \in K^{DST}, j \in Jin_{DST}} M_{j,k} Cp_k (T_{sat} - T_{amb})$$

Heat duty:

$$QH_{DST} = (1 + R) \sum_{k \in K^{DST}, j \in Jtop_{DST}} F_{j,k} MW_k \lambda_k^{vap}$$

Cooling:

$$QC_{DST} = R \sum_{k \in K^{DST}, j \in Jtop_{DST}} F_{j,k} MW_k \lambda_k^{vap}$$

Steam required:

$$Mstm_{DST} \lambda_{stm} = QS_{DST} + QH_{DST}$$

Cooling water required:

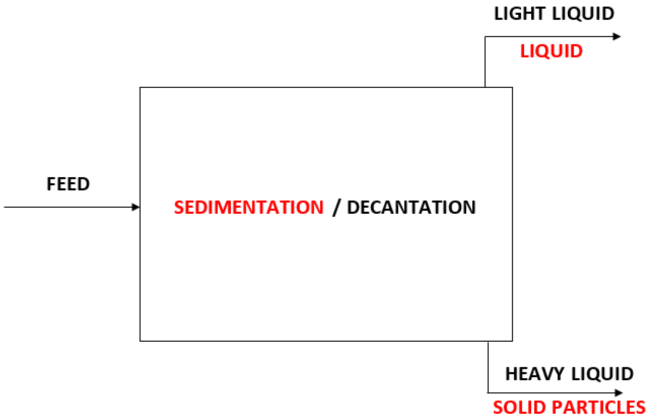
$$Mcw_{DST} Cp_w (Tcw_{out} - Tcw_{in}) = QC_{DST}$$

Variable bounds:

$$N_{min} \geq y_{DST}$$

$$R_{min} \geq 1.01 y_{DST}$$

Sedimentation (SDM)



Unit Specific Parameters

Ce_i^0 (\$) – equipment cost for technology *i* of known capacity

n_i – cost exponent for technology *i*

V_i^0 (m^3) – vessel volume for technology *i* of known capacity A_i^0 (m^2) – area for technology i of known capacity

W_i^0 (kW) – power consumption for technology *i* of known capacity

θ_i^R (hr) – residence time in technology *i*

ρ_k (kg/m3) – density of component k

π_k (\$/kg) –market price of kth component

η_{SDM} (−) – efficiency of removal in typical sedimentation unit (75%)

Variables

V_i (m^3) – vessel volume for technology *i*

A_i (m^2) – area for technology *i*

CP_k (\$/hr) – cost price for component k consumed per hour

Ce_i (\$) – equipment cost for technology *i*

Equations:

Settling velocity (evaluated parameter):

$$U_{S,SDM} = \frac{gD_p^2(\rho_s - \rho_L)}{18\mu}$$

$U_{S,SDM}$ – settling velocity (m/s)

D_p – particle diameter (m) (5E-3 m or 5 mm)

g – acceleration due to gravity (m/s^2)

ρ_s – density of solid (kg/m^3)

ρ_l – density of liquid (kg/m^3)

μ – viscosity of fluid (N-s/m^2)

Efficiency:

$$\eta_{SDM} = \frac{M_{Jtp_{SDM},Sol}}{M_{Jin_{SDM},Ssol}}$$

Concentration factor: (volume concentration factor)

$$CF_{SDM} = \frac{\sum_{k\in K_j, j\in Jin_i}\left(\frac{M_{j,k}}{\rho_k}\right)}{\sum_{k\in K_j, j\in Jtp_{SDM}}\left(\frac{M_{j,k}}{\rho_k}\right)}$$

$$1.01 \leq CF_{SDM} \leq 15$$

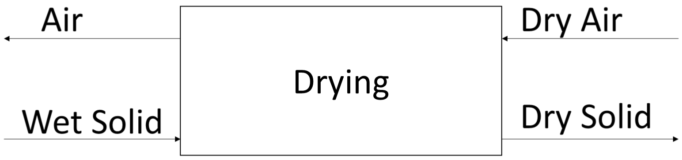
Surface overflow rate:

$$SOR_{SDM} = \frac{U_{S,SDM}}{\eta_{SDM}}$$

Area of sedimentation tank:

$$A_{SDM} = \frac{\sum_{k\in K_j j\in Jin_{SDM}}\left(\frac{M_{j,k}}{\rho_k}\right)}{SOR_{SDM}}$$

Dryer (DRY)



Unit specific parameters

v_{air}(m/s) = velocity of air flow in the dryer

Moisture Content in stream j:

$$X_j = \frac{M_{j,Wtr}}{M_{j,k}}; \forall\ k \in K_j$$

Diameter of the Drum:

$$D_{DRY} = \frac{M_{Jda_{DRY},k}}{\sqrt{v_{air}\pi * 900\rho_{air}}}; \forall k \in K_j$$

Length of Drum:

$$L_{DRY} = B_{DRY} * D_{DRY}$$

$$4 \leq B_{DRY} \leq 15$$

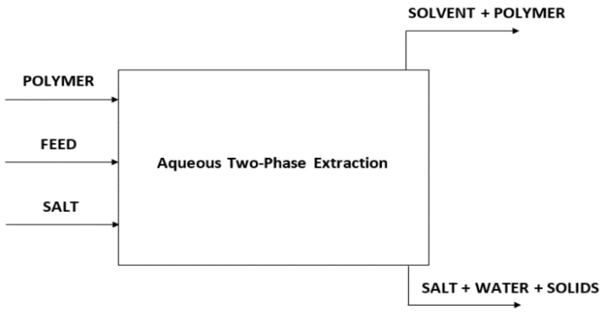
Heat required for vaporization:

$$Q_{c,DRY} = \frac{\pi}{4} D_{DRY}^2 L_{DRY}$$

Power required:

$$PW_{DRY} = \frac{3.19995 M_{Jda_{DRY},k}}{MW_{air}};\ k \in K_j$$

Aqueous Two-Phase Extraction (ATPE)



Unit Specific Parameters

$\Psi_{k\text{-}k'}$- solubility of component k in component k’

κP_k- partition coefficient of component k

Solubility Equations:

$$M_{Jbp_{ATPE},Hexane} = \psi_{Hexane-bp} M_{Jbp_{ATPE},salt}$$

$$M_{Jtp_{ATPE},salt} = \psi_{salt-tp} M_{Jtp_{ATPE},Hexane}$$

Extraction Factor:

$$EF_{ATPE} = \frac{\kappa P_k M_{JHexane_{ATPE},k}}{M_{Jsalt_{ATPE},k}}$$

Number of Stages:

$$\left(\frac{EF-1}{EF^{NAE+1}-1}\right) = \frac{M_{Jfeed_{ATPE},k} - M_{Jtop_{ATPE},k}}{M_{Jfeed_{ATPE},k}}$$

Size of unit:

$$Q_{c,ATPE} = \sum_{k\in K_j, j\in Jfeed_{ATPE}} \frac{M_{j,k}}{\rho_k} + \sum_{k\in K_j j\in Jpoly_{ATPE}} \frac{M_{j,k}}{\rho_k} + \sum_{k\in K_j, j\in Jsalt_{ATPE}} \frac{M_{j,k}}{\rho_k}$$

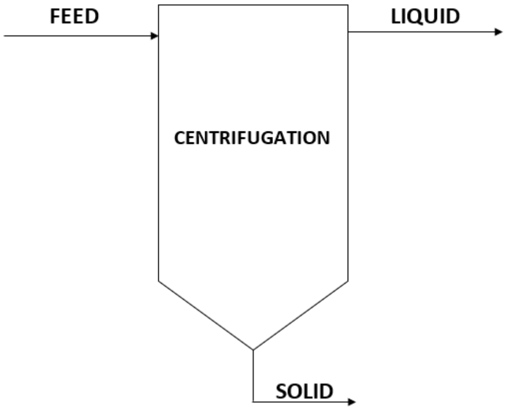
Power Required:

$$PW_{ATPE} = Wsp_{ATPE}\, Qc_{,ATPE}$$

Cooling Duty:

$$M_{cw,ATPE} = \frac{3600\, PW_{ATPE}}{c_p\left(T_{cw,out} - T_{cw,in}\right)}$$

Centrifugation (CNF)



Unit Specific Parameters

Efficiency Equation:

$$\eta_{water} = \frac{M_{Jsld_{CNF},WTR}}{M_{Jsld_{CNF},WTR}}$$

$$\eta_{solvent} = \frac{M_{Jliq_{CNF},solvent}}{M_{Jfeed_{CNF},solvent}}$$

Concentration Factor:

$$CF_{CNF} = \frac{\left[\sum_{k\in K_j, j\in Jfeed_{CNF}}\left(\frac{M_{j,k}}{\rho_k}\right)\right]}{\left[\sum_{k\in K_j j\in Jliq_{CNF}}\left(\frac{M_{j,k}}{\rho_k}\right)\right]}$$

$$2 \leq CF_{CNF} \leq 20$$

Sigma Factor Equation:

$$Qc_{CNF}U_{CNF} = \left[\sum_{k\in K_j j\in Jfeed_{CNF}}\left(\frac{M_{j,k}}{\rho_k}\right)\right]$$

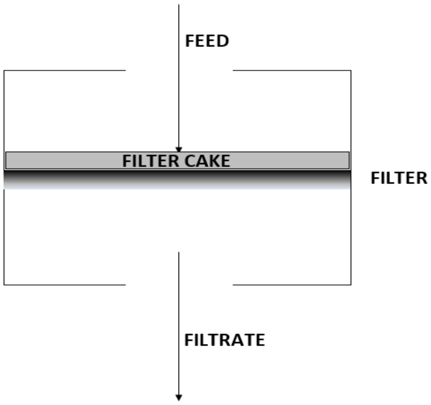
Power Required:

$$PW_{CNF} = Wsp_{CNF}\left[\sum_{k\in K_j, j\in Jfeed_{CNF}}\left(\frac{M_{j,k}}{\rho_k}\right)\right]$$

Power dissipation to heat it about 40%, therefore cooling duty is required:

$$Mcw_{CNF}c_{pw}\left(T_{cw,out} - T_{cw,in}\right) = 0.4PW$$

Filtration (FLT)



Retention factor:

$$\xi_{k,FLT} = \frac{M_{Jflt_{FLT},k}}{M_{Jfeed_{FLT},k}}; \forall k \in K_j$$

Concentration factor:

$$CF_{FLT} = \frac{\sum_{k \in K_j, Jfeed_{FLT}} \left(\frac{M_{j,k}}{\rho_k}\right)}{\sum_{k \in K_j, Jflt_{FLT}} \left(\frac{M_{j,k}}{\rho_k}\right)}$$

$$2 \le CF_{FLT} \le 30$$

Flux balance:

$$\zeta_{FLT} Q_{C_{FLT}} = \sum_{k \in K_j, j \in Jfeed_{FLT}} \left(\frac{M_{j,k}}{\rho_k}\right) \left(1 - \frac{1}{CF_{FLT}}\right)$$

Power required:

$$PW_{FLT} = Wsp_{FLT} Qc_{FLT}$$

Incineration (INCN)

Process Equations

Heating value of waste stream:

$$Q_{solv,INCN} * 1000 = 14544 * C + 62208\left(H - \frac{O}{8}\right) + 4050 * S \; [=] \; MJ/kg$$

Mass of fuel needed for heating:

$$m_{fuel,INCN} * NE_{fuel} = Q_{solv} * m_{solv} \; [=] \; MJ/s$$

$$NE_{fuel} = 38.9 \; [=] \; MJ/kg$$

*Fuel oils are products of petroleum distillation, consists of hydrocarbons

Mass of air fed (textbook):

$$m_{air,INCN} = air_{rate} * O * m_{solv} \; [=] \; kg/s$$

$$air_{rate} = 4.35$$

Energy consumed during process:

$$E_{con,INCN} = Q_{solv,INCN} * m_{solv,INCN} \; [=] \; MJ/s$$

Energy produced during process:

$$E_{prod,INCN} = eff_{INCN} * E_{con,INCN} \; [=] \; MJ/s$$

Efficiency of energy production ranges from 30-45%

Net energy:

$$E_{net,INCN} = E_{prod,INCN} - E_{con,INCN} \; [=] \; MJ/s$$

Costing Equations

Annual fuel cost:

$$Mat_{INCN} = m_{fuel} * C_{fuel} * 3600 * 24 * 340 \; [=] \; \$/yr$$

$$Cost \; of \; fuel = C_{fuel} = 0.81 \; [=] \; \$/kg$$

Annual energy cost:

$$E_{cost,INCN} * 3.6 = E_{net} * Ce * 3600 * 24 * 340 \; [=] \; \$/yr$$

$$Ce = 0.10 \; [=] \; \$/kWh$$

Conversion factor: 3.6 MJ/kWh

Annual air cost (hydraulics and pneumatics):

$$OC_{INCN} * \rho_a = C_{air,INCN} * Mass_{air} * 3600 * 24 * 340 \; [=] \$ \frac{kg}{m^3 \; yr}$$

$$C_{air,INCN} = 0.0004 \; [=] \; \$/m^3$$

Capital cost:

$$Cap_{cost,INCN} = Cap_{old,INCN} * \left(\frac{m_{solv,incn} * 3600}{m_{std,incn}} \right)^{nc} \; [=] \; \$$$

$$Cap_{old,INCN} = \; 967000 \; [=] \; \$$$

$$M_{std,INCN} = \; 100000 \; [=] \; kg/hr$$

Number of laborers (SuperPro):

$$Nlb_{INCN} * m_{std,INCN} = Nlabr_{INCN} * m_{solv,INCN} * 3600$$

$$Nlab_{INCN} = 0.1$$

Annual cost of labor:

$$Ncost_{INCN} = Nlb_{INCN} * Pay * 24 * 340 \; [=] \; \$/yr$$

$$Pay = 30 \; [=] \; \$/hr$$

Total annual cost (objective to be minimized):

$$CCT_{INCN} = N_{cost,INCN} + Cap_{cost,INCN} + OC_{INCN} + Mat_{INCN} + E_{cost,INCN}$$

C.7 Degree of Freedom Analysis

Table C.7.1.

Degree of Freedom Analysis for Individual Technologies in Solvent Recovery Evaluation

Unit operation	Variables	Equations	Degrees of Freedom
Sedimentation	14	11	3
Filtration	14	11	3
Centrifuge	16	14	2
Distillation	14	12	2
Pervaporation	13	12	1
Aqueous Two-Phase Extraction	18	13	5
Ultrafiltration	12	11	1
Dryer	12	9	3

C.8 Model specifications and input data (standard capacities and costs, parameters, feed compositions)

Table C.8.1.

Table for Standard Capacity, Costs, Scaling Factors, Labor Requirements for Technologies

Unit operation (costing capacity)	**Standard capacity (units)**	**Base costs (million $)**	**Scaling exponent (n)**	**Laborers required (#/hr)**	**Power required (kWh)**	**Consumable Costs ($/unit)**
Sedimentation (Area)	2500 m^2	1.128	0.67	0.1	0	0
Filtration (Area)	80 m^2	0.039	0.67	0.5	0.1	400 ($\$/m^2$)[c]
Microfiltration (Area)	80 m^2	0.75	0.67	1	0.1	400 ($\$/m^2$)[c]
Centrifuge (Sigma factor)	60000 m^2	0.66	0.67	1	19.2	0
Distillation (Volume)	22.58 m^3	0.082	0.67	1	0	0
Pervaporation (Area)	80 m^2	0.0261	0.67	1	0.33	400 ($\$/m^2$)[c]
Aqueous Two-Phase Extraction (volumetric flowrate)	185 m^3/hr	0.362	0.67	1	0.5	2.6 ($/kg)[a]
Ultrafiltration (Area)	80 m^2	0.938	0.67	1	0.2	400 ($\$/m^2$)[c]
Dryer (Volume)	106 m^3	0.024	0.67	0.5	0	0
Incineration (Mass flowrate)	100000 kg/hr	.967	0.67	0.1	~ [b]	0

[a] This cost is the consumable cost associated with adding in the hexane and salt into the aqueous two-phase extraction unit. The unit cost of hexane is $2/kg and the unit cost of sodium chloride salt is $0.6/kg

[b] This value dependent on the composition of the incoming stream. Different compound have different heat of combustions, which will cause variation in the power required.

[c] The replacement time for all filter consumables in assumed to be 2000 hours.

Table C.8.2.

Utility and Labor Costs (SuperPro Designer v8.5)

Utility	**Cost per unit ($/unit)**
Electricity	$0.1/kWH
Cooling Water	$5E-5/kg
Steam	$0.012/kg
Labor	$30/laborer*hr

Table C.8.3.

Input Component Parameters for Case Study 1 – Pharmaceutical Waste Stream

Component	**Molecular weight of component (g mol^{-1})**	**Density (Kg cm^{-3})**	**Heat of vaporization of component c(kJ kg^{-1})**	**Heat capacity of component c (kJ kg^{-1} C^{-1})**	**Feed mass fraction(kg component c kg feed^{-1})**
Isopropanol	60	786	664	2.32	0.51
Water	18	1000	a.	4.2	0.49
Salt	138	2160	a.	a.	a.
Hexane	86	655	a.	1.58	a.

[a.] This value was not a required input for the model

C.8.1 Aqueous two-phase extraction (ATPE):
Residence time: 2 h
Partition coefficient: Isopropanol – 8, Water – 0.05
Solubility Parameter: Hexane in bottom phase – 0.005, Salt in top phase – 0.005

C.8.2 Sedimentation (SDM):
Residence time: 6 h
Efficiency: 70%

C.8.3 Ultrafiltration (UF):
Flux: 0.0856 $m^3 m^{-2} h^{-1}$
Retention Factor (UF1): Isopropanol – 0%, Water – 100%, Salt -100%, Hexane – 100%
Retention Factor (UF2): Isopropanol – 0%, Water – 100%

C.8.4 Pervaporation (PVP):
Flux: 0.55 $m^3 m^{-2} h^{-1}$
Retention Factor (PVP1): Isopropanol – 5%, Water – 90%
Retention Factor (PVP2): Isopropanol – 1%, Water – 90%

C.8.5 Parameters for Case Study 2 (Solvent Recovery)

Table C.8.4.

Input Component Parameters for Case Study 2 – Specialty Chemical Waste Stream

Component	**Molecular weight of component (g mol^{-1})**	**Density (Kg cm^{-3})**	**Heat of vaporization of component c(kJ kg^{-1})**	**Heat capacity of component c (kJ kg^{-1} C^{-1})**	**Feed mass fraction(kg component c kg feed^{-1})**
Dimethoxyethane	90	867	418.6	1.42	0.167
Water	18	1000	a.	4.2	0.276
Toluene	92	876	401.6	1.71	0.323
1-Ethoxy-1-methoxyethane	104	800	400	1.5	0.01
Salt	142	2671	a.	0.9	0.218
Air	29	0.864	a.	a.	a.

a. This value was not a required input for the model

C.8.6 Filtration (FLT):

Flux: 0.2 m^3 m^{-2} h^{-1}

Retention Factor: Dimethoxyethane - 10%, Toluene – 10%, 1-Ethoxy-1-methoxyethane – 10%, Salt – 100%, Water – 100%

C.8.7 Pervaporation (PVP):

Flux: 0.55 m^3 m^{-2} h^{-1}

Retention Factor: Dimethoxyethane - 5%, Toluene – 97%, 1-Ethoxy-1-methoxyethane – 5%

C.8.8 Ultrafiltration (UF):

Flux: 0.0856 m^3 m^{-2} h^{-1}

Retention Factor: Dimethoxyethane - 5%, Toluene – 5%, 1-Ethoxy-1-methoxyethane – 97%

C.8.9 Logic Equations for Case Study 1: Pharmaceutical Waste Stream

$$\begin{gathered} Y_{ATPE} \\ \left[M_{1,k} = M_{2,k}\right] \end{gathered} \qquad \begin{gathered} \neg Y_{ATPE} \\ \left[M_{2,k} = 0\right] \end{gathered}$$

$$\begin{gathered} Y_{PVP1} \\ \left[M_{1,k} = M_{3,k}\right] \end{gathered} \qquad \begin{gathered} \neg Y_{PVP1} \\ \left[M_{3,k} = 0\right] \end{gathered}$$

$$\begin{gathered} Y_{DST} \\ \begin{bmatrix} M_{1,k} = M_{4,k} \\ M_{20,IPA} \geq 0.87 * M_{4,IPA} \end{bmatrix} \end{gathered} \qquad \begin{gathered} \neg Y_{DST} \\ \left[M_{24,kC} = M_{19,kC} * Y_{DST}\right] \end{gathered}$$

$$Y_{ATPE} \vee Y_{PVP1} \vee Y_{DST}$$

C.8.10 Logic Equations for Case Study 2: Specialty Chemical Waste Stream

$$\begin{gathered} Y_{FLT} \\ \left[M_{1,k} = M_{3,k}\right] \end{gathered} \qquad \begin{gathered} \neg Y_{FLT} \\ \left[M_{3,k} = 0\right] \end{gathered}$$

$$\begin{gathered} Y_{SDM} \\ \left[M_{1,k} = M_{4,k}\right] \end{gathered} \qquad \begin{gathered} \neg Y_{SDM} \\ \left[M_{4,k} = 0\right] \end{gathered}$$

$$\begin{gathered} Y_{CNF} \\ \left[M_{1,k} = M_{5,k}\right] \end{gathered} \qquad \begin{gathered} \neg Y_{CNF} \\ \left[M_{5,k} = 0\right] \end{gathered}$$

$$\begin{gathered} Y_{PVP} \\ [M_{17,kC} = M_{15,kC}] \end{gathered} \qquad \begin{gathered} \neg Y_{PVP} \\ [M_{17,kC} = 0] \end{gathered}$$

$$\begin{gathered} Y_{DST1} \\ [M_{16,kC} = M_{15,kC}] \end{gathered} \qquad \begin{gathered} \neg Y_{DST1} \\ [M_{19,kC} = M_{32,kC} * Y_{DST1}] \end{gathered}$$

$$\begin{gathered} Y_{UF1} \\ [M_{26,kC} = M_{22,kC}] \end{gathered} \qquad \begin{gathered} \neg Y_{UF1} \\ [M_{26,kC} = 0] \end{gathered}$$

$$\begin{gathered} Y_{DST2} \\ [M_{23,kC} = M_{22,kC}] \end{gathered} \qquad \begin{gathered} \neg Y_{DST2} \\ [M_{25,kf} = M_{33,kf} * Y_{DST2}] \end{gathered}$$

$$Y_{FLT} \vee Y_{SDM} \vee Y_{CNF}$$

$$Y_{PVP} \vee Y_{DST1}$$

$$Y_{UF1} \vee Y_{DST2}$$

C.9 Relative Volatility Calculation of DME and EME

DME and EME Relative Volatility Estimation, α:

$$\log(\alpha) = \frac{t_2 - t_1}{T}(3.99 + 0.001939T)$$

T- mean boiling point of the two compounds in Kelvin

t_2-EME boiling point in °C

t_1-DME boiling point °C

$$\log(\alpha) = \frac{87°C - 85°C}{359.15\ K}(3.99 + 0.001939 * 359.15K)$$

$$\alpha = 1.062$$

C.10 Additional Information from EPA's Toxics Release Inventory

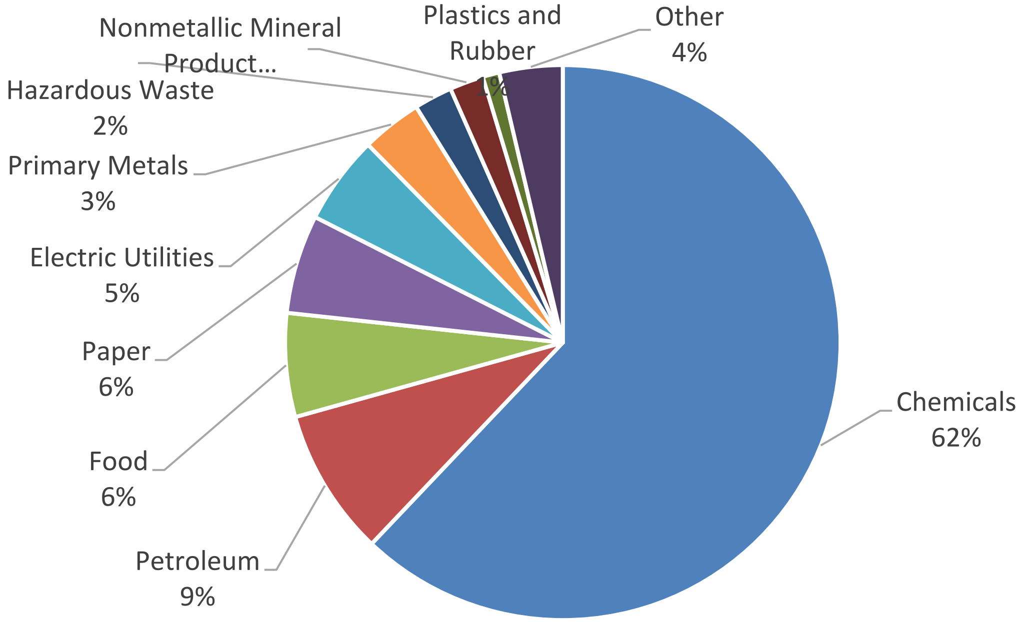


Figure C.10.1. Chemical waste emission breakdown for major sectors in 2017

Appendix D

Supporting Information for Chapter 6

D.1 General Assumptions Used for the Material Flow Analyses of Plastics in End-Of-Life (EoL) Stages

Table D.1.

Assumptions Used in the Generic Scenario Calculations

Assumptions	**Justification**
Accumulation during the consumer use phase is 0	It is difficult to predict the use-time of a particular plastic product. Thus, in reality, this assumption is not perfectly accurate. For example, in some applications such as food storage, people will use the container for years before discarding/recycling it. Alternatively, some plastics are used as single-use items (food wrapping, utensils, plates).
10% of plastic produced ends up in the environment/ocean	Realistically, plastics sent to landfills are likely to migrate to another environment. Plastic landfills do hold plastics within the containment barrier. However, a fraction of plastics does not make it into the containment. Transportation between stages, collection, sorting, and littering are all factors that contribute to plastics release.
Additives composition varies between a specific range based on types. To ensure that the general mass balance of all additive types are accounted for in a given stream, the lowest composition of additive was used for all material balances	Refer to the Material Flow Analysis spreadsheet available in: https://github.com/USEPA/GS_End-of-Life_Plastic_Additives Plastics manufactured do not necessarily always use every additive possible. In some cases, one plastic product may use fillers, while another type uses none. Using minimum composition lets us assume that, on average, the fraction of added additives to omitted additives balances the minimum composition. This assumption was made because the average additive composition for "Other plastics" nets a negative polymer resin mass, which is not possible in reality. For instance, suppose that a plastic product is made out of base resin (A), additive B, and additive C. Additive B can range between 5 – 70% of the total mass, while additive eC can range between 10 - 50% of the total mass. The highest additive composition mixture in this situation would result in 120% additives, an impossible scenario. The lowest additive composition equates to 15% additives and 85% base resin. Our work considers a longer list of additives that could be present. Using the compositions still the additive content to a value higher than 100%. Instead, low composition for all chemical additives is chosen because we also considered the possibility that some additives may not be found in all plastics generated.
2% of total plastic waste generated becomes litter	Jambeck *et al.* (2015) reported a 2% littering rate for plastic waste in their analysis

Degradation of plastic waste in landfill is too slow for appreciable mass loss	Plastic waste can take hundreds of years to degrade in the environment. When performing a material flow analysis on the basis of one year, the mass loss of plastic waste can be considered negligible. However, mass loss to the environment such as the ocean should be considered. This assumption is valid only for material flow analysis involving plastic components. If we factor in the rest of the MSW that ended up in the landfill, the degradation products cannot be neglected.
Incineration of plastic waste results in ash content equal to 1% of the original volume	Refer to the Material Flow Analysis spreadsheet available in: https://github.com/USEPA/GS_End-of-Life_Plastic_Additives Using the average ash density of 2.05 g/cm^3, average polymer density of 0.000413367 tons/cm^{3,} or 0.375 kg/cm^3 (calculated in the generic polymer stream tab), we can calculate the ash content generated. The remaining mass has already been converted to a standardized unit of CO2-eq and thus will not appear balanced.
2% of additives migrated during the use phase	We have very limited information on migrated chemicals during the use phase because it is difficult and time-consuming to do individual studies. However, we have compiled and estimated this migration using existing data from Crompton (2007), who analyzed additive migration over 30 days at 20°C. Source: T. R. Crompton, Additive migration from plastics into food: a guide for analytical chemists, New ed. Shawbury: Smithers Rapra Technology, 2007.
0.00047% of polymer/plastic/monomer migrated during use phase	Like the previous assumption, Crompton (2007)'s migration data was used. This value of 0.00047% came from the possibility of PDMS dissolving in oily products. This value is the only contributing factor to polymer migration at this time. More available data will improve the accuracy. Source: T. R. Crompton, Additive migration from plastics into food: a guide for analytical chemists, New ed. Shawbury: Smithers Rapra Technology, 2007.
Emissions in the unit of tons CO2 equivalent is not considered part of the mass	The emissions calculated were based on average endpoint data. The specifics of the identity of the "emission" are unspecified. However, for this study, we assumed that the emissions come from running the process, using substances integral to the operation, and other releases that do not include plastics/additives. Note that tons of CO_2 equivalent are simply a way of standardizing the impacts of different released substances. A higher mass of CO_2 equivalent signifies a high environmental impact. Therefore, different chemicals are assigned different values of CO_2 equivalency.
Microplastics/Plastic components make up 0.01% of the compost's mass	Plastic-coated products have the potential to contaminate compost. Brinton *et al.* (2018) tested the content of microplastics in plastic-coated paper products (milk and juice cartons, hot and cold paper drinking cups, frozen food containers, take-out containers, paper plates, and plastic-lined paper bags). During composting, these plastic coatings break down into smaller components (microplastics) rather than succumbing to biodegradation. Unfortunately, these microplastics can produce persistent organic pollutants such as

	DDT, PCBs, and dioxins. Eventually, these toxic chemicals may find their way into wildlife and the food chain. Source: W. Brinton, C. Dietz, A. Bouyounan, and D. Matsch, “Microplastics in Compost: The Environmental Hazards Inherent in the Composting of Plastic-Coated Paper Products,” p. 19, 2018.
The incineration of 1 MT (1.1 US tons) of MSW releases approximately 0.95 MT CO2-eq (or 1.05 tons CO2-eq)	A background paper on "Good Practice Guidance and Uncertainty Management in National Greenhouse Gas Inventories" reported that the incineration of 1 MT of MSW releases between 0.7-1.2 MT of CO2. An average value of 0.95 MT was used. Source: Intergovernmental Panel on Climate Change (IPCC), IPCC Expert Meetings on Good Practice Guidance and Uncertainty Management in National Greenhouse Gas Inventories. Institute for Global Environmental Strategies (IGES) for the IPCC, 2002.
Polymer recovery rate = 66.7-94%	van Velzen *et al.* (2017) performed a study on the polymer recovery efficiency via mechanical recycling and determined that the net polymer yields have varied between 66.7 – 94% for a standard recycling process. Some contaminants are partially removed following the same process. Additionally, a recent material recycling facility constructed in Philadelphia has demonstrated a recycling efficiency of 64%. We estimated a 66.7% efficiency for this one iteration. Opportunities for sensitivity analysis are available for this parameter Source: E. U. T. van Velzen, M. Jansen, M. T. Brouwer, A. Feil, K. Molenveld, and T. Pretz, “Efficiency of recycling post-consumer plastic packages,” Lyon, France, 2017, p. 170002. doi: 10.1063/1.5016785.
2% of the additives subjected to mechanical recycling have migrated from the polymer matrix	van Velzen *et al.* (2017) reported that approximately 1-3% of the recovered polymer mass appeared as dissolved substances that were separated during the polymer wash. Although they were not specific about the identity of the dissolved substances, we can approximate that the dissolved substances are volatile/semi-volatile additives Source: E. U. T. van Velzen, M. Jansen, M. T. Brouwer, A. Feil, K. Molenveld, and T. Pretz, “Efficiency of recycling post-consumer plastic packages,” Lyon, France, 2017, p. 170002. doi: 10.1063/1.5016785.
Additives added to help the polymer processability is lumped into the contamination stream #19	Refer to the Material Flow Analysis spreadsheet available in: https://github.com/USEPA/GS_End-of-Life_Plastic_Additives The spreadsheets available provides the calculations that this assumption is referencing. Please also refer to Section C diagrams for stream #19’s relation to the rest of the plastic life cycle. Horodytska (2020) study focuses on determining chemicals found in recycled plastic after being subjected to mechanical recycling. During recycling, we know that more additives are added to improve

	processability. However, some of the same additives can migrate out. Therefore, the contamination stream is the "net" mass flow rate of chemicals into recycled plastics. Source: O. Horodytska, A. Cabanes, and A. Fullana, “Non-intentionally added substances (NIAS) in recycled plastics,” Chemosphere, vol. 251, p. 126373, Jul. 2020, doi: 10.1016/j.chemosphere.2020.126373.
The contamination/degradation products entering the manufacturing phase are neglected from Stream 4	Refer to the Material Flow Analysis spreadsheet available in: https://github.com/USEPA/GS_End-of-Life_Plastic_Additives Please also refer to Section C diagrams for streams #4 and #20 and their relations to the rest of the plastic life cycle. If we account for the contamination/degradation of chemicals from stream 20 (recycled), we will enter a calculation loop. The contaminants/degradation from the plastic's previous life would get added to the next cycle.
Plastic Waste Import/Export - Ethylene = HDPE/LDPE are evenly split “Other plastics” include uncategorized plastics and polyethylene terephthalate at a 60:40 wt % ratio	UN COMTRADE database grouped all ethylene polymers into one category rather than specifying HDPE, LDPE, and PET. Therefore, dividing the values into three is chosen as an assumption for calculation. According to Ma *et al.* (2020), PET imports account for 40% of the world’s total export. Although variation is expected between countries, using a global average to estimate an unknown fraction should be reasonable. Therefore, based on the UN COMTRADE data regarding plastic waste import/export/re-export, we assume that 40% of “Other plastics” are PET and 60% contains other uncategorized plastic wastes. Source: Z. Ma, M. W. Ryberg, P. Wang, L. Tang, and W.-Q. Chen, “China’s Import of Waste PET Bottles Benefited Global Plastic Circularity and Environmental Performance,” ACS Sustainable Chemistry & Engineering, vol. 8, no. 45, pp. 16861–16868, Nov. 2020, doi: 10.1021/acssuschemeng.0c05926. United Nations, “UN Comtrade,” 2021. [Online]. Available: https://comtrade.un.org/data/
1/3 of Domestically Recycled Plastic is sent to incineration/landfill due to inefficiency problem	Only 3.9% has been domestically recycled in the United States, while 4.5% has been exported for recycling in 2018. State-of-the-art technology could realistically recover 2/3 of the plastics sent for recycling, leaving 1/3 as waste. This assumption is a "best-case scenario."

Landfill leachate release additive at a 0.001% rate	Landfill sites in industrialized countries have been known to perform leachate treatments such as aerobic and membrane bioreactors to reduce the BPA concentration to 0.11 – 30 μg/L. Without proper leachate treatment, plastic additives and BPA could be released into the environment and contaminate the nearby water supply. The rate of leachate release has been estimated to vary between 20 – 30% of the wastes placed in the landfill [23]. Our generic scenario holds that over 146 million tons of waste have been sent for landfilling in 2018, with each landfill receiving on average 55,000 tons of MSW/day. The potential leachate generated from landfills may approach 29.2 – 43.8 million tons/yr, or 11,000 – 16,500 tons/(yr·site). For a given site, the estimated yearly chemical additive release through leachate equates to 0.11 – 0.165 tons/(yr·site) (0.001% additive in leachate). Source: E. L. Teuten, J. M. Saquing, D. R. U. Knappe, M. A. Barlaz, S. Jonsson, A. Björn, S. J. Rowland, R. C. Thompson, T. S. Galloway, R. Yamashita, D. Ochi, Y. Watanuki, C. Moore, P. H. Viet, T. S. Tana, M. Prudente, R. Boonyatumanond, M. P. Zakaria, K. Akkhavong, Y. Ogata, H. Hirai, S. Iwasa, K. Mizukawa, Y. Hagino, A. Imamura, M. Saha and H. Takada, Transport and release of chemicals from plastics to the environment and to wildlife, *Philosophical Transactions of the Royal Society B: Biological Sciences*, 2009, **364**, 2027–2045.

D.2 Incineration Process Requirements and Crucial Parameters for Modeling the Dispersion of Pollutants

Table D.2.

The Typical Concentration of Pollutants Generated from Incineration Furnace, Maximum Admissible Exhaust, and Removal Efficiency Required for Gas Cleaning Systems

Pollutant	Before Gas Treatment (mg/Nm^3)	After Gas Treatment (mg/Nm^3)	Legal Limits (mg/Nm^3)
Dust	1000 – 5000	0.1 – 4	10
CO	5 – 50	2 – 45	50
Total Organic Carbon	1 – 10	0.1 – 5	10
Fly Ash	1500 – 2000	10	10
HCl	500 – 2000	10	10
SO_2	200 – 1000	0.2 – 20	50
NO_x	200 – 500	20 – 180	200
HF	5 – 20	0.01 – 0.1	1
Hg	0.05 – 0.5	0.0002 – 0.05	0.05
Heavy metals (Cd, Tl, Sb, As, Pb, Cr, Co, Cu, Mn, Ni, V)	< 50	0.0002 – 0.05	0.05
Dioxins and Furans (ng I-TEQ/Nm^3)	0.5 – 10	0.0002 – 0.08	0.1
CO_2	5 – 10%	-	-
H_2O	10 – 20%	-	-

Reference: M. J. Quina, J. Bordado and R. Quinta-Ferreira, in the Impact of Air Pollution on Health, Economy, Environment and Agricultural Sources, ed. M. Khallaf, InTech, 2011.

D.3 Dispersion Modeling Parameters

Table D.3.

Parameters Used to Estimate the Ground-Level Concentration Based on Dispersion of Plume from a Point Source (Incinerator)

Dispersion Model Parameter	Value
Average Wind Speed (m/s)	4.06
Average Temperature (°F)	52
Average Pressure (psia)	14.73
Night/Day	Day (1hr after dawn)
Condition	Moderate
Weather Stability	Neutrally Stable
Location	Urban/Rural
Incineration Stack Height (ft)	15 - 200
Gas Release Rate (SCFM)	500 – 50,000

Additional Information:

Time of day (day/night), weather stability (extremely unstable/moderately unstable/slightly unstable/neutrally stable/slightly stable/moderately stable), condition (strong/moderate/slight), and location (urban/rural) are used to determine the recommended equations for Pasquill-Gifford Dispersion Coefficients.

Weather stability depends on windspeed and quantity of sunlight.

Night time is defined as 1 hour before sunset, while daytime is defined as 1 hour after dawn. Weather stability is a function of the time of day.

The "strong" condition corresponds to a sunny midday in midsummer in England. "Slight" condition corresponds to a sunny midday in midwinter. "Moderate" condition is in between strong and slight condition.

Location (urban/rural) considers the effects of obstruction that may prevent the wind from dispersing gaseous pollutant from reaching a longer distance. Rural area generally has less obstruction, leading to a longer-range dispersion than urban environment.

Crowl and Louvar 2011 contains different correlations for all cases of gas dispersion, based on the chosen assumptions.

References:

D. A. Crowl and J. F. Louvar, Chemical process safety: fundamentals with applications, Prentice Hall, Upper Saddle River, NJ, 3rd ed., 2011.

Barometric Pressure Summary, https://www.planoweather.com/wxbarosummary.php.

Annual Average Wind Speed in US Cities, https://www.currentresults.com/Weather/US/wind-speed-city-annual.php.

Average annual temperature in the US from 1895 to 2020, https://www.statista.com/statistics/500472/annual-average-temperature-in-the-us/.

US EPA, "Air Pollution Control Technology Fact Sheet - Thermal Incinerator." US Environmental Protection Agency, 2003. [Online]. Available: https://www3.epa.gov/ttnchie1/mkb/documents/fthermal.pdf

D.4 Overall Material Flow Analysis Results for Sensitivity Analysis Scenarios

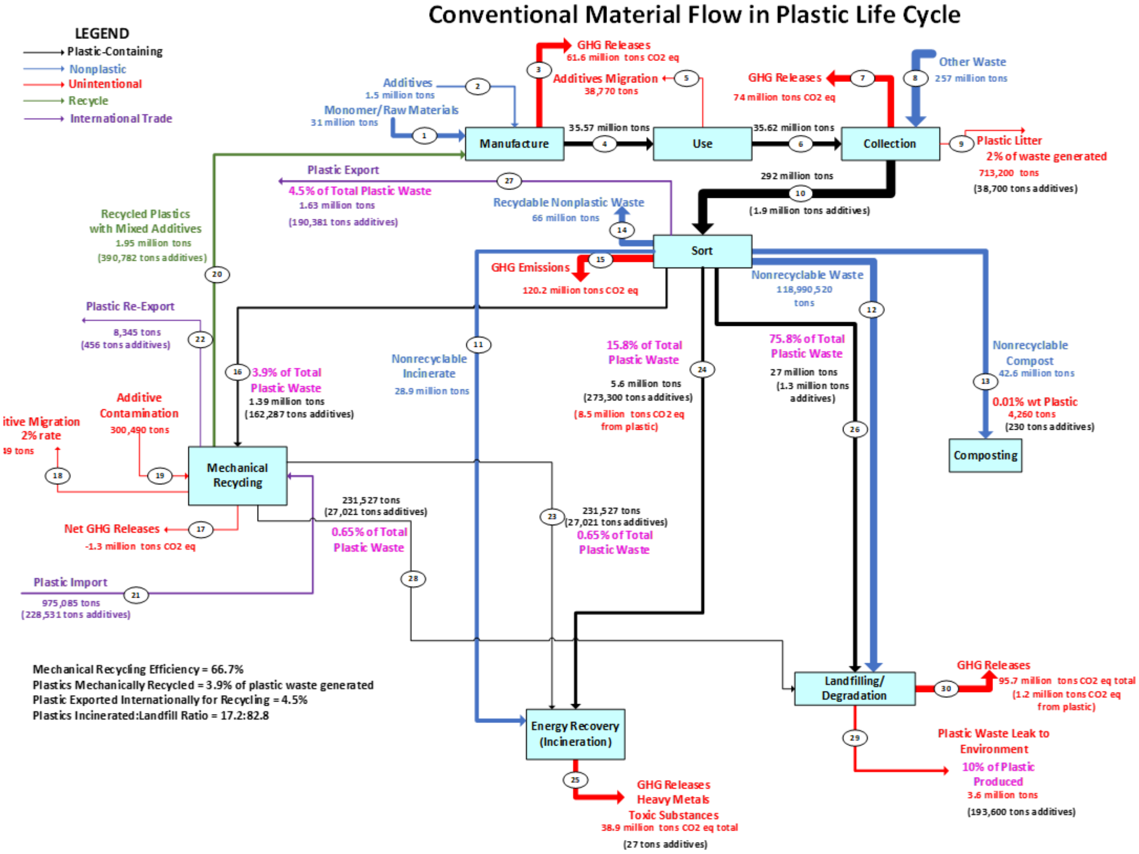
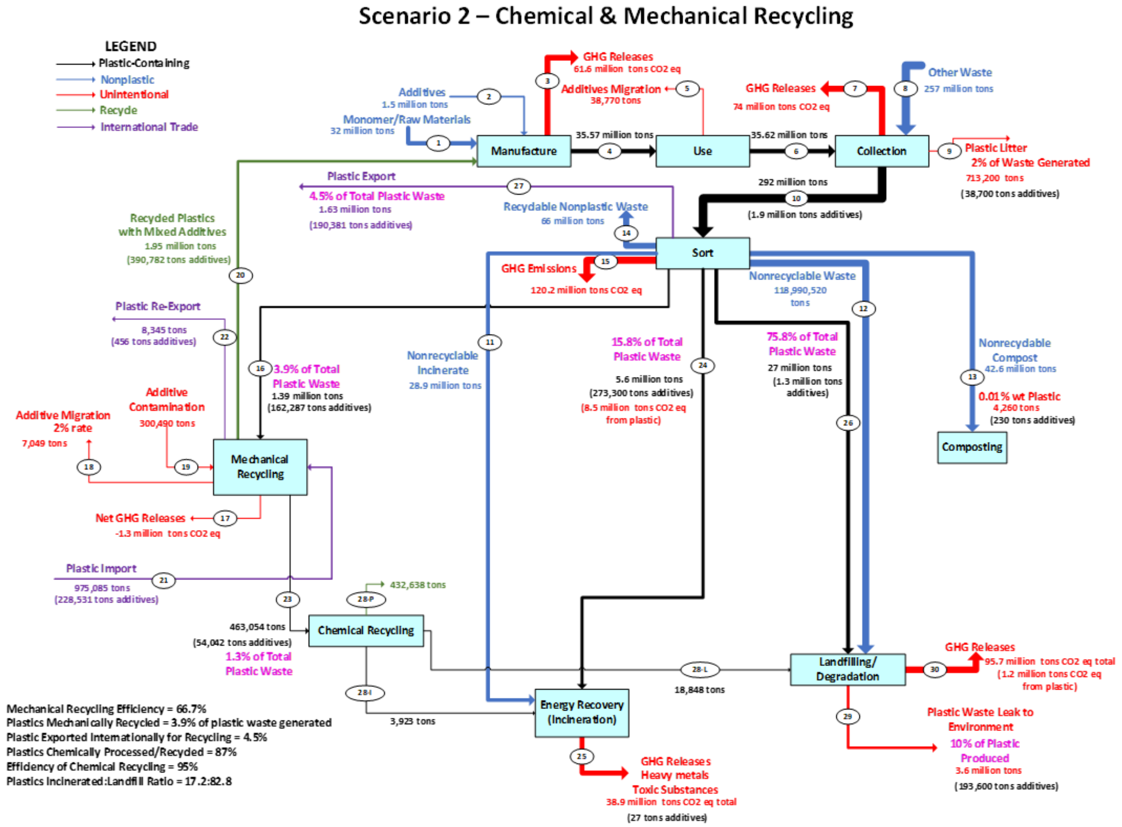


Figure D.4.1. Scenario 1 – only utilizing mechanical recycling (the state of plastic wastes management in 2018)



Mechanical Recycling Efficiency = 66.7%
Plastics Mechanically Recycled = 3.9% of plastic waste generated
Plastic Exported Internationally for Recycling = 4.5%
Plastics Chemically Processed/Recycled = 87%
Efficiency of Chemical Recycling = 95%
Plastics Incinerated:Landfill Ratio = 17.2:82.8

Figure D.4.2. Scenario 2 – the combination of chemical and mechanical recycling

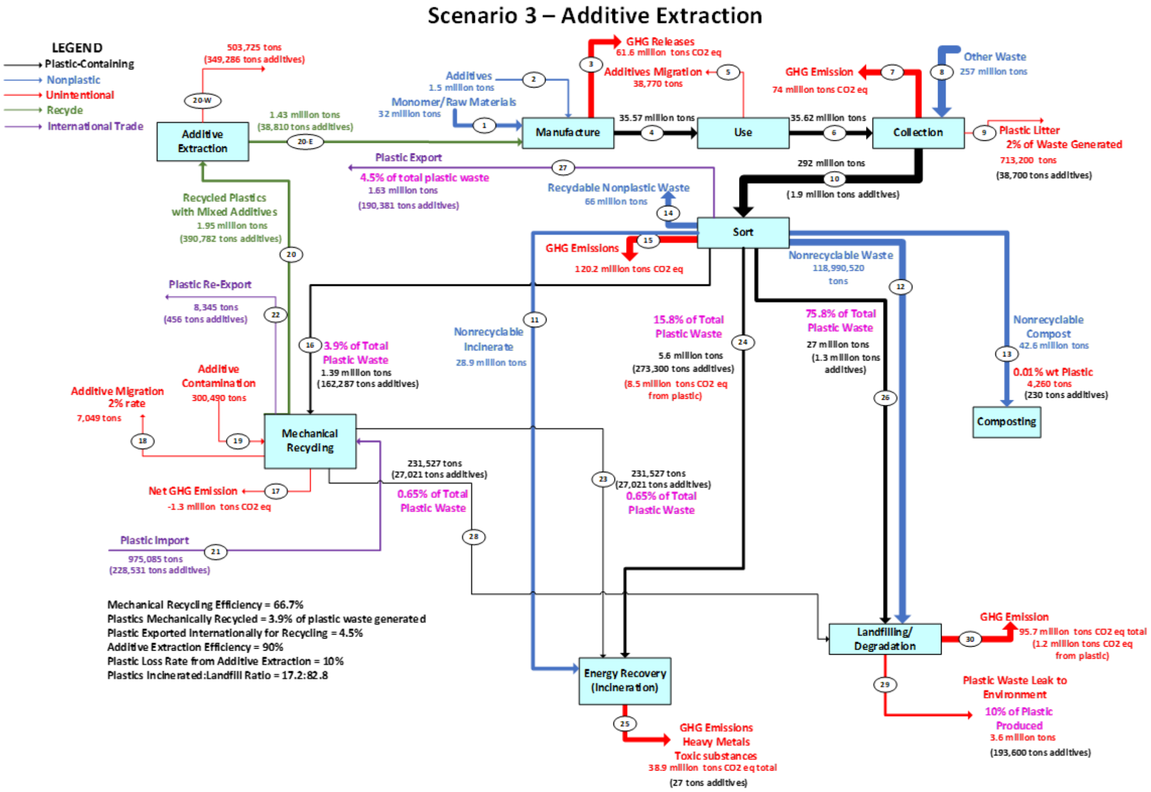


Figure D.4.3. Scenario 3 – implementing chemical additive extraction stage post-mechanical recycling

Table D.4.

Material Flow Analysis Stream Summary, in which the Result Corresponds to Figure D.4.1. (Scenario 1)

Stream	**1**	**2**	**3**	**4**	**5**
	[US tons]	[US tons]	[US tons]	[US tons]	[US tons]
Polyethylene Terephthalate (PET)	4,639,200	0	0	5,217,459	25
High Density Polyethylene (HDPE)	5,912,896	0	0	6,142,207	29
Polyvinyl Chloride (PVC)	710,974	0	0	743,395	4
Low Density Polyethylene (LDPE)	8,192,691	0	0	8,366,180	39
Polylactic Acid (PLA)	66,336	0	0	66,336	0
Polypropylene (PP)	7,982,685	0	0	7,997,513	38
Polystyrene (PS)	2,200,480	0	0	2,225,960	10
Other Plastics	2,403,445	0	0	2,977,806	14
Plasticizer	0	407,991	0	508,715	10,147
Flame Retardant	0	211,396	0	227,303	4,534
UV/Heat Stabilizer	0	253,672	0	273,497	5,455
Antioxidant	0	143,797	0	151,865	3,029
Slip Agents	0	22,693	0	23,987	478
Lubricants	0	3,990	0	4,997	100
Antistatics	0	9,980	0	11,703	233
Curing Agents	0	3,187	0	4,158	83
Blowing Agents	0	15,935	0	20,788	415
Biocides	0	33	0	42	1
Colorant	0	51,592	0	55,569	1,108
Organic Pigment	0	269	0	293	6
Clarifier/Toner	0	2,381	0	2,639	53
Inorganic Pigments	0	319	0	416	8
Fillers	0	33	0	42	1
Reinforcement	0	491,550	0	637,143	12,708
Misc. Inorganic Wastes	0	0	0	0	0
Other	0	0	0	0	0
Yard Trimmings	0	0	0	0	0
Food	0	0	0	0	0
Rubber, Leather, Textiles	0	0	0	0	0
Wood	0	0	0	0	0
Metals	0	0	0	0	0
Glass	0	0	0	0	0
Paper and Paperboard	0	0	0	0	0
Contaminants	0	0	0	0	0
Additive Degradation Products	0	0	0	0	0
Ash	0	0	0	0	0
Total Mass excluding emissions	32,108,707	1,618,817	0	35,660,011	38,518
Total Plastics	32,108,707	0	0	33,736,855	159
Total Additives	0	1,618,817	0	1,923,156	38,359

Stream	**6**	**7**	**8**	**9**	**10**
	[US tons]	[US tons]	[US tons]	[US tons]	[US tons]
Polyethylene Terephthalate (PET)	5,217,434	0	214,534	104,291	5,327,678
High Density Polyethylene (HDPE)	6,142,178	0	448,038	122,522	6,467,693
Polyvinyl Chloride (PVC)	743,391	0	121,749	14,860	850,281
Low Density Polyethylene (LDPE)	8,366,140	0	448,498	167,230	8,647,408
Polylactic Acid (PLA)	66,336	0	0	1,326	65,010
Polypropylene (PP)	7,997,475	0	0	159,861	7,837,615
Polystyrene (PS)	2,225,949	0	27,664	44,494	2,209,119
Other Plastics	2,977,792	0	233,554	59,523	3,151,823
Plasticizer	498,568	0	46,359	10,169	534,758
Flame Retardant	222,769	0	10,248	4,544	228,473
UV/Heat Stabilizer	268,042	0	15,301	5,719	277,624
Antioxidant	148,836	0	7,061	3,036	152,861
Slip Agents	23,508	0	952	479	23,981
Lubricants	4,898	0	464	100	5,261
Antistatics	11,470	0	572	234	11,808
Curing Agents	4,075	0	326	83	4,318
Blowing Agents	20,374	0	1,630	416	21,589
Biocides	42	0	3	1	44
Colorant	54,460	0	3,530	1,111	56,880
Organic Pigment	287	0	16	7	296
Clarifier/Toner	2,586	0	82	53	2,615
Inorganic Pigments	407	0	33	8	432
Fillers	42	0	3	1	44
Reinforcement	624,435	0	48,914	12,736	660,613
Misc. Inorganic Wastes	0	0	4,063,804	0	4,063,804
Other	0	0	4,560,816	0	4,560,816
Yard Trimmings	0	0	35,375,560	0	35,375,560
Food	0	0	63,120,524	0	63,120,524
Rubber, Leather, Textiles	0	0	26,195,456	0	26,195,456
Wood	0	0	18,097,084	0	18,097,084
Metals	0	0	25,610,736	0	25,610,736
Glass	0	0	12,249,884	0	12,249,884
Paper and Paperboard	0	0	67,388,980	0	67,388,980
Contaminants	0	0	0	0	0
Additive Degradation Products	0	0	0	0	0
Ash	0	0	0	0	0
Total Mass excluding emissions	35,621,493	0	258,292,372	713,200	293,201,065
Total Plastics	33,736,696	0	1,494,035	674,106	34,556,625
Total Additives	1,884,797	0	135,493	38,695	1,981,595

Stream	11	12	13	14	15
	[US tons]	[US tons]	[US tons]	[US tons]	[US tons]
Polyethylene Terephthalate (PET)	0	0	623	0	0
High Density Polyethylene (HDPE)	0	0	732	0	0
Polyvinyl Chloride (PVC)	0	0	89	0	0
Low Density Polyethylene (LDPE)	0	0	999	0	0
Polylactic Acid (PLA)	0	0	8	0	0
Polypropylene (PP)	0	0	955	0	0
Polystyrene (PS)	0	0	266	0	0
Other Plastics	0	0	356	0	0
Plasticizer	0	0	61	0	0
Flame Retardant	0	0	27	0	0
UV/Heat Stabilizer	0	0	34	0	0
Antioxidant	0	0	18	0	0
Slip Agents	0	0	3	0	0
Lubricants	0	0	1	0	0
Antistatics	0	0	1	0	0
Curing Agents	0	0	0	0	0
Blowing Agents	0	0	2	0	0
Biocides	0	0	0	0	0
Colorant	0	0	7	0	0
Organic Pigment	0	0	0	0	0
Clarifier/Toner	0	0	0	0	0
Inorganic Pigments	0	0	0	0	0
Fillers	0	0	0	0	0
Reinforcement	0	0	76	0	0
Misc. Inorganic Wastes	794,880	3,215,960	0	0	0
Other	656,640	2,923,600	0	966,000	0
Yard Trimmings	2,557,440	10,524,960	22,279,800	0	0
Food	7,534,080	35,229,380	20,320,200	0	0
Rubber, Leather, Textiles	5,736,960	16,225,980	0	4,181,400	0
Wood	2,833,920	12,132,940	0	3,098,100	0
Metals	2,937,600	13,887,100	0	8,714,700	0
Glass	1,624,320	7,601,360	0	3,056,700	0
Paper and Paperboard	4,216,320	17,249,240	0	45,954,000	0
Contaminants	0	0	0	0	0
Additive Degradation Products	0	0	0	0	0
Ash	0	0	0	0	0
Total Mass excluding emissions	28,892,160	118,990,520	42,604,258	65,970,900	0
Total Plastics	0	0	4,026	0	0
Total Additives	0	0	231	0	0

Stream	**16**	**17**	**18**	**19**	**20**
	[US tons]	[US tons]	[US tons]	[US tons]	[US tons]
Polyethylene Terephthalate (PET)	406,666	0	0	0	578,259
High Density Polyethylene (HDPE)	246,870	0	0	0	229,311
Polyvinyl Chloride (PVC)	0	0	0	0	32,420
Low Density Polyethylene (LDPE)	163,278	0	0	0	173,489
Polylactic Acid (PLA)	0	0	0	0	0
Polypropylene (PP)	22,231	0	0	0	14,828
Polystyrene (PS)	8,925	0	0	0	25,480
Other Plastics	360,014	0	0	0	574,361
Plasticizer	50,266	0	1,005	17,874	100,723
Flame Retardant	9,510	0	190	3,382	15,907
UV/Heat Stabilizer	11,964	0	239	4,254	19,825
Antioxidant	4,778	0	96	1,699	8,068
Slip Agents	702	0	14	250	1,293
Lubricants	503	0	10	179	1,007
Antistatics	924	0	18	328	1,724
Curing Agents	503	0	10	179	971
Blowing Agents	2,513	0	50	894	4,853
Biocides	5	0	0	2	10
Colorant	2,332	0	47	829	3,977
Organic Pigment	14	0	0	5	23
Clarifier/Toner	141	0	3	50	258
Inorganic Pigments	50	0	1	18	97
Fillers	5	0	0	2	10
Reinforcement	75,399	0	1,508	26,811	145,593
Misc. Inorganic Wastes	0	0	0	0	0
Other	0	0	0	0	0
Yard Trimmings	0	0	0	0	0
Food	0	0	0	0	0
Rubber, Leather, Textiles	0	0	0	0	0
Wood	0	0	0	0	0
Metals	0	0	0	0	0
Glass	0	0	0	0	0
Paper and Paperboard	0	0	0	0	0
Contaminants	0	0	0	8,889	8,889
Additive Degradation Products	0	0	0	70,431	70,431
Ash	0	0	0	0	0
Total Mass excluding emissions	1,367,592	0	3,192	136,075	1,932,487
Total Plastics	1,207,985	0	0	0	1,628,148
Total Additives	159,607	0	3,192	56,755	304,339

Stream	21 [Import]	22 [Re-Export]	23	24	25
	[US tons]	[US tons]	[US tons]	[US tons]	[US tons]
Polyethylene Terephthalate (PET)	307,423	410	67,710	745,139	81
High Density Polyethylene (HDPE)	68,182	3,534	41,104	963,296	100
Polyvinyl Chloride (PVC)	32,451	30	0	128,227	13
Low Density Polyethylene (LDPE)	68,112	3,531	27,186	1,380,910	141
Polylactic Acid (PLA)	0	0	0	11,442	1
Polypropylene (PP)	0	0	3,701	1,371,015	137
Polystyrene (PS)	19,553	27	1,486	380,554	38
Other Plastics	334,678	446	59,942	376,585	44
Plasticizer	50,393	66	8,369	68,612	8
Flame Retardant	6,430	58	1,583	35,587	4
UV/Heat Stabilizer	7,911	81	1,992	44,793	5
Antioxidant	3,318	40	795	24,376	3
Slip Agents	594	4	117	3,870	0
Lubricants	504	1	84	671	0
Antistatics	799	1	154	1,667	0
Curing Agents	467	1	84	526	0
Blowing Agents	2,336	3	418	2,629	0
Biocides	5	0	1	5	0
Colorant	1,659	20	388	8,697	1
Organic Pigment	10	0	2	56	0
Clarifier/Toner	117	0	23	402	0
Inorganic Pigments	47	0	8	53	0
Fillers	5	0	1	5	0
Reinforcement	70,093	93	12,554	81,196	9
Misc. Inorganic Wastes	0	0	0	0	79
Other	0	0	0	0	66
Yard Trimmings	0	0	0	0	256
Food	0	0	0	0	753
Rubber, Leather, Textiles	0	0	0	0	574
Wood	0	0	0	0	283
Metals	0	0	0	0	294
Glass	0	0	0	0	162
Paper and Paperboard	0	0	0	0	422
Contaminants	0	0	0	0	0
Additive Degradation Products	0	0	0	0	0
Ash	0	0	0	0	307
Total Mass excluding emissions	975,085	8,345	227,704	5,630,312	3,475
Total Plastics	830,399	7,977	201,130	5,357,168	556
Total Additives	144,686	368	26,575	273,145	30

Stream	26	27 [Export]	28	29	30
	[US tons]	[US tons]	[US tons]	[US tons]	[US tons]
Polyethylene Terephthalate (PET)	3,580,248	214,534	67,710	521,746	0
High Density Polyethylene (HDPE)	4,628,451	448,038	41,104	614,221	0
Polyvinyl Chloride (PVC)	616,106	121,749	0	74,339	0
Low Density Polyethylene (LDPE)	6,635,009	448,498	27,186	836,618	0
Polylactic Acid (PLA)	54,978	0	0	6,634	0
Polypropylene (PP)	6,587,461	0	3,701	799,751	0
Polystyrene (PS)	1,828,490	27,664	1,486	222,596	0
Other Plastics	1,809,417	233,554	59,942	297,781	0
Plasticizer	329,667	46,359	8,369	50,875	0
Flame Retardant	170,988	10,248	1,583	22,732	0
UV/Heat Stabilizer	215,219	15,301	1,992	27,352	0
Antioxidant	117,123	7,061	795	15,188	0
Slip Agents	18,596	952	117	2,399	0
Lubricants	3,222	464	84	500	0
Antistatics	8,010	572	154	1,170	0
Curing Agents	2,526	326	84	416	0
Blowing Agents	12,632	1,630	418	2,079	0
Biocides	26	3	1	4	0
Colorant	41,788	3,530	388	5,557	0
Organic Pigment	270	16	2	29	0
Clarifier/Toner	1,930	82	23	264	0
Inorganic Pigments	253	33	8	42	0
Fillers	26	3	1	4	0
Reinforcement	390,133	48,914	12,554	63,718	0
Misc. Inorganic Wastes	0	0	0	0	0
Other	0	0	0	0	0
Yard Trimmings	0	0	0	0	0
Food	0	0	0	0	0
Rubber, Leather, Textiles	0	0	0	0	0
Wood	0	0	0	0	0
Metals	0	0	0	0	0
Glass	0	0	0	0	0
Paper and Paperboard	0	0	0	0	0
Contaminants	0	0	0	0	0
Additive Degradation Products	0	0	0	0	0
Ash	0	0	0	0	0
Total Mass excluding emissions	27,052,568	1,629,528	227,704	3,566,015	0
Total Plastics	25,740,159	1,494,035	201,130	3,373,686	0
Total Additives	1,312,408	135,493	26,575	192,329	0

D.5 Greenhouse Gas (GHG) Releases and Energy Footprint of all EoL Practices for Plastics

Table D.5.

A Compilation of Greenhouse Gas Emission Factors and Energy Footprint used for the Sensitivity Analysis Study

	Mechanical Recycling		**Incineration**		**Landfilling/Littering**	
Plastic Types	**GHG (MT CO_2-eq/ton)**	**Energy Footprint (MJ/kg)**[a]	**GHG (MT CO_2-eq/ton)**	**Energy Footprint (MJ/kg)**	**GHG (MT CO_2-eq/tons)**	**Energy Footprint (MJ/kg)**[b]
PET	-1.13	80.1	1.24	40.0	0.04	-
HDPE	-0.88	78.5	1.27	54.3	0.04	-
PVC	0	57.9	0.67	28.1	0.04	-
LDPE	0	82.6	1.27	51.6	0.04	-
PLA	0	77.2	1.25	35.6	0.04	-
PP	0	90.0	1.27	55.7	0.04	-
PS	0	80.0	1.64	46.3	0.04	-
Other (Mixed)	-1.03	50.8	2.33	35.6	0.04	-

	Chemical Recycling (Pyrolysis)		**Additive Extraction (Dissolution-Precipitation)**	
Plastic Types	**GHG (MT CO_2-eq/ton)**	**Energy Footprint (MJ/ton)**	**GHG (MT CO_2-eq/tons)**	**Energy Footprint (MJ/kg)**
PET	0.238	3260	0.37	24.8
HDPE	0.238	3260	0.38	34.0
PVC	0.238	3260	0.20	17.0
LDPE	0.238	3260	0.38	33.1
PLA	0.238	3260	0.38	18.4
PP	0.238	3260	0.38	33.1
PS	0.238	3260	0.49	37.3
Other (Mixed)	0.238	3260	0.70	23.5

[a] Estimated from REMADE Calculator

[b] Not used for the calculation of material flow analysis

References:

US EPA, “Warm Version 13 - PLASTICS,” US EPA, 2015.

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D.6 Sustainable Process Index - Environmental Footprint Contribution

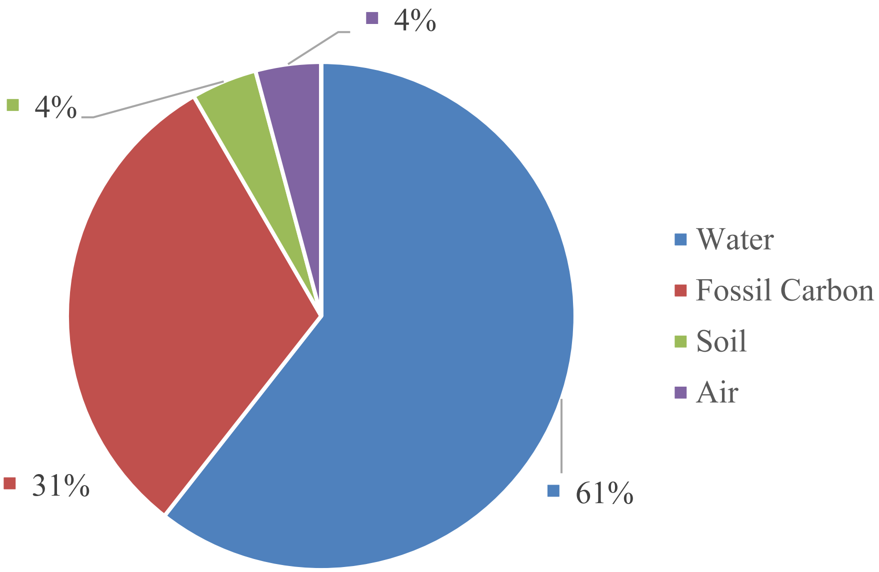

Figure D.6. Environmental footprints on the available resources. The total resource impact is equivalent to 371 m^2.a/kg of plastic recycled

D.7 Additional Information

All datasets and spreadsheets used to generate our results are available at https://github.com/USEPA/GS_End-of-Life_Plastic_Additives

Appendix E

List of Acronyms, Abbreviations, and Symbols

AHY	Acid Hydrolysis
APC	Advanced polymer chromatography
a_{incd}	Mass value expected in an incident (additive, ash, leachate)
$A_{surface}$	Surface area of contact
ATPE	Aqueous two-phase extraction
ATR	Attenuated total reflection
BARON	Branch and Reduce Optimization Navigator
BBE	Birch bark extracts
$b_{liq,skin,landfill}$	Liquid-skin contact in landfill
BPA	Bisphenol A
BYP	Bypass
C_{12} diacid	1,12-dodecanedioic acid
CHRM	Chromatography
CNF	Centrifugation
CRYS	Crystallization
Đ	Dispersity
DCM	Dichloromethane
DFDA	5,5′-methylenedifurfurylamine
DGEBBE	Diglycidyl ether of birch bark extracts
DGEBet	Diglycidyl ether of betulin
DGEBA	Diglycidyl ether of bisphenol A
DMA	Dynamic mechanical analysis
DME	Dimethoxyethane
DMF	Dimethylformamide
DRY	Drying
DSC	Differential scanning calorimetry
DST	Distillation
E'	Storage modulus
E''	Loss modulus
EEW	Epoxy equivalent weight
EME	1-ethoxy-1-methoxy ethane
EoL	End-of-life
EPA	Environmental Protection Agency
EpCl	Epichlorohydrin
EXP	Exposure rate (inhalation, dermal)
$F_{additive}$	Fraction of chemical additives (plastic, ash, leachate)
FLT	Filtration
FTIR	Fourier transform infrared
GAMS	General Algebraic Modeling Systems
GHG	Greenhouse gas
GRD	Grinding

GS	Generic scenario
GUI	Graphic user interface
HDPE	High-density polyethylene
HPLC	High-performance liquid chromatography
IDT	Initial decomposition temperature after 5% mass loss
INCN	Incineration
IPA	Isopropanol
L	Loss fraction
LDPE	Low-density polyethylene
M	Annual mass flow rate (collection, mechanical recycling, incineration)
MC	Maceration
MF	Microfiltration
MINLP	Mixed-integer nonlinear programming
M_n	Number-average molecular weight
M_w	Weight-average molecular weight
MIR	Mid-infrared
MSW	Municipal solid waste
N	Number (sites, exposure incidents)
N_2	Nitrogen gas
NIR	Near-infrared
NMR	Nuclear magnetic resonance
NT	Neutralization
O_2	Oxygen gas
OSN	Organic solvent nanofiltration
PET	Polyethylene terephthalate
PFD	Process Flow Diagram
PLA	Polylactic acid
PP	Polypropylene
PRC	Precipitation
PS	Polystyrene
PVC	Polyvinyl chloride
PVP	Pervaporation
R	Plastics released rate for a given site
$r_{breathing}$	Rate of breathing
RCRA	Resource Conservation and Recovery Act
R_{total}	Total annual plastics released (kg/yr)
SDM	Sedimentation
SFE	Supercritical fluid extraction
SPI	Sustainable process index
t	Duration of time (operating, exposure)
Tan δ	Tan delta
TBAHS	Tetra-butyl-ammonium-hydrogen-sulfate
TE	Turbo-extraction
T_g	Glass transition temperature

TGA	Thermogravimetric analysis
T_{max}	Maximum decomposition temperature
UAE	Ultrasound-assisted extraction
UF	Ultrafiltration

Appendix F

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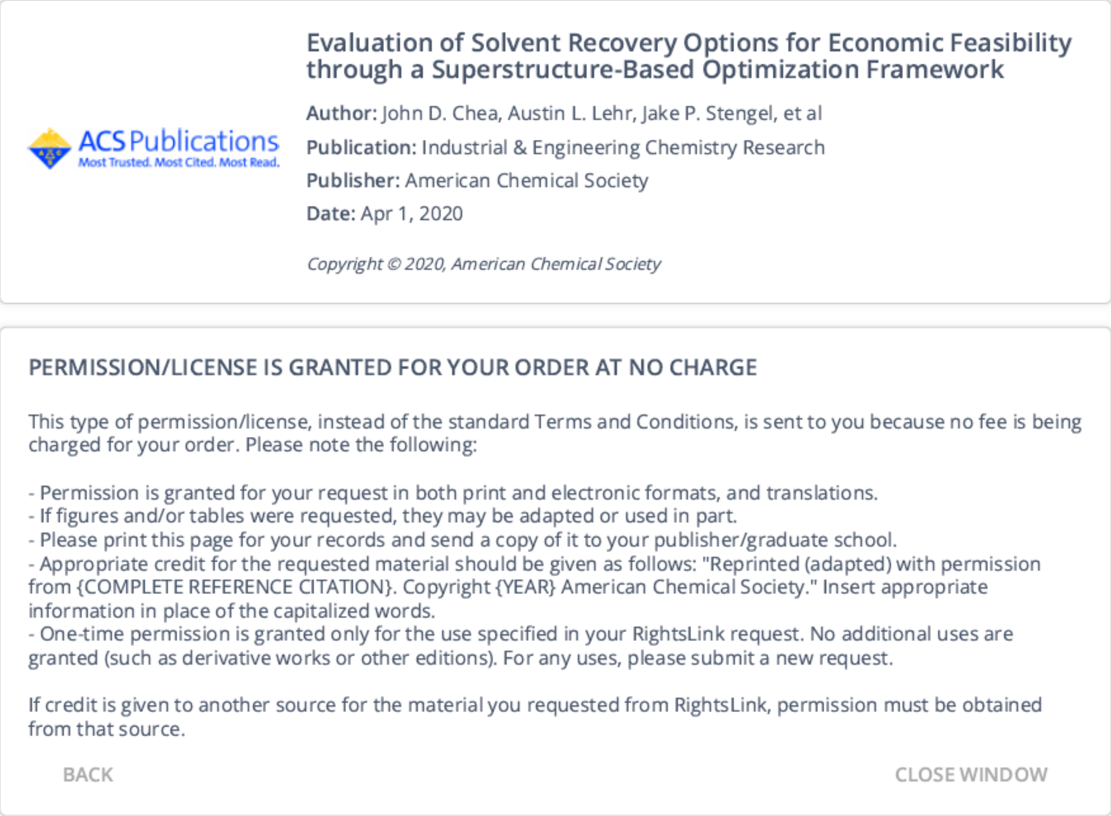

Evaluation of Solvent Recovery Options for Economic Feasibility through a Superstructure-Based Optimization Framework

Author: John D. Chea, Austin L. Lehr, Jake P. Stengel, et al
Publication: Industrial & Engineering Chemistry Research
Publisher: American Chemical Society
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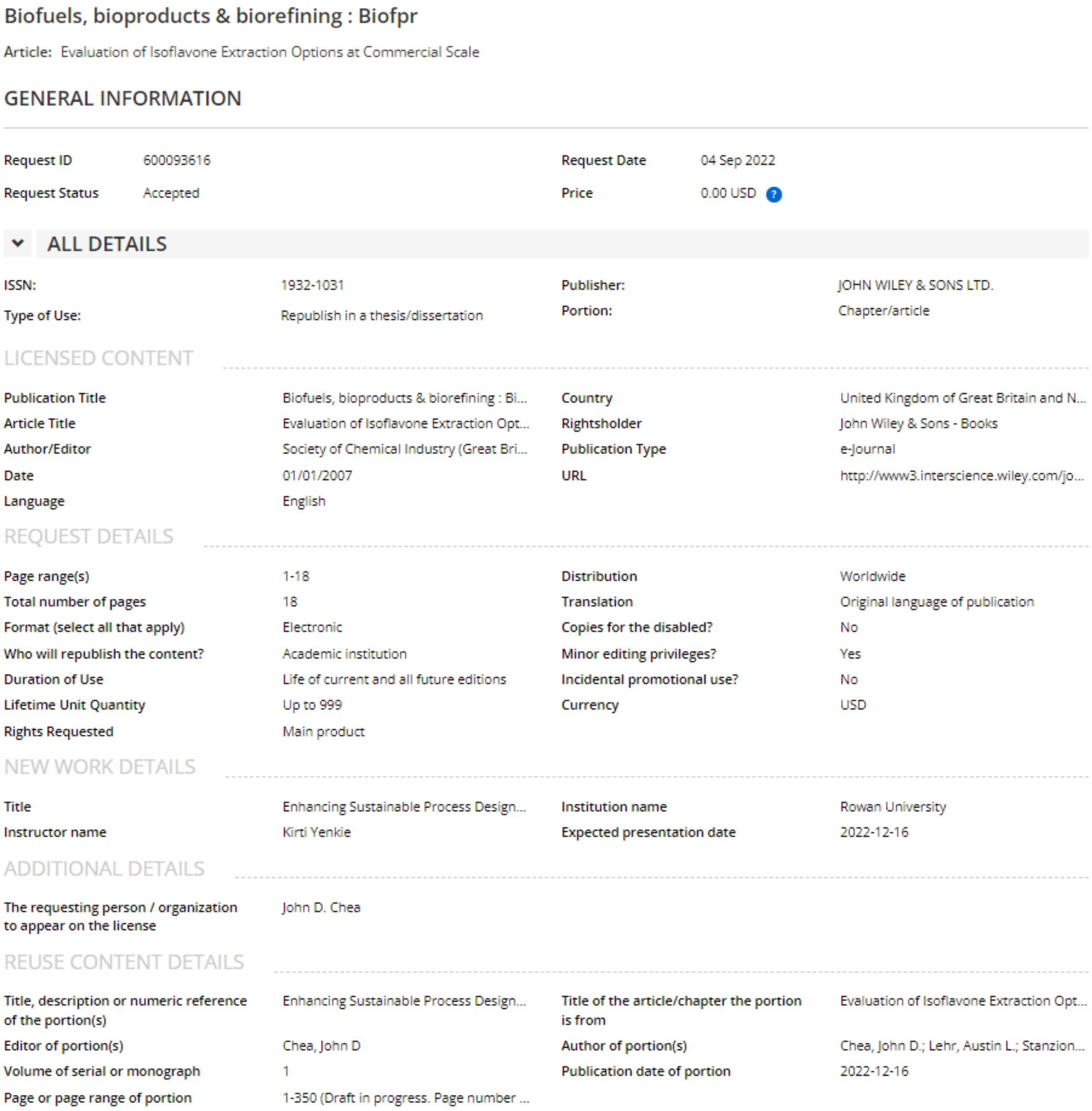

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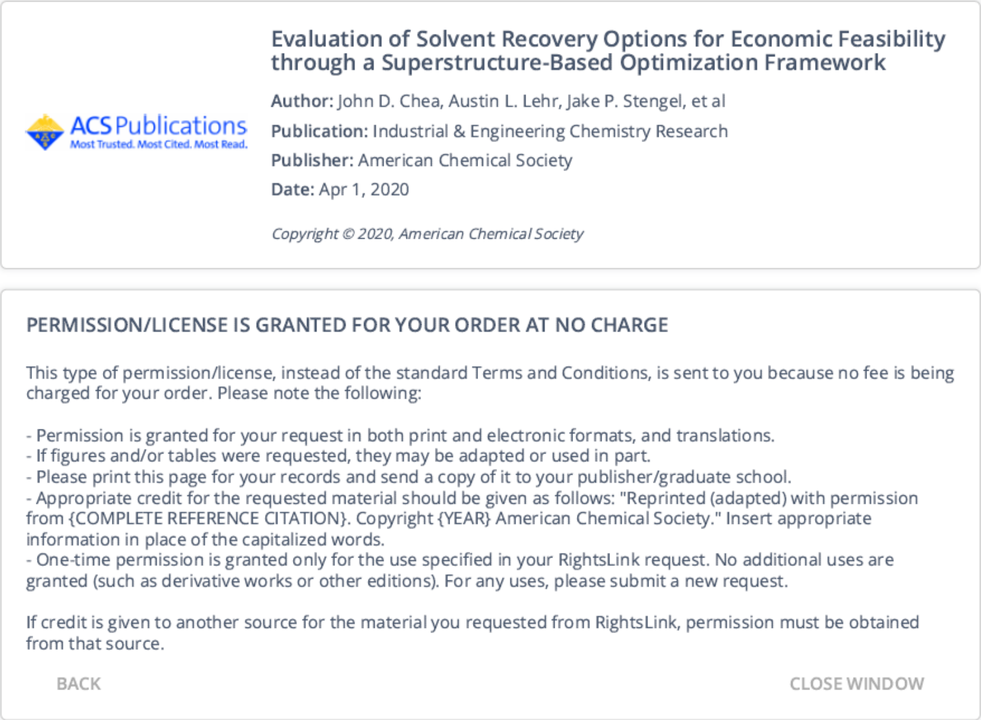

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Systematic Design of Solvent Recovery Pathways: Integrating Economics and Environmental Metrics

Author: Emmanuel A. Aboagye, John D. Chea, Austin L. Lehr, et al

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Chapter 6 Text, Figures, & Tables

A Generic Scenario Analysis of End-of-Life Plastic Management: Chemical Additives

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