Techno-Economic Comparison of Bio-Cycling Processes for Mixed Plastic Waste Valorization

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Mixed plastic waste is challenging for any recycling process. Here, an enzymatic recycling process is compared with a biotechnological upcycling process for valorizing mixed plastic waste constituted by PLA, PET, and PP. Both process routes are modeled in Aspen Plus, analyzed for bottlenecks, cost drivers, and sensitivity regarding enzymatic and microbial performance. While enzymatic recycling is only viable for uniform plastic feedstock, biotechnological upcycling operating at optimized process conditions reveals the potential to produce carbon-neutral succinic acid from mixed plastic waste.

Keywords: Enzymatic, Microbial, Mixed plastic, Recycling, Succinic acid

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1 Introduction

The global plastic crisis is a genuine and pressing issue that demands urgent action, particularly regarding the management of plastics at the end of their useful life. Synthetic plastics have become ubiquitous due to their benefits as functional materials, extreme durability, longevity, low weight, and low price in work and social environments, and as contaminants in natural systems. The overwhelming challenges are the 4.8 billion tons of plastics in (poorly managed) landfills [1] and the annually production of nearly 400 Mt of new plastic. Without measures to reduce plastic usage, this amount will likely increase significantly [2], in addition to the already 8 billion tons in Earth's system, and less than 10 % of plastic recycled [3]. Social costs from plastic pollution (including clean-up and ecosystem destruction) already exceed 100 billion $ per year [4].

The linearity of the current plastic economy is its unintended drawback. The commonly implemented concept of consumer disposal shifts the costs of recycling away from producers and retailers, eventually leading to the fact that the value of plastic waste is low, too low for alternative end-of-life options. Reuse and recycling are difficult and expensive, especially for mixed plastic (e.g., main packaging polymers: 40 % PET, 22 % HD/LD PE, 10 % PP, < 2 % PVC/PS [5]), as it is cheaper (and often less energy-intensive) to use virgin polymers for packaging. The drawback of mechanically recycled plastic is its poor quality because of the mechanical strain. Moreover, 80 % of nowadays produced plastics are based on C-C-backbones, thus durable, making it difficult for bio- or chemical recycling [6]. Biobased plastics (bioplastics) with increasing volumes emerged as non-fossil alternatives in the last decennium's plastic markets, with a market share under one percent of overall plastic produced annually. According to recent estimates, the global bioplastics market is expected to grow at a compound annual growth rate of around 5 % between 2021 and 2025 [7]. Currently, the most essential fully biobased, and biodegradable amorphous or semi-crystalline polyester is polylactic acid (PLA), with excellent properties like high mechanical strength, transparency and biocompatibility. New additives and processing methods made PLA a highly-suited polymer beyond packaging for textiles, mulch films, adhesives, biomedical and electronic applications [9, 10]. In

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2022, 470 kt PLA were produced, making it the dominant global biobased/biodegradable bioplastic (21 % of global production) with an expected 3-fold growth prognosis for 2027 [8]. However, confident predictions are challenging as they depend on various factors, e.g., consumer behavior, recycling technology developments, and product type trends. Persistent and thus non-biodegradable biomass-derived plastic materials represent 41 % of all bioplastics (2 Mt), including biobased polyethylene terephthalate (PET), polyamides, and polyethylene (PE) [11]. Polymer and product designs for recycling and (bio)degradation are crucial for transitioning from a linear to a circular plastics economy [5, 7]. Essential for a circular economy is the intense utilization of every side stream to minimize waste production or redundant CO_2 release.

Temperature-sensitive plastics, composites, and thermosets that cannot be melted at high temperatures are typical limitations for mechanical recycling. The main polyolefins used in the packaging industry, PE and PP, were shown to have different degradation mechanisms due to chain attack primarily occurring in the amorphous polymer phase, as oxygen diffusion seems limited in crystalline domains. Generally, recycled PEs reveal higher crosslinking rates than PP, which tends to chain scission [12–15]. However, the only ones recovered by mechanical recycling are two of the most prominent commodity plastics, PET and PE, mainly used in packaging. The melted and remolded polymers are often blended with virgin plastics to correct lost properties [16–21]. Mechanical and physicochemical recycling usually requires pure waste feedstocks, free of impurities and contaminants, to produce high-quality end-products obtained after resource-intensive sorting. Solvolytic processes may convert polymers into monomers and oligomers, which can be re-polymerized after purification. However, recycling processes within circular approaches should not only produce monomers for later polymerization ("bottle to bottle" principle) but instead focus on value-added products or intermediates for alternative supply chains with a minimized remaining waste fraction [22, 23]. Hydrogenolysis using advanced catalysts and pyrolysis (thermolysis) to produce gases, fuels, diols, or waxes are competitive alternatives to this end [18–21].

Biotechnological recycling supplemented with physicochemical techniques to tackle the more recalcitrant plastic polymers may promote complementing end-of-life plastic treatment options. For example, depolymerizing plastic waste under mild conditions to mixed oligo- or monomers enables their use for later polymerization (after selective building block recovery) or as feedstock for microbes in biotechnology to upcycle the waste to value-added products using ideally renewable energy. Typical enzymes for polymer hydrolysis are cutinases, lipases, and carboxylesterases [24–26].

A challenge of enzymatic degradation is the fraction of plastic polymers based on persistent and robust chemical groups, which resist hydrolysis with common biological enzymes. This fraction can be converted to valuable products with additional steps of chemical catalysis [6, 27, 28]. However, a prior separation of the non-hydrolyzable plastic fraction would be required, which comes at the expense of carbon yield losses and adds costs for the mechanical separation.

This study aims to compare enzymatic recycling and recovery of the monomers with the biotechnological upcycling of mixed plastic waste and asses the techno-economic potential of each process. In addition, a sensitivity study evaluates the impact of varying microbial performance indicators and operational parameters like plastic loading and feedstock composition. Finally, the techno-economic assessment (TEA) is used to derive technological targets to direct further research and development of biotechnological re- and upcycling for mixed plastic waste valorization.

2 Methods

In the following, the two compared processes are described, and the utilized Aspen Plus® models are introduced, as well as the basic assumptions for the techno-economic comparison.

2.1 Biochemical Recovery

Mixed plastic (MP) consisting of polylactic acid (PLA), PET, and polypropylene (PP) is decomposed by enzymatic hydrolysis into lactic acid, ethylene glycol (EG), and terephthalic acid (TA) with PP as an inert component. The hydrolysis products are recovered by the process (P1) shown in Fig. 1, consisting of a precipitation, ion exchange and rectification process. The necessary enzymes are produced in a fermentation step with glucose (Gl) as substrate and fed into the hydrolysis after removing the biomass by filtration. With the addition of calcium hydroxide (CaOH), the pH value in the hydrolysis is kept neutral, which causes lactic acid to be present as calcium lactate (CaLa). The resulting stream is centrifuged to remove leftover plastic and other solids. In the following precipitation, CaLa is acidified with sulfuric acid to lactic acid and calcium sulfate, which is separated by centrifugation, and washed out as gypsum. In this step, the TA fraction is removed as well. The product stream is purified of all remaining ions with ion exchange chromatography and an activated carbon column. These columns prevent unwanted racemization in the following rectification step. Most of the process water is separated at the column head in the first rectification column, while lactic acid, EG, and a water rest remain in the bottom stream. The bottom stream is further purified in a second rectification step to obtain lactic acid with a purity of 80 % as the head product and EG as the bottom product.

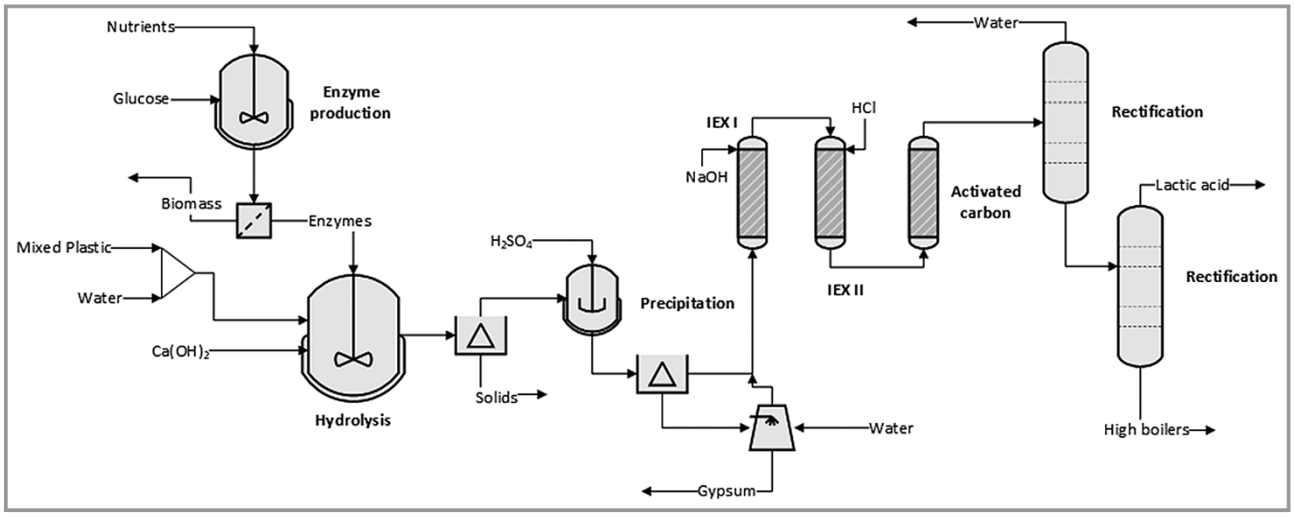

Figure 1. Mixed plastic recycling by enzymatic hydrolysis of PLA and lactic acid recovery (P1).

2.2 Biotechnological Upcycling

The upcycling process (P2) is schematically depicted in Fig. 2. Here, mixed plastic is decomposed by enzymatic hydrolysis as well. In contrast to the recovery process, a fermentation step with seed fermentation occurs after hydrolysis. Here, TA, EG, and lactic acid are converted into succinic acid, which forms calcium succinate (CaSu) with the added CaOH. The biomass and other remaining solids are removed by centrifugation. Succinic acid is recovered by adding sulfuric acid, resulting in the precipitation of calcium sulfate (gypsum). The succinic acid solution is separated from the solid gypsum by centrifugation. The crude succinic acid is subsequently resolved in water, purified of all remaining ions in an ion exchange chromatography, and finally, an activated carbon column. Pure succinic acid is achieved with a third crystallization step and a dryer.

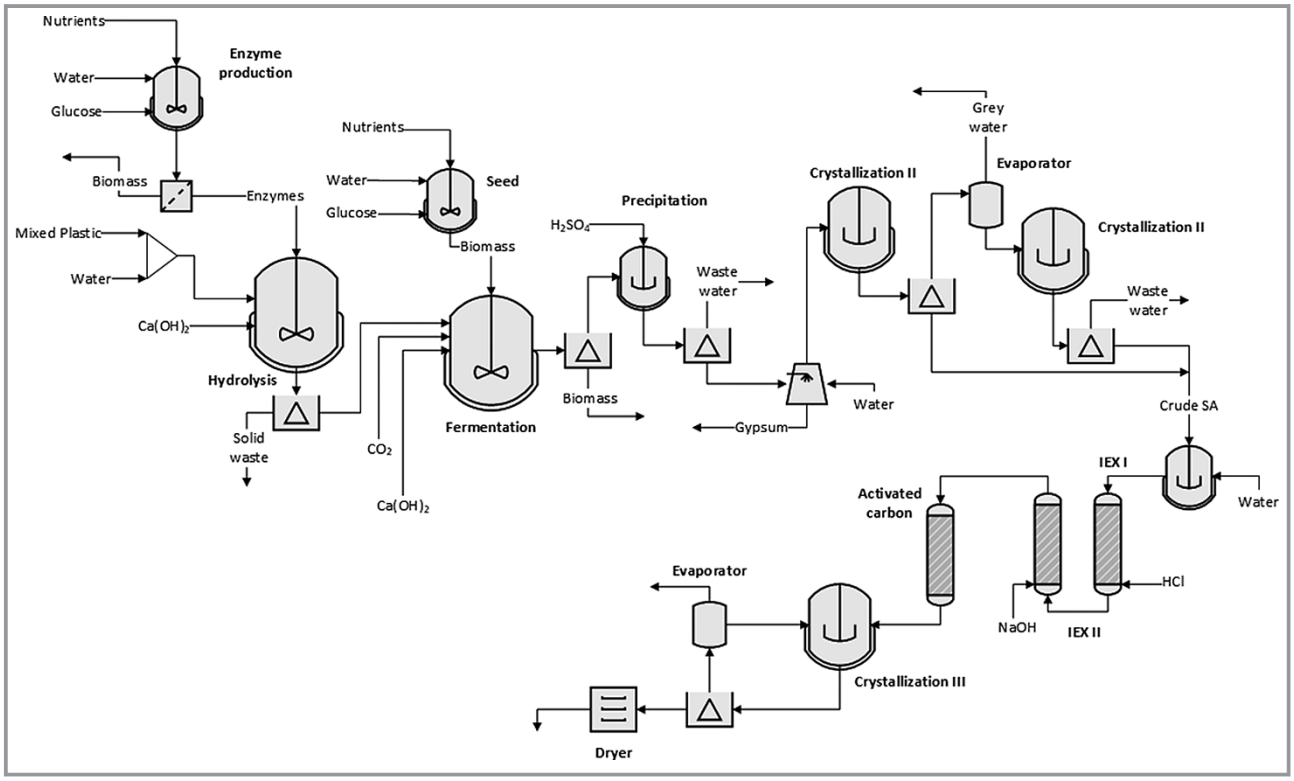

Figure 2. Mixed plastic upcycling by enzymatic hydrolysis of PLA and microbial conversion to succinic acid (P2).

2.3 Flowsheet Simulation

The simulations were carried out in Aspen Plus® V11. ELECNRTL was used as the property model, and missing model parameter values were estimated with the UNIFAC method. ELECTNRTL was chosen as property model because modeling pH changes is required for describing the dissociation of acids and bases used for precipitation. In addition, ELECNRTL is the well-established NRTL model's ionic extension characterized by robust performance in process simulation at moderate pressure and a wide temperature range. The considered substances were modeled as *conventional* substances, except biomass, enzymes, PP, PLA, PET, TA, CaSu, and CaLa, which are modeled as *solids*. Succinic acid is implemented as *conventional* until the crystallization, whereafter succinic acid is modeled as a *solid*. In global chemistry, the self-dissociation of water and lactic and succinic acid dissociation are implemented. The associated property tables, Aspen flowsheets, and detailed information on the assumptions made for the model are shown in the SI.

2.4 Process Parameters for Basis Scenario

To compare the two introduced processes and calculate the resulting operational and capital costs, a base scenario with the process parameter in Tab. 1 was simulated. The yearly productivity of each process should reach 50 kt of lactic and succinic acid, respectively. As a feedstock, a uniform MP composition was chosen to consider the influence of the different products emerging from the hydrolysis on the downstream. The MP loading of the feed stream was chosen to ensure the solubility of CaLa in the product stream of the hydrolysis, which is at approx. 60 g L^{-1} for 70 °C [29]. The considered hydrolysis, enzyme production, and fermentation properties, such as space-time yield, titer, yield, and reaction equations, are documented in the SI.

Table 1. Process parameters basis scenario.

Parameter	Value
Plant capacity [kt a^{-1}]	50
MP weight composition (PLA: PET: PP) (60 g L^{-1} each)	1:1:1
MP loading feed stream [g L^{-1}]	180

2.5 Cost Estimation

With the results of the performed simulations, the cost of manufacturing (COM) is calculated. These consist of the sum of product-specific costs c_i for feed streams, waste disposal, by-products, heating, cooling, electricity, CO_2 tax, labor, maintenance, and depreciation.

$$\mathrm{COM} = \sum_{i}^{n} c_i \tag{1}$$

The specific costs for the feed streams, waste disposal, and by-products are based on a literature review and shown in the SI. The Aspen Plus® default data is taken for heating, cooling, electricity costs, and CO_2 tax. By solving the mass and energy balances for each process in Aspen Plus®, the costs for all streams and utilities can be estimated. The labor costs are considered with 36 employees and two plant engineers. Plant maintenance is calculated as 6 % of the total plant capital cost. For the calculation of the depreciation, a 10-year plant lifetime is expected with a 5 % interest rate and a capital cost of four times the capital cost estimated by the Aspen Plus® economics calculation.

The sensitivity analysis is carried out by varying variables with a significant influence on the COM. The new COM* is calculated by linear extrapolation from the price of the base scenario p_0 to the new price p*.

$$\mathrm{COM}^{\star} = \mathrm{COM} + \left(\frac{p^{\star}}{p_0} - 1\right) c_i \tag{2}$$

2.6 Footprint Analysis

Footprints F_i were calculated in terms of equivalent carbon dioxide emissions, freshwater consumption, total wastewater production, and solid waste production from the mass flow of each category in relation to the mass flow of the respective product. The carbon dioxide footprints account for direct CO_2 emissions from the process and indirect emissions from utilities (heating, cooling, and electricity).

$$F_i = \frac{\dot{m}_i}{\dot{m}_p} \tag{3}$$

2.7 Sensitivity Analysis

A sensitivity analysis was carried out to show the influence of different parameters on the resulting COM. The varied parameters are shown in Tab. 2. One parameter at a time was varied, while the others were fixed at the base scenario. The fractional conversion of hydrolysis and fermentation was kept at 100 % for the base scenario and represents ideal reactions derived from the corresponding metabolism. A lower fractional conversion was investigated to represent non-ideal reaction conditions. For both reactions, representative space-time yields are taken from the literature [30, 31] and are varied to larger values to quantify potential economic benefits. A wide range of mixed plastic loading was explored to assess the impact of suspending polymers in water to achieve good flow properties. Cost parameters

Table 2. Varied parameter values for the sensitivity analysis.

Parameter	Base scenario	Range
MP composition (PLA: PET: PP)	1:1:1	–
Fractional conversion hydrolysis & fermentation [%]	100	50–100
MP loading feed stream [g L^{-1}]	180	60–300
Space time yield hydrolysis & fermentation [g $L^{-1}h^{-1}$]	hydrolysis: 3.6; fermentation: 6.03	3.5–15
Electricity cost [€ MWh^{-1}]	70	10–170
Steam cost [€ t^{-1}]	20	11–30
MP cost [€ t^{-1}]	150	50–250
Solid waste cost [€ t^{-1}]	110	20–210

are part of the sensitivity analysis to represent market fluctuations.

3 Results and Discussion

The results are presented in two steps. First, the costs of manufacturing (COM) and footprint calculations for the base scenario are presented. Based on these figures, a qualitative comparison of the two processes is carried out. A sensitivity study was carried out to account for the uncertainty in the selected assumptions. Here, the sensitivity of each process regarding raw material and energy prices, as well as emission constraints, are analyzed. The sensitivity study is used to identify technological constraints imposed by thermodynamic limits and calculate targets for key process parameters (space-time yield, MP loading, and biotechnological conversion).

Fig. 3 displays the COM for the recovery process (P1) and the ratios of the stream costs. An overall COM of 4.10 € kg^{-1} is calculated for lactic acid recovered from PLA containing mixed plastic waste in the base scenario. The overall COM is significantly above the market sales price for virgin lactic acid, which is in the range of 1.2–1.5 € kg^{-1} [32]. The prospect of an economically successful application is thus unlikely.

Raw material costs account for the most significant fraction of the production costs, followed by depreciation and heating costs. The raw material costs consist mainly of MP costs, followed by the expenses for NaOH and HCl. MP is the primary substrate, and the PLA content and its conversion determine the substrate costs, which increase with low PLA content, incomplete conversion, and high product losses. The high ionic strength in this stream causes high costs for acid and base. The significance of depreciation and heating costs indicates that separating lactic acid from the hydrolysate is cumbersome and results in a costly rectification. The costly rectification results from an unfavorable vapor-liquid equilibrium (VLE) of lactic acid and water at low lactic acid concentrations. The VLEs of lactic acid and water at 1 bar(a) and 0.5 bar(a) are shown in Fig. 4.

Above 80 wt % water, the equilibrium curve approaches the bisectrix resulting in a rapid increase in the total number of stages and high reflux ratios. Considering a reasonable number of stages (35) and reflux ratio (4) leads to a high product loss in the first rectification column, where about 30 wt % of lactic acid is lost. Therefore, a lactic acid concentration in the hydrolysate of at least 5 wt % (~0.5 M) is desirable to foster efficient lactic acid recovery by rectification. Preferably the lactic acid concentration in the hydrolysate should be 10 wt % (~ 1.1 M) to 20 wt % (~2.2 M). As a result, the maximal solubility of CaLa must be considered when $Ca(OH)_2$ is used for pH control in hydrolysis. Another possible optimization of the process would be the implementation of a low-pressure rectification

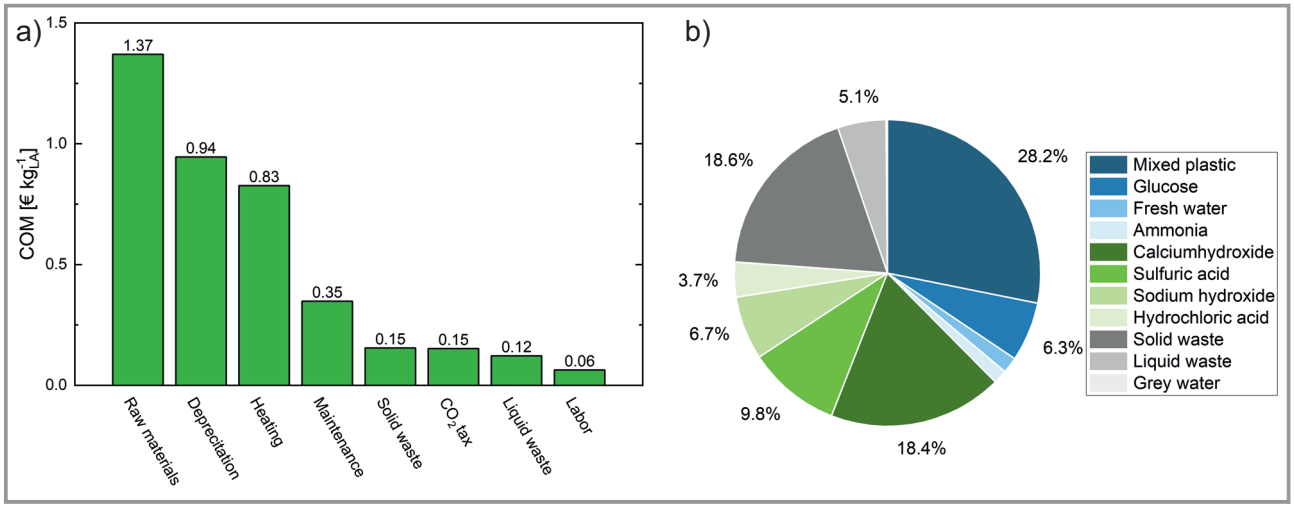

Figure 3. a) Cost of manufacturing (COM) for lactic acid and b) composition of stream costs for the enzymatic recovery process for PLA (P1) containing mixed plastic waste with the base scenario input according to Tab. 2.

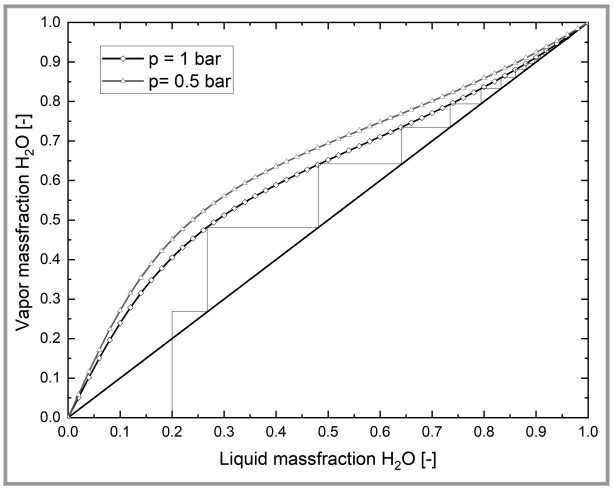

Figure 4. *xy*-diagram of lactic acid and water at 1 bar(a) and 0.5 bar(a).

for the second column. This process alternative could lead to a complete separation of lactic acid and ethylene glycol (EG), even considering the maximum temperature of 180 °C. Taking a prize for EG of 2 € kg_{EG}^{-1} into account, a decrease in the COM to 3.2 € kg_{LA}^{-1} could be achieved.

Depending on the operating temperature of the hydrolysis, the solubility limit of CaLa is found in the range of 0.5–2 M [29]. The use of other bases like NaOH or KOH is possible. Sodium and potassium salts are generally highly soluble but would cause a high ionic strength in the remaining hydrolysate. High ionic strength during the rectification can induce undesired racemization of the lactic acid and should be avoided [33]. The ionic strength in this process is already high, resulting in a need for high amounts of NaOH and HCl to regenerate the ion exchange chromatography. Alternatively, adsorption [34], reactive extraction [35–37], or membrane-supported reactive extraction [38, 39] can be applied to recover the LA and increase its concentration before the rectification.

Fig. 5 displays the COM for the biotechnological upcycling of MP waste to succinic acid and the composition of the raw material costs. The COM for succinic acid derived from mixed plastic waste hydrolysate as feedstock is calculated to be 2.22 € kg^{-1}. This COM is comparable to previously reported prices for bio-based or petrochemically derived succinic acid [40–43]. Maintenance and depreciation account for almost 50 % of the overall costs, followed by raw material, heating, and waste disposal costs. Consequently, biotechnological upcycling can be considered a CAPEX-intensive process route. This implies that the overall process performance largely depends on the efficient usage of equipment, and that space-time yields of the fermentation must be paid close attention.

The stream costs are evenly distributed between feedstock, auxiliary chemicals, and waste disposal. The waste disposal costs directly depend on using acid and base for pH control throughout the process, and both sum up to approximately 60 % of the raw material costs. The extensive use of auxiliary chemicals is a known issue in the biotechnological production of succinic acid [43, 44].

The investigated processes for the enzymatic recovery and the biotechnological upcycling of mixed plastic waste have in common that efficient product separation is a crucial aspect of the overall economy of biotechnological plastic waste valorization. While the recycling process is less capital-intensive, a cost cut of at least 50 % is essential to become economically competitive. The reduction of raw material costs by high-yield enzymatic conversion and the limitation to feedstock with high PLA content are potential levers to reduce the expenses for raw materials, lactic acid concentrations above 10 wt % are required to make the rectification step cost-efficient. Therefore, the initial loading of mixed plastic waste in the hydrolysis should be selected

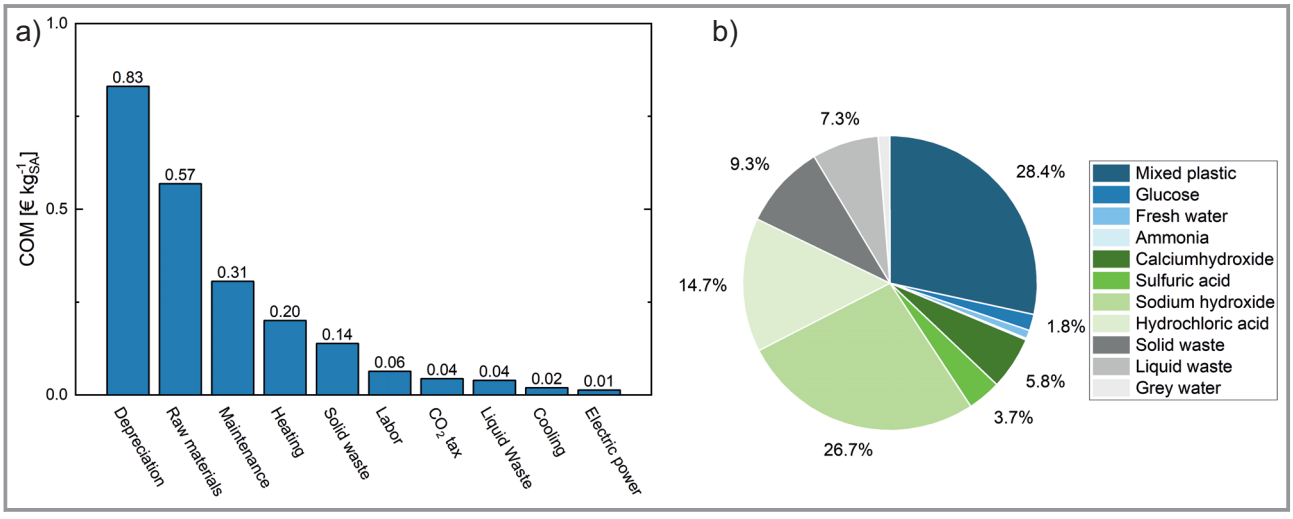

Figure 5. a) Cost of manufacturing for succinic acid and b) composition of stream costs for biotechnological upcycling of mixed plastic waste (P2) total COM: 2.22 € kg^{-1}. Input according to Tab. 2.

accordingly. If the required plastic loading cannot be obtained in the hydrolysis, reactive extraction could be considered to recover the lactic acid from a diluted hydrolysate [34, 39, 45].

A severe drawback of the enzymatic recycling process is the inability to recover monomers besides lactic acid in the current layout. The non-hydrolyzed polymer fraction is removed and disposed of as waste, as well as the TA, which precipitates with calcium sulfate. EG may be recovered as a high boiling compound from the bottom of the second lactic acid distillation column, but it accounts for less than 30 wt % of the PET fraction. Using TA and EG as feedstock for microbial upcycling in parallel would be an economical alternative. Another drawback is inorganic acid, base, and solid waste deposition costs, which constitute 46.8 % of the total raw material expenses. Thereof, two conclusions can be drawn for the applicability of enzymatic recovery:

1) The distillation of lactic acid, produced by enzymatic hydrolysis, requires a plastic feedstock with high PLA content. Processing of mixed plastic appears challenging from an economic point of view due to low process yields and additional costs for pre-sorting.
2) Reducing auxiliary chemicals usage leverages the economic competitiveness of enzymatic plastic recycling.

In contrast to enzymatic recycling, the biotechnological upcycling of MP waste appears as the more viable option regarding economic competitiveness.

3.1 Footprint Analysis

The footprint analysis shown in Fig. 6 reveals an advantage of the biotechnological upcycling in each category. The carbon footprint of the succinic acid produced by biotechnological upcycling is calculated at 1.75 $kgCO_2e\,kg^{-1}$, which is comparable to the carbon footprint of bio-based succinic acid derived from sugarcane [46] and below the carbon footprint of petroleum-based succinic acid (3.3 $kgCO_2e\,kg^{-1}$) [47]. The biotechnological upcycling process has the advantage that each metabolized lactate molecule fixes one molecule of CO_2 per mole of succinic acid. Thus, up to 25 % of the carbon in the succinic acid produced via the reductive pathway of the TCA cycle comes from external CO_2. This feature enables biotechnological upcycling to act as a sink that prevents CO_2 emissions into the atmosphere. When 90 % PLA is used as feedstock, the process (without utilities) becomes a carbon sink at 7 $gCO_2e\,kg^{-1}$ succinic acid, accounting for the emission through seeding, enzyme production, and metabolism in the fermenter. The carbon sink rate can be derived from the stoichiometry of the reactions occurring in the fermentation of lactic acid, TA, and EG and in the seeding reactor. Reaction equations for fermentation and seeding can be found in the SI. The freshwater consumption during the process results from MP loading and product titer. Increased MP loading and product titer would reduce the necessary amount of fresh water and wastewater. Especially fresh- and wastewater requirements are high for the recovery process due to the high ionic strength (0.22 mol L^{-1}) in the downstream process, which causes high consumption of NaOH and HCl for the regeneration of the ion exchange resin. The high ionic strength leads to significant emissions of salt-containing wastewater from the process. In addition, solid waste is an inherent problem that results from the precipitation of calcium sulfate in the downstream process.

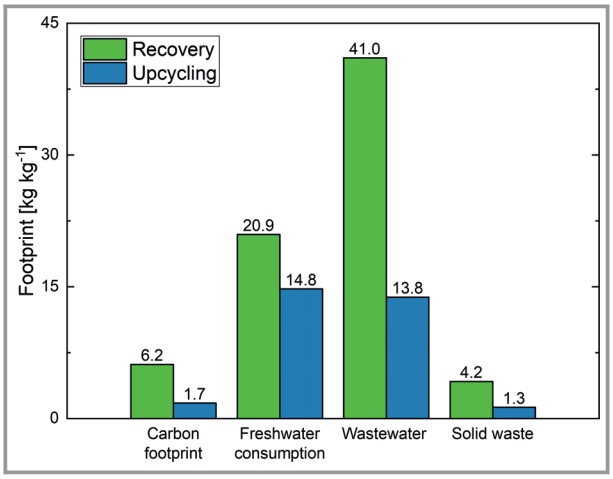

Figure 6. Footprint analysis to compare lactic acid recovery (P1) and the upcycling to succinic acid (P2) from mixed plastic wastes.

3.2 Sensitivity of Materials and Energy Costs

Fig. 7 shows the sensitivity of the COM regarding expenses for MP waste, heating energy, electricity, and solid waste disposal costs for the enzymatic recovery (P1) and the biotechnological upcycling (P2) of mixed plastic waste. As discussed, feedstock costs account for the most significant fraction of raw material expenses. The most common and mature valorization technology for MP waste is incineration. A mixture that contains equal ratios of PP, PET, and PLA has a calorific value of approximately 29.5 MJ kg^{-1}. This value is comparable to the energy content of coal (25–33 MJ kg^{-1}) [48]. The average price for coal used in power plants in Germany from 2000–2020 was 72.5 € t_{HCE}^{-1} [49], with recent peak prices between 150 € and 300 €. Consequently, any (bio-)chemical recycling process must operate economically at similar or higher prices for the MP waste feedstock to secure the supply and successfully compete with the utilization of MP waste as an alternative energy source.

The enzymatic recovery is unlikely to compete economically with incineration since COM is far above the market prices of virgin lactic acid, even with MP waste that costs less than 70 € t^{-1}. Upcycling, however, is found to be competitive even at high energy prices.

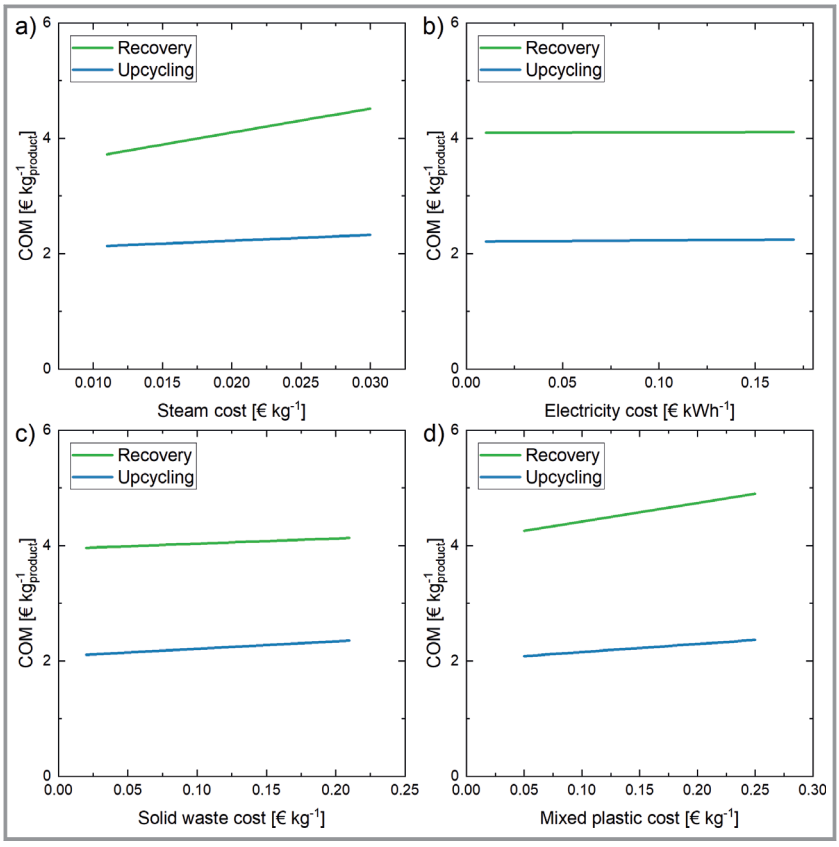

Figure 7. Sensitivity analysis: a) energy costs (heating), b) electricity costs, c) solid waste disposal costs, d) mixed plastic costs.

The high energy demand of the lactic acid separation makes the recovery process more sensitive to increases in the costs for heating than the upcycling process. The energy demand of the recovery process could be further reduced by energy integration measures like vapor compression in the rectification. At the current stage, both approaches show no significant sensitivity toward changes in electricity prices. This, however, may change when energy integration measures are implemented, as these measures reduce the consumption of heating energy at the expense of higher electricity consumption.

Solid waste disposal costs are relevant, as both processes require the disposal of gypsum and residual plastics that are inert to hydrolysis. PP is a major constituent of the solid fraction separated during the recycling process. The production of gypsum is comparable in both approaches. TA has negligible solubility in water and thus potentially precipitates in the acidification step together with the gypsum if it is not completely converted in the fermentation. The solid waste stream from the enzymatic recycling process contains up to 18 wt % of TA.

3.3 Sensitivity of Process Conditions

Fig. 8a displays the influence of MP loading on the COM of the recovery and upcycling process. The recovery process is more sensitive to MP loading than the upcycling process. A lower plastic loading results in an increased water fraction that needs to be separated. The energy-intensive and challenging lactic acid and water rectification explains the higher sensitivity in the recovery process. Contrarily, in the upcycling process, the additional water is separated by the first centrifuge and directed to the wastewater stream resulting in a smaller sensitivity of MP loading. The MP loading is limited in the recovery process due to the solubility limit of calcium lactate. A further increase in plastic loading would result in product losses in the first centrifugation step. Solid calcium lactate would be separated together with the remaining solids in the solid waste stream. The highest COM for the recovery and upcycling process is 8.1 € kg_P^{-1} and 5.9 € kg_P^{-1}, respectively. At low MP loadings, the separation of lactic acid in the rectification column becomes challenging due to the unfavorable shape of the VLE curve at low lactic acid concentrations. An increase in the theoretical stages or the reflux ratio could enable the separation at the expense of higher capital costs and increased energy demand. A reasonable target for MP loading appears to be 200 g L^{-1}. Below 150 g L^{-1}, the COM begins to increase drastically, and above 250 g L^{-1} no significant reduction is observed. 200 g L^{-1} are also reported for second-generation biomass processes that require arguably even more challenging hydrolyzation.

Fig. 8b depicts the sensitivity of COM regarding the fractional conversion of the hydrolysis and fermentation. The recovery process is more sensitive to fractional conversion than the upcycling process. In the recovery process, the steep increase in COM at lower fractional conversion is explained by the lower lactic acid concentration and the resulting challenging rectification, as shown in Fig. 4. Conversely, a decrease in the fractional conversion of the fermentation leads to a shallow increase in COM, resulting in a lower product stream and an increase in waste streams. The results show that for the recovery process, enzymatic hydrolysis is a crucial step in the process. Enzyme engineering is thus essential to obtain an efficient overall process. For the upcycling process, the biological systems (enzymes, bacteria) are not as decisive. The highest COM for the recovery and upcycling process is 11.7 € kg_{LA}^{-1} and

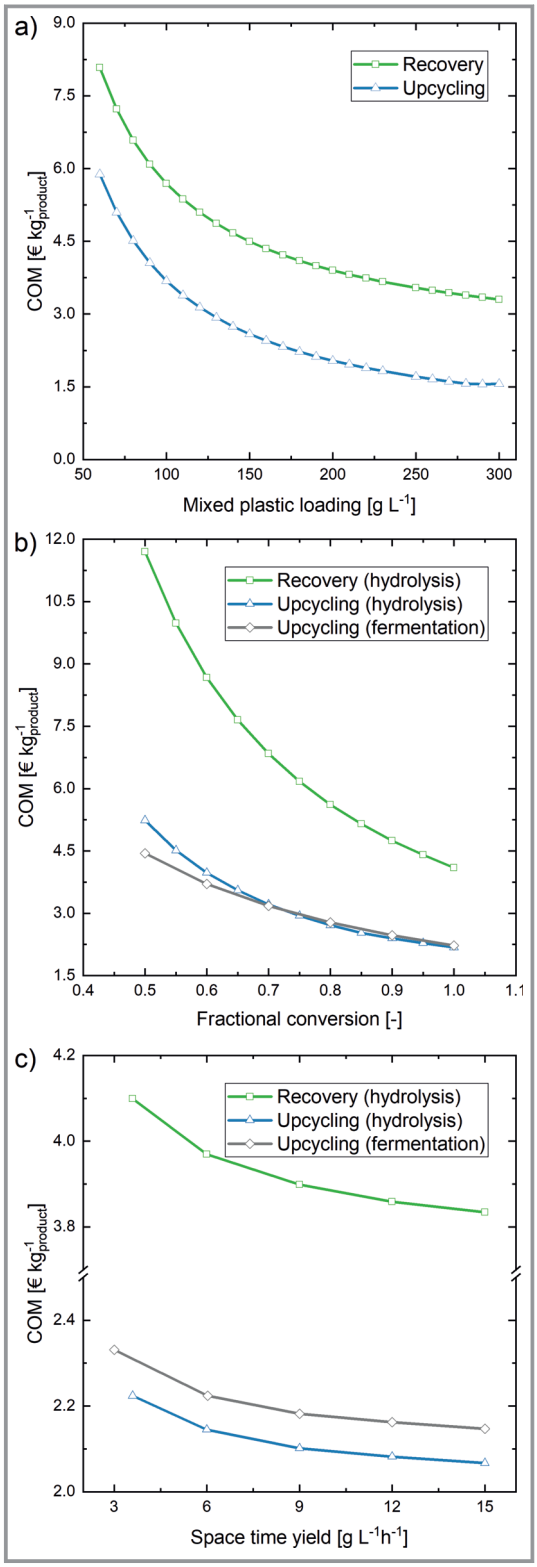

Figure 8. Sensitivity analysis: a) mixed plastic loading in the feed stream, b) fractional conversion in the hydrolysis and fermentation, c) space-time yield (STY) of hydrolysis and fermentation.

5.2 € kg_{SA}^{-1}, respectively. A conversion of >90 % is therefore desirable.

Fig. 8c displays the sensitivity of COM depending on the space-time yield. The space-time yield is relevant because a higher space-time yield results in smaller reactor volumes reducing the capital costs. The capital expenses for the hydrolysis reactor account for about 0.41 € kg_{LA}^{-1} of the recycling and 0.22 € kg_{SA}^{-1} of the upcycling CAPEX costs. The fermentation CAPEX contributes an additional 0.15 € kg_{SA}^{-1} to the COM. Therefore, a rational target for space-time yield optimization appears to be in the range of 6–9 g $L^{-1}h^{-1}$. This value seems feasible because a space-time yield of 6.02 g $L^{-1}h^{-1}$ was already obtained in the literature [30].

Using an MP feed, including PET, comes with challenges in both processes. Ethylene glycol resulting from hydrolyzed PET is an impurity requiring a second rectification column in the recovery process. In the upcycling process, digesting PET and its monomers to succinic acid produces CO_2 increasing the carbon footprint of the succinic acid. Therefore, both processes are simulated with a 90 % PLA feed stream consisting of 90 wt % PLA, 5 wt % PET and 5 wt % PP, and their COM are shown in Fig. 9. The COM of the recovery process is significantly reduced to 3.08 € kg_{LA}^{-1} due to an easier separation problem in the first rectification column and avoiding the second rectification column. In the upcycling process, the COM remains roughly constant. However, the net carbon stream is −0.03 $kg_{CO2}kg_{SA}^{-1}$ neglecting CO_2 emissions of utilities, as can be seen in Fig. 9b.

4 Conclusion

Plastic recycling by hydrolysis with subsequent lactic acid recovery or upcycling to succinic acid is techno-economically analyzed by modeling both processes in Aspen. The base scenario showed a clear advantage of the biotechnological upcycling of mixed plastic waste over the recovery. Enzymatic recycling requires plastic feedstock with high PLA content, while biotechnological upcycling can process mixed plastic feedstock. High plastic loadings of 150–250 g L^{-1} of valorizable carboxylates are desirable in both cases to avoid costly separation. Process optimization should focus on energy integration, improving space-time yields of hydrolysis and fermentation, and alternative downstream technologies that overcome the usage of auxiliary chemicals and avoid the co-production of gypsum. In addition, the economic perspective of recycling technologies would improve if all other monomers released in the hydrolysis were recovered as well. Space-time yields of 6–9 g $L^{-1}h^{-1}$ should be achieved to reduce the equipment costs for enzymatic hydrolysis and fermentation. Next, alternative downstream technologies must be developed to overcome the co-production of solid waste and enable the reuse of process water. If the consumption of auxiliary

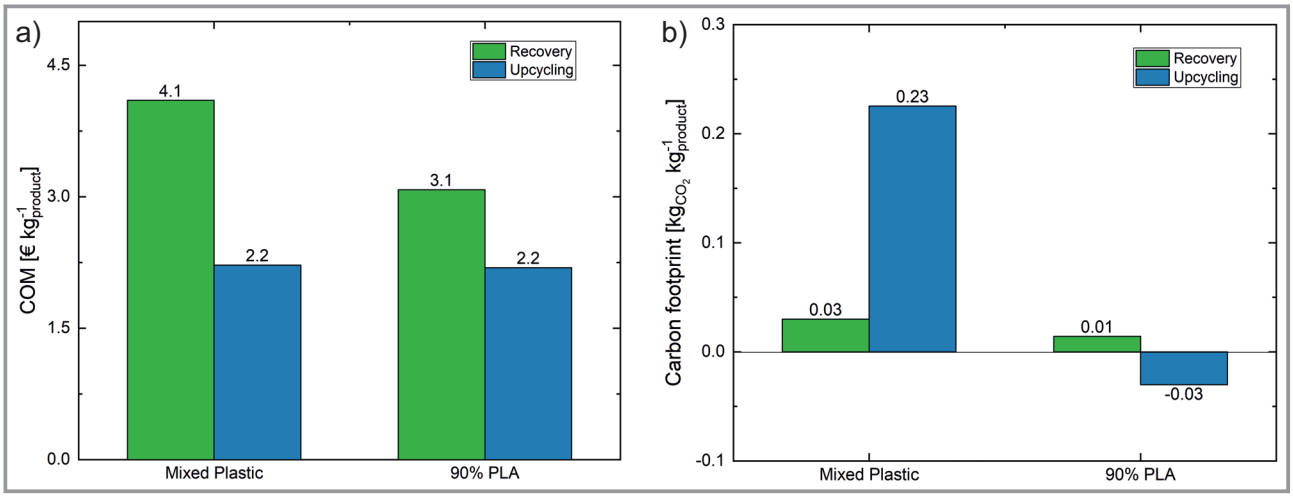

Figure 9. a) Comparison of the COM for the mixed plastic feed stream and the 90 % PLA feed stream, b) carbon footprints without utilities for the mixed plastic and 90 % PLA scenario.

chemicals and waste disposal is eliminated, savings of up to 27 % of the COM for succinic acid are expected. Consequently, biotechnological upcycling could produce succinic acid from mixed plastic waste at lower prices than petrochemically sourced succinic acid. If 90 % PLA feedstock is used and carbon-neutral utilities are available, the fixation of CO_2 in the fermentation can offset carbon emission from the process and enable carbon-negative production of succinic acid.

Supporting Information

Supporting Information for this article can be found under DOI: https://doi.org/10.1002/cite.202300021. This section includes additional references to primary literature relevant for this research [50–62].

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Abbreviations

CaLa	Calcium lactate
CAPEX	Capital expenditure
CaSu	Calcium succinate
COM	Cost of manufacturing
EG	Ethylene glycol
HCE	Hard coal equivalent
LA	Lactic acid
MP	Mixed plastic
OPEX	Operational expenditure
PET	Polyethylene terephthalate
PLA	Polylactic acid
PP	Polypropylene
SA	Succinic acid
TA	Terephthalic acid
TEA	Techno economic assessment
VLE	Vapor-liquid-equilibrium

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