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A Fast Computational Framework for the Design of Solvent-Based Plastic Recycling Processes

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ABSTRACT

Multilayer plastic films are widely used in packaging applications because of their unique properties. These materials combine several layers of different polymers to protect food and pharmaceuticals from external factors such as oxygen, water, temperature, and light. Unfortunately, this design complexity also hinders the use of traditional recycling methods, such as mechanical recycling. Solvent-based separation processes are a promising alternative to recover high-quality pure polymers from multilayer film waste. One such process is the Solvent-Targeted Recovery and Precipitation (STRAP™) process, which uses sequential solvent washes to selectively dissolve and separate the constituent components of multilayer films. The STRAP™ process design (separation sequence, solvents, operating conditions) changes significantly depending on the design of the multilayer film (the number of layers and types of polymers). Quantifying the economic and environmental benefits of alternative process designs is essential to provide insights into sustainable recycling and film (product) design. In this work, we present a fast computational framework that integrates molecular-scale models, process modeling, techno-economic and life-cycle analysis to evaluate STRAP™ designs. The computational framework is general and can be used for complex multilayer films or multicomponent plastic waste streams. We apply the proposed framework to a multilayer film commonly used in industrial food packaging. We identify process design configurations with the lowest economic and environmental impact. Our analysis reveals trends that can help guide process and product design.

Keywords: Polymers, Process Design, Modelling and Simulations, Technoeconomic Analysis, Life Cycle Analysis

INTRODUCTION

A wide range of packaging applications use multilayer plastic films to protect products from external factors (e.g., oxygen, water, temperature, and light). Multilayer films are complex and diverse because they combine several layers of distinct polymers to leverage their unique properties. The multilayer film design can vary for different applications; for instance, industrial films can include more than ten polymer layers. This complexity hinders direct mechanical recycling. Solvent-based approaches have emerged as a promising alternative to recover and recycle their constituent polymers. One such technology is the Solvent-Targeted Recovery and Precipitation (STRAP™) process, which uses sequential solvent washes to selectively dissolve and separate the constituent components of multilayer plastic films [1]. The solvents used need to be properly selected to dissolve only a target component in each step. Thus, each selected solvent must have a high solubility for the target component and a low solubility for the other components of the multilayer film. This target component can refer to one or multiple polymers [2].

Molecular-scale models have been employed to predict polymer solubilities for solvent selections in such recycling processes. We recently introduced a joint computational and experimental workflow that can perform large-scale temperature-dependent polymer solubility predictions. Based on this approach, we generated a solubility database for common polymers and a large number of solvents [3]. The database has enabled the creation of a computational tool that automates solvent selections for solvent-based processes. This tool can screen and rank solvent candidates based on the solubility requirements of separation sequences. Once the solvent for the target component is selected, the next steps of the STRAP™ process can be taken as described below.

Figure 1 provides an example of the modules and process flow diagram that we use to represent the separation of different components using the STRAP™ process. For instance, for a multilayer film of 4 components, the first component can be separated as shown in the process flow diagram. In this example, each component comprises one polymer. The process steps are as follows: first, the multilayer film is mixed with a previously chosen solvent (that selectively dissolves only the target polymer P_1) and heated; next, the solution is filtered to separate the undissolved solids (polymers P_2, P_3, P_4); finally, the target polymer P_1 is precipitated via temperature reduction, filtered, and recovered. Most of the solvent is also recovered and recycled. Then, the process is repeated to separate the remaining components (polymers P_2, P_3, P_4). Hence, the separation of an n-component multilayer film requires n-1 separation stage(s).

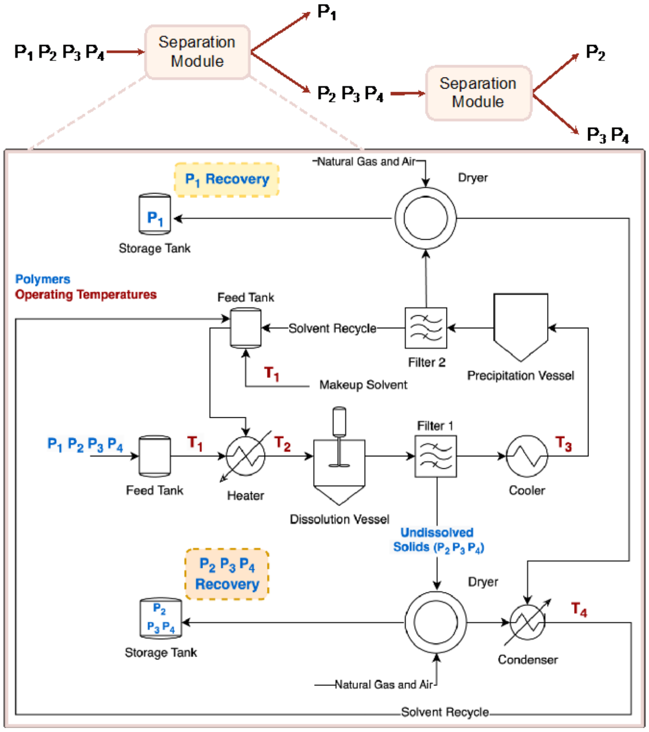

Figure 1. Simplified flow diagram of the STRAP™ process for one separation module.

A couple of precipitation techniques have been previously reported [2]. One is temperature-driven precipitation, which is economically and environmentally feasible and can be used for several polymer-solvent combinations. If the precipitation cannot be done via temperature, an antisolvent can be added to enable precipitation. However, adding an antisolvent leads to higher energy requirements because a distillation unit is required to separate the resulting mixture of solvents. Previous research has shown that the economic and environmental performance of the process is better when the precipitation is temperature-driven [4]. Therefore, in this work, we will select solvents that can enable temperature-driven precipitation only. It is worth highlighting that the solvent and operating temperatures can change if the separation sequence changes (for example, with P_2 as the target polymer). These changes can impact the economic and environmental benefits of the process. Additionally, identifying the proper conditions to achieve a high solvent recovery rate is key for the process benefits. Previous techno-economic analysis (TEA) and life cycle assessment (LCA) of the different STRAP™ process variations have also shown significant differences in costs and CO_2 emissions due to solvent selection and separation sequence [5,6]. While these models have been useful to determine the economic and environmental feasibility as well as process design bottlenecks, they have also shown the need for a general framework to guide the design of solvent-based processes.

In this work, we present a fast computational framework that integrates molecular-scale models, process modeling, TEA and LCA to provide insights into sustainable solvent-based process design. We also aim to provide guidelines for multilayer film designs that are easier to recycle or have a lower recycling impact. This framework can determine the economic and environmental impacts of several process design scenarios, including different separation sequences, solvents that enable temperature-driven precipitation, and process operating conditions (for dissolution, precipitation, and solvent recovery). The computational framework is general and can be used for complex multilayer films or multicomponent plastic waste streams.

COMPUTATIONAL FRAMEWORK

Our computational framework follows a series of steps to determine the economic and environmental impacts of each process design feasible scenario. The computational steps are summarized in **Figure 2**.

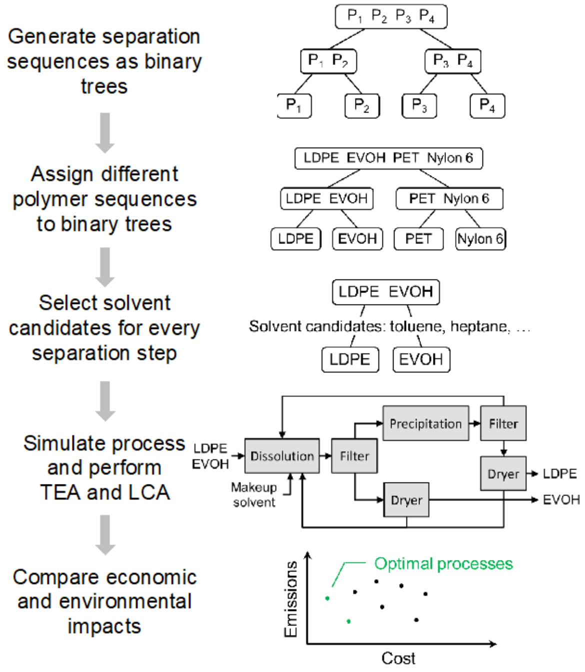

Figure 2. Schematic representation of the proposed framework.

First, for any given multilayer film, the framework generates all possible separation sequences. **Figure 3** provides an example of the binary trees that we use to represent the separation sequences for a multilayer film composed of 4 polymers. Here, we use the left branch to denote the dissolved polymer(s) and the right branch to refer to the undissolved polymer(s). For this example, we can see that every separation step only dissolves one polymer. Therefore, this example has a $D^n = 1$, which represents the number of polymers being dissolved in each step. Also, this binary tree only shows such separation sequence. Changing the separation order of the sequence provides all possibilities for the case of $D^n = 1$. Therefore, the permutation of the set of polymers $\{P_1, P_2, P_3, P_4\}$ results in 24 different sequences.

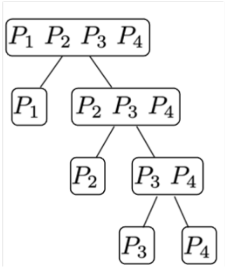

Figure 3. Binary tree illustrating a possible separation sequence for a multilayer film composed of 4 polymers.

To determine all the possible sequences, we also consider the binary trees where 2 polymers are dissolved in a certain step ($D^n = 2$), resulting in 2 different binary trees and 48 sequences. Similarly, when there are 3 polymers dissolved together, 2 different binary trees and 48 sequences are possible. Therefore, the separation of a 4-polymer mixture has in total 5 possible binary tree structures, which correspond to 120 sequences. **Table 1** presents a summary of the number of sequences and binary trees generated based on the value of D^n for the 4-polymer mixture. It is worth highlighting that this combinatorial complexity increases rapidly with the number of polymers. For example, a 5-polymer mixture will have 14 different binary tree structures, which leads to 1680 possible sequences.

Table 1: Possible binary trees and sequences for a 4-polymer mixture considering the different possible numbers of dissolved polymers in a certain step (D^n).

D^n	**Binary Trees**	**Sequences**
1	1	24
2	2	48
3	2	48

As shown in **Figure 2**, the next step is to assign different polymer sequences to the binary trees and eliminate the unfeasible sequences based on empirical rules from previous research (e.g., composition, polymer solubility, and maximum number of polymers dissolved in each step) [3-6]. After this, we use the computational tool to identify all the solvent candidates for the target polymer(s) in each separation step. This tool selects solvents (only based on solubility) from the previously reported database that includes predicted temperature-dependent polymer solubilities from molecular-scale models [3]. The criteria to select the feasible solvents is that the solubility of the target polymer(s) should be greater than 15 wt% and the solubility of the non-target polymer(s) should be lower than 3 wt%. Once the solvents have been identified, we estimate the required temperature of the condenser to achieve a high solvent recovery rate (~99.90%) given the inlet temperature from the dryer. Previous studies indicate that achieving a solvent recovery of ~99.99% enhances the economic viability of the separation process. However, solvents with low boiling points, such as toluene, pyridine, and acetic acid, face challenges in attaining this recovery rate. In contrast, solvents like glycol, dodecane, and diethylene glycol can achieve this target. It is equally essential to avoid solvents with high boiling points, as they can escalate the energy consumption in the distillation process during solvent mixture recovery (which occurs in precipitation via antisolvent addition). Therefore, the solvent recovery is

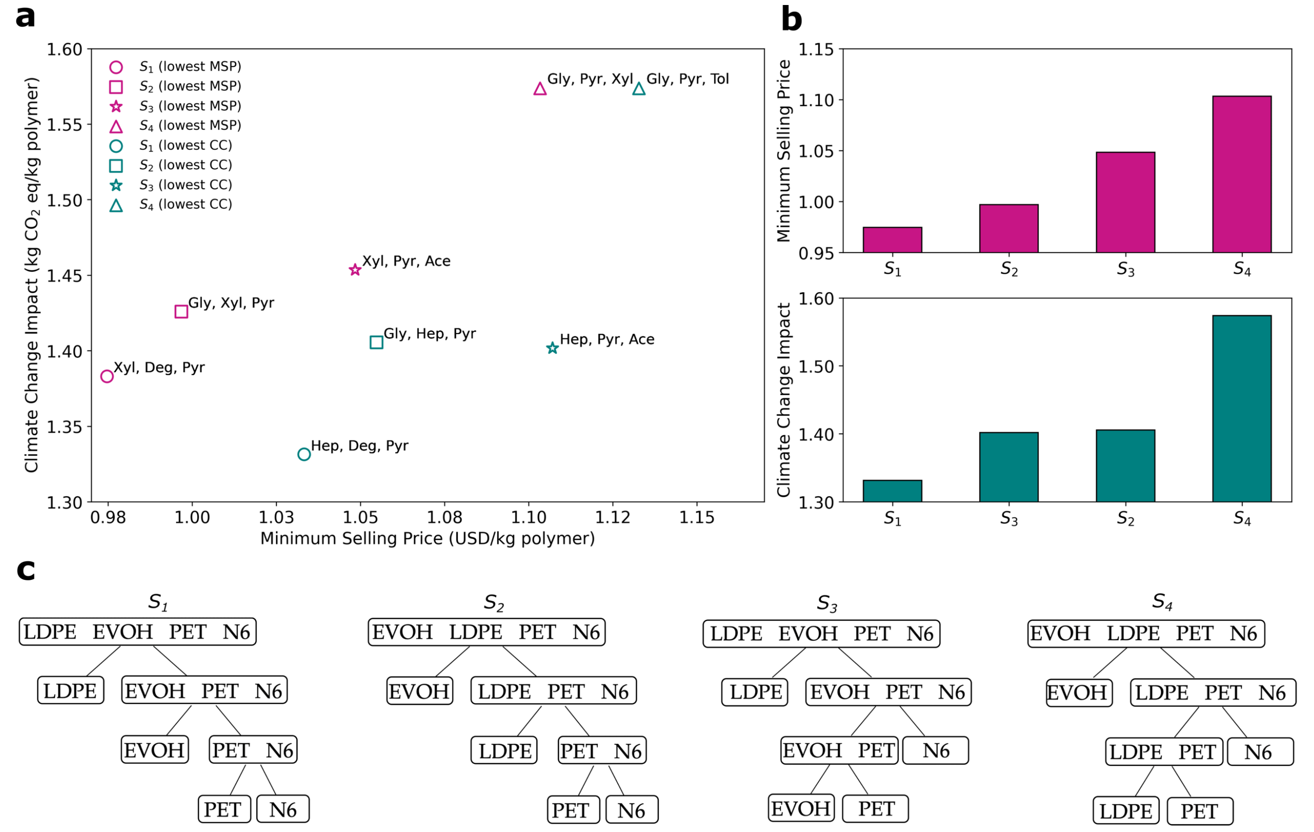

Figure 3. (a) Scenarios with the lowest MSP and CC impacts. The pink symbols represent the sequences (S_n) with the lowest MSP and the green symbols represent the sequences (S_n) with the lowest CC impacts. The abbreviations of the solvents used for each scenario are shown next to each symbol (see **Table 1**). (b) Pink bars represent only the MSP for each sequence and green bars refer only to the CC. (c) Separation sequences shown

set at ~99.90%, and future considerations will include evaluating the trade-offs associated with each solvent. The condenser temperature is estimated by simulating a heat exchanger and iterating over different temperatures to achieve the recovery rate specification as a pre-process simulation. The process model simulation for the heat exchanger is performed in the open-source platform BioSTEAM [7]. This Python process simulator has been validated against proprietary software (SuperPro Designer and Aspen Plus).

Next, we use the collected inputs (mass, polymers, composition, separation sequence, solvent, and operating conditions) to simulate the STRAP^{TM} process and perform the TEA in BioSTEAM. We use the minimum selling price (MSP) as the economic metric to compare different scenarios. After this, we evaluate the environmental impact of each scenario using an LCA methodology. The LCA was performed using the open-source software openLCA [8], the Environmental Footprint and AGRIBALYSE databases and the Environmental footprint impact assessment method [9,10]. We consider all the inputs to the process (electricity, steam, water) and we estimate the climate change (CC) impact for each scenario. Since there are limited data for solvents in the LCA databases and we are considering high recycling rates, we do not include the impact of solvents for this analysis. Finally, we store the economic (MSP, expressed in USD per kg of polymer sold) and environmental (CC impact, expressed in kg CO$_2$ per kg of polymer) outputs of all feasible process design scenarios (including different sequences and solvents).

RESULTS AND DISCUSSION

We applied the proposed computational framework to a multilayer film composed of LDPE, EVOH, PET, and Nylon 6 (N6). This 4-polymer multilayer film is commonly used for food packaging applications [11]. As mentioned above, there are 120 possible sequences for a 4-polymer mixture.

To identify the sequences and solvents that lead to the best economic and environmental performance, we compare the MSP and CC impact of all the generated scenarios. We consider all the separation modules required to recover the 4 constituent polymers of the multilayer film using the STRAP^{TM} process. As a benchmark, we also estimate the climate change impact of producing the 4 polymers from fossil sources and their average market prices.

First, we identify the solvents that lead to the lowest MSP in each separation step of the different generated sequences and report the corresponding CC impact of these sequence-solvent combinations. Similarly, we identify the solvents that lead to the lowest CC impact and their corresponding MSP. **Figure 3a** presents the scenarios with the lowest MSP (pink symbols) and the lowest CC impact (green symbols). It should be noticed that each symbol refers to a different sequence (represented by S_n) and set of solvents used for all the required separation modules. Solvents are represented by an abbreviation which is related to the solvent common name in **Table 2.** From **Figure 3a**, we can see that there are trade-offs between the economic and environmental metrics. For instance, the sequence S_1 with the set of solvents p-Xylene, Diethylene glycol and Pyridine (represented by the pink circle) leads to the lowest MSP (0.97 USD/kg), but it does not lead to the lowest CC impact. On the other hand, the sequence S_1 with the set of solvents n- heptane, Diethylene glycol and Pyridine (represented by the green circle) leads to the lowest CC impact (1.33 kg CO_2/kg) but leads to a higher MSP.

We compare these results with previous STRAP™ studies to show the viability of the proposed framework. A TEA [2] and an LCA [4] for a similar multilayer film composed of LDPE, EVOH, PET, and EVA are used as references. Here, the sequence used was similar to sequence S_1 and was demonstrated experimentally. We find that the reported MSP is 1.1 USD/kg and the CC is 1.18 kg CO_2/kg. Although the polymers, composition, and solvents used are not equal to the multilayer film addressed in this study, we can see that the economic and environmental impacts are similar which highlights the applicability of the proposed framework. Future work will include evaluating the previously reported multilayer film (LDPE, EVOH, PET, and EVA) with our framework to identify other feasible sequences and solvents that could be tested experimentally. **Figure 3b** provides a summary of the MSP (pink bars) and CC impact (green bars) for each sequence. To compare these values to the price and climate change impact of virgin polymers we consider the following. As a reference, we find that the average market prices of the recovered polymers are 1.2–2.6 USD/kg. Furthermore, the multilayer film addressed in this study has a market price of 2.9 USD/kg [11, 12]. From previous research, we know the range of the required scale to achieve an MSP comparable to these market prices [5]. Therefore, the results presented in this work were obtained for a fixed plant capacity of 6,400 tons per year. As we can see in **Figure 3b**, the MSP of the recovered polymers is comparable to the average market prices. However, this trend is sensitive to the scale of the process and can change with other capacity factors.

Table 2: Common name of selected solvents for the scenarios with the lowest impacts.

Solvent Abbreviation	Solvent Common Name
Ace	Acetic acid
Deg	Diethylene glycol
Gly	Glycol
Hep	n-heptane
Xyl	p-Xylene
Pyr	Pyridine
Tol	Toluene

Regarding the environmental impact of virgin polymers, we estimate the CC impact of the production from fossil sources of the constituent polymers of the multilayer film considered in this work (LDPE, EVOH, PET, and N6). Considering that every polymer represents 25 wt% of the film, we find that 4.81 kg CO_2 per kg of polymer are generated. From **Figure 3b**, we can see that all the different STRAP™ sequences have a lower CC impact. Specifically, sequence S_1 results in around 60% fewer emissions than the production of the multilayer film from fossil sources.

Figure 3c presents the different sequences as binary trees showing the dissolved polymers in each separation step (left branch). From the MSP and CC plots, we observe that sequence S_1 results in the lowest economic and environmental impacts. This sequence refers to dissolving one polymer in each separation step in the following order: LDPE, EVOH, PET, and N6. However, the set of solvents that lead to the lowest MSP and CC are different for each sequence. There are different factors that determine if one sequence and solvent is better for the economic or environmental metrics, such as the amount of required solvent (which is determined by the polymer solubility) and the thermodynamic properties of the solvents. This first analysis provides initial suggestions of the key variables that impact the economic and environmental performance. For instance, the dissolution temperature is dependent on the boiling point of solvents. Therefore, solvents with low boiling points result in lower energy requirements and environmental impacts. On the other hand, we found that the solvents that require a lower polymer-solvent ratio (due to higher solubility) were selected for the scenarios with the best economic performance. Such solvents had a higher boiling point.

CONCLUSIONS AND FUTURE WORK

This work presented a fast computational framework to provide insights into the STRAP™ process design. The proposed framework helps identify the separation sequence, solvents, and process operating conditions with the lowest economic and environmental impact. We use the framework to identify process designs with low impacts for a multilayer film composed of 4 polymers. From these results, we conclude that the environmental performance is mainly driven by the boiling point of solvents while the economic performance is guided by the polymer solubility. Our framework is general and can help guide the design of other solvent-based processes to efficiently treat complex multilayer waste streams. Therefore, future work will include analyzing case studies with different polymers and number of layers. Furthermore, we will consider varying recycling rates for the solvents. We will also evaluate other processing plant scales and the recovery of only selected polymers (for streams with large number of polymers).

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