TECHNO-ECONOMIC AND LIFE CYCLE ASSESSMENT OF CHEMICAL RECYCLING AND UPCYCLING OF MIXED PLASTICS WASTE CONTAINING POLY-VINYL-CHLORIDE (PVC)

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Abstract

Developing technologies that completely remove chlorine from plastics waste can allow its chemical recycling and upcycling with catalytic methods. This study compares eight processes involving different dechlorination methods (absorption columns, adsorption in beds of zeolites, catalytic dechlorination, and dissolution in ionic liquids) and chemical conversion technologies (incineration, pyrolysis, hydrogenolysis) to upgrade mixed plastics waste to various products (e.g., electricity, fuels, virgin polymers, and lubricant oil). The analysis determines that the absorption of chlorine in columns with basic aqueous solutions is limited to plastics waste with PVC concentrations below 0.1%. Dissolution in ionic liquids is not cost-competitive. On the contrary, two-step processes with catalytic dechlorination followed by thermochemical catalytic depolymerization, either pyrolysis or hydrogenolysis, significantly improve process economics and emissions. The most economically viable alternative is hydrogenolysis for producing lubricants, while the technology with the lowest global warming potential is chemical recycling via catalytic pyrolysis.

KEYWORDS: Plastic recycling, upcycling, dechlorination, life cycle assessment, circular economy.

INTRODUCTION

Plastics waste has become a critical issue for the environment, with 400 million metric tons produced each year[1,2] and an expected increase to 1,200 million metric tons by 2050. This has led to a significant increase in plastics pollution,[3] harming marine life and affecting ecosystems.[4] Plastics waste poses other threats to the environment and human health, such as an increase in occupied land and microplastic generation. Currently 75% of global plastics waste is landfilled, 16% is incinerated and only 9% is recycled.[2] In the United States (US), landfilled plastics result in a loss of 3.4 EJ (approximately 3% of the total energy consumption in the US) and an economic loss opportunity of $7.2 billion.[5] These concerns and the export ban of plastics waste to China[6] have increased interest in recycling in Western countries.

Most plastics recycling is mechanical due to its low processing costs. While this technology produces low CO_2 emissions (~1 kg_{CO2} per kg of plastics waste recycled),[7] it cannot separate polymers with the same density and degrades them, limiting recyclability.[8,9] Chemical recycling has emerged to address these drawbacks.[8,10] Solvent-based recycling through the dissolution-precipitation method has shown promising economic and environmental results at the pilot plant scale.[11–14] However, it has not been industrially commercialized since the use of solvents, like toluene, restricts the commercialization in sectors such as food packaging,[15] and the low diffusivity of polymers limits scalability.[16] Only, the use of target solvents, like in glycolysis[14,17] or methanolysis[18] of PET, have shown promising economic results with an easy scale-up. Thermochemical technologies, like pyrolysis followed by cracking and polymerization,[19,20] or gasification followed by methanol-to-olefins and polymerization,[21] can produce virgin-quality polymers (recycling). Recycling competes with the generation of more valuable products, known as upcycling.[7,22] Techno-economic analyses (TEA) have been conducted on multiple high-temperature thermochemical upcycling (e.g., gasification to produce hydrogen[23] and methanol, hydrothermal liquefaction,[24,25] pyrolysis to produce a naphtha for producing lubricant oil[7] or aldehydes[26]) and mild-temperature thermo-catalytic technologies (e.g., catalytic pyrolysis, hydrocracking for fuels production,[27] and hydrogenolysis to produce lubricant oil,[28–30]). Among them, pyrolysis is the most profitable one.[19,24] Its advantage lies in the high yield of aromatics and olefins, achieved by selecting an adequate catalyst, temperature, and heat transfer method.[10] Similarly, hydrogenolysis can also yield a high olefin content at a higher cost, but with less energy use as it operates at lower temperatures.[24]

Despite multiple studies utilizing pure polymers in experiments and associated TEA and life cycle assessment (LCA) studies,[31] plastics waste is mixed in nature.[32] It consists of multiple polymers, including polyolefins (polypropylene (PP), low-density polyethylene (LDPE), and high-density polyethylene (HDPE), polyvinyl chloride (PVC), and polyethylene terephthalate (PET). Among them, LDPE and PET can be sorted with high recovery efficiencies through mechanical methods,[33] whereas the remaining mixture is unsuitable for catalytic processing due to poisoning of the depolymerization catalysts.[34] PVC degradation[35,36] during

depolymerization forms highly corrosive HCl or halogenated organic compounds, which degrade the quality of the naphtha products.[34] Advancing catalytic chemical recycling and upcycling technologies therefore requires efficient dechlorination methods.

Dechlorination has been implemented before depolymerization (two-step method), during depolymerization (co-pyrolysis), and after depolymerization.[37] [32]Absorption of HCl from depolymerized gas products with a neutralizing agent, such as lime or a NaOH solution, has been a common practice.[34] Removing chlorine from liquid depolymerization products (e.g., naphtha) can be achieved using several adsorbents, such as calcium hydroxides,[38] carbonates,[39] red mud,[40] iron oxide,[41,42] and zeolites.[43]

Adsorbents can also be employed in depolymerization reactors. Zeolites, metal oxides (MgO and Al_2O_3[37,44]), silica-alumina and fluid catalytic cracking (FCC)[45,46] catalysts can reduce chlorine content from 55,000 ppm to 4,400 ppm. These values are still higher than EPA's (Environmental Protection Agency) for petroleum products (1000 ppm),[47,48] some oils (~40 ppm for lubricants), and other products: a maximum of 500 ppm for waste oil,[49] 100 ppm for naphtha,[50] or 1 ppm for ethanol-based fuels.[51] To meet chlorine concentration standards, two-step processes have been proposed:[34,52,53] preprocessing (a dechlorination step) at around 300 ºC, followed by depolymerization.[39] This two-step method is more effective in reducing chlorine than a single step catalytic pyrolysis process, but it entirely removes chlorine from the feed, only resulting in organo-chlorinated compounds.[39,53] This two-stage process has recently been intensified by pressurizing the dechlorination reactor with hydrogen. The dechlorination of PVC with hydrogen and MgO as an adsorbent achieved complete chlorine removal from plastics waste, converting PVC into PE and $MgCl_2$.[54] The chlorine-free plastics mixture can then be depolymerized catalytically to value-added products. Novel processes utilizing selective solvents have also recently been explored. Ionic liquids (ILs) combined with chloromethanes can depolymerize mixed plastics waste containing PVC into a fuel-range mixture of paraffins at low temperatures (25 ºC – 100 ºC).[55] The chlorine is selectively transformed into gaseous HCl, which is removed by neutralization with NaOH.[56] Despite no utilities being required, significant costs are incurred due to the use of solvents. In this regard, TEA studies can help compare multiple processes.

This work conducts TEA and LCA to compare process alternatives for managing mixed plastics waste to different products such as fuels, lubricant oil, and polyolefins. Furthermore, the work also evaluates the role of PVC concentration on the feasible operating ranges of each technology. The process description, models, and TEA and LCA assumptions are provided in Section 2. Section 3 presents the results, and Section 4 concludes this study.

METHODOLOGY

OVERVIEW OF PROCESS ALTERNATIVES

The processes studied are summarized in Figure 1 with the main assumptions presented in the following subsections. All of them are designed to treat 35 kt/y of plastic waste, the largest pyrolysis plant built in Europe nowadays.[10] More details about the role of plant size are given in Hernández et al.[24] Process models have been developed in Aspen Plus® v12.1 employing PolyNRTL as a thermodynamic package.[20] The Pyomo package within Python has also been used to create custom models for the reactive absorption tower employed in dechlorination, as the technology is unavailable in Aspen Plus. After the process simulation, heat integration was performed using the pinch method. The aim of the study is to systematically compare the role of PVC content on the recycling and depolymerization of mixed plastics waste, while maintaining operating conditions constant. Following this approach, all the cases except those processes employing pyrolysis are evaluated using a PP-PVC mixture. This mixture is the only one assessed across all technologies, with PVC contents varied between 0 %wt. and 20%wt. within each study. Processes 3, 4, and 5, which employ pyrolysis, are modeled with the composition reported by Miskolczi et al. (0% - 3% wt. of PVC, 47% - 50% HDPE, 40% PP, 10% PS)[57] since PP-PVC mixtures with different PVC content are not available in literature. Using this composition still enables comparison of PVC effects under a consistent pyrolysis configuration. More details of process models and assumptions are available in the Supplementary Information (SI).

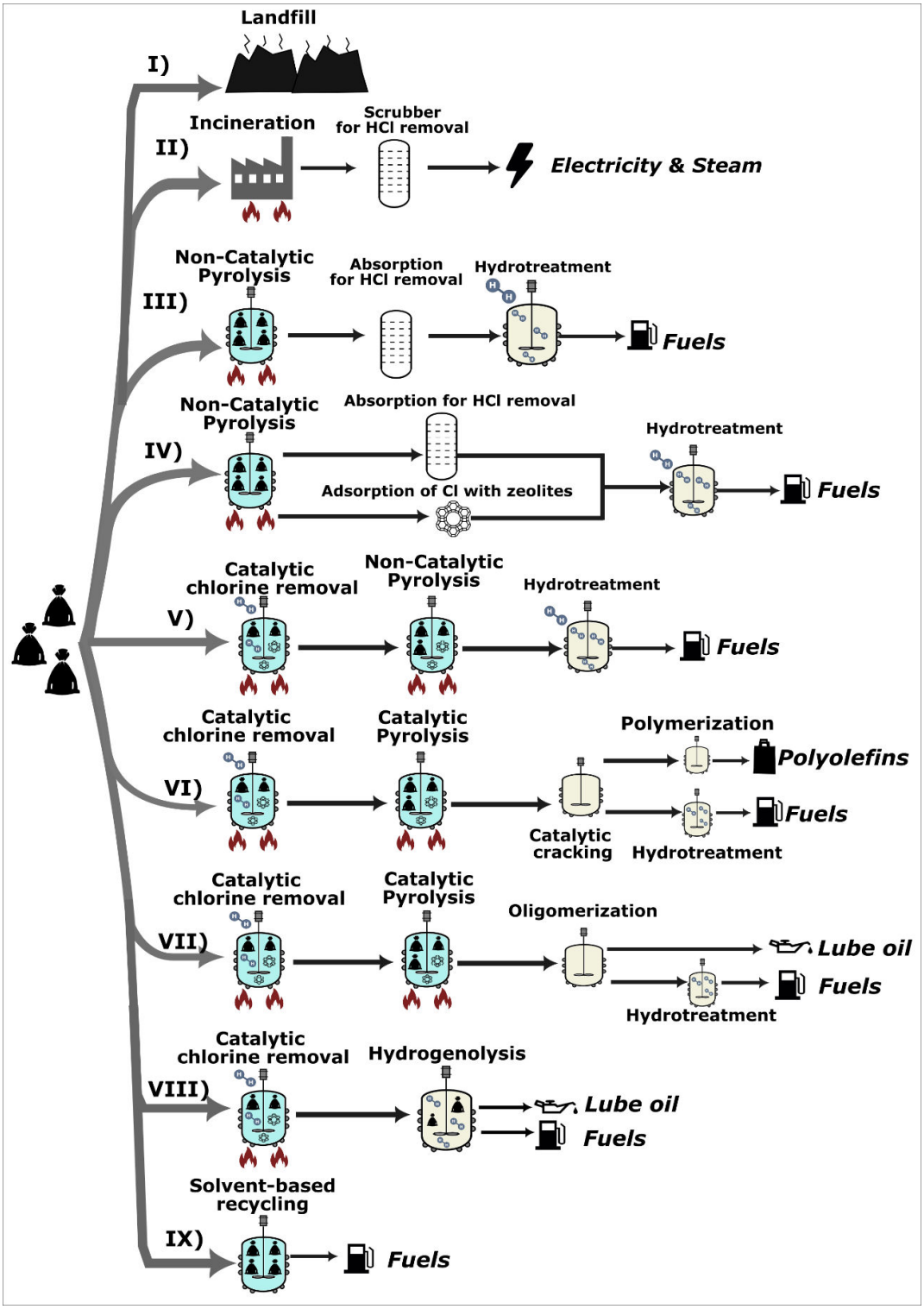

Figure 1. Summary of plastics waste management technologies considered and their processing steps.

I) Landfill

As the most common end-of-life scenario of plastics waste, landfill was included here as a benchmark. The cost of landfill is taken as the average cost of landfilling municipal solid waste in the US, $53/ton.[58] The environmental impacts of landfill are taken from the ecoinvent database for the operation of unsanitary landfills treating plastics waste mixture.

II) Incineration

Incineration is the second most popular method for managing plastics waste according to OECD.[2] The process designed is similar to the one described in previous work.[59] Plastics waste is burnt in a combustion chamber, generating hot gases that evaporate water in a boiler. The water is in a Rankine power cycle with three turbines at high, middle, and low pressure. The flue gases follow the gas cleaning steps outlined in the Waste Incineration Reference Document of the European Commission.[60] They are first sent to a dust bag filter to remove the particles and then treated in a scrubber with a solution of NaOH in water to remove HCl. This incineration system has been studied under two configurations. The first configuration solely produces power, while the second one produces both power and steam at high, middle, and low pressures.

III) Non-catalytic pyrolysis with HCl removal via absorption for naphtha production for fuels

The first thermochemical process involves non-catalytic pyrolysis, followed by chlorine removal through absorption. The pyrolysis unit operates at 530 ºC in nitrogen atmosphere at 1.5 bar with yields as reported in Miskolczi et al.[57] Since HCl is released, the unit is made of stainless steel SAE-304. A mixture with 3% of PVC is selected as a base case. Sensitivity analyses for other PVC concentrations are based on data reported and extrapolations (see SI).

The product from the pyrolysis reactor is cooled and sent to a flash drum, which divides the streams into liquid and gas phases. The gas stream contains most of the HCl from pyrolysis, which is removed in an absorption column with a sodium hydroxide solution. The distribution of components, including HCl, varies with temperature in the flash separator. Elevated flash temperatures release more HCl into the gas phase, removing more chlorine by absorption but also losing more hydrocarbon products. To evaluate this trade-off, a sensitivity analysis was conducted, varying the flash separator temperature from 25 ºC to 90 ºC (not exceeding 100 ºC, to retain water in liquid form). The absorption column is modeled using custom equations coded in Python and interfaced with Aspen Plus ®, see more details in the SI. The outlet stream is sent to a debutanizer, obtaining two fractions: a gas fraction that can be sold as liquefied petroleum gas (LPG), and a liquid fraction that is blended with the naphtha fraction recovered at the bottom of the previous flash drum. This dilutes the traces of chlorine in the naphtha stream coming from the flash.

The naphtha, mainly composed of paraffins, is sent to a hydrotreatment reactor operating at high hydrogen pressures, ranging from 30 to 70 bar (70 bar requires a higher cost), and temperature of 200 ºC.[61–65] In this reactor, olefins are converted into paraffins, and aromatics are converted into cycloalkanes. This saturated

naphtha is finally separated into gasoline, diesel, and heavy fuel oil fractions based on their boiling points. Blending stages for tuning the octane rating are not considered.

IV) Non-catalytic pyrolysis with chlorine removal via gas-phase absorption and liquid-phase zeolite adsorption for naphtha production for fuels

This process evaluates the same non-catalytic pyrolysis reactor, but the removal of chlorine is enhanced by passing the liquid naphtha through a bed filled with zeolites. Two adsorption beds are considered in parallel: one in operation and another in regeneration by oxidation. Adsorption with 13X zeolite has been demonstrated to remove up to 90% of the chlorine present in the naphtha when the bed operates at 150 ºC.[42] The LPG fraction is recovered by a debutanizer. The liquid fraction is then sent to a hydrotreating unit, where it is separated into gasoline, diesel, and fuel oil fractions, as described above.

V) Catalytic pyrolysis following catalytic chlorine removal to produce naphtha for fuels

The third dechlorination alternative uses a two-stage system consisting of a catalytic dechlorination unit followed by non-catalytic pyrolysis for depolymerization. The dechlorination process hydrogenates PVC in the mixed plastics waste to PE in the presence of MgO at 30 bar and 250 ºC.[54] The process is carried out in batch mode with two units working in parallel to ensure continuous operation. Apart from the raw materials and heat consumption, the reactor also employs power for agitation. The energy consumption is determined from the power number of agitation, which is a function of the Reynolds number.[66] In scale up from laboratory to industrial scale, the same Reynolds number of agitation is maintained. More details are given in the SI. The reactions are summarized in Eqs. (1) and (2), where chlorine is absorbed by MgO.

$$\frac{1}{n}-(C_2H_3Cl)-_n + \frac{1}{2}H_2 \rightarrow (C_2H_4)_n + HCl \quad (1)$$

$$HCl + \frac{1}{2}MgO \rightarrow \frac{1}{2}MgCl_2 + \frac{1}{2}H_2O \quad (2)$$

The chlorine sorption agent, MgO, is transformed into $MgCl_2$, which is later generated by oxidizing it with steam at 550 ºC, via the following reaction:

$$MgCl_2 + H_2O \rightarrow MgO + 2\,HCl \quad (3)$$

The HCl gas from the regeneration reactor is sent to an absorption column for neutralization. As a result of this pretreatment, a mixture of plastics wastes without chlorine is sent to the pyrolysis reactor. In this case, the yield of the non-catalytic pyrolysis reactor also follows the 0% PVC results of Miskolczi et al.[57] The pyrolysis products are then separated and hydrotreated to obtain LPG, gasoline, diesel, and fuel oil fractions as reported in Process III.

VI) Catalytic pyrolysis following catalytic chlorine removal to produce naphtha for polyolefins

The complete removal of chlorine by pretreatment enables chemical conversion of plastics waste with catalytic methods. One option is to perform a two-step catalytic thermochemical depolymerization by catalytic pyrolysis with HZSM-5, achieving the yields reported by Lin and Ye.[67] The fluidized bed reactor

operates at 360 ºC with nitrogen as fluidization gas. In the pyrolysis reactor, the conversion of PE (generated from the PVC dechlorination reactor) is assumed to be the same as that of PP. The reactor shows a high yield to light olefins (C2 to C4) and a significant fraction of liquid naphtha. To enhance the overall yield of light olefins, the naphtha is converted to light olefins using catalytic cracking with $CaO\text{-}Al_2O_3$ with conversion and selectivity based on the work of Pant and Kunzru.[68] The light fractions of this catalytic cracking and the catalytic pyrolysis are mixed and recovered individually through a sequence of debutanizer, depropanizer, dethanizer, and demethanizer columns. All the olefin components are then used to produce polyethylene, polypropylene, and polybutylene as in our previous work.[7] The remaining naphtha is sent to a hydrotreatment unit and a distillation column to recover gasoline and diesel.

VII) Catalytic pyrolysis following catalytic chlorine removal to produce naphtha for lubricant oil

This process employs the same catalytic method as processes V) and VI) for removing the chlorine and the same catalytic pyrolysis unit for thermochemical depolymerization. However, the naphtha product, with a significant concentration of light olefins, is used to produce lubricant. This requires separating the light olefins from the liquid stream and sending them to an oligomerization reactor. The fixed-bed oligomerization reactor operates at 70 bar and 200 ºC, over HZSM-5 zeolite catalyst, with a conversion to alpha-olefins of 90%.[69] The paraffins and unreacted olefins are separated from the alpha-olefins by distillation and sold as LPG. The alpha-olefins are mixed with the liquid stream from the pyrolysis reactor and are introduced into a second oligomerization reactor operating at 40 bar and 220 ºC with HZSM-5 zeolite.[70] This second oligomerization in liquid form grows the molecular chain to a carbon number above 20 in batch units. The main product, the lubricant, is separated at the bottom of a distillation column. The naphtha recovered at the top is sent to a hydrotreatment reactor to increase the concentration of paraffins. Finally, this saturated naphtha is sent to a fractionation column to recover gasoline, diesel, and fuel oil.

VIII) Hydrogenolysis with catalytic chlorine removal to produce naphtha for lubricant oil

The catalytic dechlorination technology presented in the previous processes is combined with a hydrogenolysis reactor reported by Kots et al.[54] The dechlorination reactor converts PVC in a mixture with PP into PE as in Eqs (1) and (2). Next, the resulting mixture of PE and PP is introduced into a hydrogenolysis reactor that operates at 30 bar and 250 ºC with Ru/TiO_2 as a catalyst. In this reactor, the polymers are converted into olefins and paraffins; see SI. It was observed that a higher concentration of PVC in the original mixed plastics waste reduces the yield of lubricant oil in this second step. The yield to each fraction has been implemented in Aspen Plus® with a stoichiometric reactor. The power due to agitation and the design of two batch reactors in parallel are estimated offline, as described in the SI. Next, the reactor effluent is sent to a flash drum for separation. The gas fraction is primarily composed of hydrogen gas, which is separated from hydrocarbons with a molecular weight below C_3 using a pressure swing adsorption system. Given that the liquid fraction is highly viscous and contains traces of polymers, hexane is used for extracting the lubricants.[30] The mixture of lubricant, hexane and catalyst pellets are then separated into two steps.

First, a filter is placed to remove the catalyst, which also contains part of hexane and lubricants (5% is assumed). Second, a flash drum separates hexane, which is recycled back to the extraction. The catalyst pellets still contain unreacted solid PP, absorbed hexane and lubes, requiring regeneration with hydrogen. Methane is a byproduct of this catalyst regeneration and can be sold as fuel, similar to natural gas.

IX) Dissolution-based depolymerization for fuel production

This process depolymerizes the mixed plastics waste with dichloromethane (DCM) and ILs.[55,56] Upon agitation at atmospheric conditions (25 ºC and 1 bar), the polymers (PP and PVC) dissolve into the dichloromethane mixture and release HCl gas. HCl is diluted with argon and removed from the reactor overhead with a fan. This gas stream is sent to an absorption column using a caustic soda solution, converting HCl into NaCl.[56] The extraction system and reactor are made of stainless steel 316 to prevent corrosion. Two batch reactors are considered to ensure continuous operation of the plant.

The liquid fraction of the depolymerization reactor effluent is first sent to a filter to remove the traces of undissolved polymer. Then, it is sent to an extraction system where chloroform (TCM) and water are added to separate the stream into aqueous and organic phases. The aqueous fraction recovers the ILs after distillation and the organic fraction contains the mixture of dissolved hydrocarbons in DCM and TCM.[56] The organic phase is sent to a set of distillation columns to recover the solvents and the liquid mixture of hydrocarbons that could be split into gasoline and diesel.

TECHNO-ECONOMIC AND LIFE CYCLE ASSESSMENT

Techno-Economic Analysis (TEA)

TEA is carried out following the discounted cash flow method with an amortization period of 20 years. A plant capacity of 35 kt/y is taken to compare with the largest plastic pyrolysis plant in Europe nowadays.[10] TEA employs 2024 as cost year with the Capital Expenses (CAPEX) updated with the Chemical Engineering Plant Cost Index of the Chemical Engineering magazine.[71] In the calculation of the CAPEX, Aspen Economic Analyzer is employed to determine the costs of the conventional units (e.g. distillation columns, flash drums, heat exchangers). Specific units like the PSA beds and the reactors employ custom models for their design, with the costs determined by the Catcost tool of the National Renewable Energy Laboratory (NREL)[72] and Matches[73] cost estimator. The CAPEX and the operating expenses (OPEX) are employed to determine the minimum selling price (MSP) of the main product obtained in each process, the return on investment (ROI), the internal rate of return (IRR) in case a process is profitable, and the value generated per kilogram of plastics waste as economic indicators for each technology. A more detailed description of the assumptions, the costs, and the prices is given in the SI.

Sensitivity analyses have been carried out for i) the price of mixed plastics waste, which corresponds to plastics waste collection costs (between \$0.15/kg and \$0.3/kg[74]), and ii) the concentration of PVC in the mixed plastics waste, as summarized in Table 1. Sensitivity analyses have also been conducted to

understand the impacts of flash drum temperatures before the absorber on chlorine removal and hydrotreatment pressure (between 40 bar and 70 bar) in the fuel production cases. These cases producing fuels are selected to evaluate the pressure in hydrotreatment, since these are the ones mostly affected by hydrotreatment costs.

Table 1. Summary of sensitivity analyses carried out in the process.

Process	PVC content evaluated (% wt.)*	Other sensitivity analyses
I) Landfill	-	-
II) Incineration	0 - 20	Power VS Steam and Power production
III) Non-catalytic Pyrolysis – Absorption. Fuels production.	0 - 6	Temperature in flash before the absorber (30 ºC to 90 ºC). Hydrotreatment pressure (40 bar to 70 bar).
IV) Non-catalytic Pyrolysis – Adsorption- Fuels production.	0 - 6	Temperature in flash before the absorber (30 ºC to 90 ºC). Hydrotreatment pressure (40 bar to 70 bar).
V) Catalytic chlorine removal – Non-Catalytic Pyrolysis – Fuels production.	0 - 10	Hydrotreatment pressure (40 bar to 70 bar)
VI) Catalytic chlorine removal - Catalytic Pyrolysis – Chemical Recycling	0-20	-
VII) Catalytic chlorine removal - Catalytic Pyrolysis – Lubricant oil production	0 - 20	-
VIII) Catalytic chlorine removal – Hydrogenolysis to lubricant oil	0 - 20	-
IX) Dissolution-based depolymerization for fuel production	20	-

*Non-catalytic pyrolysis explores a range of PVC content up to 6% based on literature data. Catalytic dechlorination and dissolution-based depolymerization cover a range of up to 20% following the experimental reports in literature. Only when catalytic dechlorination is followed by non-catalytic pyrolysis, the range is reduced to 10% since with the other technologies, there is no data available with PVC content above 6%.

Life Cycle Assessment

LCA is performed to determine the main contributors to the environmental impacts of the systems listed in Figure 2. In evaluating the environmental impacts, only materials in continuous operation of the processes are considered. The impacts related to the construction of the plant are not included. The impact factors have been determined following the Tool for the Reduction and Assessment of Chemical and Other Environmental Impacts (Traci) v2.1 method,[75] from ecoinvent v.3.8 database. The analysis is based on a bin-to-gate boundary without recycling outlet streams. A system expansion, substituting all products in each of the processes, is followed. This allows allocating the emissions per kg of plastics waste to be treated, facilitating the comparison between the different waste management methods.[20,24] More details for the system boundaries, the emission factors, and the background processes employed for substitution in each case study are given in the SI.

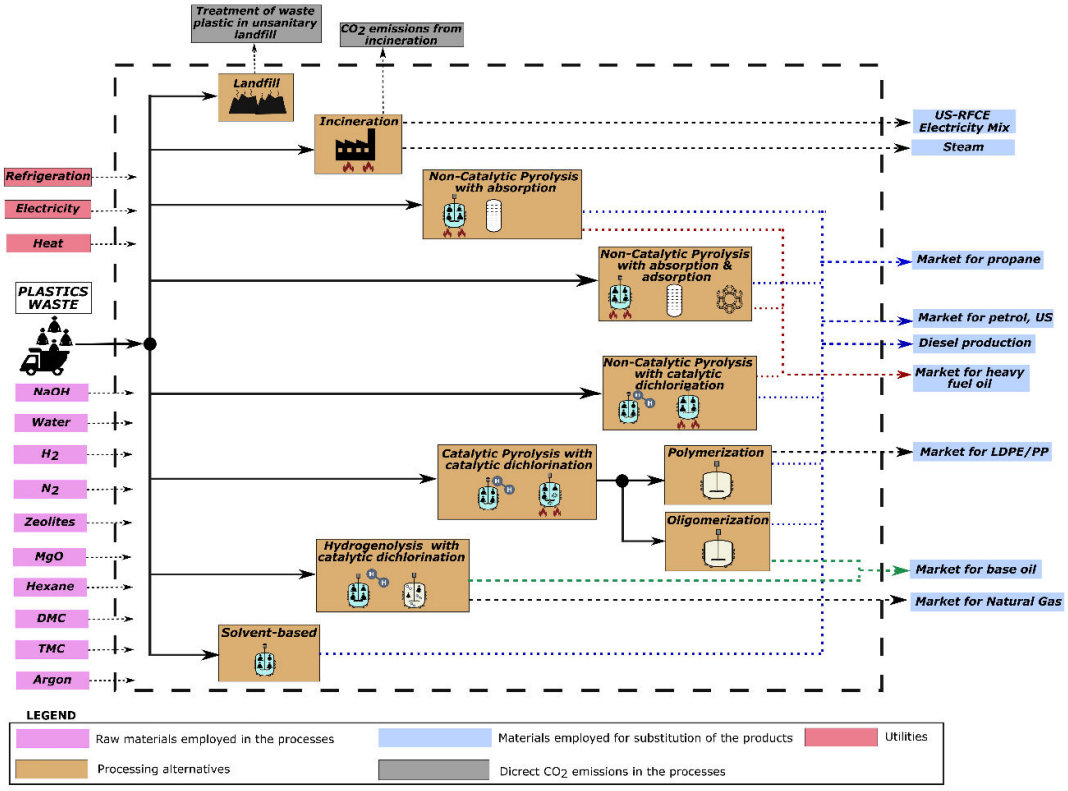

Figure 2. Boundaries of the systems evaluated in LCA. In the Figure, US-RFCE refers to the electricity mix in the "Region of the Five-State-Area).

RESULTS

TEA RESULTS

The resulting economic indicators for recycling mixed plastics waste with 3% wt. PVC are summarized in Table 2. The profit generated per kg of plastics waste is employed for comparing different technologies. The technologies with the highest profitability are those producing lubricant oil. As demonstrated in other

works[7,19] and shown in Figure 3A, a highly profitable product governs the process economics. Among the two alternatives, hydrogenolysis stands out as the most profitable with higher returns (ROI and IRR) than pyrolysis. Its IRR, greater than 20%,[76] suggests that this process holds significant potential for treating mixed plastics waste. The high profitability of hydrogenolysis is due to the highest yield of lubricant oil (see Table 3), resulting in the highest income among processes (see Figure 3A). On the other hand, the operating costs of most processes are not that high, with the main contributors associated with collecting plastics waste and amortization of the CAPEX. The importance of these two factors justifies why the facility location is an important topic.[74,77] Hydrogenolysis has a lower amortization cost, as it invokes fewer distillation sequences and only a single reactor. However, it consumes raw materials like hexane and, H_2; and the market for lubricant oils is around 10 times smaller than the plastic waste generated.[78,79] The next low-cost option with similar a market size is the production of polyolefins. Polyolefins are produced through a two-step process that involves catalytic dechlorination and catalytic pyrolysis, followed by catalytic cracking and polymerization. Despite the large number of processing steps involved, the CAPEX is less than fuel production. Figure 3B shows that most of the CAPEX stems from the separation and hydrotreatment of large chains for fuel production as a co-product. Separation of products and enhancing the yield to light olefins by cracking requires more energy than in other processes (e.g., fuel production), which results in a higher energy consumption.

The production of low-value products, like electricity or fuels, is the worst economic alternative. Incineration plants producing only electricity are less profitable than landfilling plastics waste. These higher costs rationalize why incineration systems have not been widely deployed worldwide. In Europe, incineration has a share of 23% in plastics waste management, primarily due to the emphasis on reducing uncontrolled degradation to microplastics. In contrast, in the United States, incineration of plastics waste is less common due to the associated costs.[2] TEA shows that incineration is better if a co-generation unit produces steam at high, medium, and low pressures, but this requires a plant within industrial complexes for easy transportation through pipelines. The cost breakdown further reveals that, as in other processes, the main cost drivers are the amortization of the CAPEX and the plastics waste collection, followed by the raw materials, mostly for cleaning the gases. Cleaning gases entails a higher cost than in other processes (pyrolysis for the production of fuels with absorption) since almost all HCl is gas at high temperature which is more diluted in air employed for combustion.

The production of fuels via thermochemical methods (pyrolysis) also shows low profitability due to the high OPEX and CAPEX, and low revenue from selling the products. H_2, which is primarily used in hydrotreatment for producing fuels, contributes significantly. The CAPEX is high since the unit operates at high pressures, 70 bar; see Figure 3B. Among the three dechlorination alternatives, absorption has the lowest costs but also has the lowest chlorine removal efficiency (see Table 3), which limits its implementation as presented in the next sub-section. In addition to thermochemical routes, dissolution has also been evaluated to produce fuels

from PVC-containing plastics waste. This process is highly expensive due to the use of chloromethanes. Even though chloromethanes could be theoretically recovered by distillation, separating them from C5's and C6's fractions without significant loss is challenging. The high cost of chloromethanes and low revenue from fuels render the process the least competitive among the options considered.

Table 2. Summary of economic indicators for the plastics waste management alternatives studied with 3% wt. of PVC content in the mixed plastics waste. All case studies are for a plant treating 35 kt/y. The ROI, IRR and profit generated per kg of plastic waste are computed considering the MSP of the target product in the market.

Process	CAPEX (MM$)	MSP main product	MSP of product in the market	ROI (%)	IRR (%)	Profit per kg of plastics waste ($/kg$_{plastics\ waste}$)
I) Landfill	-	-	-	-	-	-0.053
II) Incineration-Elect	26.5	$0.220/kWh	$0.07/kWh	-43%	-	-0.354
II) Incineration-Steam	55.3	$0.015/kWh	$0.07/kWh	34%	0.8%	0.141
III) Non-catalytic Pyrolysis – Absorption - Fuels	63.2	$2.20/kg	$0.56/kg	-35%	-	-0.513
IV) Non-catalytic Pyrolysis – Absorption and Adsorption-Fuels	65.4	$2.24/kg	$0.56/kg	-35%	-	-0.525
V) Catalytic chlorine removal – Non-Catalytic Pyrolysis – Fuels	78.2	$2.41/kg	$0.56/kg	-32%	-	-0.585
VI) Pretreatment for chlorine removal - Catalytic Pyrolysis – Chemical Recycling	66.4	$1.28/kg	$1.1/kg - $1.3/kg	0.6%	0.4%	0.128
VII) Pretreatment for chlorine removal - Catalytic Pyrolysis – Upcycling to lubricant oil	59.6	$0.92/kg	$1.5/kg - $1.8/kg	31.6%	20.1%	0.563

VIII) Pretreatment for chlorine removal – Hydrogenolysis to lubricant oil	39.5	$0.90/kg	$1.5/kg - $1.8/kg	63.6%	34.7%	0.671
IX) Dissolution-based depolymerization for fuel production	48.0	$3.60/kg	$0.56/kg	-124%	-	-1.65

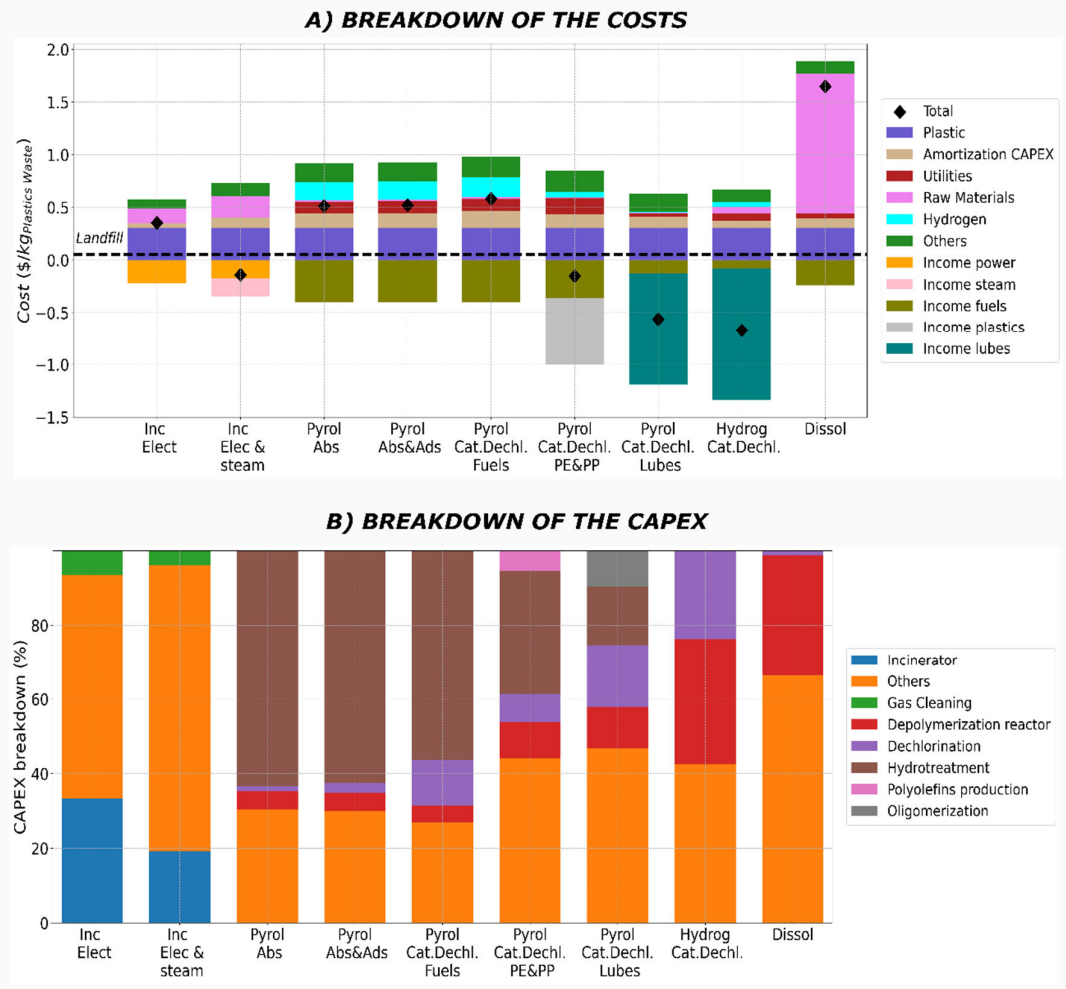

Figure 3. Breakdown of the A) costs and B) CAPEX for each process with a PVC content of 3% wt. In the horizontal axis: Inc Elect. refers to process II when electricity is only produced. Inc Elec & steam refers to process II when electricity and steam are produced. Pyrol Abs refers to Process III, Pyrol Abs & Ads is for process IV, Pyrol Cat. Dechl. Fuels is for process V, Pyrol Cat. Dechl. PE & PP refers to process VI, Pyrol Cat. Dechlor. Lubes is for process VII, Hydrog. Cat. Dechl. refers to process VIII, and Dissol. refers to process IX.

Table 3. Summary of chlorine removal efficiency and yields to each product for each of the processes.

Process	Chlorine removal efficiency from product	Yield to each product	
		Product	Yield to product
I) Landfill	-	-	-
II) Incineration-Elect	-	Electricity (kWh/kg $_{\text{plastics waste}}$)	2.60
II) Incineration-Steam	-	Electricity (kWh/kg $_{\text{plastics waste}}$)	2.02
		HP Steam (kg/kg $_{\text{plastics waste}}$)	16.7
		MP Steam (kg/kg $_{\text{plastics waste}}$)	11.5
		LP Steam (kg/kg $_{\text{plastics waste}}$)	3.53
III) Non-catalytic Pyrolysis – Absorption – Fuels*	98.27 %	Gasoline (kg/kg $_{\text{plastics waste}}$)	0.08
		Diesel (kg/kg $_{\text{plastics waste}}$)	0.34
		Heavy fuel-oil (kg/kg $_{\text{plastics waste}}$)	0.07
IV) Non-catalytic Pyrolysis – Absorption and Adsorption-Fuels*	99.79%	Gasoline (kg/kg $_{\text{plastics waste}}$)	0.08
		Diesel (kg/kg $_{\text{plastics waste}}$)	0.34
		Heavy fuel-oil (kg/kg $_{\text{plastics waste}}$)	0.07
V) Catalytic chlorine removal – Non-Catalytic Pyrolysis – Fuels	100%	Gasoline (kg/kg $_{\text{plastics waste}}$)	0.08
		Diesel (kg/kg $_{\text{plastics waste}}$)	0.34
		Heavy fuel-oil (kg/kg $_{\text{plastics waste}}$)	0.07
VI) Pretreatment for chlorine removal - Catalytic Pyrolysis – Chemical Recycling	100%	LDPE (kg/kg $_{\text{plastics waste}}$)	0.10
		PP (kg/kg $_{\text{plastics waste}}$)	0.29
		Poly-Butylene (kg/kg $_{\text{plastics waste}}$)	0.18
		Gasoline (kg/kg $_{\text{plastics waste}}$)	0.06
		Diesel (kg/kg $_{\text{plastics waste}}$)	0.08
		LPG (kg/kg $_{\text{plastics waste}}$)	0.19
VII) Pretreatment for chlorine removal - Catalytic Pyrolysis – Upcycling to lubricant oil	100%	Lubricants (kg/kg $_{\text{plastics waste}}$)	0.56
		Gasoline (kg/kg $_{\text{plastics waste}}$)	0.13
		Diesel (kg/kg $_{\text{plastics waste}}$)	0.04
		Heavy fuel-oil (kg/kg $_{\text{plastics waste}}$)	$4.4 \cdot 10^{-4}$
VIII) Pretreatment for chlorine removal – Hydrogenolysis to lubricant oil	100%	Lubricants (kg/kg $_{\text{plastics waste}}$)	0.66
		Natural gas (kg/kg $_{\text{plastics waste}}$)	0.15
IX) Dissolution-based depolymerization for fuel production	100%	Natural gas (kg/kg $_{\text{plastics waste}}$)	$2.6 \cdot 10^{-3}$
		Gasoline (kg/kg $_{\text{plastics waste}}$)	0.71
		Diesel (kg/kg $_{\text{plastics waste}}$)	0.30

*Note that only thermodynamic equilibrium is considered for the distribution of HCl between gas and liquid phases. The presence of metal oxides in the liquid phase or the formation of organochlorides that increase chlorine in liquid phase are not considered.

Sensitivity analyses on TEA results

Sensitivity analyses were performed on the price of plastics waste, the PVC content, and the hydrotreatment operating conditions, as summarized in Table 4. The cost of collecting plastics waste, the main driver identified in previous works, has more influence than PVC when the PVC content is below 10 % wt. When the PVC content is up to 20% wt., its impact is more than the plastics waste price; see processes VI to VIII in Table 4. The pressure in hydrotreater shows the lowest variability; see the production of fuels (processes III to V). To better understand the effect of PVC, a more detailed analysis is presented in the next sub-section.

Table 4. Results from several sensitivity analyses carried out in the economics of the process.

	Profit per kg of plastics waste (lowest and highest value evaluated in each case) ($/kg $_{\text{plastics waste}}$)		
Process	**Effect of plastics waste price***	**Effect of PVC content****	**Effect of hydrotreatment pressure*****
I) Landfill		-	-
II) Incineration-Elect	-0.43 ~ -0.24	-1.10 ~ -0.22	-
II) Incineration-Steam	0.07 ~ 0.25	-	-
III) Non-catalytic Pyrolysis – Absorption - Fuels	-0.59 ~ -0.40	-0.527 ~ -0.498	-0.51 ~ -0.47
IV) Non-catalytic Pyrolysis – Absorption and Adsorption- Fuels	-0.60 ~ -0.41	-0.545 ~ -0.504	-0.52 ~ -0.48
V) Catalytic chlorine removal – Non-Catalytic Pyrolysis – Fuels	-0.66 ~ -0.47	-0.64 ~ -0.52	-0.58 ~ -0.54
VI) Pretreatment for chlorine removal - Catalytic Pyrolysis – Chemical Recycling	0.06 ~ 0.26	-0.13 ~ 0.18	-
VII) Pretreatment for chlorine removal - Catalytic Pyrolysis – Upcycling to lubricant oil	0.69 ~ 0.88	0.41 ~ 0.62	-
VIII) Pretreatment for chlorine removal – Hydrogenolysis to lubricant oil	0.84 ~ 1.03	-0.22 ~ 0.90	-
IX) Dissolution-based depolymerization for fuel production	-1.73 ~ -1.53	-	-

* Plastics waste price is evaluated between 0.15 and 0.3 $/kg$_{\text{plastics waste}}$. The lowest profit corresponds to the highest plastics waste price.

**PVC content is evaluated between 0 and 20 %wt. for processes II, VI, VII and VIII, between 0 and 6% for processes III and IV, and between 0 and 10% for process V. The lowest profit corresponds to the highest PVC content.

*** Pressure in the hydrotreatment is varied between 40 bar and 70 bar. The lowest profit corresponds to the highest pressure.

Effect of PVC content on economics

Further sensitivity analysis on the PVC concentration is summarized in Figure 4. Lubricant oil production consistently remains the most economically attractive option across the entire range of PVC concentrations studied. However, the leading depolymerization technology to produce it changes as the PVC content in the feed increases. At concentrations below 12% wt. (below the average PVC content in plastic waste, ~8%wt.), hydrogenolysis is the preferred technology, and at higher concentrations, pyrolysis is better. The preferred technology can also be affected by the assumptions considered in the modeling of the process. During catalytic dechlorination, PVC is converted into PE, altering the composition of the plastics mixture. In hydrogenolysis[52], the effect of modifying this mixture has been studied experimentally,[51] which provides a quantitative understanding of the yield reduction of lubricants when PE is increased and its subsequent impact on profit reduction. However, for pyrolysis, the modification of the mixture has been assumed to retain the yields reported by Lin and Yen.[67] For more accurate conclusions, more catalytic pyrolysis experiments are needed. Apart from this difference between the two processes, it is also important to highlight the "S" shape obtained for hydrogenolysis in Figure 4. This shape emerges because the yields at 3% have been obtained by interpolation between 0 and 10%. As a result, the cost increases at low PVC concentrations due to the CAPEX of new units introduced for dechlorination, then they have a slight reduction, and after 10% the reduction is more significant due to the drop in the yield to lubricant oil. This analysis suggests that, despite the use of plastics waste mixtures in generating value-added products, identifying the right catalyst or process for the entire system is not straightforward. Compositional changes introduced by pretreatment can negatively impact the catalyst yields. Therefore, identifying a robust catalyst capable of maintaining high performance across feedstock compositions remains a key challenge for future research.

PVC content was also evaluated in incineration and the production of polyolefins and fuels by pyrolysis. Polyolefins production has the best economic performance of this set of technologies. However, it is not profitable when the PVC content exceeds 10% wt. These results illustrate the challenges of polyolefin's chemical recycling and rationalize some of the risks associated with industrial implementation, despite some works estimating profitability.[20,24] Incineration is more sensitive to PVC content than pyrolysis for fuel production, with better economic performance at concentrations below 10% wt. of PVC. This high sensitivity of incineration is due to the lower OPEX and CAPEX per revenue generated, as well as the higher share of cleaning. In the production of fuels by pyrolysis, other costs like the H_2 employed in hydrotreating and the amortization of the CAPEX contribute more. As a result, the change in cost with increasing PVC content is relatively small, below $\$0.2/kg_{plastics\ waste}$. Furthermore, the presence of additives (e.g., plasticizers, chalk, and cement powder attached to PVC from the demolition of buildings) further limits the application of this technology as the content of chlorine in the liquid phase increases due to the formation of organo-chlorides and char.

PVC content in pyrolysis to produce fuels is only studied until 6% wt. since at higher concentrations, absorption and adsorption systems are unable to produce naphtha with chlorine below 50 ppm; see Figure 5. This threshold of 50 ppm is reported for products like lubricants, with a stricter limit of 1 ppm suggested for commercial fuels.[51] Achieving 1 ppm is only possible when both absorption and adsorption are implemented for treating mixed plastics waste with PVC content below 1% wt. When using only an absorption column, the chlorine concentration in the naphtha is reduced to 8 ppm, even when the mixed plastics waste feedstock contains 0.1% wt. PVC. This suggests that the use of absorption alone is insufficient to achieve the chlorine purity required for producing commercial fuels.

To further enhance this chlorine removal in the absorption column, a sensitivity analysis has been performed in the flash separator after pyrolysis; see Figure 5A. Higher temperatures in the flash (below 100 ºC at atmospheric pressure) result in higher chlorine in the gas phase, improving subsequent removal. By increasing the temperature from 30 ºC to 90 ºC, the concentration of chlorine in the naphtha is reduced by nearly one-half; see "Naptha" line in Figures 5C and 5D. Most of the chlorine is removed by absorption and a small part by adsorption, necessary for achieving the purity. For PVC concentrations above 6% wt, the removal is insufficient. This underscores the necessity of developing technologies such as catalytic dechlorination or dissolution for removing chlorine, which enables the recycling of PVC with higher concentrations, given that the typical average PVC content in mixed plastics waste is around 8% wt. In addition, these technologies can be implemented before depolymerization, facilitating chemical recycling and allowing the upgrade of the naphtha to value-added products.

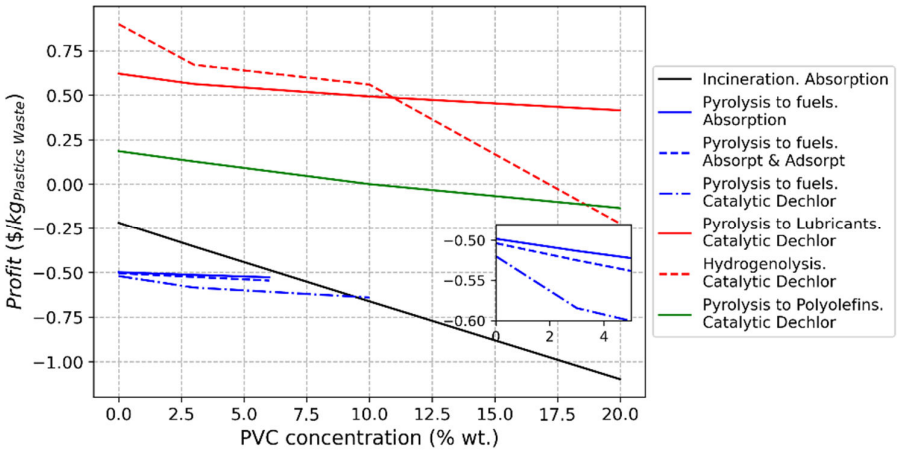

Figure 4. Effect of PVC content (%wt.) in the feed on the economics of several processes.

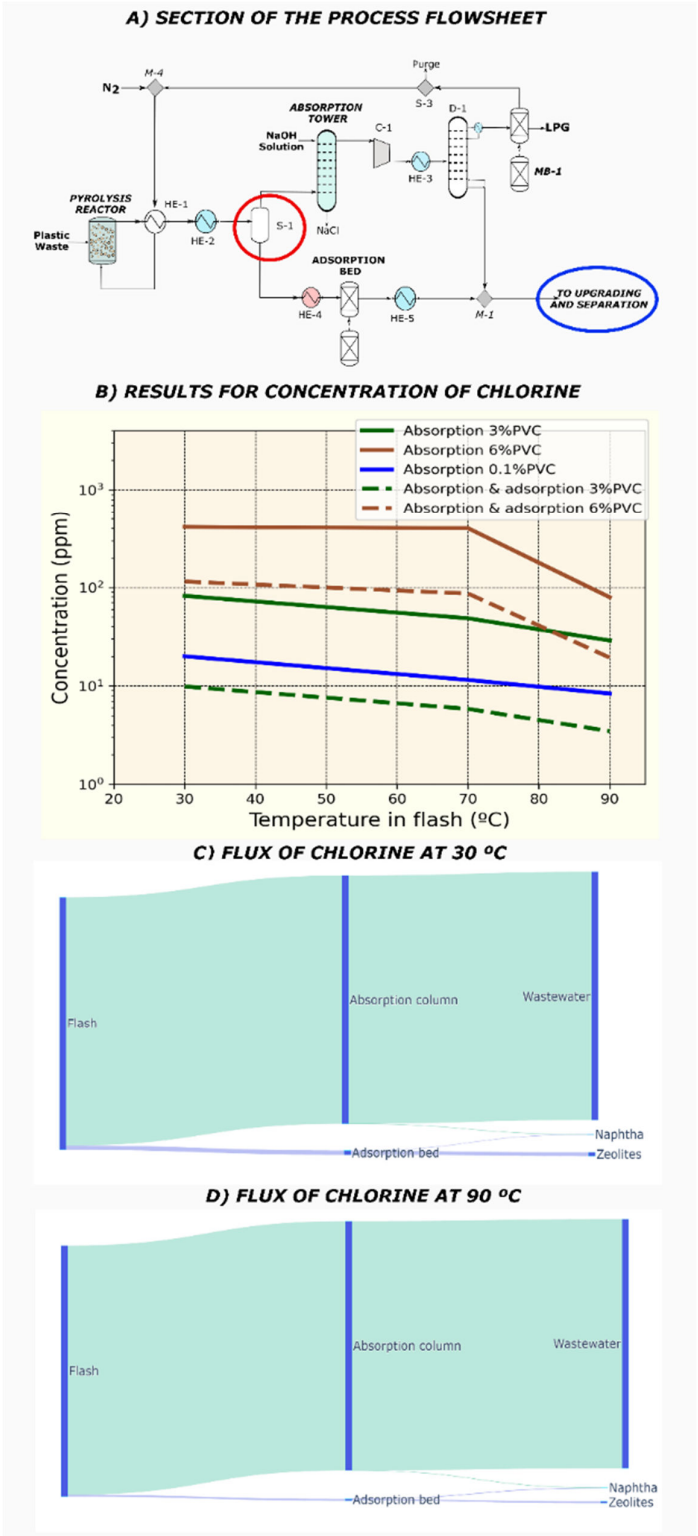

Figure 5. A) Section of the process flowsheet with the flash drum where temperature is modified (red circle) and location of the naphtha (blue circle) where a target concentration of chlorine must be achieved. B) Results for the concentration of chlorine under different temperatures in Flash S-1. C) Flux of chlorine at 30 ºC and D) at 90 ºC when the process is fed with a mixture of 3% wt. of PVC.

LCA results

The results of the LCA, summarized in Figure 6, illustrate that alternative plastics waste management methods to landfilling have environmental benefits in most assessed environmental indicators. Ecotoxicity, eutrophication, and ozone depletion potential are reduced with all management methods except in the dissolution-based process. Acidification is also lowered in all processes except for non-catalytic pyrolysis, while photochemical oxidation is increased in all cases, mainly due to H_2 consumption. Only in the case of chemical recycling to polyolefins, the photochemical oxidation is reduced due to product substitution. The substitution of other plastics makes the chemical recycling path the most interesting for all the indicators evaluated, except for ozone depletion, which is more favourable for lubricant production. In this case, the conventional production of lubricants involves higher equivalent emissions of Chlorofluorocarbons (CFCs) that are then substituted by plastics routes presented in this work. The assessment of the global warming potential (GWP) reveals more balanced results, with only four alternatives reducing the GWP of landfill. The reduction of the GWP is mainly attributed to the product generated. The production of lubricant oil, polyolefins, and steam determines the processes with the lowest GWP. Interestingly, steam production significantly reduces the GWP, primarily because it displaces steam generated from natural gas in a less efficient method. The process with the next lowest GWP corresponds to catalytic pyrolysis to produce polyolefins. This result is in line with previous works,[7,20] indicating that chemical recycling of plastics waste reduces the GWP of the business-as-usual scenario. However, chemical recycling has other drawbacks, such as higher costs compared to mechanical recycling. Apart from polyolefins, production of lubricant oil results in negative GWP, suggesting that this use is also better than landfills. When the emissions are reported per kg of lubricant oil, the GWP is lower than lubricant oil produced from petroleum, remarking that this path is sustainable from both points of view. The reduction of the GWP is due to the utilization of cleaner raw material, which also involves fewer emissions in transportation. The oligomerization section is similar in the plastic pyrolysis and petroleum routes, so the analysis suggests plastic depolymerization against petroleum extraction, transportation and fractionation. Pyrolysis and hydrogenolysis processes have similar emissions, with hydrogenolysis being slightly higher due to additional power (assumed to be sourced from the grid) and hydrogen (from the steam reforming of natural gas) consumption, as shown in the breakdown in Figure 7. The remaining cases exhibit higher GWP than landfilling. Dissolution has the worst environmental performance due to the high contribution from its raw material consumption of chloromethane and NaOH. Comparison of different dechlorination technologies in processes III to V shows that catalytic dechlorination has a 3% higher GWP than absorption. The increase is primarily due to hydrogen use, though its overall impact on total emissions is modest. Nevertheless, catalytic dechlorination, able to achieve lower chlorine concentrations than absorption and adsorption, is the recommended alternative.

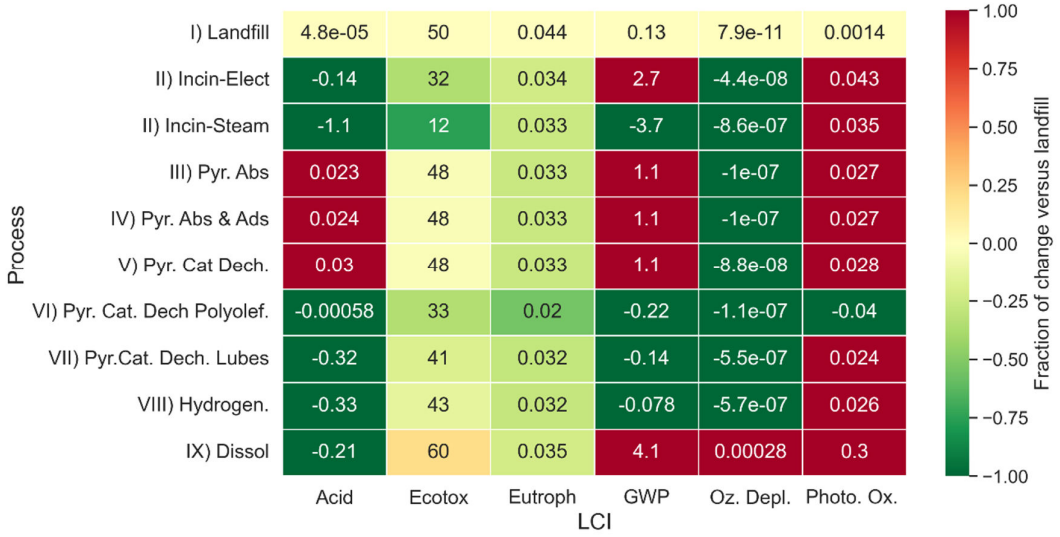

Figure 6. Summary of Environmental metrics for each of the processes. Acid. corresponds to acidification in $kg_{SO2}/kg_{plastics\ waste}$. Ecotox. refers to ecotoxicity of freshwater in $CTU/kg_{plastics\ waste}$, Eutroph refers to eutrophication in $kg_{N}/kg_{plastics\ waste}$, GWP refers to global warming potential in $kg_{CO2}/kg_{plastics\ waste}$, Oz. Depl. corresponds to ozone depletion in $kg_{CFC\text{-}11}/kg_{plastics\ waste}$ and Photo. Ox. refers to photochemical oxidation in $kg_{O3}/kg_{plastics\ waste}$.

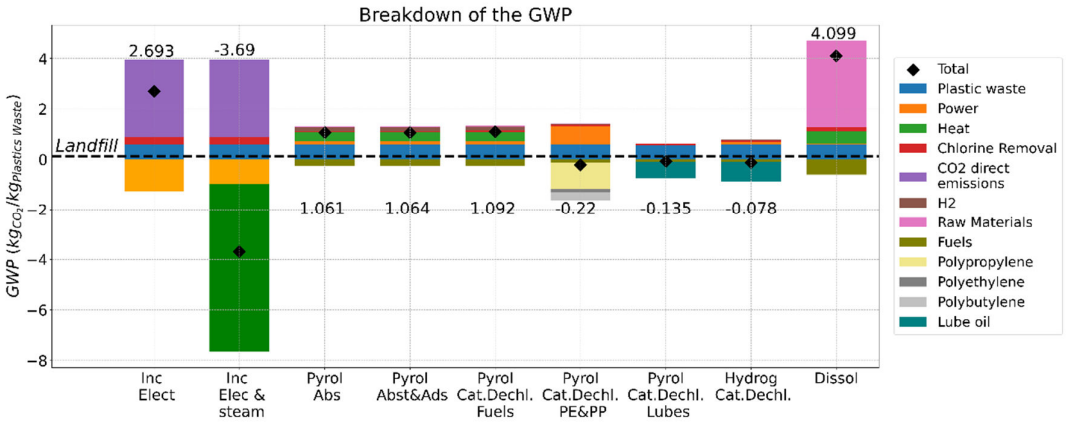

Figure 7. Breakdown of GWP for each of the processes. In the horizontal axis: Inc Elect. refers to process II when electricity is only produced. Inc Elec & steam refers to process II when electricity and steam are produced. Pyrol Abs refers to Process III with fuels as the main product, Pyrol Abs & Ads is for process IV producing fuels, Pyrol Cat. Dechl. Fuels is for process V producing fuels, Pyrol Cat. Dechl. PE & PP refers to process VI producing polyolefins (mostly polyethylene (PE) and polypropylene (PP)), Pyrol Cat. Dechlor. Lubes is for process VII producing lubricants, Hydrog. Cat. Dechl. refers to process VIII also producing lubricants, and Dissol. refers to process IX.

Effect of PVC concentration on the GWP

Sensitivity analysis has been conducted to better understand the influence of PVC concentration on the GWP of different technologies. As in TEA, incineration is the most sensitive management method to the concentration of PVC (Figure 8, A)). This high sensitivity is due to the significant contribution of chlorine removal technologies compared to other processes; see Figure 7. A similar effect occurs when producing polyolefins and lubricants. The amount of polyolefins produced is less than that of lubricants, resulting in higher sensitivity. In the case of lubricants, the sensitivity against GWP is less than the sensitivity with the price, see Figure 8,A). This is because from an economic perspective lubricants have higher market prices than polyolefins, meanwhile from an environmental perspective the GWP is more similar between both. The comparison of the two technologies employed in the production of lubricant oils shows that at concentrations higher than 1.5% wt. of PVC, catalytic pyrolysis has lower emissions than hydrogenolysis, see Figure 8,B). However, at lower concentrations, hydrogenolysis exhibits better performance, as the yield obtained from lubricant oil increases when the PVC content decreases, which suggests hydrogenolysis for treating average plastic waste (typical PVC content of 8%wt.). Analysis of hydrogenolysis reveals a sharp increase in GWP at a PVC content of 20% wt., due to the significant drop in lubricant production observed at this concentration. Such effects have not been included in the modeling of pyrolysis; experiments will be needed. Finally, the processes for producing fuels via pyrolysis were compared. The highest GWP corresponds to the catalytic dechlorination process and the lowest to the absorption process. However, as discussed in previous sections, catalytic dechlorination is the only method that ensures plastics waste with a small concentration of chlorine. Thus, this technology achieves a more robust operation and is recommended despite the ~3% higher GWP than absorption.

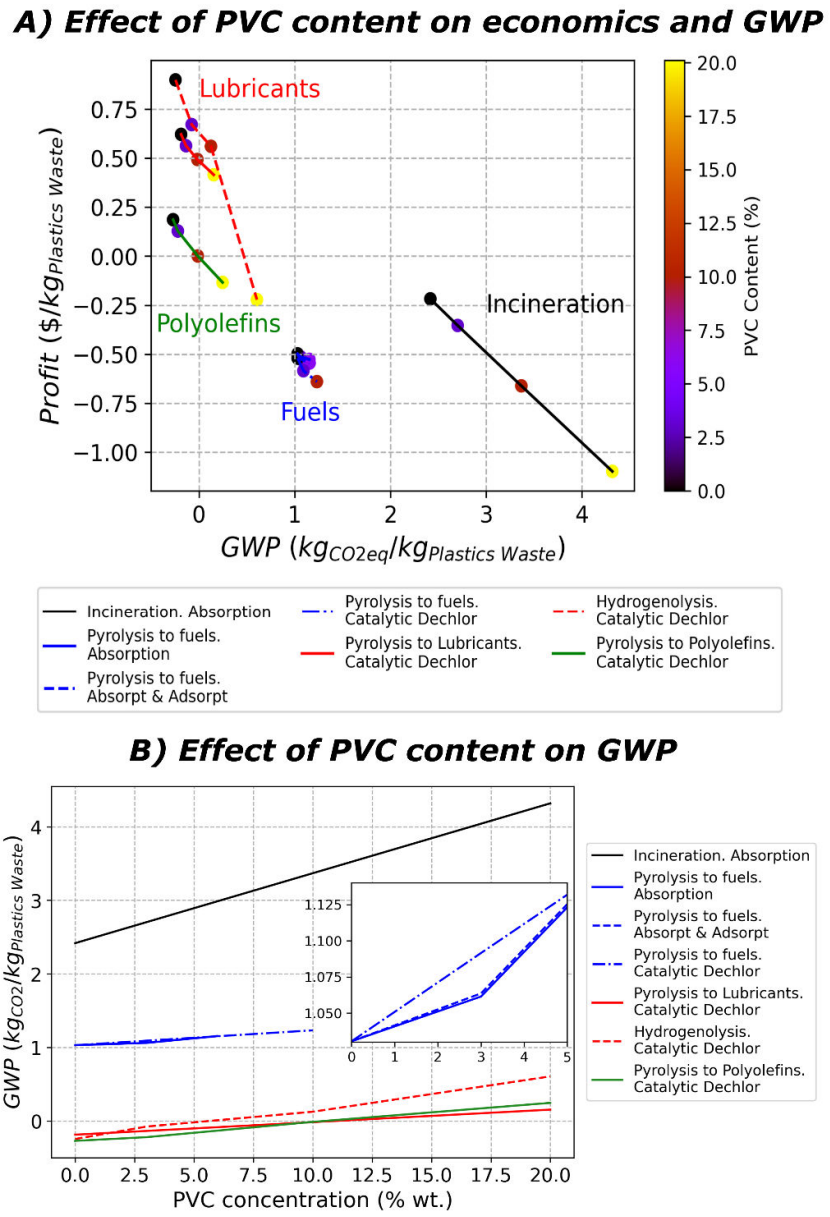

Figure 8. A) Plot comparing the profit generated on plastics waste and GWP of different technologies under different PVC content. B) Effect of PVC content on the emissions generated by different processes.

CONCLUSIONS

TEA and LCA analyses conducted for several processes treating mixed plastics waste with PVC have demonstrated that the final product highly governs economics and emissions. Developing technologies that effectively remove chlorine from mixed plastics waste is necessary to increase the yields of desired products. A two-step catalytic dechlorination with MgO and H_2 at high pressures, followed by hydrogenolysis to lubricant oil, has the best economic performance among the management strategies compared and reduces the GWP over landfill or incineration for electricity production. Both economics and emissions are highly influenced by the PVC content, with the minimum selling price of lubricant oil doubling and the GWP

increasing from -0.0759 $kg_{CO2}/kg_{plastics\ waste}$ to 0.6062 $kg_{CO2}/kg_{plastics\ waste}$ when the PVC concentration increases from 3% to 20% wt. The two-step method with catalytic dechlorination also opens the opportunity for catalytic pyrolysis to produce olefins. This chemical recycling method is the best alternative in terms of GWP reduction. On the other hand, the best economic performance for pyrolysis is obtained when it is employed to produce lubricant oil, with results very similar to those of hydrogenolysis. Performing detailed analyses of the influence of operating conditions (pressure, temperature) and catalysts will help decision-making.

This two-step method is the best choice to produce value-added products, as it removes chlorine and allows the use of catalytic depolymerization technologies. However, it is not recommended in other cases. For example, when aiming to produce fuels by non-catalytic pyrolysis of mixed plastics waste, the selection of the technology is dictated by the concentration of PVC. At PVC concentrations below 3% wt., treating the gas phase of the depolymerized product with an absorption column and the liquid phase with an adsorption bed is cheaper for reducing chlorine concentration below 5 ppm (maximum required for fuel). It is essential to note that this PVC content is below the average concentration of PVC in mixed plastics waste, at 8%, so the two-step treatment with catalytic dechlorination is still recommended as a generic solution for treating mixed plastics waste. However, further development is required for identifying optimal catalysts in the depolymerization step. Chlorine removal alters the plastics waste composition, resulting in a complex mixture, requiring catalyst re-optimization. Identifying a catalyst that performs well across a range of PVC concentrations could significantly improve the overall process. The effect of the composition of plastics waste on the yield of each product also requires further understanding. For comparison, this work has evaluated two mixtures between them (one containing several polymers and another based only on PP and PVC); yet, further experimental work is needed. Even though dissolution with ILs and chloromethanes can achieve complete chlorine removal, further intensification (e.g., increase the plastics waste to solvent ratio) is required to make these methods competitive.

SUPPORTING INFORMATION

Detailed description of process models, assumptions of techno-economic analyses and life cycle assessment, fluxes, and detailed economic and LCA results.

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