Integrated synthesis, modeling, and assessment (iSMA) of waste-to-resource alternatives towards a circular economy

The case of the chemical recycling of plastic waste management

Pacheco-López, Adrián; Gómez-Reyes, Edward; Graells, Moisés; Espuña, Antonio; Somoza-Tornos, Ana

DOI
10.1016/j.compchemeng.2023.108255

Publication date
2023

Document Version
Final published version

Published in
Computers and Chemical Engineering

Computers and Chemical Engineering 175 (2023) 108255

Contents lists available at ScienceDirect

Computers and Chemical Engineering

journal homepage: www.elsevier.com/locate/compchemeng

Integrated synthesis, modeling, and assessment (iSMA) of waste-to-resource alternatives towards a circular economy: The case of the chemical recycling of plastic waste management

Adrián Pacheco-López [a], Edward Gómez-Reyes [a], Moisés Graells [a], Antonio Espuña [a,*], Ana Somoza-Tornos [a,b]

[a] Department of Chemical Engineering, Universitat Politècnica de Catalunya, EEBE, C/ Eduard Maristany 16, Barcelona 08019, Spain
[b] Department of Chemical Engineering, Delft University of Technology, Van der Maasweg 9, Delft 2629 HZ, Netherlands

A R T I C L E I N F O

Keywords:
Circular economy
Waste-to-resource, Ontologies
Chemical recycling
Plastic waste treatment
Integrated modeling

A B S T R A C T

The need to transform economic models to implement a circular use of resources is crucial due to the current waste accumulation crisis. New waste-to-resource alternatives are constantly emerging to close material loops; therefore, tools are needed to identify the best synergies to upcycle waste. An approach has been developed to identify and assess waste-to-resource processing routes not currently implemented at the industrial level to valorize waste. The proposed framework consists of several interconnected modules that include ontologies for knowledge management, graph theory and short-path algorithms for the generation of paths and pre-assessment of processes, a Mixed-Integer Linear Programming (MILP) model for superstructure optimization; and the rigorous design, simulation, and optimization exclusively of those alternatives that show the best performance in previous steps. A case study for the treatment of mixed plastic waste reveals chemical recycling and the production of pyrolytic fuels as tentatively favorable options, both environmentally and economically.

1. Introduction

Traditional economic paradigms, following the current driving forces and trends, are proven to be unsustainable due to the exponential growth of the world population, the rapid industrialization of emerging economies, and the massive resources consumption in developed countries (Ellen MacArthur Foundation, 2019). This model corresponds to the so-called linear economy, where materials flow in a straight line from the extraction of finite natural resources, production of consumer goods (often single- use), and disposal to landfills or incineration. This linear consumption of materials and energy is putting a strain on ecosystems. Therefore, the awareness of the fact that people's lives and businesses rely on the world's ecosystem has increased notably (Valeche-Altinel et al., 2021).

As a result, the circular economy concept arises as a suitable solution to this problem and offers an attractive path forward since it creates value and growth in ways that benefit customers, businesses, society, and the environment. It is estimated that applying circular economy principles to five of the most used resources (cement, aluminum, steel, plastics, and food) could reduce more than 50% of the GHG emissions, corresponding to 9.3 gigatonnes of CO_{2eq} by 2050 (Ellen MacArthur Foundation, 2019). This amount is equivalent to all global emissions from transport during the same period. This transformation can be achieved by extending the useful life of assets and recycling the materials used to make them, therefore reducing the demand for raw materials and the generation of waste, which in turn helps improve air quality, reduce water contamination, and protect biodiversity.

Among the abovementioned materials, plastics play a key role in the

Abbreviations: BAU, Business as usual; CO2eq, Carbon dioxide equivalent; CX (X: number), Hydrocarbon with X carbon atoms; ECO, Endpoint indicator for the environmental impact on Ecosystems; GHG, Greenhouse gases; GPI, Global performance indicator; HDPE, High density polyethylene; HH, Endpoint indicator for the environmental impact on Human Health; HUSY, Hierarchical ultra-stable Y zeolite; ISBL, Inside battery limits; LCA, Life cycle assessment; MILP, Mixed-integer linear programming; M€, Million euros; MPW, Mixed plastic waste; MSW, Municipal solid waste; OSBL, Outside battery limits; PE, Polyethylene; PET, Polyethylene terephthalate; PP, Polypropylene; PS, Polystyrene; PVC, Polyvinyl chloride; RES, Endpoint indicator for the environmental impact on Resources; SAHA, Amorphous silica-alumina catalyst; TRL, Technology readiness level; ZSM-5, Zeolite socony mobil–5.

* Corresponding author.
E-mail address: antonio.espuna@upc.edu (A. Espuña).

https://doi.org/10.1016/j.compchemeng.2023.108255
Received 11 November 2022; Received in revised form 4 April 2023; Accepted 6 April 2023
Available online 7 April 2023

transition to the circular economy. Plastics are widely spread materials due to their versatility, good performance in a wide range of applications, lightweight, and low production cost. Over the last decades, this fact has led to the rapid increase of plastic items production, especially in segments showing low costs and short useful life. To put it into context, their use has increased twentyfold in the last 50 years, reaching almost 370 million tonnes of plastic produced in 2019 worldwide (PlasticsEurope, 2020), which is expected to double in the next 20 years. The problem arises when this plastic is destined for single-use applications and/or its end-of-life is poorly managed. For instance, after a short first-use cycle, 95% of plastic packaging material value is lost to the economy and a staggering 32% of it escapes collection systems (Ellen MacArthur Foundation, 2017). Thus, waste accumulation and resources depletion concerns are growing recently due to the lack of effective and efficient resources and waste management policies in most countries worldwide (Kakadellis and Rosetto, 2021). In an effort to improve the situation, there has been an increasing interest in developing waste-to-resource processes to obtain valuable products from plastic waste, opening up a wide range of upcycling options.

Conventional plastic reclamation methods are commonly based on mechanical methods, incineration, or landfilling. Mechanical recycling is the main technology applied to large-scale plastic waste treatment. However, this treatment poses important limitations since each type of plastic responds differently to the process depending on its mechanical behavior, chemical structure, and thermal properties. For instance, temperature-sensitive plastics, composites, and plastics that do not flow at elevated temperatures (thermosets e.g.) cannot be processed mechanically. Therefore, only two types of plastic are recovered this way: polyethylene terephthalate (PET) and polyethylenes (Garcia and Robertson, 2017), in addition, mechanical methods usually result in lower-quality products than the original plastic material. On the other hand, incineration recovers energy from the waste as heat but with low efficiency (Rahimi and Garcia, 2017), and with landfilling, the value of the material is lost to the economy and potentially destroys natural habitats.

In addition to mechanical recycling, recent research is focusing on repurposing chemically recyclable polymers and depolymerization of commercially available plastics (Hong and Chen, 2017). Among these resource recovery technologies, the one drawing more attention lately is chemical recycling that consists of thermo-catalytic processes such as pyrolysis, hydrocracking, and gasification, which are being studied under a wide range of conditions (Zhang et al., 2021), and chemolysis processes such as methanolysis, ammonolysis, aminolysis, glycolysis, hydrolysis, etc. (Chanda, 2021; Zhang et al., 2021). Relevant reviews are available on thermal and catalytic pyrolysis of plastic waste to produce a wide range of products ranging from pyrolytic oils and gasses to fuel-range chemicals, among others (Al-Salem et al., 2017; Lee et al., 2021; Miandad et al., 2016). Other reviews focus on gasification as a valorization route to produce syngas (Lopez et al., 2018), hydrocracking to produce high-quality fuels (Kunwar et al., 2016; Munir et al., 2018), and the co-conversion of biomass and plastic waste to obtain gaseous fuels (Mariyam et al., 2022). In addition, Kazemi et al. (2021) proposed the use of chemolysis and thermolysis processes for recycling plastics applied to the construction sector.

Bio-upcycling of plastic waste shows that microbial plastic metabolism might open new pathways to substitute fossil-based synthesis routes (Tiso et al., 2022). Muñoz Meneses et al. (2022) reviewed technological solutions that generate new uses for discarded polymeric materials or turn them into novel materials, such as carbon nanotubes, graphene, or other carbonaceous high added-value materials. Formela (2021) reported the recent progress in the sustainable development of waste rubber tire recycling technologies and discussed the main challenges affecting the future trends of their industrial application. Despite being very promising for chemical recycling or energy recovery, most of these alternatives currently present low technology readiness levels (TRL) and their industrial implementation requires extra modeling and assessment efforts.

Considering that the field of possibilities to upcycle waste keeps widening and most of the new developments do not evolve further than the lab scale, new potentially beneficial implementations may never get to see the light. For this reason, and due to the knowledge management challenges that the great availability of alternatives and information present, new synthesis tools are necessary to find the best possible routes for each kind of waste as well as to manage these substantial amounts of data more efficiently. Therefore, there is a surging need for holistic and efficient tools to systematically retrieve and evaluate the available alternatives for the treatment of given wastes (Yang et al., 2013).

There have been some attempts to develop models for the integration of upcycling technologies for the treatment of available plastic waste, as it is mixed plastic waste (MPW), such as the one proposed by Somoza-Tornos et al. (2021). The authors presented a systematic framework for the synthesis and optimization of circular economy networks and used it to identify the most promising paths to upcycle plastic waste. An optimization-based systematic and rigorous computational framework with integrated life cycle assessment was used in the work by Thakker and Bakshi (2021) to build general circular value chains. They evaluated a given network and find the best alternatives holistically with a special focus on LCA (Life Cycle Assessment) and design methods. Juárez-García et al. (2021) extended their previous works on carbon-hydrogen-oxygen symbiosis networks (i.e. Farouk et al., 2021) and detailed the process simulations to better assess the process-dependent parameters. Despite their success to solve the problem of closing material loops, they addressed it from a global perspective and assessed each alternative in detail, which adds extra complexity and would require significant computational efforts when the number of alternatives to consider is very large. Baratsas et al. (2021) proposed a novel CE system-engineering framework and decision-making tool for the modeling and optimization of food supply chains. This framework identifies all the possible pathways for the manufacture of a desired product and the valorization of wastes and by-products, from which a Resource-Task-Network was built, and a MILP model applied to optimize the supply chain considering multiple objectives, thus allowing a holistic modeling and optimization approach of the entire food supply chain. Robles et al. (2020) developed a waste supply chain optimization to recover value-added products from the organic fraction of municipal solid waste. Their systems-modeling approach integrates spatial data analysis, MILP optimization, and technology performance evaluation to aid the design of waste-to-resource value chains to recover nutrient and carbon-rich resources. These works show the potential of decision-making tools in a particular domain and their application needs to be extrapolated to other fields. To promote information exchange, Soldatos et al. (2020) proposed a digital platform that aims to facilitate knowledge exchange in cross-sectorial scenarios which could potentially promote new insights and opportunities towards the paradigm of the circular economy. In the same direction, Cecelja et al. (2015), proposed a semantic algorithm for the synthesis of industrial symbiosis networks based on the use of ontologies for knowledge modeling. This tool enables the acquisition of knowledge from the user through ontology instantiation and input-output matching based on semantic relevance between participants. They were able to form innovative networks by the decomposition of process properties and optimize it to maximize environmental performance. However, they identified issues with the availability of data and the efficiency of knowledge acquisition and management.

On a different note, graph theory and modular process representations have been used in a multitude of process synthesis approaches (Affery et al., 2021; Medina-González et al., 2020; Pastore De Lima and Maravelias, 2022; Proios et al., 2005; Tian and Pistikopoulos, 2019). Modular optimization approaches have also been successfully applied to several process syntheses case studies, such as biorefineries (Tay et al., 2012) and waste management systems (Batista et al., 2021; Flower et al., 1995; Kuznetsova et al., 2019). Finally, the integration of different tools into a unified framework has been applied to the circular economy and industrial symbiosis problems with promising results (Balgobin and

Evrard, 2020; Cagno et al., 2023; Hamilton et al., 2015; Silk et al., 2020). Ontologies have emerged in the last decades as a useful tool for knowledge management within decision-making frameworks, which proves their potential to address the identified challenges (Muñoz et al., 2012; Poveda-Villalón et al., 2022; Wilde et al., 2022; Zhou et al., 2018). To address these identified challenges, and paying attention to the recent developments and emerging tools in the field, the framework proposed in this work seeks to efficiently identify and build pathways to connect waste and resources to promote sustainability, as well as to reduce the required human and computational efforts.

Since the number of alternatives available to treat a specific material or waste might be too large to be studied through rigorous traditional methods, a multi-stage, sequential approach is proposed to perform consecutive filtering and discard those alternatives that are less promising or underdeveloped. The initial stages of the framework perform a simplified analysis and reduce the number of alternatives from an unmanageable set to one that can be more easily processed by an optimization algorithm. Each step of the framework adds gradually more detail and complexity to the analysis, taking advantage of the fact that the number of options has been previously reduced, and a more thorough assessment and optimization is performed only on the most promising alternatives. By doing so, the set of decisions is sequentially divided into various stages, thus avoiding dealing with a large volume of data all at once. This way, a sub-optimal solution might be obtained at first; however, this can be sorted out with an iterative procedure.

2. Problem statement

The integrated problem of waste-to-resource path generation and assessment with rigorous process design can be structured as follows:

- Given:
  - A set of waste-to-resource transformations with their associated costs, environmental impacts, processing capacity, and product yields.
  - A list of available waste sources, including information about their compositions, costs, and environmental footprints.
  - A list of potential resources demands, including information about their market prices, quality requirements, and other technical specifications.
- Obtain:
  - A prioritized list of the most promising routes and alternatives, according to aggregated economic, environmental, and maturity performance indicators.
  - The optimal material processing superstructures connecting waste streams with raw material demands according to different objectives such as economic profit and environmental damage on different impact categories.
  - Perform the rigorous process design, including process integration of the selected processes.

3. Materials and methods

We present a hierarchical multi-stage framework that integrates different Process Systems Engineering tools: ontologies for knowledge management, short-path algorithms to build processing routes, mathematical programming for superstructure optimization, and process integration and design techniques.

The set of decisions is divided into several stages to reduce the computational effort required by traditional optimization and decision-making procedures. This is done at the expense of the chance of losing global optimality in small datasets, but it is the only option to get solutions in a reasonable time for large cases. Thus, the steps of the methodology were designed to sequentially filter out the least appealing alternatives. The decisions go from general (i.e., if a technology is attractive or not), to more specific (i.e., which technologies should be used to treat a specific waste stream) towards a final rigorous technology design (i.e., process conditions for optimal performance).

The methodology is structured in four interoperable modules as depicted in Fig. 1. The core or central module consists of a knowledge management system (*I*), while the other three modules exchange the necessary information with it. These three modules are executed sequentially towards route synthesis and rigorous process design. Module II entails the routing, pre-assessment, and pre-selection of alternatives to narrow down the number of options based on the metrics identified by (Pacheco-López et al., 2021b). In module III, the most promising alternatives are then represented as the superstructure developed in Somoza-Tornos et al. (2021), considering the actual waste flow rates to be managed in each particular case study. Finally, module IV consists of the rigorous design of the processes identified in the network optimization. The modules are described in detail in the sections below.

The different modules are centralized and managed with a program script coded in Python 3. This program interacts with the tools implemented in the four modules to perform sequentially all the steps of the methodology. It can read/write data from/into the ontology and generate reports with the results to ease their interpretation. In the same way, an accessory program has also been developed to read information from a spreadsheet, create new instances, and assert their relevant information and relationships into the ontology. The whole framework (see Fig. 1) has been designated as *iSMA* (after the acronym for integrated Synthesis, Modeling, and Assessment).

3.1. Knowledge management (module I)

All the input and output data used in the framework are managed within an ontology-based system. Ontologies have proven to be an efficient and flexible repository of information and knowledge that allows versatile interrelation between concepts at multiple levels of detail. They are usually programmed in OWL language (OWL Working Group, 2012), which is a semantic language designed to represent rich and complex knowledge about things, groups of things, and relations between things. This way, the knowledge can be represented in a machine-readable way, but also allowing the use of semantic operators to query information, making access to data very efficient and intuitive for human interaction. Further clarification of how knowledge was represented in the ontology can be seen in previous contributions (Pacheco-López et al., 2021b).

Within the domain of Process Systems Engineering (PSE), a modified version of OntoCAPE (Marquardt et al., 2010) was used (Pacheco-López et al., 2020). The ontology includes all the axioms needed in the methodological framework: the definition of classes and instances and the object and data property assertions. All the processes, waste materials, intermediate products, and tentative final products have been instantiated in the ontology with their corresponding costs, prices, yields, and environmental indicators assertions. The results of the other modules are fed back into the ontology, enabling communication between modules II, III, and IV.

3.2. Path generation and pre-assessment (module II)

This module was developed and tested as a standalone application in Python code, as reported in a previous contribution (Pacheco-López et al., 2021b). The ontology is queried to implicitly generate all possible routes connecting available wastes with valuable products in a P-Graph. Bounds for partial and complete routes are assessed according to economic, maturity, and environmental aspects for the identification of the most promising alternatives. To do so, a Bellman-Ford short-path algorithm is used (Bellman, 1954), where the shortest paths to all tentative final nodes are built and assessed. All these paths are compared and sorted according to the proposed global performance indicator (GPI) which is also used as a weight to measure path length. The GPI is

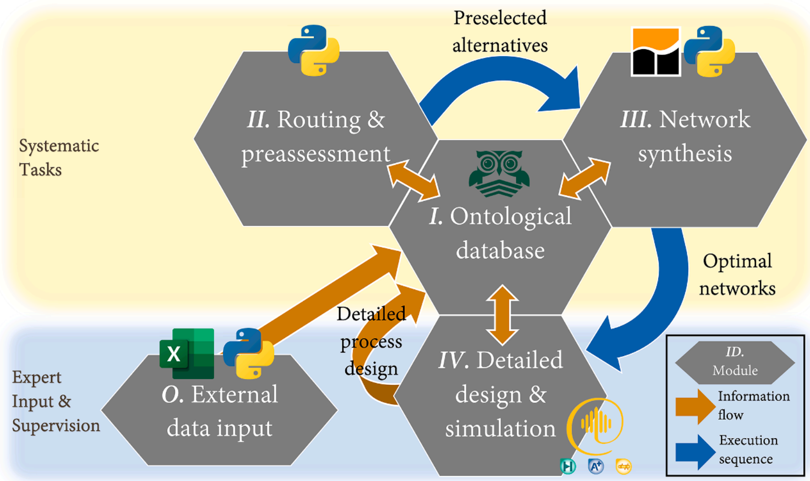

Fig. 1. Schematic representation of the proposed framework.

calculated using the economic and monetized environmental impact balances, as well as economic, environmental, and maturity performance pondering factors as shown in Eq. (1) (for more details about this metric refer to Pacheco-López et al. (2021b)).

$$GPI = (P^{eco} + P^{env}) \cdot f^{eco} \cdot f^{env} \cdot f^{TRL} \quad (1)$$

Where:

- P^{eco} is the economic profit of a concrete route
- $P^{env}$is the environmental monetized profit of the route
- f^{eco} is the economic pondering factor
- f^{env} is the environmental pondering factor
- f^{TRL} is the technology readiness level pondering factor

A limited list of alternatives is passed through to the next stage, making sure to select a heterogeneous set of options based on clusters according to the type of technology (e.g., pyrolytic semi-batch reactors, pyrolytic fluidized bed reactors, gasification, etc.). This clustering is defined in the ontology as a property that is used by the algorithm to identify each type of technology. The algorithm limits the number of technologies chosen for each cluster depending on the total number of alternatives, the number of clusters, and the number of alternatives that are set to be sent to the next stage. It guarantees that at least one technology from each cluster is selected and only the best ones of those with several similar options.

3.3. Superstructure optimization (module III)

This module starts with the pre-selected alternatives from the previous module, whose necessary parameters are already available in the ontology and are read directly from it. Superstructure representation is used to link these technologies with sources of waste and demands for raw materials. The superstructure is optimized using the model developed by Somoza-Tornos et al. (2021) that was developed in GAMS and embedded within the previously mentioned Python code. It is a useful tool to select the most suitable processing networks based on economic profit and three environmental endpoint indicators (impacts on human health, ecosystems, and resources). The assessment of these environmental objectives is done against economic profit through the representation of Pareto bicriteria fronts, which reduces the complexity and computational expense of dealing with four objectives simultaneously.

Each one of the resulting configurations is defined by which processes are used, the amount of material that is processed in each one of them, the products and byproducts amounts obtained to be sold, and the amount of waste or byproducts that are sent to waste management (i.e., landfill or incineration). Along with these results, the maximized economic objective (tentative profit) and the endpoints resulting from the LCA of the whole superstructure are also obtained.

It is important to remark that the techno-economic and environmental assessment performed on the processes to estimate parameters, such as process cost and environmental impacts, are common for both pre-assessment and superstructure optimization stages but used differently. In the former, they are used to assess and filter alternatives while in the latter they are used in a network optimization that yields a set of Pareto solutions to aid decision-making.

3.4. Process design and optimization (module IV)

This module includes process simulation (using the commercial simulator Aspen Plus) and integration (e.g., heat integration, energy recovery, CO_2 capture). The goal is to obtain a rigorous design for processes resulting from the network configurations in the previous module. This part of the framework entails the most expert-intervention requirement of the whole methodology and the most detailed design among all three. In this stage, the designers must make several decisions based on their expertise, on the available information in the literature source for the process under development, and using the latest available and more adequate design tools and techniques. They must choose each piece of equipment, piping, and accessories, and their configuration based on the process conditions and most costly efficient materials. Additionally, they must choose and optimize their specific working conditions, such as pressure, temperature, employed technology, internal configuration, etc.

4. Case study

The effectiveness of the integrated decision-making framework is illustrated through a case study that considers the use of mixed plastic waste to obtain valuable products and reduce the environmental footprint of plastics.

The chosen feedstock corresponds to a simulated mixed plastic waste (MPW) sample from sorting plants where mainly packaging plastic is separated from municipal solid waste (MSW). It was assumed to be composed of 40% of polyethylene (PE), 35% of polypropylene (PP), 18% of polystyrene (PS), 4% of polyethylene terephthalate (PET), and 3% of polyvinyl chloride (PVC) as proposed by Adrados et al. (2012).

The ontology was filled with processes from several publications (e.g.: Brandrup et al., 1996; Kaminsky et al., 2004; Kannan et al., 2014; Onwudili et al., 2019, 2009; Anuar Sharuddin et al., 2016; Kunwar et al., 2016; Rahimi and Garcia, 2017; Thiounn and Smith, 2020; Vollmer et al., 2020; Zhang et al., 2021). Among these processes, there is the one proposed by López et al. (2011) who tested the pyrolysis of MPW at different temperatures in a semi-batch reactor with and without the presence of catalysts (ZSM-5 zeolite and Red Mud). Lin et al. (2010) proposed the utilization of post-use commercial FCC catalysts using a fluidizing reaction system that operates isothermally and at atmospheric pressure. They tested four different catalysts obtaining good yields of valuable hydrocarbons and proposed a model to predict the behavior of the reactor under different conditions, such as different temperatures, different catalysts, particle size, and rate of fluidizing gas. For the elimination of plastic waste, gasification, and co-gasification processes have also been studied by several authors (Aznar et al., 2006; Kannan et al., 2013; Saebea et al., 2020; Toledo et al., 2011). To do so, they used an air-fluidized bed using dolomite as a tar-cracking catalyst at different bed temperatures and co-gasification ratios with coal and biomass. The main products from these operations were syngas, char, and light hydrocarbons. MPW can also be previously sorted into different materials and treated separately. For the treatment of PE waste, Uemichi et al. (1999) used a fixed bed tubular flow reactor catalyzed by the presence of zeolite (HZSM-5) and amorphous silica-alumina (SA) obtaining significantly favorable results when they were combined in a weight ratio of 9:1 at 375 °C. They obtained an oil phase that was transformed into high-quality gasoline. Sharma et al. (2014) pyrolyzed HDPE grocery bags and obtained an alternative fuel, mainly composed of paraffinic hydrocarbons, with properties complying with diesel standards, such as cetane number and lubricity among other specifications. Therefore, they are suitable to be used in blends with conventional petroleum diesel fuel. Miskolczi et al. (2009) investigated a pilot-scale process where packaging wastes (mainly PE and PP) were cracked in a horizontal gas-heated tube reactor at 520 °C using ZSM-5 catalyst and obtaining a wide range of fuels such as gasses, gasoline, light, and heavy oil. In addition, data for the pyrolysis of PE at different temperatures, residence times, and heating rates were added according to the results from Quesada et al. (2019), who characterized the oil obtained with the pyrolysis of plastic film (mostly composed by PE). They found that this oil had similar chemical and physical characteristics to those of commercial fuels (gasoline and diesel).

Recently, the authors (Pacheco-López et al., 2021a) also proposed a techno-economic and environmental assessment of the alternatives to fossil fuels, finding the use of pyrolytic oil from PP very promising against biomass and fossil-based alternatives. In addition, the hydration of ethylene to ethanol was proposed to replace gasoline-like fuels, with complementary results depending on the objective. Finally, Dimitrov et al. (2013), analyzed the potential of recycling PET bottles by pyrolysis-gas chromatography at 600 °C obtaining substantial amounts of acetaldehyde and benzoic acid.

The alternatives added to the ontology were chosen to include a diverse set of processes:

- thermal and catalytic pyrolysis at different temperatures and heating rates, gasification, co-gasification, catalytic cracking, etc.;
- various kinds of reactors such as stirred or unstirred batch reactors, fluidized or fixed bed reactors, horizontally heated-extruder tube reactors, etc.;
- different catalysts such as ZSM-5, HZSM-5, HUSY zeolites, red mud (a byproduct of the aluminum industry), SAHA (amorphous silica-alumina); and
- different operation modes such as continuous, semi-continuous, or discontinuous.

Product market prices were retrieved from the PRODCOM database of 2019 (Eurostat - European Union, 2021). Environmental impacts were obtained via a life cycle assessment following the ReCiPe2016 method and additionally monetized (for the pre-assessment in module II) following the Environmental Prices Handbook for the European Union (de Bruyn et al., 2018). The used life cycle inventory came from the database EcoInvent 3.6 (Wernet et al., 2016), accessed via SimaPro with gate-to-gate system boundaries and 1 tonne of waste as a functional unit. Technology readiness levels (TRL) were estimated following the guidelines from the European Commission (European Commission, 2017). More details on these assessment methods were presented in previous contributions (Pacheco-López et al., 2021b; Somoza-Tornos et al., 2021).

Specific products demand satisfaction was considered in this case and all obtained products were assumed to be sold at market price. Products demands were obtained from the PRODCOM database and escalated to a scenario of 32.71 tonnes of MPW per hour (volume of post-consumer plastic waste collected in the EU28 in 2018, 29.1 million tonnes, and escalated to a region of around 5 million inhabitants such as the Province of Barcelona). The plant costs and environmental impacts have been considered to vary linearly with the plant's capacity for a limited range of capacities.

5. Results and discussion

Following the same structure as the methodology, the results of each one of the different modules previously described for the proposed case study are presented below. The process information used in these modules was obtained from the literature (e.g., market prices, demands, process yields) or estimated following standard procedures (i.e., techno-economic and environmental assessments). This information is available in Supplementary Material's section 7. The methods and assumptions for the techno-economic analysis and life cycle assessment of the technologies can also be consulted in Somoza-Tornos et al. (2021).

5.1. *Path generation and pre-assessment (module II)*

Departing from a total of 58 different tentative steps included in the ontology which were directly or indirectly related to this specific case study, approximately 180 potential paths were obtained, from which around 40 complete paths were deployed, and 140 partial routes were also analyzed. A simplified version of the resulting P-graph is depicted in Fig. 2.

Then, the algorithm builds all shortest paths between the initial node and all other material nodes resulting in the set of paths shown in Table 1, sorted according to the proposed indicator. The pyrolysis of MPW at 500 °C seems to be the most attractive alternative, followed by this same kind of pyrolysis with catalysts such as red mud and ZSM-5 zeolite, as opposed to landfilling and incineration that were heavily penalized due to their inferior performance both in economic and environmental terms. As seen in Table 1, the alternatives with the worst economic and/or environmental performances are always at the bottom of the list with a GPI value equal to zero. This is due to the multiplying effect of the defined factors, which values were standardized comparatively among all alternatives, and ranged from zero to one, being zero for the last alternative in that category, and one for the first.

Once the pre-assessment is performed, the pre-selected alternatives are sent to the network synthesis stage, where an actual superstructure optimization is performed. As mentioned above, to perform equitable filtering of alternatives, they can be clustered, and only those more promising from each cluster were selected. The criteria for screening alternatives may depend on the total number of alternatives and can be tuned accordingly to each scenario.

5.2. *Superstructure optimization (module III)*

This network optimization model was implemented in GAMS 37.1.0 and solved using CPLEX 20.1.0.1 on a machine running an Intel i7–2600 with 4 cores @3.40/3.70 GHz processor. The optimization model features 230 equations, 458 continuous variables, and 56 discrete variables, which takes an average time of 3.5 s to be solved 34 times.

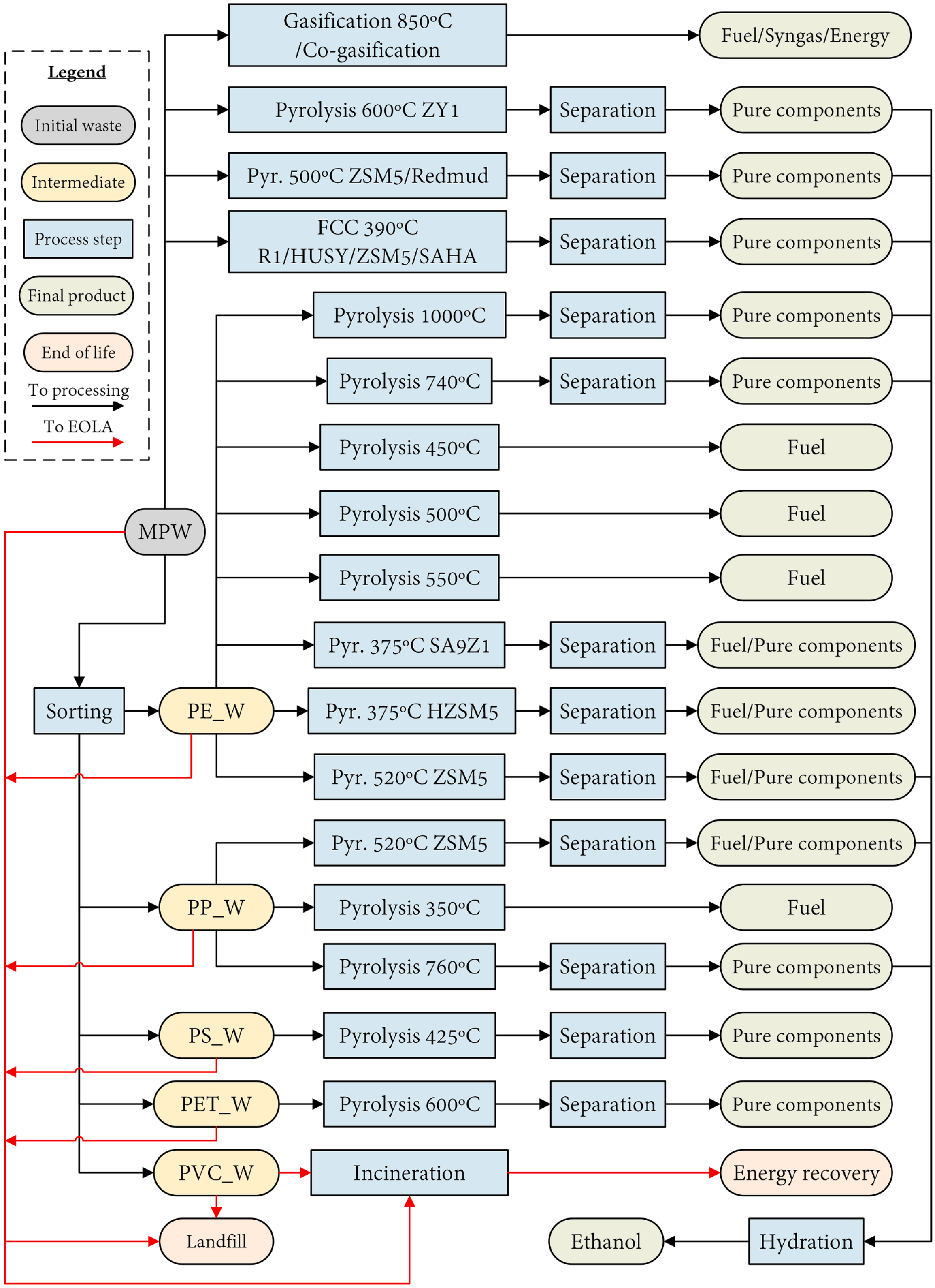

Fig. 2. Implicitly generated graph in the pre-assessment stage with tentative connections. Pyr.: Pyrolysis; ZY1: Y zeolite (Onwudili et al., 2019); ZSM5: ZSM-5 zeolite (López et al., 2011); FCC: fluid catalytic cracking; R1: FCC-R_1 commercial FCC equilibrium catalysts with different levels of rare earth oxides, zeolite, and a silica-alumina matrix; HUSY: Ultra stabilized Y zeolite; SAHA: amorphous silica-alumina (Lin et al., 2010); HZSM: HZSM-5 zeolite; SA9Z1: hybrid catalyst combining 9 parts of silica-alumina(SA) and 1 part of HZSM-5 zeolite (Uemichi et al., 1999); EOLA: End of life alternative; PE: polyethylene; PP: polypropylene; PS: polystyrene; PET: polyethylene terephthalate; PVC: polyvinyl chloride. For more details about the composition of “Pure Components”, see Table 1 below.

Table 1
Deployed process paths for MPW treatment, outputs, and GPI for the illustrative 20 alternatives. Sort.: Sorting; r.t.: residence time; FBR: Fluidized bed reactor; ZY1: Y zeolite (Onwudili et al., 2019); ZSM5: ZSM-5 zeolite (López et al., 2011); FCC: fluid catalytic cracking; R1: FCC-R_1 commercial FCC equilibrium catalysts; HUSY: Ultra-stabilized Y zeolite; SAHA: amorphous silica-alumina (Lin et al., 2010); HZSM: HZSM-5 zeolite; SA9Z1: hybrid catalyst combining 9 parts of silica-alumina(SA) and 1 part of HZSM-5 zeolite (Uemichi et al., 1999); LPG: liquefied petroleum gasses; WPPO: waste plastic pyrolysis oil.

	Processes	Outputs	GPI
1	Pyrolysis 500 °C + Separation	Methane, ethane/ene, propane, butane, hydrogen, pentane, hexene, toluene, ethylbenzene, styrene, naphthalene, xylene, 2,4-dimethyl-heptene & C9-C14 compounds	784
2	Pyrolysis 500 °C /Red Mud/ + Separation	Methane, ethane/ene, propane, butane/ene, hydrogen, pentane, hexene, toluene, ethylbenzene, styrene, methyl naphthalene, xylene, 2,4-dimethyl-heptene & C9-C14 compounds	723
3	Pyrolysis 500 °C /ZSM5/ + Separation	Methane, ethane/ene, propane, butane/ene, hydrogen, pentane, hexene, toluene, ethylbenzene, styrene, methyl naphthalene, xylene, 2,4-dimethyl-heptene & C9-C14 compounds	548
4	Pyrolysis 500 °C	Pyrolysis gas & pyrolysis oil	473
5	Pyrolysis 600 °C /ZY1/ + Separation	Methane, ethylene, propene, ethane, butane, butane, hydrogen, benzene, toluene, ethylbenzene & styrene	464
6	Pyrolysis 600 °C /ZY1/	Pyrolysis gas & pyrolysis oil	460
7	Acid FCC 390 °C /ZSM5/ + Separation	Gasoline, LPG, aromatics mixture, C9-C14 compounds, char & hydrochloric acid	318
8	Acid FCC 390 °C /HUSY/ + Separation	Gasoline, LPG, aromatics mixture, C9-C14 compounds, char & hydrochloric acid	316
9	Acid FCC 390 °C /SAHA/ + Separation	Gasoline, LPG, aromatics mixture, C9-C14 compounds, char & hydrochloric acid	313
10	Acid FCC 390 °C /R1/ + Separation	Gasoline, LPG, aromatics mixture, C9-C14 compounds, char & hydrochloric acid	311
11	Co-gasification 850 °C	Methane, ethane, syngas & char	195
12	Gasification 850 °C	Methane, ethane, syngas & char	190
13	Sort. + PE pyrolysis 740 °C + Separation	PP, PS, PET, PVC sorted wastes + Methane, ethane, ethylene, propene, benzene, toluene, indane & pyrene	78
14	Sort. + PE pyrolysis /SA9Z1/ FBR 375 °C	Gasoline, ethane, propane, butane + char	70
15	Sort. + PP pyrolysis 760 °C + Separation	Methane, ethylene, propene, ethane, benzene, toluene & naphthalene	60
16	Sort. + PE pyrolysis 1000 °C + Separation	Methane, ethylene, propene, butadiene & benzene	57
17	Sort. + PP pyrolysis 350 °C + Separation	WPPO (pyrolysis oil – diesel substitute) & char	50
18	Sort. + PE pyrolysis 550 °C; r.t.: 40 min	WPPO (pyrolysis oil – diesel substitute) & char	40
19	Incineration	Energy Recovery	0
20	Landfill	None	0

In this module, a multi-objective optimization was performed. First, the superstructure was optimized to maximize economic profit allowing the variation of the material flows entering each one of the pre-selected alternatives. Then, the ε-constraint method was applied to obtain the Pareto fronts for each bi-criteria pair (Branke et al., 2008; Cohon, 1978; Haimes, 1973; Mavrotas, 2009). In this case, the anchor point's configuration from the optimization to minimize environmental impacts on human health and ecosystems was considered coincidental since the Pareto obtained for human health dominates the one for ecosystems. Although this is not the general case, here the midpoints with the most weight are shared by both endpoints (such as global warming potential or fine particle matter formation); therefore, resulting in three different anchor points: one for the maximum profit, one for the minimum impact on human health and ecosystems, and one for the minimum impact on resources. Each Pareto front was built up using epsilon intervals between the mentioned anchor points and solving the model to maximize profit subject to their respective ε-constraints. Each one of the points of the Pareto fronts represents a different process configuration. The configurations that were leading to significant economic losses (profit below −1000 €/h) were disregarded from the solution set since they would be turned down by any decision-makers under current standards due to the importance of economic feasibility. As an illustrative example, Fig. 3 shows the configuration obtained for the best economic performance.

Fig. 4 below shows the Pareto plots for each one of the three environmental objectives against the economic profit, the coordinates for these points can be seen in Table S1. Table S2 presents the level of production matrix for each technology in each configuration.

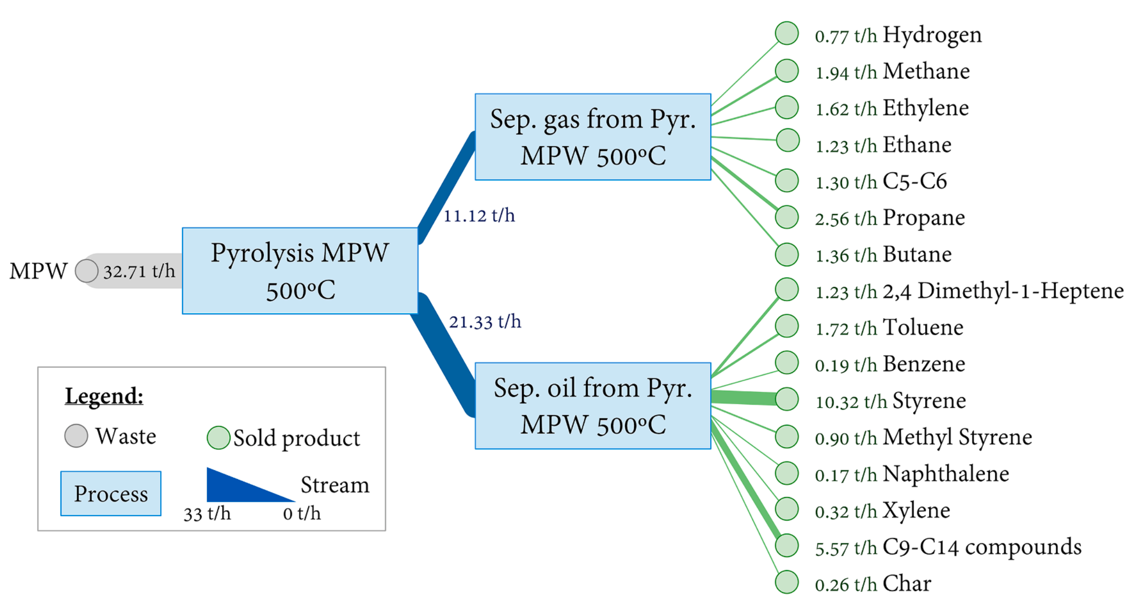

Fig. 3. Configuration obtained for maximized profit. Color-coded as orange (point number 10) in Fig. 4.

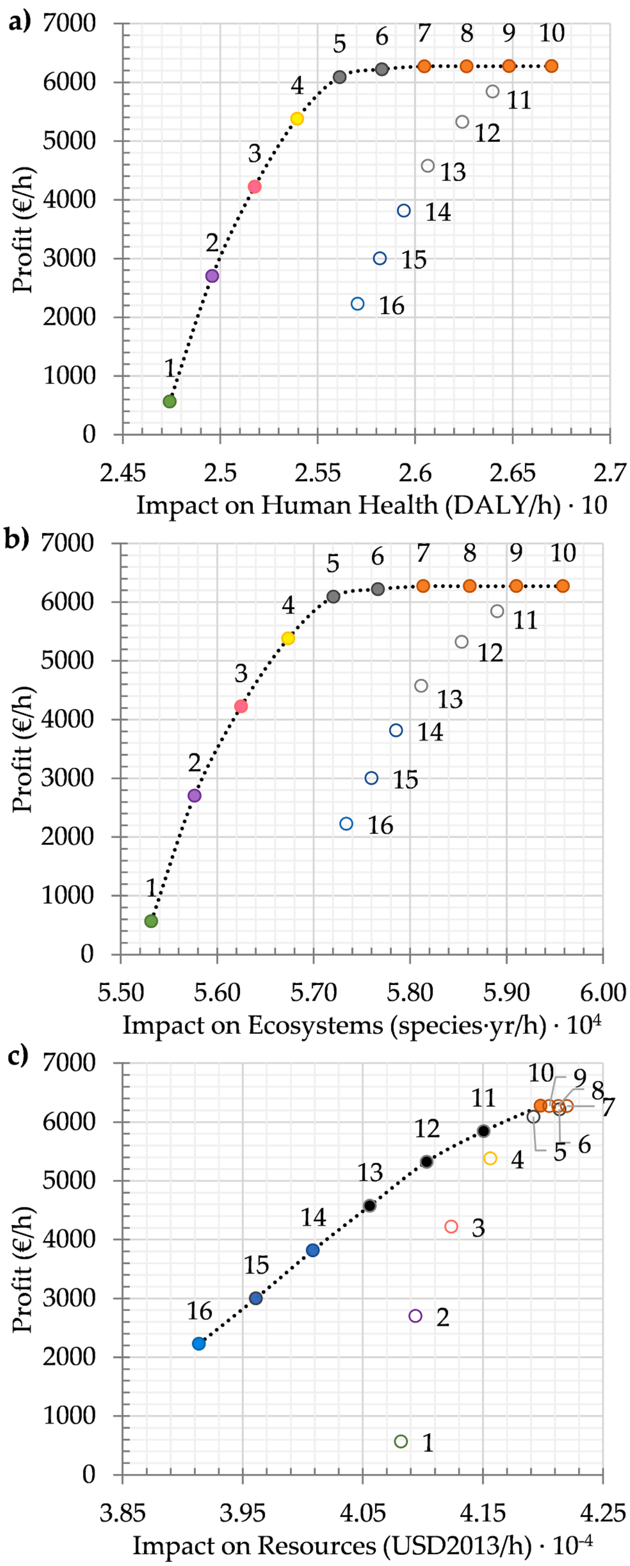

Fig. 4. Pareto optimal solutions of each two-dimensional space (two objectives) for the trade-off between profit and the three environmental endpoint indicators, i.e.: a) Human health, b) Ecosystems, and c) Resources. Filled points correspond with optimal solutions for that bicriteria Pareto front, while hollow points are the projections of others bicriteria Pareto optimal solutions. The points are color-coded to represent different configurations, as shown in Table S2 and Figures S1-S16. The dotted line represents fictitious points in the Pareto front.

The anchor points are situated at the end of each Pareto front. More specifically, point number 10 corresponds to the configuration with maximum profit, point 1 to the one with minimum impact on human health (HH) and ecosystems (ECO), point 16 to the one with the lowest impact on resources (RES), and the rest of the points are solutions in between. As seen in Fig. 4a and 4b, both Pareto tendencies are equivalent, as opposed to Fig. 4c in which the tendency is notably different.

Configuration 10 has a maximum profit of 6274.65 €/h and configurations 9, 8, 7, 6, and 5 have similar profits (above 6000€/h) but their impacts on HH and ECO decrease considerably for slight changes in their economic profit. This is due to the decrease in the amount of pyrolysis gas sent to separation and sold as a byproduct instead. The environmental impact of the separation, in this case, is relatively high and the profit obtained from separating the gas is not as significant (around 100 €/t of separated gas) as it is the environmental impact associated with this process.

Comparing the variation of each objective, configuration 5 for instance seems to be particularly promising compared to number 1. The profit for configuration 5 has decreased by 3% from the maximum profit and the resulting impacts on HH and ECO have decreased by 4% each. However, the profit for configuration 1 against the maximum profit has decreased by 92% while only a reduction of 7.5% impact on HH and ECO was obtained. This means that configurations 1 to 4 have a significant impact on economic performance while slightly reducing their impact on HH and ECO, in contrast with configurations 5 to 9, where the impact on profit when reducing environmental damages is very subtle. The main change introduced in configurations 1 to 4 corresponds with the inclusion of the preliminary sorting of plastics. This change has a greater economic influence (the cost of sorting is 314.56 €/t against 80.71 €/t for direct pyrolysis at 500 °C, 75% less) compared to the reduction on the environmental indicators (for instance, the impact of sorting on ecosystems is $4.09{\cdot}10^{-7}$ against $2.34{\cdot}10^{-7}$ species·year/t for direct pyrolysis at 500 °C, 43% less).

A similar phenomenon can be observed in the Resources vs Profit Pareto space (Fig. 4c) for configurations from 1 to 10, but with more noticeable changes. The impact on Profit is small when reducing environmental damage for points 5 to 10, but a much greater impact can be observed for points 4 and below. This indicates that the impact on resources when reducing the amount of gas separated from unsorted plastic pyrolysis, and therefore sold as a byproduct, is very small when

Table 2
Net flow rates of the process, utility requirements, and CO_2 emissions.

Concept	Units	Amount	Cost (€/h)
Feedstock			
Mixed plastic waste	kg/h	35,420	10,838.52
Products			
Syngas (methane, hydrogen)	kg/h	2533	−2356.69
Ethane	kg/h	1313	−1221.45
Ethylene	kg/h	1640	−1193.07
Hydrogen chloride	kg/h	667	−31.41
Propane	kg/h	2430	−1940.60
C4-C5 mixture	kg/h	2298	−2138.10
2,4 dimethyl-1-heptene	kg/h	3755	−2742.01
Cyclohexane	kg/h	1117	−755.88
Styrene	kg/h	8400	−7180.99
Toluene	kg/h	1652	−916.48
Utilities			
Electricity	kW	2295	177.79
Cooling water	m^3/h	765	24.26
Refrigerant - Propane	kg/h	1.34	1.09
Refrigerant - Ethylene	kg/h	2.70	1.96
Refrigerant - Freon 12	kg/h	12.95	34.84
Generated electricity (Rankine)	kW	1139	−88.30
Total carbon emissions			
CO_2	kg/h	18,588	Not considered
CO_2 referenced to initial waste	kg CO_2/t MPW	525	Not considered
CO_2 emissions from incineration	kg CO_2/t MPW	3106	Not considered

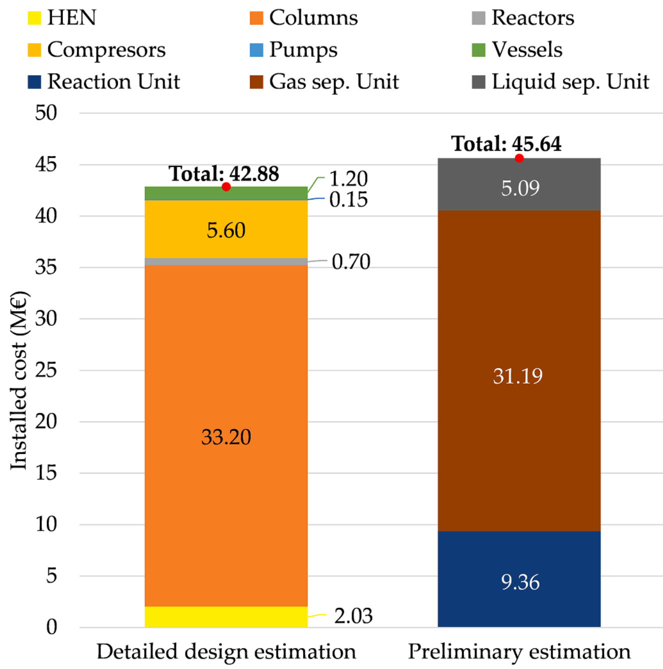

Fig. 5. Capital cost breakdown for preliminary and detailed design estimations. HEN: heat exchanger network; Sep.: separation. Reactors refer exclusively to the reactors' equipment after performing the detailed design in module IV, while in the preliminary estimation, it might include other equipment that goes in the reaction unit.

compared to the changes observed when including sorting plastics, which entails a high economic burden.

As for configurations 11 to 16, although they are dominated in the Pareto frontiers for HH and ECO, they are dominating in the RES one. Here, the tendency is almost linear, where the slope shows a reduction of 10% profit for each 1% reduction in RES impact, with a minor change in the slope around point 13. For instance, when changing the amount of plastic waste sent to pyrolysis with or without a catalyst, the environmental indicators are almost identical, while using a catalyst increases the cost noticeably (especially seen in points 11 to 13). When observing all these points (11 to 16) on the HH and ECO Pareto fronts, again there seem to be two linear tendencies with a change of slope in point 13, too (smoother from 10 to 13, but steeper from 13 to 16). This change in slope is due to the inclusion of plastic sorting in points 14 to 16, which has a higher cost in proportion to environmental endpoints than other processes. The same can be observed from points 1 to 4, where a notable change is observed, also due to the sorting being included in the configurations. This fact can be associated with inefficiencies in the sorting process, which results in a costly process with a lower yield than other processes and obtaining in turn another waste to deal with.

From these observations, it can be extracted that:

- Direct chemical treatment on MPW has better economic performance than introducing a previous sorting stage to manage the different plastic materials individually.
- Sorting and treating various kinds of plastic separately gives better results from the environmental point of view since those alternatives have lower unitary impacts when compared to unsorted treatment, as opposed to the economic performance that is penalized due to the cost of sorting.
- In contrast, for configurations without sorting, slight changes in the configurations, such as the inclusion of catalysts, can significantly reduce the environmental impact with a very small sacrifice in profit.

To summarize, for the considered waste, different pyrolysis processes followed by the separation of the pyrolytic products to obtain commercial-grade chemicals or fuels can be applied. There are different combinations according to the different tentative objectives, either economic or environmental (see Fig. 3, Fig. 4, and the Supplementary Material's Section 3), therefore yielding a different range of products depending on the solution.

The application of the methodology to this case study has shown that the most suitable alternatives are those that promote chemical recycling and simultaneously obtain fuels from plastic waste, therefore reducing the need for fossil fuels. Even though chemical recycling is not the only approach towards the implementation of a circular economy, it is necessary to recover materials from those products that cannot be directly recycled, reused, or refurbished to extend their life cycle as much as possible. To sum up, emerging waste transformation businesses are a cornerstone for the transition to the circular economy.

Among these recently developed alternatives for the chemical recycling of plastic waste, pyrolytic processes are promising alternatives for obtaining valuable chemicals that can be used as raw materials for other processes. New combinations of pyrolysis processes and separations were identified, and the material network was optimized to fulfill current demands in a more circular way than business as usual. In this case, the solution corresponding with point number 10 (color-coded as orange in Fig. 4, which process block diagram is shown in Fig. 3) was chosen for further study as an illustrative example. Although a multi-criterial decision-making approach could be applied to find the most suitable trade-off solution according to the objectives of each case, it remains out of the scope of this paper.

5.3. *Process design and optimization (module IV)*

Fig. 6 depicts the process flowsheet of the simulated plant for the pyrolysis of MPW. Design details can be seen in Section 3.4 and a more detailed explanation as well as the used simulation tools can be found in the Supplementary Material's Section 4. To account for the uncertainty of waste availability, at this step the design procedure assumed a 10% extra nominal capacity (i.e.: 35.4 t MPW/hour). Since the sample considered as a feedstock is a mixture of plastics, including PVC, a 2-stage reaction process has been proposed to avoid harmful emissions to the atmosphere. Here, the first reactor with a lower temperature than the main reactor (300 °C vs 500 °C) has been proven to be efficient to remove most of the present chlorine in the form of hydrogen chloride (López et al., 2011). The main pyrolytic reactor has been modeled as a stoichiometric reactor based on the data provided in the literature (Adrados et al., 2012). The hot gaseous pyrolysis products are sent to the evaporator of a steam Rankine cycle to generate electricity and recover energy. Then, these products are separated via flash separation into gaseous and liquid phases at room conditions (25 °C, 1 atm). Each one of these phases is fractionated and purified to separate their main components as marketable products. The gas stream is compressed up to 27 atm and enters the distillation train after passing through an amine scrubbing unit for CO_2 capture (Wang and Song, 2020). The liquid phase is sent to a different distillation train at a pressure of 10 atm. The main purified products obtained are syngas (a mixture of methane and hydrogen), ethane, ethylene, propane, and a mixture of C_4—C_5 components from the gaseous phase. From the liquid fraction, the main products are styrene, cyclohexane, 2,4 dimethyl-1-heptene, toluene, and a heavy oil mixture consisting of aromatics and aliphatic C_8+ compounds where further separation was not feasible, and it can be used as a fuel in other units of the process. Feedstock composition can be seen in Section 4 above.

Table 2 summarizes the flow rates for the feedstock and products, the usage of utilities, energy requirements along with their associated cost, as well as total CO_2 emissions. As seen in the results more than 70 wt.% of the mixed plastic waste entering the process can be recovered as a marketable purified product and around 25% as heavy fuel. Among the utilities, the most critical in terms of cost is electricity due to the high-energy demand of compressors, although nearly 50% of that energy

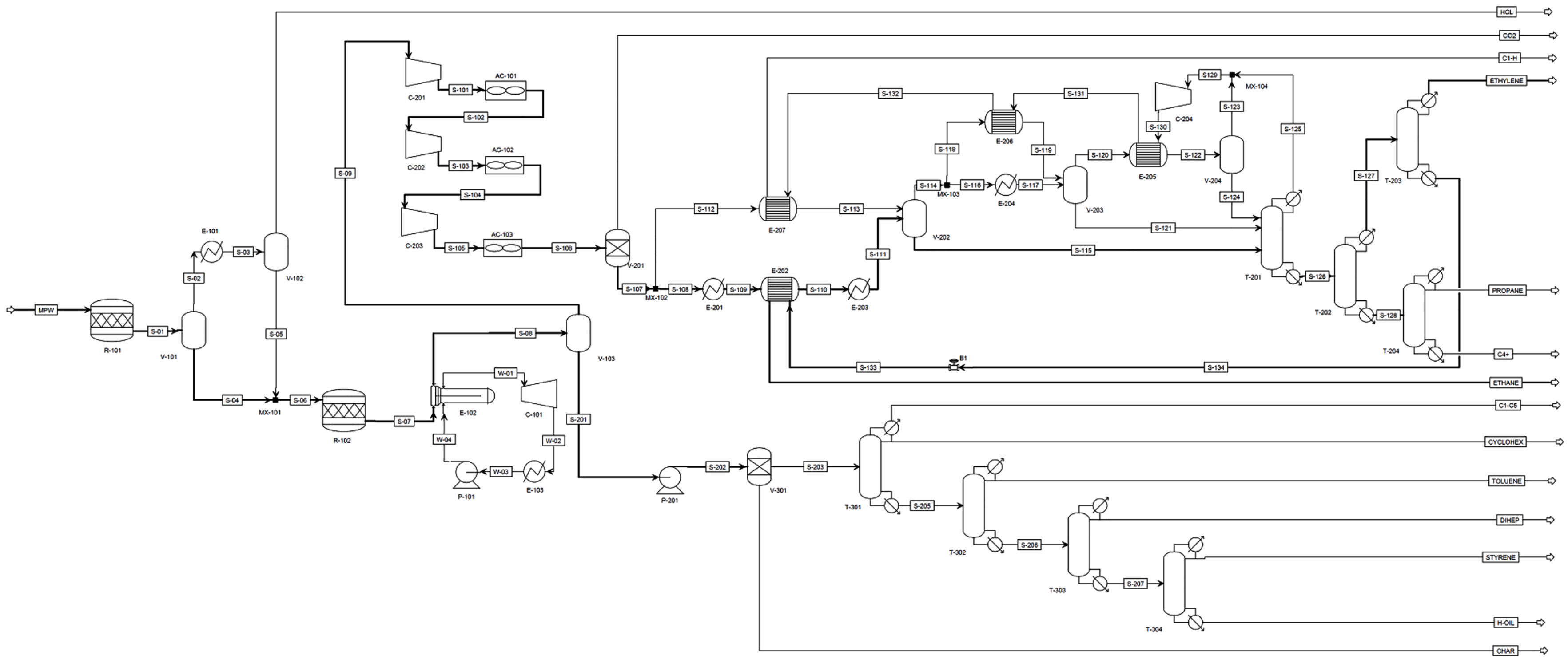

Fig. 6. Snapshot of the detailed simulation performed in the last stage of the methodology. For detailed equipment operating conditions and sizing or extensive information on each stream involved in the process, see Sections 5 and 6 in the Supplementary Material.

can be covered by the energy produced in the Rankine cycle. Regarding the direct carbon emissions, it appears as a prominent issue to address since the total emissions account for a near half tonne of CO_2 per tonne of treated MPW, even though these emissions are lower (83%) than the emissions from business as usual (BAU) treatment, i.e., incineration for energy recovery. Consequently, the flue gasses from the fired heated reactors should be treated with a Carbon Capture Unit before releasing them into the atmosphere to reduce the environmental impact of the process; however, the design of this part rests out of the scope of this paper.

The breakdown of capital costs from the new design and preliminary estimations are shown in Fig. 5, bearing in mind that each category in the preliminary estimation is grouped per unit and in the detailed design per equipment type. The total estimated capital cost of the detailed design ascends to almost 43 M€ (against almost 46 in the preliminary one), where the distillation columns (77%) and the gas compressors (13%) are the most expensive units, which in turn correspond to the gas and liquid separation units (over 90% of the total cost when combined) within ISBL (Inside Battery Limits) capital costs. In the preliminary estimations, they are distributed as 68% gas for the separation unit, 11% for the liquid separations, and 21% for the reaction unit. Accounting for OSBL (Outside Battery Limits), engineering, and contingencies, the estimated capital expenditure reaches 70.75 M€ (against 75.31 M€ in the preliminary estimations). In both, capital costs were annualized accounting for 8000 h of yearly operation, and a 10-year linear depreciation scheme with a fixed interest rate of 15%. The comparison of the detailed design results with the preliminary estimation for modules II and III shows that those estimations were accurate enough since the difference between both is only 6%.

Table 3
Techno-economic assessment summary.

Concept	Units	Amount
Operational costs		
Feedstock	€/h	10,838.52
Utilities	€/h	2007.95
Total variable cost	€/h	12,846.47
Total fixed cost	€/h	642.32
Total operational cost	€/h	13,488.79
Capital cost		
ISBL (total installed cost)	M€	42.88
OSBL	M€	17.15
Engineering cost	M€	4.29
Contingency cost	M€	6.43
Total fixed capital cost	M€	70.75
Annualized capital cost	M€	14.15
Total costs, revenues, and profit		
Operational expenditure	€/h	13,488.79
Capital expenditure	€/h	1768.76
Products revenue	€/h	22,276.93
Profit	€/h	7019.38
Relative profit	€/t MPW	198.18

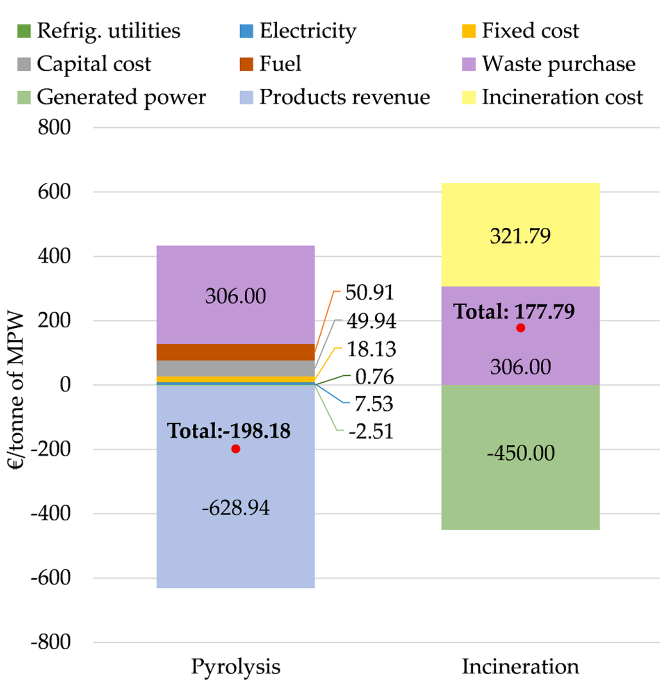

Fig. 7. Total cost per tonne of processed waste through pyrolysis vs. incineration (BAU).

Table 3 shows the breakdown of the techno-economic assessment on a time basis, while Fig. 7 shows the unitary cost per tonne of MPW treated via the designed pyrolysis process against BAU procedures, as it is incineration in this case. Pyrolysis entails feedstock cost (waste collection) as the highest operational cost, while the cost drivers of incineration are evenly distributed among all operational costs. When compared, the pyrolysis process is overall economically and environmentally more beneficial than BAU, since the tentative profit ascends to 198.18 €/t of MPW, while incineration has a total cost of 177.79 €/t despite the credits of the generated heat power.

To assess how the process might have been improved in the simulation and design stage, we compared the total profit estimated in previous stages against the one obtained here. As mentioned in Section 5.2 above and shown in Fig. 4, the total profit obtained by the Pyrolysis of MPW at 500 °C followed by products purification was around 6274.65 €/h, or 191.83 €/t MPW, while the new improved design is up to 7019.38 €/h, or 198.18 €/t MPW. Therefore, even after including new significant elements into the design of the process, such as chlorine and CO_2 reclamation or heat recovery through a Rankine cycle, the profit per tonne of MPW can be tentatively improved by more than 3%. However, there is great room for improvement if separation capital costs are reduced consistently or the feedstock cost is subsidized by the administrations.

The framework's cycle can be repeated every time new alternatives emerge, being either new instances from the literature or improved pre-existing ones, to test if new and better configurations can be synthesized and identify if a new optimum is available.

6. Conclusions

This work addresses the development of systematic methods and tools for the identification, synthesis, and rigorous process design of new alternatives for the treatment of waste that can be integrated into new circular approaches, which are aimed at reducing anthropogenic environmental damage as well as providing economic development. The methodological framework proposed in this work allows the systematic identification and assessment of new technologies, as well as providing new combinations of processes that narrow down the list of alternatives available to a more manageable set according to several predefined objectives. The application of this framework is not limited to the identification of circular approaches, but it can also be used to synthesize and optimize symbiosis networks since the ontology can be populated with any kind of process. Thus, the framework might use any of these processes to build new connections not previously identified either at the strategic or tactical level.

The general methodology has been applied to the case of plastic waste management to illustrate its practicality. Results show that it is useful to identify possible routes fairly and objectively for closing the material loops and to select only those that were most promising, before a more detailed route assessment. Additionally, an optimized network of alternatives according to different objectives or scenarios can be obtained, which is a useful aid for decision-making. The detailed design and simulation of the MPW pyrolysis path showed the technological need to find less energy-intensive, more efficient separation technologies, and the use of carbon capture technologies to minimize CO2 emissions. Despite these identified challenges, the overall process appears as a better alternative than conventional BAUs.

New waste transformation businesses can emerge as a necessary part of the circular economy's paradigm. They can potentially benefit from waste and produce valuable chemicals or fuels while keeping materials within the cycle and being economically profitable. In consequence, systematic methods and tools such as the one developed in this work will be required to devise which are the best alternatives for each kind of waste. Our framework combines automated procedures for the systematic synthesis, assessment, and filtering of alternatives with expert process design for the final solution (see Fig. 1) to enrich decision-making problems and allow finding better trade-off solutions based on the objectives.

The scaling-up of the processes was not addressed in the modeling in the first stages of the methodology, since it is a challenging task for multiphase processes like pyrolysis, therefore potentially introducing a considerable source of uncertainty whose effect could be studied performing a sensitivity analysis. Despite this fact, the differences between the preliminary estimations and eventual rigorous design results were not significantly different for our case study (around 3% for profit and 6% for capital cost). Future work will focus on considering this fact in the first stages, as well as the implementation and systematization of the process parameters optimization, further integrating other useful tools, such as automated information extraction, flowsheet development, and the study of the benefit of including circularity metrics. Additionally, the reintroduction of new detailed designs in the ontology, broadening the field of alternatives with new instances from the literature, and re-iteration within the framework for verification, sensitivity analysis, and robustness assessment purposes are planned to be performed, as well as including some multi-objective decision-making approaches to select which alternatives should qualify from module II to module III.

CRediT authorship contribution statement

Adrián Pacheco-López: Conceptualization, Methodology, Software, Data curation, Visualization, Validation, Resources, Formal analysis, Investigation, Writing – original draft, Writing – review & editing. **Edward Gómez-Reyes:** Software, Resources. **Moisés Graells:** Conceptualization, Writing – original draft, Writing – review & editing, Supervision, Project administration, Funding acquisition. **Antonio Espuña:** Conceptualization, Writing – original draft, Writing – review & editing, Supervision, Project administration, Funding acquisition. **Ana Somoza-Tornos:** Conceptualization, Methodology, Data curation, Resources, Supervision, Investigation, Validation, Writing – original draft, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

Financial support received from the Spanish "Ministerio de Economía, Industria y Competitividad" and the European Regional Development Fund, both funding the research Project CEPI (PID2020–116051RB-I00) is fully acknowledged. Adrián Pacheco-López thanks the financial support received from the "Ministerio de Ciencia e Innovación" (grant ref. PRE2018–087135).

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.compchemeng.2023.108255.

References

Adrados, A., de Marco, I., Caballero, B.M., López, A., Laresgoiti, M.F., Torres, A., 2012. Pyrolysis of plastic packaging waste: a comparison of plastic residuals from material recovery facilities with simulated plastic waste. Waste Manag. 32, 826–832. https://doi.org/10.1016/j.wasman.2011.06.016.

Affery, A.P., Tan, J.X., Yan, I., Ong, B., Lim, J.Y., Yoo, C., Shen How, B., Ling, G.H.T., Foo, D.C.Y., 2021. Optimal planning of inter-plant hydrogen integration (IPHI) in eco-industrial park with P-graph and game theory analyses. Process Saf. Environ. Prot. 155, 197–218. https://doi.org/10.1016/j.psep.2021.08.016.

Al-Salem, S.M., Antelava, A., Constantinou, A., Manos, G., Dutta, A., 2017. A review on thermal and catalytic pyrolysis of plastic solid waste (PSW). J. Environ. Manag. 197, 177–198. https://doi.org/10.1016/j.jenvman.2017.03.084.

Aznar, M.P., Caballero, M.A., Sancho, J.A., Francés, E., 2006. Plastic waste elimination by co-gasification with coal and biomass in fluidized bed with air in pilot plant. Fuel Process Technol. 87, 409–420. https://doi.org/10.1016/j.fuproc.2005.09.006.

Balgobin, T., Evrard, D., 2020. A framework for modelling emerging processes' upscaling from an environmental perspective. Procedia CIRP 90, 154–158. https://doi.org/10.1016/j.procir.2020.01.055.

Baratsas, S.G., Pistikopoulos, E.N., Avraamidou, S., 2021. A systems engineering framework for the optimization of food supply chains under circular economy considerations. Sci. Total Environ. 794, 148726 https://doi.org/10.1016/j.scitotenv.2021.148726.

Batista, M., Goyannes Gusmão Caiado, R., Gonçalves Quelhas, O.L., Brito Alves Lima, G., Leal Filho, W., Rocha Yparraguirre, I.T., 2021. A framework for sustainable and integrated municipal solid waste management: barriers and critical factors to developing countries. J. Clean. Prod. 312 https://doi.org/10.1016/j.jclepro.2021.127516.

Bellman, R., 1954. The theory of dynamic programming. Bull. Am. Math. Soc. 60, 503–515. https://doi.org/10.1090/S0002-9904-1954-09848-8.

Brandrup, J., Bittner, M., Michaeli, W., Menges, G., 1996. Recycling and Recovery of Plastics. Hanser Verlag.

Branke, J., Deb, K., Miettinen, K., Słowinski, R., 2008. Multiobjective optimization. Interactive and Evolutionary Approaches, LNCS 5252. Springer. https://doi.org/10.1007/978-3-319-29392-9_4.

Cagno, E., Negri, M., Neri, A., Giambone, M., 2023. One framework to rule them all: an integrated, multi-level and scalable performance measurement framework of sustainability. Circular Economy and Industrial Symbiosis Sustain. Prod. Consum. 35, 55–71. https://doi.org/10.1016/J.SPC.2022.10.016.

Cecelja, F., Trokanas, N., Raafat, T., Yu, M., 2015. Semantic algorithm for Industrial Symbiosis network synthesis. Comput. Chem. Eng. 83, 248–266. https://doi.org/10.1016/j.compchemeng.2015.04.031.

Chanda, M., 2021. Chemical aspects of polymer recycling. Adv. Ind. Eng. Polym. Res. https://doi.org/10.1016/j.aiepr.2021.06.002.

Cohon, J.L., 1978. Multiobjective Programming and Planning. Dover Publications ed. Dover Publications.

de Bruyn, S., Bijleveld, M., de Graaff, L., Schep, E., Schroten, A., Vergeer, R., Ahdour, S., 2018. Environmental Prices Handbook - EU28 version. Delft, CE Delft. Oct. 2018 Publ. code 18.7N54.125.

Dimitrov, N., Kratofil Krehula, L., Ptiček Siročić, A., Hrnjak-Murgić, Z., 2013. Analysis of recycled PET bottles products by pyrolysis-gas chromatography. Polym. Degrad. Stab. 98, 972–979. https://doi.org/10.1016/j.polymdegradstab.2013.02.013.

Ellen MacArthur Foundation, 2017. The new plastics economy: Rethinking the future of plastics & catalysing action. Ellen MacArthur Found, p. 68. https://ellenmacarthurfoundation.org/the-new-plastics-economy-rethinking-the-future-of-plastics-and-catalysing.

Ellen MacArthur Foundation, 2019. Completing the picture: how the circular economy tackles climate change. https://ellenmacarthurfoundation.org/completing-the-picture.

Eurostat - European Union, 2021. Overview - Prodcom - statistics by product - Eurostat [WWW Document]. https://ec.europa.eu/eurostat/web/prodcom (accessed 9.21.21).

European Commission, 2017. EN HORIZON 2020 WORK PROGRAMME 2016 –2017 20 . General Annexes. European Commission Decision C, pp. 1–39, 20172468 of 24 April 2017)Annex G, Technology Readiness Levels (TRL).

Farouk, A.A., El-Halwagi, M.M., Foo, D.C.Y., Mei, I., Chew, L., 2021. Development of a C−H−O symbiosis network during conceptual design via economic. Sustain. Saf. Metr. https://doi.org/10.1021/acssuschemeng.0c08553.

Flower, J.R., Bikos, S.C., Johnson, S.W., 1995. A Modular approach to synthesis of cleaner processes. Comput. Chem. Eng. 19 (45) https://doi.org/10.1016/0098-1354(95)87013-X.

Formela, K., 2021. Sustainable development of waste tires recycling technologies – recent advances, challenges and future trends. Adv. Ind. Eng. Polym. Res. 4, 209–222. https://doi.org/10.1016/J.AIEPR.2021.06.004.

Garcia, J.M., Robertson, M.L., 2017. The future of plastics recycling. Science 358, 870–872. https://doi.org/10.1126/SCIENCE.AAQ0324/ASSET/53AC3A00-0BBA-41D7-A05A-BE986DAF5476/ASSETS/GRAPHIC/358_870_F1.JPEG.
Haimes, Y.Y., 1973. Integrated system identification and optimization. Control Dyn. Syst. 10, 435–518. https://doi.org/10.1016/B978-0-12-012710-8.50013-3.
Hamilton, S.H., ElSawah, S., Guillaume, J.H.A., Jakeman, A.J., Pierce, S.A., 2015. Integrated assessment and modeling: overview and synthesis ofsalient dimensions. Environ. Model. Softw. 64, 215–229. https://doi.org/10.1016/j.envsoft.2014.12.005.
Hong, M., Chen, E.Y.X., 2017. Chemically recyclable polymers: a circular economy approach to sustainability. Green Chem. 19, 3692–3706. https://doi.org/10.1039/C7GC01496A.
Juárez-García, M., El-Halwagi, M.M., Ponce-Ortega, J.M., 2021. Systematic approach for synthesizing carbon-hydrogen-oxygen networks involving detailed process simulations. Ind. Eng. Chem. Res. 60, 16378–16393. https://doi.org/10.1021/acs.iecr.1c02738.
Kakadellis, S., Rosetto, G., 2021. Achieving a circular bioeconomy for plastics. Science 373, 49–50. https://doi.org/10.1126/SCIENCE.ABJ3476/ASSET/AB5F3BB7-50C8-4E95-B31A-D91CA953A229/ASSETS/GRAPHIC/373_49_F1.JPEG.
Kaminsky, W., Predel, M., Sadiki, A., 2004. Feedstock recycling of polymers by pyrolysis in a fluidised bed. Polym. Degrad. Stab 85, 1045–1050. https://doi.org/10.1016/j.polymdegradstab.2003.05.002.
Kannan, P., Al Shoaibi, A., Srinivasakannan, C., 2014. Temperature effects on the yield of gaseous olefins from waste polyethylene via flash pyrolysis. Energy Fuels 28, 3363–3366. https://doi.org/10.1021/ef500516n.
Kannan, P., Al Shoaibi, A., Srinivasakannan, C., 2013. Energy recovery from co-gasification of waste polyethylene and polyethylene terephthalate blends. Comput. Fluids 88, 38–42. https://doi.org/10.1016/j.compfluid.2013.09.004.
Kazemi, M., Faisal Kabir, S., Fini, E.H., 2021. State of the art in recycling waste thermoplastics and thermosets and their applications in construction. Resour. Conserv. Recycl. https://doi.org/10.1016/j.resconrec.2021.105776.
Kunwar, B., Cheng, H.N., Chandrashekaran, S.R., Sharma, B.K., 2016. Plastics to fuel: a review. Renew. Sustain. Energy Rev. https://doi.org/10.1016/j.rser.2015.10.015.
Kuznetsova, E., Cardin, M.A., Diao, M., Zhang, S., 2019. Integrated decision-support methodology for combined centralized-decentralized waste-to-energy management systems design. Renew. Sustain. Energy Rev. 103, 477–500. https://doi.org/10.1016/j.rser.2018.12.020.
Lee, J., Kwon, E.E., Lam, S.S., Chen, W.H., Rinklebe, J., Park, Y.-K., 2021. Chemical recycling of plastic waste via thermocatalytic routes. J. Clean. Prod. 321, 128989 https://doi.org/10.1016/j.jclepro.2021.128989.
Lin, Y.H., Yang, M.H., Wei, T.T., Hsu, C.T., Wu, K.J., Lee, S.L., 2010. Acid-catalyzed conversion of chlorinated plastic waste into valuable hydrocarbons over post-use commercial FCC catalysts. J. Anal. Appl. Pyrolysis 87, 154–162. https://doi.org/10.1016/j.jaap.2009.11.006.
López, A., De Marco, I., Caballero, B.M., Laresgoiti, M.F., Adrados, A., 2011. Dechlorination of fuels in pyrolysis of PVC containing plastic wastes. Fuel Process. Technol. 253–260. https://doi.org/10.1016/j.fuproc.2010.05.008.
López, A., de Marco, I., Caballero, B.M., Laresgoiti, M.F., Adrados, A., Aranzabal, A., 2011. Catalytic pyrolysis of plastic wastes with two different types of catalysts: ZSM-5 zeolite and red mud. Appl. Catal. B 104, 211–219. https://doi.org/10.1016/j.apcatb.2011.03.030.
Lopez, G., Artetxe, M., Amutio, M., Alvarez, J., Bilbao, J., Olazar, M., 2018. Recent advances in the gasification of waste plastics. a critical overview. Renew. Sustain. Energy Rev. https://doi.org/10.1016/j.rser.2017.09.032.
Mariyam, S., Shahbaz, M., Al-Ansari, T., Mackey, H.R., McKay, G., 2022. A critical review on co-gasification and co-pyrolysis for gas production. Renew. Sustain. Energy Rev. https://doi.org/10.1016/j.rser.2022.112349.
Marquardt, W., Morbach, J., Wiesner, A., Yang, A., 2010. OntoCAPE-A *Re*-Usable Ontology For Chemical Process Engineering, RWTHedition. Springer Berlin Heidelberg. https://doi.org/10.1007/978-3-642-04655-1.
Mavrotas, G., 2009. Effective implementation of the ε-constraint method in multi-objective mathematical programming problems. Appl. Math. Comput. 213, 455–465. https://doi.org/10.1016/j.amc.2009.03.037.
Medina-González, S., Gkioulekas, I., Dua, V., Papageorgiou, L.G., 2020. A graph theory approach for scenario aggregation for stochastic optimisation. Comput. Chem. Eng. 137, 106810 https://doi.org/10.1016/j.compchemeng.2020.106810.
Miandad, R., Barakat, M.A., Aburiazaiza, A.S., Rehan, M., Nizami, A.S., 2016. Catalytic pyrolysis of plastic waste: a review. Process. Saf. Environ. Prot. 102, 822–838. https://doi.org/10.1016/j.psep.2016.06.022.
Miskolczi, N., Angyal, A., Bartha, L., Valkai, I., 2009. Fuels by pyrolysis of waste plastics from agricultural and packaging sectors in a pilot scale reactor. Fuel Process. Technol. 90, 1032–1040. https://doi.org/10.1016/j.fuproc.2009.04.019.
Munir, D., Irfan, M.F., Usman, M.R., 2018. Hydrocracking of virgin and waste plastics: a detailed review. Renew. Sustain. Energy Rev. https://doi.org/10.1016/j.rser.2018.03.034.
Muñoz, E., Capón-García, E., Espuña, A., Puigjaner, L., 2012. Ontological framework for enterprise-wide integrated decision-making at operational level. Comput. Chem. Eng. 42, 217–234. https://doi.org/10.1016/j.compchemeng.2012.02.001.
Muñoz Meneses, R.A., Cabrera-Papamija, G., Machuca-Martínez, F., Rodríguez, L.A., Diosa, J.E., Mosquera-Vargas, E., 2022. Plastic recycling and their use as raw material for the synthesis of carbonaceous materials. Heliyon 8, e09028. https://doi.org/10.1016/J.HELIYON.2022.E09028.
Onwudili, J.A., Insura, N., Williams, P.T., 2009. Composition of products from the pyrolysis of polyethylene and polystyrene in a closed batch reactor: effects of temperature and residence time. J. Anal. Appl. Pyrolysis 86, 293–303. https://doi.org/10.1016/j.jaap.2009.07.008.
Onwudili, J.A., Muhammad, C., Williams, P.T., 2019. Influence of catalyst bed temperature and properties of zeolite catalysts on pyrolysis-catalysis of a simulated mixed plastics sample for the production of upgraded fuels and chemicals. J. Energy Inst. 92, 1337–1347. https://doi.org/10.1016/j.joei.2018.10.001.
Pacheco-López, A., Lechtenberg, F., Somoza-Tornos, A., Graells, M., Espuña, A., 2021a. Economic and environmental assessment of plastic waste pyrolysis products and biofuels as substitutes for fossil-based fuels. Front. Energy Res. 9, 236. https://doi.org/10.3389/fenrg.2021.676233.
Pacheco-López, A., Somoza-Tornos, A., Graells, M., Espuña, A., 2021b. Synthesis and assessment of waste-to-resource routes for circular economy. Comput. Chem. Eng. 153 https://doi.org/10.1016/j.compchemeng.2021.107439.
Pacheco-López, A., Somoza-Tornos, A., Muñoz, E., Capón-García, E., Graells, M., Espuña, A., 2020. Synthesis and assessment of waste-to-resource routes for circular economy. Comput. Aided Chem. Eng. https://doi.org/10.1016/B978-0-12-823377-1.50323-2. Elsevier Masson SAS.
Pastore De Lima, A.E., Maravelias, C.T., 2022. A generalized framework for reactor network synthesis: a graph theoretic approach. Comput. Chem. Eng. 160, 107722 https://doi.org/10.1016/j.compchemeng.2022.107722.
PlasticsEurope, 2020. Plastics – the Facts 2020. PlasticEurope, pp. 1–64.
Poveda-Villalón, M., Fernández-Izquierdo, A., Fernández-López, M., García-Castro, R., 2022. LOT: an industrial oriented ontology engineering framework. Eng. Appl. Artif. Intell. 111 https://doi.org/10.1016/J.ENGAPPAI.2022.104755.
Proios, P., Goula, N.F., Pistikopoulos, E.N., 2005. Generalized modular framework for the synthesis of heat integrated distillation column sequences. Chem. Eng. Sci. 60, 4678–4701. https://doi.org/10.1016/j.ces.2005.02.072.
Quesada, L., Calero, M., Martín-Lara, M.A., Pérez, A., Blázquez, G., 2019. Characterization of fuel produced by pyrolysis of plastic film obtained of municipal solid waste. Energy 186, 115874. https://doi.org/10.1016/j.energy.2019.115874.
Rahimi, A.R., Garcia, J.M., 2017. Chemical recycling of waste plastics for new materials production. Nat. Rev. Chem. https://doi.org/10.1038/s41570-017-0046.
Robles, I., O'Dwyer, E., Guo, M., 2020. Waste-to-Resource value chain optimisation: combining spatial, chemical and technoeconomic aspects. Water Res. 178, 115842 https://doi.org/10.1016/j.watres.2020.115842.
Saebea, D., Ruengrit, P., Arpornwichanop, A., Patcharavorachot, Y., 2020. Gasification of Plastic Waste For Synthesis Gas Production. Energy Reports. Elsevier Ltd, pp. 202–207. https://doi.org/10.1016/j.egyr.2019.08.043.
Sharma, B.K., Moser, B.R., Vermillion, K.E., Doll, K.M., Rajagopalan, N., 2014. Production, characterization and fuel properties of alternative diesel fuel from pyrolysis of waste plastic grocery bags. Fuel Process. Technol. 122, 79–90. https://doi.org/10.1016/j.fuproc.2014.01.019.
Silk, D., Mazzali, B., Gargalo, C.L., Pinelo, M., .A, Udugama, I., Mansouri, S.S., 2020. A decision-support framework for techno-economic-sustainability assessment of resource recovery alternatives. J. Clean. Prod. 266, 121854 https://doi.org/10.1016/j.jclepro.2020.121854.
Soldatos, J., Kefalakis, N., Despotopoulou, A.M., Bodin, U., Musumeci, A., Scandura, A., Aliprandi, C., Arabsolgar, D., Colledani, M., 2020. A digital platform for cross-sector collaborative value networks in the circular economy. Procedia Manuf. 54, 64–69. https://doi.org/10.1016/j.promfg.2021.07.011.
Somoza-Tornos, A., Pozo, C., Graells, M., Espuña, A., Puigjaner, L., 2021. Process screening framework for the synthesis of process networks from a circular economy perspective. Resour. Conserv Recycl. 164, 105147 https://doi.org/10.1016/j.resconrec.2020.105147.
Tay, D.H.S., Ng, R.T.L., Ng, D.K.S., 2012. Modular optimization approach for process synthesis and integration of an integrated biorefinery. Comput. Aided Chem. Eng. 31, 1045–1049. https://doi.org/10.1016/B978-0-444-59506-5.50040-7.
Thakker, V., Bakshi, B.R., 2021. Toward sustainable circular economies: a computational framework for assessment and design. J. Clean. Prod. 295, 126353 https://doi.org/10.1016/j.jclepro.2021.126353.
Tian, Y., Pistikopoulos, E.N., 2019. Generalized modular representation framework for the synthesis of extractive separation systems. Comput. Aided Chem. Eng. 47, 475–480. https://doi.org/10.1016/B978-0-12-818597-1.50076-X.
Tiso, T., Winter, B., Wei, R., Hee, J., de Witt, J., Wierckx, N., Quicker, P., Bornscheuer, U. T., Bardow, A., Nogales, J., Blank, L.M., 2022. The metabolic potential of plastics as biotechnological carbon sources – review and targets for the future. Metab. Eng. 71, 77–98. https://doi.org/10.1016/J.YMBEN.2021.12.006.
Toledo, J.M., Aznar, M.P., Sancho, J.A., 2011. Catalytic air gasification of plastic waste (polypropylene) in a fluidized bed. Part II: effects of some operating variables on the quality of the raw gas produced using olivine as the in-bed material. Ind. Eng. Chem. Res. 50, 11815–11821. https://doi.org/10.1021/ie200145p.
Uemichi, Y., Nakamura, J., Itoh, T., Sugioka, M., Garforth, A.A., Dwyer, J., 1999. Conversion of polyethylene into gasoline-range fuels by two-stage catalytic degradation using silica-alumina and HZSM-5 zeolite. Ind. Eng. Chem. Res. 38, 385–390. https://doi.org/10.1021/ie980341+.
Valeche-Altinel, C., Wachholz, C., Engström, M., 2021. A low-carbon and circular industry for Europe. Think 2030 policy paper by. Ellen Macarthur Foundation and the Institute for European Environmental Policy. https://think2030.eu/a-low-carbon-and-circular-industry-for-europe/.
W3C OWL Working Group, 2012. OWL 2 Web Ontology Language Document Overview (Second Edition) [WWW Document]. OWL 2 Web Ontol. Lang. http://www.w3.org/TR/owl2-overview/ (accessed 4.30.21).
Wang, X., Song, C., 2020. Carbon capture from flue gas and the atmosphere: a perspective. Front. Energy Res. 8, 265. https://doi.org/10.3389/FENRG.2020.560849/BIBTEX.
Wernet, G., Bauer, C., Steubing, B., Reinhard, J., Moreno-Ruiz, E., Weidema, B., Zah, R., Wernet wernet, G., 2016. The ecoinvent database version 3 (part I): overview and

methodology. Int. J. Life Cycle Assess. 21, 1218–1230. https://doi.org/10.1007/s11367-016-1087-8.

Wilde, A.S., Wanielik, F., Rolinck, M., Mennenga, M., Abraham, T., Cerdas, F., Herrmann, C., 2022. Ontology-based approach to support life cycle engineering: development of a data and knowledge structure. Procedia CIRP 105, 398–403. https://doi.org/10.1016/J.PROCIR.2022.02.066.

Yang, X.S., Koziel, S., Leifsson, L., 2013. Computational optimization, modelling and simulation: recent trends and challenges. Procedia Comput. Sci. 18, 855–860. https://doi.org/10.1016/j.procs.2013.05.250.

Zhang, F., Zhao, Y., Wang, D., Yan, M., Zhang, J., Zhang, P., Ding, T., Chen, L., Chen, C., 2021. Current technologies for plastic waste treatment: a review. J. Clean. Prod. https://doi.org/10.1016/j.jclepro.2020.124523.

Zhou, L., Zhang, C., Karimi, I.A., Kraft, M., 2018. An ontology framework towards decentralized information management for eco-industrial parks. Comput. Chem. Eng. 118, 49–63. https://doi.org/10.1016/j.compchemeng.2018.07.010.