

SYSTEMATIC DESIGN AND ANALYSIS OF SOLVENT ASSISTED PLASTIC RECYCLING PROCESSES

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Abstract

In 2019, approximately 368 million metric tons of plastic were produced, with nearly 50% of those plastics being single use. By the year 2050 plastic production is projected to triple and this expansion has generated concern over the end of life of plastics. Currently the waste management system is faced with two issues when it comes to plastics recycling: inefficient sorting methods and low-efficiency recycling methods. Mechanical recycling is the most common recycling method but presents with lower value recycled materials due to the material incompatibilities introduced via the inefficient sorting methods. These problems lead to over 90% of plastics to either be landfilled or incinerated. Chemical recycling presents a promising alternative as it potentially allows for plastics to maintain their original properties. To that end, there is the need to investigate the feasibility of chemical recycling methods to help mitigate the challenging problem posed by plastics end-of-life stage. This work proposes a conceptual solvent-assisted plastics recycling framework based on a superstructure optimization approach. This framework is evaluated using a representative case study for the recovery of Polyethylene Terephthalate (PET). In this case study it is found that polymer recovery is both economically and environmentally favorable to incineration.

Keywords

Optimization, Superstructure, Plastics Recycling

Introduction

In 2019, approximately 368 million metric tons of plastic were produced globally and by the year 2050 plastic production is expected to triple (Tiseo, 2020). From the beginning of large-scale production of plastics in 1950 to 2019, approximately 7300 million metric tons of plastic has been produced globally (Geyer et al., 2017). The general trend for yearly global plastic production has been growing at an exponential rate for the last 70 years. With the continued growth of the polymer industry, it is estimated that between 850-950 metric tons of plastic waste will be generated per year (Degnan and Shinde, 2019). Plastic waste generation has become of increasing concern as 79% of all waste plastics end up in landfills, 12% are incinerated, and only 9% are recycled (Geyer et al., 2017). The current waste management infrastructure lacks an effective sorting method for plastic waste and as a result even a portion of

the plastics sent to material recovery facilities are rejected. As the rate of plastic waste generation grows, continuing to landfill the majority of waste plastics will become ineffective as the surface area of the earth is finite. Furthermore, waste plastics make up 80% of marine debris as these materials are either illegally dumped into the ocean or are carried from the land by natural phenomena (*Plastics | General Assembly of the United Nations*, 2018). Several chemicals used in the production of plastics are known to be carcinogens and endocrine inhibitors, leading to developmental, reproductive, neurological, and immune disorders. Currently, plastic recycling is limited by two factors: inefficient sorting techniques and low-efficiency recycling methods. Everyday use plastics such as shopping bags, bottles, wraps, and material packaging are made out of polyethylene terephthalate (PET) and low-density

polyethylene (LDPE) end up in municipal solid waste (MSW) streams. The MSW streams can vary widely in composition, physical and chemical properties, and overall recycling potential, containing other materials like; cardboard and metal that need to first be separated out (Schwarz et al., 2021). The recyclable waste streams will then go on to material recovery facilities (MRF) for further sorting. Material sent to an MRF is often first separated by polymer type, typically accomplished using near infrared (NIR) technologies, then the materials are further separated into clear and colored streams using optical sensors (Schyns and Shaver, 2021). Furthermore, the separation of multilayered plastics such as water bottles with plastic sleeves is expensive and often contain polyamides or ethylene vinyl alcohols that can affect the chemical, physical, and mechanical properties of the recycle (Mehta, 2020).

Of all the plastics that are recycled, more than 90% are recycled via mechanical recycling. Extrusion is the most widely used mechanical recycling method as it is a cheap, large-scale, and solvent-free recovery method. In this process, heat and rotating screws are used to induce plasticization of the material, then the material is fed through a temperature controlled nozzle to form fixed cross section extrudate (Schyns and Shaver, 2021). The thermal conduction and shear force applied in the extruder lead to thermo-oxidative and shear-induced chain scission, cross-linking, or chain branching, which will lead to degradation of the polymer chain. With this degradation the mechanical properties of polymer will be affected, and the performance of the polymer material degrade as well. One of the greatest barriers to mechanical recycling is the recyclability of the material. The polymer blends present in the waste stream can compromise the mechanical integrity of the recycled product due to the incompatibility in the physical properties of the different polymers. Furthermore, these polymers often have additives present in them to enhance their physical and chemical properties, which cannot be addressed by mechanical recycling techniques. As plastic waste generation continues to grow it is imperative to simultaneously address the inefficiencies in the MSW sorting system.

The fundamental mechanisms behind chemical recycling methods are different than that of mechanical recycling as it deals primarily with the breakdown of the chemical structure of the material. Chemical processes are more tolerant of contaminants and yield material that is equivalent to the original, reducing the amount of downcycling (Tullo, 2019). Chemical recycling offers the ability to reprocess the material into petrochemicals that can be used as fuel or reprocessed into new plastics (Al-Salem et al., 2009). Polymers have two potential end-of-life uses following a chemical recycling process, plastic-to-plastic or plastic-to-fuel. These materials can be converted back into the original monomers or converted into oils. (Kunwar et al., 2016; Thomas et al., 2019). Plastics-to-fuels processes do result in greenhouse gas emissions as the material is combusted. However, using these plastics-to-fuel processes

to produce hydrocarbon fuels has been shown to produce less emissions than traditional fuel production processes (Benavides et al., 2017). Recent work has been done that shows a dissolution process can be used as a viable method to recover polymer (Sherwood, 2020). Dissolution processes require an appropriate solvent to dissolve the solute. Dissolution and depolymerization processes use solvent to recover the polymer or monomer so that it can be converted again into new plastics, however, this technology requires extensive amounts of solvent as that is often the agent in excess in the reaction driving up the operational cost. In addition, these processes lead to large amounts of solvent waste which can be challenging to manage because of the emissions associated with its disposal.

Chemical recycling methods can be an economically viable and environmentally friendly recycling methods if designed using a systems thinking approach to optimize system performance. In this work we leverage a methodology from previous work by Chea et. al (Chea et al., 2020) to evaluate solvent recovery methodologies. This work utilizes a superstructure-based optimization approach to simultaneously analyze multiple possible recovery pathways and reports the most economically and environmentally favorable option. Incorporating this solvent recovery framework in the design of plastic-to-plastic processes could benefit chemical recycling technologies and will provide more options to recover waste plastic that otherwise end up in the environment. The work proposed in this study examines the techno economic and environmental assessment of the design of solvent assisted plastic recycling. This study provides an optimization framework to address the economic challenges associated with implementing large-scale plastic recycling in the current waste management infrastructure while simultaneously estimating the environmental impact.

Materials and Methods

Polyethylene terephthalate (PET) is a polyester derived from crude oil. This material is used for packaging food and beverages because of its inert properties, recyclability, and durability. Sherwood et al. (2020) have developed and patented a two-stage closed-loop recycling process that uses an organic solvent such as ethyl benzoate (EB) to recycle post-consumer PET waste (Sherwood, 2020). The proposed process consists of two steps: (1) dye removal and (2) polymer dissolution. PET waste is firstly subjected to a dye removal step by subjecting the polymer to a solvent, ethyl benzoate, at 120°C. The solvent at this temperature swells the polymer, opening up the polymer matrix and allowing for dyes and additives to permeate out. The second step of the process uses ethyl benzoate at 180°C to dissolve the swelled PET fully. Any material remaining in the solid phase is removed as contamination in a filtration step. The resulting product stream from this process consists of recycled PET, ethyl benzoate, acetaldehyde produced from PET degradation at high temperatures, and remaining

polymer additives. Figure 1 shows a flow diagram for the process developed by Sherwood.

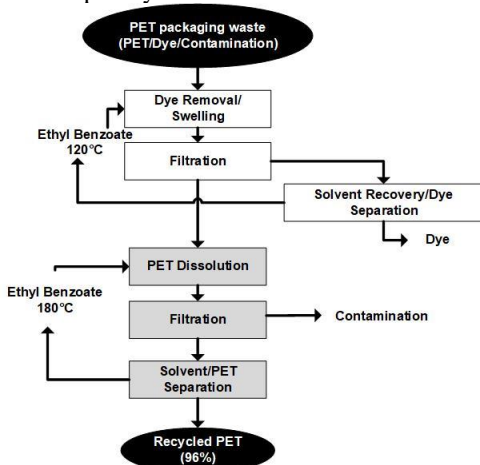


Figure 1. Process flow diagram of Sherwood process

The major limitation of this process is the demand for constant solvent to carry out both steps. This work will augment the existing process from Sherwood to increase process productivity and reduce the need for fresh solvent. Unlike other processes that have stringent solvent purity requirements, Sherwood et al. proposed that the solvent recovered can be reused within the same process for the recycling of polymer through chemical means (Sherwood, 2020).

An inlet flow of 100 kg/h was chosen for PET entering the dissolution stage as a basis for calculation. The solvent to plastic ratio required for the dissolution is 22.78 g ethyl benzoate: 1 g PET, resulting in an entering flow rate of 2278 kg Ethyl Benzoate/hour. The feed rates for the polymer additives (ADD) and acetaldehyde (ACT) were set to 0.5 kg/h based on standard PET formulation and the PET thermal degradation curve (Das and Tiwari, 2019). Most of the polymer additives are removed with dyes in the initial swelling phase of plastic recycling. Therefore, the presence of additives in the initial stream is minimal. The plastic recycling process reaches temperatures above the PET glass transition temperature, but below the decomposition temperature thus, minimal acetaldehyde byproduct was likely produced in the process. Acetaldehyde and the additives had an outlet specification of 95% removal. The polymer recovery optimization process was specified for a PET purity of 95% and a recovery of 95%.

Sustainability Model Building

The environmental impact for this work was carried out using the GREET model (Argonne National Laboratory, 2021) and life cycle impact data. Life cycle inventories (LCIs) were developed for each step in the PET recycling process. Each input was normalized using the mass of recovered polymer as the functional unit. GREET contains a variety of pre-made LCIs for chemicals however, the LCI for ethyl benzoate production is not present. Thus, an LCI was developed under the following assumptions. The

production of ethyl benzoate requires reacting benzoic acid with ethanol. Subsequently, an LCI for benzoic acid was also not present in GREET. The LCI was developed under the following assumptions. The production of benzoic acid is based on the partial oxidation of toluene with water being a byproduct. The model created for benzoic acid helps in quantifying the LCI data for the recovery process. In terms of energy requirements, we considered electricity and natural gas used in steam generation for the production processes of each component. The upstream emissions for the energy requirement models are already in-built processes within the GREET database. The final life cycle assessment for the recovery framework entails the summation of LCI data for the ethyl benzoate (ethanol + benzoic acid processes), electricity and natural gas requirements, and PET for the entire recycling process. GREET reports various types of emissions from CO to PM₁₀, each of these emissions categories are normalized over their respective global warming potentials and the final values are reported in units of kg CO₂ equivalent emissions per kg of PET recovered.

Superstructure Development

Designing a recovery process is complex as it often involves stages with multiple possible separation technologies to decide between. We use the superstructure approach to reduce this complexity. A superstructure is an approach to process synthesis that encompasses all technology alternatives, streams, mixers, and splitters for all possible flow combinations (Chea et al., 2020; Yenkie et al., 2017). We categorized our framework into four main stages: solid removal, recovery, purification, and refinement as shown in Figure 1. The solid removal or phase separation stage is the primary step in the process that can remove solid impurities from a liquid stream. The recovery stage aims to collect most of the desired component. The purification and refinement stages remove remaining impurities from the product. These stages can be repeated to reach certain industry requirements based on the application of the recovered component. Depending on the components in the stream, a recovery process may not be applicable due to inability to meet purity requirements or high operating costs associated with difficult separations. In these cases, incineration is employed instead of attempting recovery. However, the high energy costs and harmful environmental impact of incineration make it an unlikely selection. Figure 2 illustrates the superstructure which has 480 possible pathways for the recovery of PET from polymer recycling process effluent. The superstructure contains 50 streams, 4 bypasses, and 15 individual separation units for determining a recovery process with a minimized cost objective. The separation units are divided into 4 stages based on the type of separation required: solid removal, recovery, purification, and refinement. The bypass stream can skip a certain stage depending on if the purity and recovery specifications are met. The primary stage, solid removal, consists of the following technologies:

sedimentation (SDM), filtration (FLT), adsorption (ADS1), precipitation (PRC), and centrifugation (CNF). This stage aims to remove remaining solid additives from the polymer recycling process. Sedimentation, centrifugation, and filtration are similar as the separation through these methods depends on the settling velocity of the solid additives being removed. Precipitation is an effective method for solid removal that utilizes an added anti-solvent component to draw out the additives from the solvent/polymer mixture. Granulated activated carbon was chosen as the adsorbent for the solid removal adsorption technology. Binding percentages were assumed to quantify the attraction of the additives to the activated carbon surfaces. Subsequent adsorption technologies are modeled using the same activated carbon adsorbent and binding percentage method. After removal of the solid additives, the effluent stream continues into the recovery stage of the framework. This second stage contains four possible technologies for removing liquid impurities from the PET: distillation (DST), pervaporation (PVP1), adsorption (ADS2), and microfiltration (MF). Distillation is an “energy-intensive” unit that utilizes differences in boiling points to separate components. In the pervaporation unit, a membrane selectively permeates components from the feed through the membrane and vaporizes them during this passing. A vacuum is used to collect the vapor product and to create a large pressure gradient to drive the separation of the mixture. Microfiltration is another process unit that utilizes a membrane to separate PET from the remaining components in the stream. Unlike pervaporation, the product remains a liquid in the permeate stream. Additionally, the pressure gradient driving the separation is caused by a difference in partial pressure rather than a vacuum. At the end of this stage, the continuing stream contains a majority of PET with some ethyl benzoate remaining. To reach the specified polymer purity, a purification stage is implemented. This third stage includes microfiltration (MF2), ultrafiltration (UF1), and pervaporation (PVP2) as the purification process units. The pervaporation and microfiltration in this stage are designed using the same principles of separation described for the same technologies in stage two above. Ultrafiltration is another membrane process that is semi-permeable allowing the desired solvent to be separated from the mixture through a pressure driving force. The ultrafiltration unit has a more selective membrane and operates at higher pressures than the microfiltration unit. At the end of the purification stage, the polymer recovery stream still contains ethyl benzoate amounts above the allowable constraints. A refinement stage with Ultrafiltration (UF2), Nanofiltration (NF), and Pervaporation (PVP3), was implemented to satisfy the PET purity specifications. Incineration was also considered as a possible pathway despite the absence of an incineration path in the superstructure. The cost minimization was prioritized when finding the optimal solvent recovery process. For each stage in the superstructure, a bypass was included to allow for flexibility and remove any technology selection

restriction.

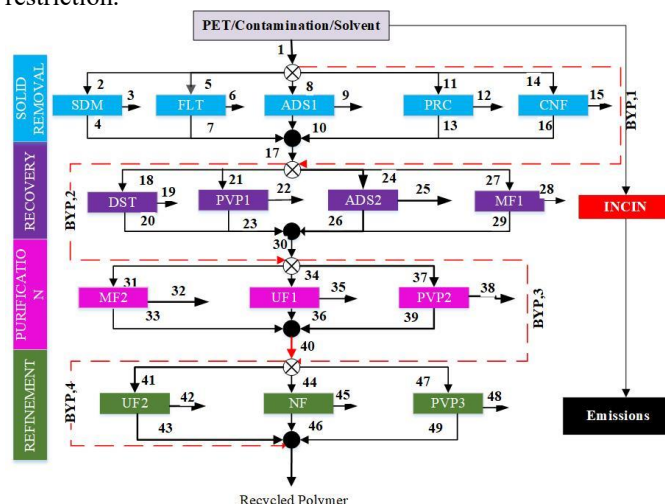


Figure 2. Generic superstructure for polymer recycling.

Results and Discussion

Table 1 displays the optimization results from GAMS, which contains the annual operating costs and the price per kg processed compared for the optimal pathway and incineration. There are 480 possible recovery pathways. The polymer recycling stream optimization model consists of 780 equations, 562 variables, and 19 discrete variables. BARON, which is the solver used, converged to a solution within 5.26 seconds with an optimality gap of 1E-05. The optimal polymer recovery pathway to recover PET from a stream containing 94% EB, 4% PET, and 0.5% ACT and ADD required the use of adsorption, pervaporation, and ultrafiltration. Figure 3 shows the optimal path highlighted in the superstructure.

Table 1. Optimization Results for PET Recycling using GAMS

Polymer Recycling Pathways	Annualized Cost (\$ million/yr)	Prices (\$/kg processed)
BYP1-ADS2-PVP2-UF2	0.0766	0.099
Incineration	3.01	0.16

This process has an annual operation cost of \$77,000/yr over a 25-year period with an annual recovery rate of 768.48 metric tons/yr of PET at a purity of 99%. The incineration of PET has an annual operation cost of \$3.01 million/yr, which is greater by a factor of nearly 39 than the annual operation cost of polymer recovery. Comparing recovery to incineration there is a 97% reduction in cost when recovering the material. Figure 4 displays the total contribution of each cost category for the feasible pathway.

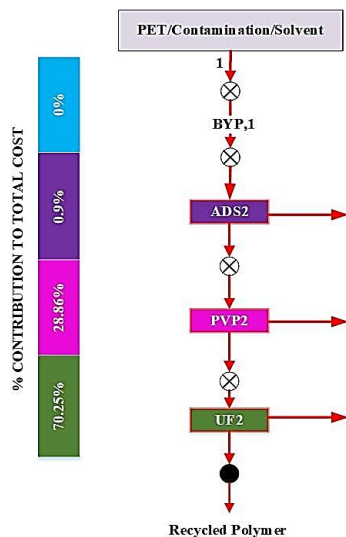


Figure 3. Optimal path for PET Recovery with the respective stage-wise cost contribution. The technologies selected are Adsorption (ADS) in the recovery stage, Pervaporation (PVP) in the purification stage, and Ultrafiltration (UF) in the refinement stage. The solid removal stage was bypassed.

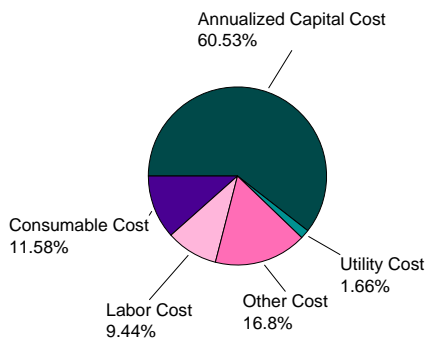


Figure 4. Cost distribution for the optimal pathway to recover PET

The annualized capital cost contributes to much of the total cost followed by the overhead (other) cost and consumables cost. The small utility cost contribution is due to the relatively low energy requirements for the technologies in this process. All three of the selected technologies require additional components/materials for separation and therefore contribute to the overall consumables cost. The annualized capital cost is directly related to the capacity of the unit operations selected. The breakdown of the stagewise contribution to the total cost of the process is shown in Figure 5. There is no cost associated with the solid removal stage since the optimal pathway bypasses that stage. The refinement stage contributes the most to the overall cost followed by the purification and recovery stages. As with the overall cost distribution, the main contributing factor in the refinement stage is annualized capital cost.

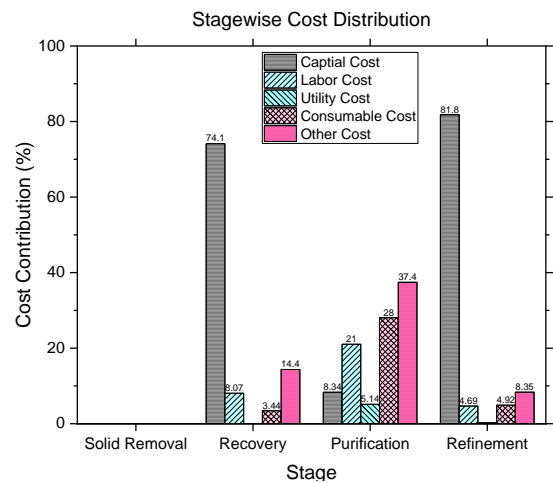


Figure 5. Stage-wise cost distribution for PET Recycling

The large capacity ultrafiltration unit selected in the refinement stage is responsible for the significant stage and overall annualized capital cost contribution. The membranes for the pervaporation and ultrafiltration units make up the majority of the contribution to the consumables cost compared to the adsorbent from the adsorption unit.

Sustainability Analysis

The emission components considered for this work include VOC, CO, NO_x, PM₁₀, PM_{2.5}, SO_x, BC, OC, CH₄, N₂O and CO₂. The total GHG for the recovery process is 7.7 kgCO₂-eq/kg PET while that of incineration is 339.3 kgCO₂-eq/kg PET. Recycling of PET waste results in a 98% reduction in over GHG emissions. Figure 6 shows the component distribution for polymer recovery and incineration. The highest emissions are associated with CO₂ for both the recycling and incineration process.

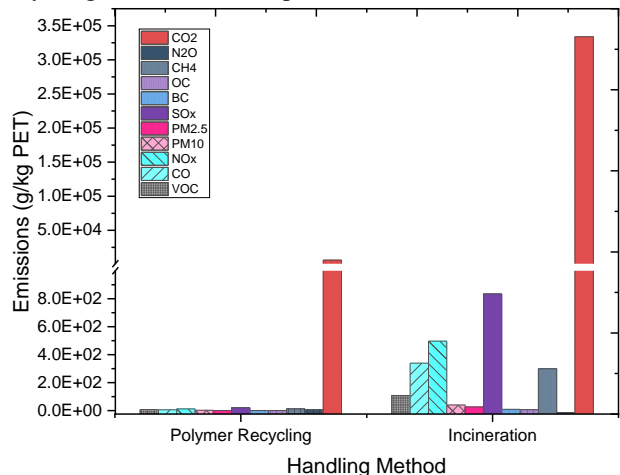


Figure 6. Emission component distribution for polymer recycling and incineration

The solvent accounted for the highest emissions while the energy inputs had a lesser contribution. Therefore, recovering the solvent (EB) for reuse in this process can be beneficial at further reducing the carbon footprint of the recycling process.

Conclusions

We have developed a super-structure based chemical plastic recycling framework that incorporates solvent recovery and considers a stage-wise analysis of multiple technologies. The viability of this framework was evaluated with the recovery of PET using ethyl benzoate solvent. Common polymer and solvent properties, separation technologies, and municipal solid waste handling information were necessary to obtain the information for solving the chemical plastic recycling related problem. Multiple polymer recovery pathways were analyzed simultaneously to obtain the optimal recovery pathway. This case has demonstrated that chemical recycling is both economically favorable, with a 97% reduction in cost, and greener, with a 98% reduction in net GHG emissions. Further investigation into solvent production processes is required to reduce both the emissions and cost of these processes, as the solvent requirement is the driving factor for both metrics. Additional work is being done to develop models for mechanical and thermal recycling technologies to be incorporated into the superstructure for further comparison. With these additional models we will conduct more case studies for different plastic types. These analyses will expand the existing framework to become an all-inclusive polymer recovery framework that can be applied to any industry that generates large amounts of plastic waste.

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