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Technoeconomic Assessment of Recycling Routes for Chemicals: A Case Study of n-Hexane

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The circular economy has become one of the most popular topics in worldwide sustainability research. The imperious necessity of reducing resource consumption and decreasing waste generation has led to reincorporating materials at the end-of-life (EoL) stage into the productive chain. Nonetheless, the presence of hazardous substances in the EoL stage materials poses a significant challenge for the transition toward the production model. The adequate transformation of these materials into feedstocks requires their correct allocation into recovery plants and final destinations. Such an allocation can be decided by resorting to optimisation by generating the best alternative networks, from where the stakeholders may decide the most suitable recycling scheme. In this work, a graph-theoretic approach is introduced to identify the best alternatives to reincorporate industrial EoL chemicals into the productive chain. This contribution presents the initial approach to this problem, demonstrated through a case study considering the data reported on the public-access release inventory data for n-hexane. Different recycling routes are proposed for the case study by optimising the total treatment cost, and their advantages and disadvantages are discussed; moreover, their efficiency concerning the circular economy is measured by comparing the amount of recovered chemicals. By generating plausible recycling alternatives, this work contributes positively to analysing potential alternatives for circular economy and resource conservation in industry.

1. Introduction

Nowadays, processing systems are expected to fulfil numerous requirements to avoid negative impacts on society and the general ecosystem. Therefore, decisions on production processes cannot be made exclusively considering the operating costs and revenues, but numerous sustainability criteria must be contemplated simultaneously. Two objectives usually pursued in sustainability evaluation are the minimisation of resource demand and the reduction of waste generated (Sheldon et al., 2022). Circular Economy is a philosophy aiming at designing products and processes so that materials at the end of their life cycle, i.e., termed here end-of-life (EoL) materials, are reincorporated in the productive chain or used as raw materials in different processes (Geisendorf and Pietrulla, 2018). The result of recycling EoL materials is that both the quantity of waste material to be treated and the new resources required are reduced for the productive chains involved.

In the industry, various compounds are used as raw materials and auxiliary substances for manufacturing valuable goods. A fraction of these substances is usually transformed into valuable products, but some other is lost or regarded as waste in EoL streams. Since various compounds are classified as toxic by the U.S. Environmental Protection Agency (EPA), disposal operations and destructive treatments are usually performed to minimise their potential release into the environment. The destructive nature of these treatments complicates their recovery and recycling. Thus, ensuring the circular economy for these substances requires the correct allocation of EoL materials to treatment facilities with plausible recovery treatments, from which it is possible to transport the recovered material to the new manufacturing facilities.

The solution to such a problem involves determining the most cost-effective recycling plan for recovering the target compound from a set of EoL materials according to the specifications of a set of plausible consumers. This can be summarised as identifying the best system constituents (i.e., treatment facilities, treatment

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alternatives, transport units, and consumers) and their most convenient connectivity so that the chemicals of interest are returned to the productive chain. The task of determining the topology of the process, i.e., the process structure, from a set of plausible units is illustrated in Figure 1 and is termed process synthesis. This generates the best system configuration (e.g., Treatment-Generator-Facility) for material recycling. It is worth noting that the streams of all generators (Gen.) must be allocated for treatment, but not all consumers (Cons.) or treatment facilities must be included in the final structure.

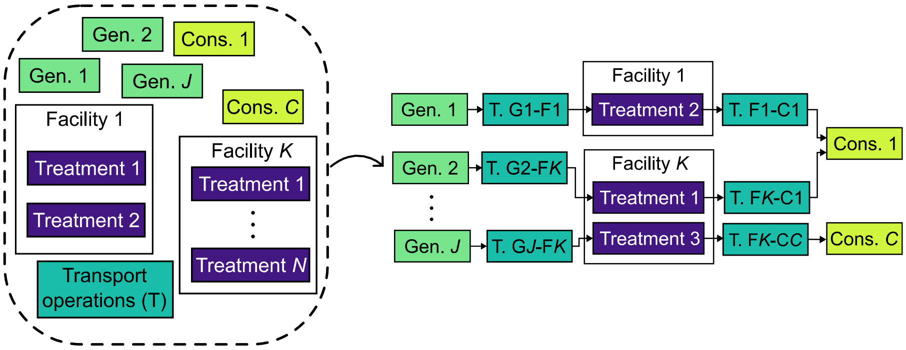

Figure 1: Representation of the synthesis problem for recycling EoL materials

Process synthesis can be solved by formulating a Mixed-Integer Programming (MIP) problem (Duran and Grossmann, 1986) that considers the total cost as the objective function and the mass balance of units (i.e., treatment facilities and transport operations) as the problem constraints. The mixed-integer nature of the problem is given by the combination of continuous variables (e.g., mass and energy flows, etc.) with binary decision variables that represent the inclusion of the units (e.g., treatment option or transport operations) in the final solution. Moreover, if a single chemical is considered, the mass balance can be formulated in terms of a set of linear expressions for mixing and dividing. However, a major challenge to overcome in recovering toxic substances is that the EoL materials usually consist of various chemicals of distinct nature, depending on the generation point and the economic activity performed in such facilities. Therefore, the mass balance of the units must be modelled in terms of non-linear functions, thus constituting a Mixed-Integer Non-Linear Programming (MINLP) problem. Another challenge is that solving the MIP formulation results in a single solution, which can be optimal from the economic point of view but may have flaws in other criteria not contemplated in the objective function. Therefore, generating multiple solutions is preferred by the stakeholders (Voll et al., 2015).

A substance worthy of examination for recovery and recycling is n-hexane. N-hexane is a hydrocarbon mainly employed as a component in fuels and other petroleum products. Moreover, it is extensively utilised as a solvent for plastics and resins, in adhesive formulations, as an edible oil extractant for seed crops, and as a solvent in biodiesel production (Schmidt et al., 2014). However, despite its extended use, n-hexane has been reported to exhibit aquatic life toxicity and damage to organs and fertility functions (Agency for Toxic Substances and Disease Registry, 1999). Therefore, due to its applications and environmental and health concerns, this chemical results in a relevant case study.

Previous contributions have addressed the tracking of EoL chemical flows by resorting to data engineering approaches (Hernandez-Betancur et al., 2022). However, no systematic and logistics strategies have been proposed for the recycling of these materials into the productive chain. Moreover, the design of recovery systems guided by MINLP optimisation was explored in the available literature (Cremaschi, 2015). Nonetheless, scarce attention has been directed to generating the set of best recovery schemes that confer the stakeholders with a range of possibilities to select the best design considering multiple criteria.

In this work, an MINLP problem is formulated to determine the best allocation of EoL materials to treatment facilities and consumers. The problem formulation is illustrated using a case study of n-hexane, looking for the most cost-effective alternatives for its recycling. The MINLP is formulated and solved by resorting to the P-graph framework (Friedler et al., 2022), a graph-theoretic approach that systematically determines a rigorous superstructure for the model and effectively deals with binary decisions when solving it; thus, it can generate the n-best operation plans from which the most convenient recycling structure can be selected.

2. Methodology

The objective is to select the set of units comprising alternative recycling schemes that minimise the total cost of the network. For this, the problem is formulated in terms of the P-graph framework. The P-graph framework is an effective resource for dealing with problems that involve binary decision variables. This framework can manage such decisions by resorting to the structure's properties to represent the synthesis problem; therefore, the integer part of the problem is handled through rigorous combinatorial algorithms. Also, the framework facilitates the optimisation procedure and generates a list of the n-best solutions to the synthesis problem. The manipulation of the problem's structure properties requires an unambiguous representation of the system. For this, the problem's elements are partitioned into two types of nodes, i.e., M-type and O-type nodes. The first type represents the system's materials, depicted as circles in the graph; the second type represents the units performing the transformation or transportation of such materials; these nodes are shown as horizontal bars. The two types of nodes are connected by arrows that indicate the direction of the material flows.

In this problem, the EoL materials located at their generation facilities are regarded as raw materials, whereas the materials allocated in the consumer facilities are considered desired products. Moreover, the recovery operations, treatment facilities, and transport operations selected by the designer are designated as the units in the synthesis problem. Figure 2 shows the conventional representation (a) and P-graph representation (b) of a system where the EoL materials from two generators are transported to treatment unit F1 and subsequently to consumer 2. It is worth noting that the residual streams of treatment facilities are not represented in the graph. However, they are involved in the problem.

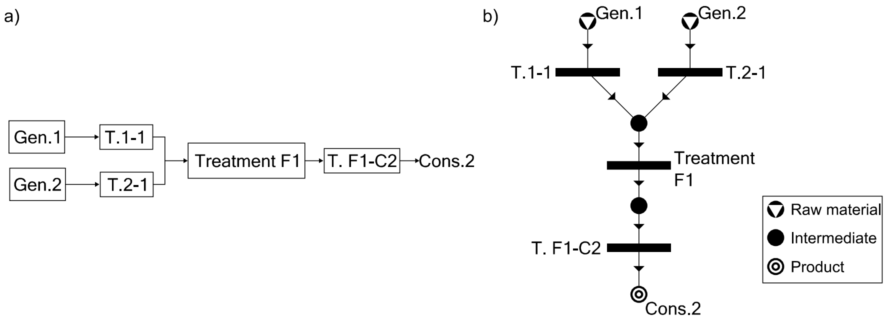

Figure 2: Representation of subsystem in conventional representation (a) and P-graph representation (b)

The solution procedure initiates by using the algorithm MSG (Maximal Structure Generation) to construct a rigorous superstructure that represents the entire synthesis problem, referred to as the *maximal structure*. This structure comprises all defined connections among the units selected. Therefore, all plausible recycling schemes are a sub-structure of it (Friedler et al., 1993). Subsequently, the algorithm ABB (Accelerated Branch and Bound) performs the optimisation via branching steps based on the maximal structure's properties and carries out the bounding of related sub-problems. The bounding is performed by solving relaxed versions of the MINLP problems, formulated by classifying the units as included, excluded, or undecided. On the one hand, the binary decision variables of included units are set to one, whereas the equations concerning the excluded units are removed from the problem. On the other hand, the binary decision variables of the undecided units are relaxed, thereby constituting an NLP problem that is solved to find the lower bound of the branch.

In this work, the model comprises the mass conservation law applied to M-type and O-type nodes. For this, the arcs of the P-graph are regarded as multicomponent streams described by C individual mass flows. The arcs are then classified as streams consumed by the units (a) or produced by the units (b). The model of the M-type nodes is not shown here because of space limitations. However, details on it may be found in previous contributions (Pimentel et al., 2022). The model of each O-type node consists of the mass balance, which represents the separation efficiency of the units, and the cost function used to estimate its performance. In this work, on the one hand, the mass balance on O-type nodes is estimated by assuming a recovery ratio for each component in each type of unit, as shown in Eq(1) where RR_j^i stands for the recovery ratio of component i in unit j. On the other hand, the general cost function in Eq(2), which accounts for fixed and operating costs of treatment and transportation, is used to estimate the cost C_j of each unit j in the set of units included in the network. Naturally, the cost of excluded units is not considered in the problem.

$$b_j^i = a_j^i \, RR_j^i \tag{1}$$

$$C_j = A_j \left(\sum_{i \in C} a_j^i \right)^{B_j} + D_j \left(\sum_{i \in C} a_j^i \right) + E_j \tag{2}$$

Parameters $A_j, B_j, D_j,$ and E_j in Eq(2) are constant values for each type of unit included in the structure. Then, the objective function is the sum of the cost of all units included in the structure. The algorithms of the P-graph framework were implemented in Python 3.9, and the bounding of the NLP was performed in Python via the API of GAMS using the solver "Xpress".

3. Case study

To illustrate the ideas expressed in previous sections, a case study based on n-hexane is formulated. Because of the risks this hydrocarbon poses to human health and the environment, releases related to it are reported and tracked by the Toxics Release Inventory (TRI) program in the United States (US EPA, 2013). The data reported to the TRI can be used to generate information concerning the amount of hexane generated as EoL material at various facilities and the available treatment plants and operations. Here, the tracking data provided by Hernandez-Betancourt et al. (2022) for 2018 defines the set of producers, consumers, and treatment facilities plausible for the recycling structures. The EoL materials are determined by selecting the three largest generators that reported n-hexane releases with no broker involved. Nevertheless, the TRI only comprises data for the quantity of substance transferred. Still, no information concerning its composition or the flow of additional components in the released streams is available in the program. Consequently, the information on the total amount of EoL material generated by the facility, retrieved from the information provided by the Resource Conservation and Recovery Act (RCRAInfo (US EPA, 2015)), is used to estimate the composition of the EoL material transfers. Here the EoL materials are partitioned into two components: n-hexane (*C6*) and the remaining components, termed *RES.* The data used in the case studio are presented in Table 1.

Table 1: Component flows in kg/y for EoL defined in the Case study

Component	EoL 1	EoL 2	EoL 3
C6	232,619	178,271	97,886
RES	1,802,618	271,729	622,514

The set of plausible treatment facilities (TF) is identified by selecting four large receivers of n-hexane reported in the tracking data, which declared non-destructive treatment methods according to the TRI information. Based on such information, four types of units were assumed to be in the distinct TF. The information related to these units, as well as their location, is reported in Table 2. The cost parameters of treatment units, i.e., coefficients in Eq(4) for each type of unit, are estimated through simulation. Because of the uncertainty on the streams' composition, the cost of recovering hexane is estimated by assuming the component *RES* consists of a mixture of four major solvents reported in TRI, specifically toluene, methanol, xylene, and water. Then, the recovery processes are simulated in Aspen Plus V10 for various mass flows, and the fixed and operating cost are regressed to generate an estimate of the cost coefficients. On the other hand, the four plausible consumers are selected from the set of facilities reported in the available tracking data. The parameters of the minimum composition of hexane and the maximum flow acceptable by the assumed consumers are shown in Table 3.

Table 2: Information on treatment facilities (TF) and treatment units for the case study

Unit identifier	Unit type	RR^{C6}	RR^{RES}	Available in TF
1	Simple evaporation	0.500	0.130	TF1
2	Settling	0.900	0.510	TF1, TF2, TF3
3	Simple distillation	0.970	0.040	TF3, TF4
4	Distillation + decanter	0.965	2.0E-04	TF4

Table 3: Requirement of n-hexane composition and maximum flow received by consumers in the case study

Facility	Minimum C6 mass fraction	Maximum flow (kg/y)
Cons 1	0.3	831,412
Cons 2	0.7	308,443
Cons 3	0.6	77,632
Cons 4	0.95	1,293

Moreover, the data on the longitude and latitude of generators, facilities, and consumers are used to estimate the distance between the plausible constituents of the network. This information, presented in Table 4, is used to estimate the cost of transporting materials as a proportional function of the distance.

Table 4: Distances in km from treatment facilities to EoL material generators and consumers

Facility	EoL 1	EoL 2	EoL 3	Cons 1	Cons 2	Cons 3	Cons 4
TF 1	2,339	389	2,141	1,348	436	2,219	1,592
TF 2	1,112	1,365	1,015	932	1,465	1,077	499
TF 3	2,281	115	1,887	1,096	13	2,162	1,195
TF 4	1,928	3,43	1,480	6,78	4,20	1,809	7,88

With this information, the algorithm MSG is implemented to automatically generate the maximal structure of the problem. Here, looking for convenience in the final solution, the set of plausible transport units is limited to those whose distance is less than 2,000 km. Consequently, the maximal structure generated consists of 40 O-type nodes and 18 M-type nodes. The full extension of the maximal structure is not shown here because of space limitations. Subsequently, the algorithm ABB is implemented in Python, together with the API of GAMS, to formulate the subproblems according to the P-graph axioms and solve the bounding via NLP solvers. The best structure for recycling n-hexane, considering the case study's data, is shown in Figure 3. In this solution, the EoL materials from generators EoL 1 and EoL 2 are distributed between TF2, TF4, TF3 and TF4. In contrast, the flow of EoL material generated by EoL 3 is handled entirely by TF4. In this solution, the recovered hexane is distributed only between consumers 1 and 2, sending 72 % of the material to consumer 2, which is consistent with its lower requirement on purity. Moreover, the amount of non-recovered hexane in this solution is 30.3 t/y. Some interesting solutions can be seen among the set of n-best solutions. Two of these are shown in Figure 4. The structure in Figure 4(a) is less than 1.5 % more expensive than the best solution found. However, this structure has the advantage of satisfying three of the consumers, which may benefit the network's flexibility. On the other hand, the non-recovered hexane in this structure is 30.8 t/y. On the other hand, Figure 4(b) shows a structure with a total cost of 172,893 USD/y. Although this structure has a cost that is 6.5 % higher than the one of solution in Figure 3, the non-recovered hexane is 20 t/y. Thus, this solution has a higher efficiency in terms of circular economy as it reincorporates 34 % more hexane back into the productive chain.

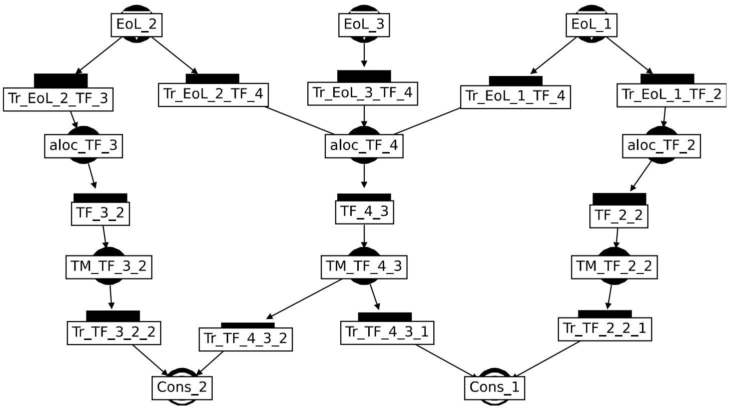

Figure 3: best recycling structure for the case study. Total cost: 162,211 USD/y

4. Conclusions

An initial method for finding the most cost-effective recycling routes for EoL materials has been presented. The method permits finding the n-best solutions for which the EoL materials from all generators are allocated into treatment facilities and subsequently into suitable consumers. TRI tracking information and RCRAInfo were utilised to construct a case study with realistic values dealing with the recycling of n-hexane into the productive chain. Distinct alternative recycling routes were generated by resorting formulating of a synthesis problem in the form of an MINLP, and its subsequent solution using the P-graph framework. The best structure and two alternatives are presented and compared regarding cost and n-hexane recovered.

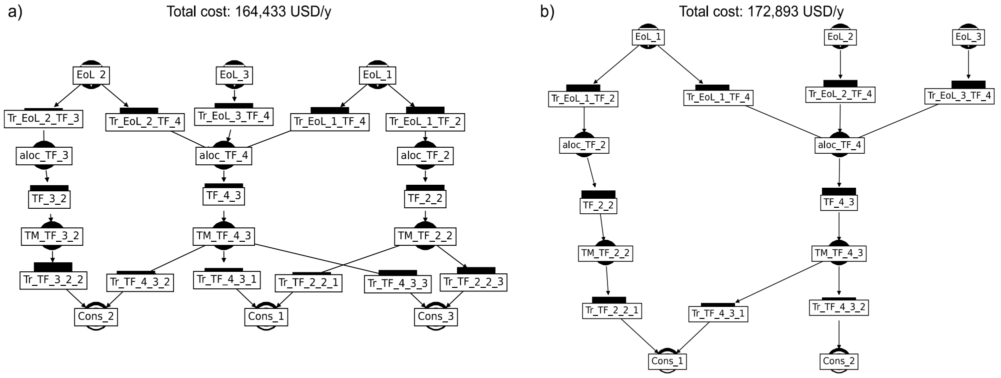

Figure 4: Alternative recycling structures for the n-hexane case study. Total cost: 164,433 USD/y (a) and 172,893 USD/y

This work presents the initial attempt at solving this problem, and future work can focus on addressing the high level of uncertainty in the data. It is expected that the method presented will contribute to achieving cost-effective models of circular economy and resource conservation in the chemical industry.

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