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The metabolic potential of plastics as biotechnological carbon sources – Review and targets for the future

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ABSTRACT

The plastic crisis requires drastic measures, especially for the plastics' end-of-life. Mixed plastic fractions are currently difficult to recycle, but microbial metabolism might open new pathways. With new technologies for degradation of plastics to oligo- and monomers, these carbon sources can be used in biotechnology for the upcycling of plastic waste to valuable products, such as bioplastics and biosurfactants. We briefly summarize well-known monomer degradation pathways and computed their theoretical yields for industrially interesting products. With this information in hand, we calculated replacement scenarios of existing fossil-based synthesis routes for the same products. Thereby, we highlight fossil-based products for which plastic monomers might be attractive alternative carbon sources. Notably, not the highest yield of product on substrate of the biochemical route, but rather the (in-)efficiency of the petrochemical routes (*i.e.*, carbon, energy use) determines the potential of biochemical plastic upcycling. Our results might serve as a guide for future metabolic engineering efforts towards a sustainable plastic economy.

1. Introduction

The world-wide plastic crisis is real. With 4.8 billion tons of plastic in poorly managed landfills (Geyer et al., 2017), with close to 400 Mt of new plastic produced in 2020 (Hundertmark et al., 2018a), and with less than 10% of this new plastic recycled even once (less than 1% recycled twice (Geyer et al., 2017)), we face a daunting challenge. While plastic in the environment reached the public debate in many countries, the outlook is dim: Borelle et al. tell us that even in a react-now scenario ("ambitious"), 20 to 50 Mt of plastic will be disposed into aquatic ecosystems every year by 2030 (Borrelle et al., 2020). Another challenge of the ever-increasing plastic use, reaching 1000 Mt by 2050 (Hundertmark et al., 2018a), is the use of fossil resources. Indeed, the chemical industry is estimated to have the highest growth rates for fossil resources by 2030 (International Energy Agency, 2018). The resulting annual greenhouse gas emissions would reach 6.5 Gt CO_2 equivalents by 2050 (Zheng and Suh, 2019). Surely, the overall challenge cannot be changed by the dismal contribution of clearly less than half a percent of plastic produced from renewable carbon sources, *i.e.*, biomass, CO_2 (plus green hydrogen in the future (Blank et al., 2020)), and waste streams yet. However, sugar as carbon source is gaining momentum, *e.g.*, for polylactic acid (PLA) produced from lactic acid (LA). A new PLA production plant is announced by TotalCorbion to be built in Europe, with a yearly production capacity of 125,000 t PLA, and other developments around the world, especially in China. The production capacity of microbial polyesters (poly-3-hydroxybutyrate (PHB) and polyhydroxyalkanoates (PHA) of various monomer compositions) are in the 5000 tonnes per annum range (*e.g.*, Kaneka, Danimer Scientific). While it is exciting to see that bioplastic finally excels, the absolute contributions to the plastic

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Abbreviations:

1,4-Butanediol BDO
2,4-Toluenediamine TDA
2,5-Furandicarboxylic acid FDCA
4,4′-methylenedianiline MDA
Acrylonitrile butadiene styrene ABS
Adipic acid AA
Biochemical recycling BC
Bis-(2-hydroxyethylterephthalate) BHET
D-Lactic acid LA
Ethylene glycol EG
Global warming impact GWI
Hydroxyalkanoyloxy alkanoate HAA
Hydroxymethylfurfural HMF
Methylene diphenyl isocyanate MDI
Mono-(2-hydroxyethylterephthalate) MHET
Poly-3-hydroxybutyrate PHB
Polyamide 6 PA 6
Polyamides PA
Polybutylene adipate terephthalate PBAT
Polybutylene succinate PBS
Polybutylene terephthalate PBT
Polycarbonate PC
Polyethylene PE
Polyethylene furanoate PEF
Polyethylene terephthalate PET
Polyhydroxyalkanoates PHA
Polylactic acid PLA
Polymethyl methacrylate PMMA
Polypropylene PP
Polystyrene PS
Polyurethanes PUR
Polyvinyl chloride PVC
Succinic acid SA
Terepththalic acid TPA
Toluene diisocyanate TDI
Tricarboxylic acid TCA
Waste treatment WT

market are currently very small.

Emergence of a sustainable plastics economy will strongly rely on fair pricing, *e.g.*, of CO_2 including its climate impact, as implemented for other industrial sectors in the EU Emissions Trading System. Wei et al. argued in a recent commentary for a zero fossil resource plastic economy, relying on the "6 R" principles - rethink, refuse, reduce, reuse, recycle, and replace (Wei et al., 2020). Such a future plastic economy would partially rely on biotechnological technologies for production and end-of-life plastic treatment (Lee et al., 2011). Importantly, all plastic that might end up in the environment should be equipped with an emergency degradation mechanism, which overcomes the observed accumulation of plastic waste in the environment. Rubber, in form of tiny particles from tire wear might be such an example, as it is estimated that in Germany alone, 100,000 tonnes per annum are lost into the environment, while no major accumulation/sinks are known to date. Indeed, a half-life of about 16 months was reported (Cadle and Williams, 1980) and vulcanized rubber is known to be biodegradable (Rose and Steinbüchel, 2005), indicating such an emergency degradation. While atmospheric oxidation seems the main mechanism, two evolutionary different enzyme systems are known that can attack the double bond in rubber (Yikmis and Steinbüchel, 2012; Jendrossek and Birke, 2019; Birke et al., 2018). Reliable studies that quantify the fate of tire wear in the environment are however urgently needed.

While environmental plastic degradation is discussed for decades and examined for example by ISO norms ISO/DIS 23832 and ISO 14855–2, the degradation to oligomers and monomers for use as substrate for microbes has received less attention. In 2018, the European Union established the "European Strategy for Plastics in a Circular Economy", funding plastic-based biotech. In this framework, the MIX-UP project focuses on changing the traditional linear value chain of plastics to a sustainable, biodegradable based one (Ballerstedt et al., 2021). Here, we briefly summarize the state-of-the-art of two alternative technologies to obtain oligomers and monomers: 1. Enzymatic plastic degradation and 2. Plastic degradation by pyrolysis. We are aware of the intensive efforts on chemical plastic recycling (Ellis et al., 2021; Vollmer et al., 2020; Weckhuysen, 2020), with exciting examples like combined polymer degradation and monomer hydrogenation (hydrogenolysis) of polyethylene terephthalate (PET) and PLA to the corresponding diols (Westhues et al., 2018). The chemical advance in PET recycling culminated in rapid hydrolysis at room temperature, a catalytic challenge that was not expected to be solved so rapidly or at all (Tanaka et al., 2021). In addition, some modified PE-like polymers were suggested, with performance parameters much resembling PE, however equipped with activatable bonds for novel end-of-life options (Baur et al., 2021; Häußler et al., 2021). Chemical plastic recycling advances are, however, not in the scope of this review.

Here, we evaluate the potential of plastic monomers as microbial substrates. With the molecular constituents of potential plastic hydrolysates in hand, we summarize their catabolic pathways and compute the theoretical yields for the production of common or potential biotechnology products (Fig. 1). Finally, we use these theoretical biochemical yields to compute replacement scenarios of products currently produced from fossil resources. The results might guide future metabolic engineering efforts, in which plastic waste is used for upcycling to generate (plastic) value. In addition, the results also highlight the shortcoming of some of the investigated native biochemical pathways and argue for synthetic pathways that support chemical synthesis routes with attractive substrate-to-product yields.

2. Polymers to monomers

In recent years, biotechnological approaches have been proposed as sustainable alternative for plastic recycling (Wei et al., 2020). The simplest mechanism for depolymerizing plastics is the direct microbial depolymerization of the polymer, which can also occur in environments contaminated with plastic. For more recalcitrant polymers like PET, enzymatic depolymerization requires dedicated enzyme reactors under specific working conditions like increased temperatures. Polymers containing highly recalcitrant C–C bonds in their backbones for which no dedicated enzymes are reported (yet), might be degraded over time by unspecific oxidases (*e.g.*, laccases, peroxidases), however at very low rates or not at all depending on the environmental conditions. These plastics can be depolymerized technically by, *e.g.*, pyrolysis, obtaining a condensate, the pyrolysis oil. In the following section, these different methods are described, starting with microbial degradation and progressing *via* enzymatic cleavage to pyrolytic plastics degradation.

2.1. Microbial depolymerization

Microbial depolymerization usually does not yield monomers for subsequent processing, since microbes take up the monomers directly and generate biomass and CO_2. We will in this section only focus on the depolymerization and the formation of the respective monomers (Table 1).

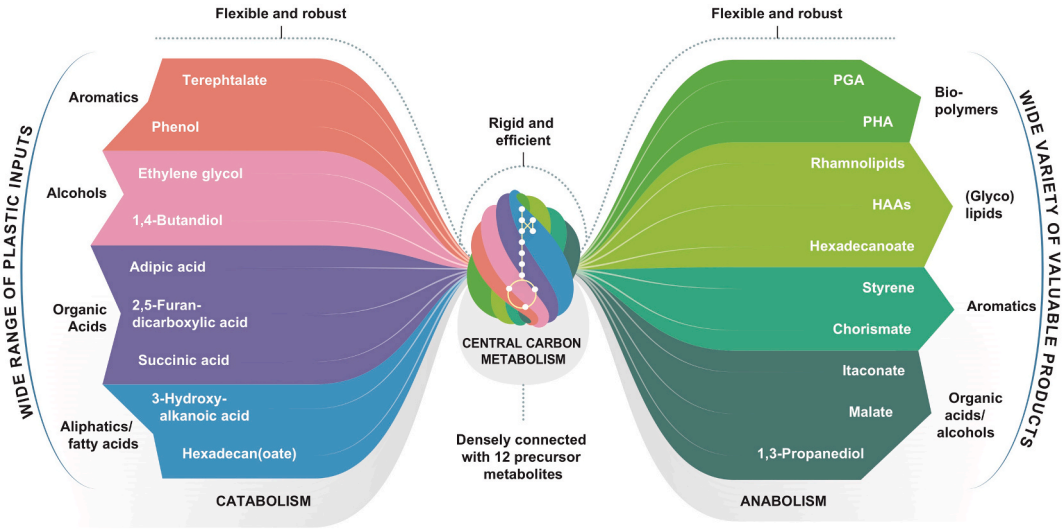

Fig. 1. The bow tie of microbial metabolism. The flexibility of the microbial metabolic arsenal facilitates the conversion of plastic monomers to valuable products. While the central carbon metabolism is rigid, the catabolic (left) and anabolic (right) pathways show a high versatility and are amenable to metabolic engineering. This versality allows researchers to modify microorganisms for the usage of many different monomers from post-consumer plastic waste for the production of a plethora of industrially interesting compounds. The groups of substances on the substrate side include monomers from industrially relevant polymers and represent a selection (*e.g.*, amines are missing). The products are industrially interesting molecules, already synthesized or suggested to be synthesized using microbes. PGA – polyglutamic acid, PHA – polyhydroxyalkanoates, HAA – hydroxyalkanoyloxy alkanoate.

Table 1
Monomers from microbial deconstruction of biodegradable polymers.

Polymer	Monomers	Refs
Polyhydroxyalkanoates	3-hydroxyalkanoic acid	Chowdhury (1963)
Polybutylene succinate	1,4-butanediol, succinic acid	Tokiwa et al. (2009)
Polybutylene adipate terephthalate	1,4-butanediol, adipic acid, terephthalic acid	Utomo et al. (2020)
Polylactic acid	D-lactic acid, L-lactic acid	Zaaba and Jaafar (2020)

Polymer utilization by microbes is so common that we usually do not give it any attention, especially for sugar polymers like cellulose or aromatic polymers like lignin. While these processes occur in nature, the technical realization of the lignocellulosic polymer degradation and subsequent monomer utilization still waits for its economic breakthrough, despite huge efforts in the last decades. This is in no small part due to the recalcitrance and complexity of lignocellulosic biomass as biotechnological substrate, requiring harsh pretreatment and complex enzyme cocktails to be degraded at biotechnologically relevant rates.

In contrast, starch is effectively used as biotechnological feedstock at very large scale due to its ease of purification and simpler structure (Mussatto et al., 2010). These features enable biotechnological utilization of plastics as carbon source, since purity and bioavailability of starch are similar to biodegradable polymers such as PHA, polybutylene succinate (PBS), polybutylene adipate terephthalate (PBAT), and polylactic acid (PLA). Starch is also widely used as biodegradable polymer for packaging and consumer goods (nova-Institute, 2020). Microbes able to degrade and assimilate polymers traditionally considered non-biodegradable were rarely found (Ru et al., 2020), although also in this field much development is ongoing. One example is the already iconic *Ideonella sakaiensis* isolate, which can depolymerize amorphous PET and grow partly on the released monomers, albeit very slowly (Yoshida et al., 2016). While the literature is full with reports on microbial plastic degradation including recalcitrant carbon-carbon bond containing plastics, the details are rarely encouraging. A recent study from Kim et al. (2021) suggested *Acinetobacter* and *Pseudomonas* strains that are capable of polystyrene degradation.

2.1.1. *Polyhydroxyalkanoates (PHA)*

PHAs are polyesters with side chains of different lengths: A short chain length PHA is for example PHB, while medium chain length PHAs feature side chains with six to fourteen carbon atoms. PHA polymers are thermoplastic and can be processed on conventional processing equipment (Cataldi et al., 2020), with potential applications in various fields such as biomedicine including tissue engineering, bio-implants, and drug delivery (Raza et al., 2018). Despite decades of research, the total global production capacity of PHAs is sub 50,000 tonnes per annum. That said, a rapid increase is envisaged due to technology readiness, CO_2 neutrality, and demand for degradable plastics. Since PHAs are internal carbon storage polymers in many microorganisms, the ability to metabolize PHAs is essential for PHA producers. However, post-consumer PHA is obviously available only extracellularly. The ability to degrade extracellular PHAs depends on extracellular carboxylesterases called PHA depolymerases (Jendrossek and Handrick, 2002; Lee and Choi, 1999), which not all PHA producers feature. While the commonly used PHA producer *Pseudomonas putida* KT2440 for example does not have an extracellular PHA depolymerase (de Eugenio et al., 2007), microbes such as the bacterial predator *Bdellovibrio bacteriovorus* possess such an enzyme (Martinez et al., 2012). The monomer resulting from PHA depolymerization is the respective hydroxyalkanoic acid, a potential substrate of β-oxidation in many microbes (see also below).

2.1.2. *Polybutylene succinate (PBS)*

The applications of PBS overlap partially with polypropylene, however usually with less favorable physical properties. For PBS synthesis, an excess of 1,4-butanediol (1,4-BDO) is used in the first step to obtain

BS oligomers. These oligomers are transesterified to high molecular weight PBS under vacuum and in the presence of a chemical catalyst. The world market of PBS is about 80,000 tonnes per annum (nova-Institute, 2020), while substantial investments have been announced in the first two months of 2021 in China alone, adding an additional 900,000 tonnes per annum in the coming years (news from Hengli Petrochemical Co., Ltd.). This rapid development is due to policy changes in China, specifically from "plastic restriction order" to "plastic prohibition order", which force products made of non-degradable plastic like current bags and disposable plastic tableware gradually out of the market, leading to rapid growth of the same products from degradable plastic. Huge metabolic engineering efforts resulted in market-ready production of 1,4-BDO (Burgard et al., 2016) and succinic acid (SA) (Chae et al., 2020) from renewable carbon sources. Still, most PBS monomers are synthesized by chemocatalysis from fossil resources.

PBS is considered biodegradable (Tokiwa et al., 2009) and this degradation can be rapid. Under laboratory conditions, a thermophilic *Microbispora rosea* strain degraded 50% of the PBS in eight days (Jarerat and Tokiwa, 2001). As described for other polyesters, esterases and cutinases show activity on PBS, while this activity depends heavily on polymer accessibility and the other physical conditions during hydrolysis. The resulting monomers 1,4-BDO and especially succinate are readily used as carbon source by many microbes (see monomer description below).

2.1.3. Polybutylene adipate terephthalate (PBAT)

PBAT is used in niche applications, in which biodegradation is practical, *e.g.*, in mulching films, often in a mix with plastics like PLA. PBAT is synthesized in two reactions from the monomers 1,4-BDO, adipic acid (AA), and terephthalic acid (TPA). The two intermediates 1,4-BDO/AA polymer and 1,4-BDO/TPA polymer are transesterified to the corresponding co-polymer (Jian et al., 2020). This random co-polymerization explains also why PBAT has no crystalline nature and is therefore accessible for enzymatic degradation. The world market was about 280,000 t in 2020 (nova-Institute, 2020), however, in the recent months, construction of an additional 600,000 tonnes per annum capacity was announced, again mainly driven by policy changes in China. While 1,4-BDO and AA can be biotechnologically produced, chemocatalysis from fossil resources still dominates.

The degradation of PBAT has been reported by enzymes like esterases (Wallace et al., 2017) and cutinases (Soulenthone et al., 2021), but also by single microbes (Soulenthone et al., 2021) and aerobic (Meyer-Cifuentes et al., 2020) or anaerobic (Perz et al., 2016) microbial consortia. Indeed, PBAT is hydrolyzed under favorable conditions like industrial composting in 60 days or even faster (Müller et al., 2001). PBAT-PLA mulching films can be left by the farmer on the field also in moderate climate, as biodegradation takes place under non-favorable conditions, although at a considerably lower rate (Kijchavengkul et al., 2008). The monomers can be utilized by microbes as sole carbon sources (Utomo et al., 2020) (see below for details).

2.1.4. Polylactic acid (PLA)

The basic mechanical properties of PLA are between those of polystyrene (PS) and PET (Lunt, 1998). While PLA can be directly synthesized by microbes (Jung et al., 2010a), the main production route is *via* chemical polymerization of microbially produced monomers. About 90% of the world-wide produced LA is derived from microbial fermentations. The production of PLA is estimated to be at least 800,000 tonnes per annum by 2020 with Japan and the USA being the two major producers (Karamanlioglu et al., 2017). The construction of 125,000+ tonnes per annum installations are announced in France and China. Being an aliphatic polyester, PLA is in principle susceptible to biodegradation, and this biodegradability and other properties can be tuned by addition of glycolic acid as co-monomer (Jem and Tan, 2020). In recent years, a few thousand studies on enzymatic and microbial degradation have been published (Zaaba and Jaafar, 2020). Several microbial species are able to degrade PLA. Usually, degradation is initiated by excreted depolymerases and subsequent uptake and metabolization of oligomers, dimers, and monomers (Zaaba and Jaafar, 2020). However, in comparison to other biodegradable materials, PLA is more recalcitrant, which results in inefficient microbial degradation (Qi et al., 2017). Enzymatic degradation of PLA is catalyzed by lipases, esterases, and proteases such as alcalases resulting in the release of LA (Zaaba and Jaafar, 2020). While degradation of PLA in natural conditions (*e.g.*, in soil) is very slow, composting under industrial conditions is significantly faster (Ho et al., 1999).

2.2. Enzymatic plastic degradation

As mentioned before, microbes able to degrade and assimilate synthetic polymers were rarely found and furthermore feature very low degradation rates. The history of plastic waste in the environment is with less than 100 years short. Natural evolution for the emergence of degradation mechanisms happens on significantly longer timespans. Thus, for polymers with very low bioavailability the adaption of the microbial metabolic clusters appears to be not fully triggered (Bornscheuer, 2016; Krueger et al., 2015). Consequently, identified microbial enzymes with notable depolymerization activities are likely still the result of moonlighting activities, mainly limited to those active on polyesters or other heteroatomic polymers with ester bonds (for example, polyester polyurethanes (PUR)) (Wei and Zimmermann, 2017a; Danso et al., 2018; Jönsson et al., 2021). Monomers released during enzymatic plastic degradation are diverse (Table 2).

2.2.1. Polyethylene terephthalate (PET)

As the most widely used polymer type in beverage bottles and synthetic fibers, PET can be synthesized by condensation reactions that start with the monomeric compounds TPA and ethylene glycol (EG). Both monomers can be readily produced by a hydrolytic reaction of amorphous PET using various enzymes (Wei and Zimmermann, 2017b). The first reported polyester hydrolase with considerable depolymerization activity on bulky PET was a cutinase (TfH) identified in the thermophilic actinomycete *Thermobifida fusca* (Müller et al., 2005). Using 0.5 mg purified TfH, up to 54% weight loss from approximately 20 mg melt-pressed PET bottle waste (10% crystallinity) was achieved within 3 weeks of incubation at 55 °C. This corresponds to a depolymerization rate of 0.043 $mg_{PET}\ h^{-1}\ mg_{enzyme}{}^{-1}$ by converting PET polymer into TPA and EG at an enzyme concentration of 25 mg per gram of PET ($mg_{enzyme}\ g_{PET}{}^{-1}$). Further studies gradually increased this conversion rate to 9.3 $mg_{PET}\ h^{-1}\ mg_{enzyme}{}^{-1}$ using homolgous *T. fusca* cutinases (Wei et al., 2014) based on either engineered process with ultrafiltration (Barth et al., 2015) or engineered enzyme variants with improved activities (Wei et al., 2016; Furukawa et al., 2019). More recently, thermostable T. fusca cutinase expressed in *Bacillus subtilis* has depolmyerized low-crystalline post-consumer PET packaging at 70 °C at a rate of >3 $mg_{PET}\ h^{-1}\ mg_{enzyme}{}^{-1}$ (Wei et al., 2019a). A higher reaction temperature up to 75 °C was found to be favorable for PET degradation as a result of

Table 2
Possible monomers arising from enzymatic depolymerization.

Polymer	Monomers	Refs
Polyethylene terephthalate	Ethylene glycol, terephthalic acid	Wei & Zimmermann, 2017b
Polyethylene furanoate	Ethylene glycol, 2,5-furandicarboxylic acid	Austin et al., 2018; Weinberger et al., 2017
Polyurethanes	Adipic acid, 2,4-toluenediamine, 4,4′-methylene dianiline, 1,4-butanediol, diethylene glycol, 6-hydroxyhexanoic acid	Magnin et al., 2019b, 2020
Polyamides	Adipic acid, azelaic acid, sebacic acid, suberic acid, hexamethylenediamine, 6-aminohexanoate	Kinoshita et al., 1981; Kakudo et al., 1993

increased polymer chain mobility (Falkenstein et al., 2020; Wei et al., 2019b). This is also evident because, for example the *I. sakaiensis* PET hydrolase (*Is*PETase) with an optimal reaction temperature at 40 °C showed at least two orders of magnitude lower specific activities in degrading the Gf PET films than its thermophilic counterparts active at 65 °C (Tournier et al., 2020). Among these thermostable and -active PET hydrolases, the leaf compost metagenome-derived cutinase LCC (Sulaiman et al., 2012) was found to be the superior biocatalyst as evidenced by the outstanding stability and activity against various amorphous PET materials of the wild-type enzyme at 70 °C (Falkenstein et al., 2020; Wei et al., 2019b; Sulaiman et al., 2014; Tiso et al., 2021). By semi-rational protein engineering, the powerful LCC variant ICCG has been created recently and revealed a maximum depolymerization rate of above 120 $mg_{PET}\ h^{-1}\ mg_{enzyme}{}^{-1}$ against amorphized post-consumer PET bottles, corresponding to a maximum productivity of 42 g of TPA per liter per hour (Tournier et al., 2020). This rate was equivalent to a >2800-fold improvement compared to that with TfH against similarly pretreated PET waste as reported in 2005. Moreover, the TPA was readily recovered and purified and finally proven to deliver a comparable product quality in the synthesis of virgin PET as those obtained with petroleum-derived TPA, thereby closing the recycling loop. Alternatively, the PET hydrolysates obtained with LCC have been used as carbon source for engineered *P. putida* to produce other value-added chemicals by enabling the one-pot use of both TPA and EG, also providing options for open-loop upcycling (Tiso et al., 2021; Meys et al., 2020).

2.2.2. Polyethylene furanoate (PEF)

During the last decade, PEF, a polyester synthesized from 2,5-furandicarboxylic acid (FDCA), has received attention from both scientific communities and industry as a bio-based alternative to PET, both for the fossil fuel saving purpose, and for superior polymer properties (Eerhart et al., 2012). As a result of the reduced flexibility of the furan moieties in PEF, a higher glass transition temperature and corresponding lower chain mobility has been determined in PEF compared to PET (Burgess et al., 2014). Nevertheless, using both the mesophilic *Is*PETase variants and thermophilic PET hydrolyzing cutinases, enzymatic hydrolysis of PEF has yielded comparable or even higher amounts of the degradation product FDCA compared to those determined with specifically synthesized PET samples in a similar manner (Austin et al., 2018; Weinberger et al., 2017). These results confirmed the broad applicability of various PET hydrolases also for a future scenario. Due to the lack of market-mature PEF products, a biotechnological process for recovered monomers from PEF is, however, still subject of ongoing research, although much can be learned from works focused on the biotechnological production of FDCA in this respect (Saikia et al., 2021).

2.2.3. Polyurethanes (PUR)

Due to the more recalcitrant bonds in PUR (*e.g.*, carbamate, amide and ether bonds), these polymers have so far not been completely depolymerized enzymatically. To date, solid experimental studies overwhelmingly report enzymes cleaving the ester bonds in polyester PUR. Recent reviews summarize the latest findings, including the use of ureases and amidases/proteases for PUR depolymerization (Magnin et al., 2020; Skleničková et al., 2020; Kemona and Piotrowska, 2020; Liu et al., 2021).

The versatility of PET-hydrolyzing cutinases has for example been verified for the degradation of polyester PUR as well as for other petrochemical polymers containing ester bonds (Schmidt et al., 2017; Bollinger et al., 2020). With the superior enzyme LCC, 3.2% weight loss of a commercial thermoplastic polyester PUR was determined following 100 h degradation at 70 °C. This corresponds to a degradation rate of approximately 0.5 $mg_{PUR}\ h^{-1}\ mg_{enzyme}{}^{-1}$, which is at least one order of magnitude lower than those with PET described above. The degradation of the urethane bond was reported in a recent patent (EP3587570A1), while the amide bond could be partially degraded using enzymes from fungi (Magnin et al., 2019a, 2020). However, these enzymatic activities were so far still verified with small-molecule PUR model compounds rather than bulk polymers. Various analytic approaches have been applied in the identification of PUR degradation products (Magnin et al., 2019b). Nonetheless, due to the highly variable chemical compositions and polymer structures of commercial PUR products which confine their biodegradability, processes aiming at the recovery and purification of specific PUR monomers derived from biocatalytic upcycling have not been yet well established.

2.2.4. Polyamides (PA)

PA can consist of various aliphatic, semi aromatic, and aromatic units leading to a variety of natural and synthetic polymer types. Among the latter, aliphatic PA such as PA 6 (polycaprolactam, Nylon-6), PA 6.6 (polyhexamethylene adipamide) or PA 6.12 (polyhexamethylene dodecanediamide) are most prominent and mainly used in the textile and automotive industry (Palmer, 2001). Due to the vast number of PA types, many different monomers might be released by enzymatic degradation that could be used as substrates for microbial growth. Depending on the PA, three groups of monomers are expected as degradation products: dicarboxylic acids (such as AA), diamines (such as hexamethylenediamine) and amino acids (*e.g.*, 6-aminohexanoate). Although amide bonds are common in nature, the biodegradation of high molecular weight PA is very rare. To our current knowledge, a manganese-dependent peroxidase (MnP) that was purified from a white rot fungus is the only enzyme reported to degrade high molecular weight PA fibers and membranes (Deguchi et al., 1998). Interestingly, the reaction mechanism for PA degradation partly differs from that reported for lignin-degrading MnPs. Nonetheless, enzymatic degradation of PA by MnP probably occurs in an unspecific way resulting in occasional chain-scission rather than depolymerization of the polymer.

In contrast, three so-called nylonases were identified in *Arthrobacter* sp. KI72, isolated from sludge near a PA 6 manufacturing plant that specifically degraded cyclic and linear 6-aminohexanoate (Ahx) oligomers. NylA (KEGG, EC 3.5.2.12) was found to convert a cyclic dimer into a linear dimer, showing no activity towards longer cyclic or linear oligomers (Kinoshita et al., 1977; Yasuhira et al., 2010). Ahx linear oligomers were hydrolyzed by NylB (KEGG, EC 3.5.1.46) *via* an exo-type hydrolysis or by the endo-acting NylC (KEGG, EC 3.5.1.117) (Kinoshita et al., 1981; Negoro et al., 1992). NylB showed highest activity towards the linear dimer, generating Ahx. The activity decreased with increasing chain-length of linear oligomers resulting in a relative activity of 8% on the hexamer and 0.3% on the icosamer compared with the linear dimer (Chibata et al., 1982). NylC degraded Ahx linear oligomers with a degree of polymerization >3 with a preference for the pentamer, and also showed activity towards the Ahx cyclic tetramer (Kakudo et al., 1993, 1995). Enzyme engineering has led to a thermo-stabilized NylC that was able to degrade thin-layered PA 6, PA 6.6, and PA 6.6-co-6.4 in which succinyl units were incorporated (Negoro et al., 2012; Nagai et al., 2014). Hence, nylonases are promising candidates for further enzyme engineering approaches to design highly efficient PA depolymerases.

2.3. Pyrolytic plastic degradation

Purely biotechnological approaches are not suited for depolymerizing polymers more recalcitrant than the ones described so far (*e.g.*, polyethylenes and polypropylenes with their stable carbon-carbon bonds). In this case, interdisciplinary approaches are required that combine highly efficient thermochemical or catalytic depolymerization methods with microbial metabolization. One example for such an efficient depolymerization method is pyrolysis.

Pyrolysis describes the endothermic process of thermochemical decomposition of material in the absence of oxygen or in an atmosphere of inert gases (Buekens and Meyers, 2012; Panda et al., 2010). Due to increased temperature and heat applied, drying, evaporation, degassing, and chemical cracking processes occur consecutively (Scholz et al., 2001). The decomposition process is characterized by a high complexity

of the occurring reactions and mechanisms, which are discussed to depend mainly on the molecular structure of the raw materials. The proportion of solid, condensable, and gaseous products depends strongly on operating parameters such as temperature, heating rate, residence time (gas and solid), and reactor design (Buekens and Meyers, 2012; Quicker, 2020).

Degrading organic macromolecules like plastics into smaller molecules or oligomers and monomers, requires temperatures above 350 °C. Polyolefins, such as polyethylene (PE) and polypropylene (PP) attain a maximum rate of decomposition at ca. 450 °C. Higher temperatures generate on average shorter chain fragments, as cracking is targeted at chain ends first, and then successively proceeds along the polymeric length (Buekens and Meyers, 2012; Panda et al., 2010).

The derived solid residue contains inorganic components (*e.g.*, mineral impurities, fillers from plastics) and carbonized char of high calorific value and carbon content (Czajczyńska et al., 2017). Heavy metals like Cd, Pb, Zn, and Cu concentrate in the solid residues but may also be released partially into the volatile phase at high temperatures and rapid heating rates (Quicker, 2020; Yu et al., 2016). Pyrolysis may also be called 'dry distillation' as the yielded pyrolytic gas can be divided into gaseous products and a condensable fraction of liquid or wax consistency at ambient temperature. In general, the condensate comprises paraffins, olefins, and BTX (benzene, toluene, xylene) aromatic compounds. The presence of oxygen leads to the formation of decomposition water, methanol or formaldehyde (Scholz et al., 2001; Ragaert et al., 2017). The organic phase of the condensate is commonly known as 'pyrolysis oil' and can be further processed into products by distillation and refining steps. The gaseous products consist mainly of permanent gases and a variety of olefin gases (Scholz et al., 2001). Some polymers contain halogens or other possible pollutants that improve the material properties when integrated into the macromolecule. The degradation of polyvinyl chloride (PVC) for example leads to the formation of gaseous hydrochloric acid. Integrated sulphur compounds of other polymers may enter the gas phase in low quantities as hydrogen sulphide or carbonyl sulphide when degraded (Quicker, 2020).

Highly fluctuating product distribution and low reproducibility pose a great challenge to process control for industrial application of pyrolysis if mixed plastic waste streams are processed. Additionally, certain impurities may have a catalytic effect or can inhibit reactions and substantially affect the product distribution and composition (Ragaert et al., 2017). However, pyrolysis of mono-fraction waste streams such as polystyrene (PS), PA, and polymethyl methacrylate (PMMA) can be adapted by optimizing heating and cooling rates to yield products containing mostly their respective monomers recovering high value chemical precursors (Czajczyńska et al., 2017; Lehrle et al., 2000). PA formed by ring-opening can be transformed into its respective monomers for purification and repolymerization, for example, PA 6 to caprolactam (Punkkinen et al., 2017). PE and PP show random chain fragmentation along polymer length resulting in a broad naphtha-like product spectrum characterized by branched chain products (Table 3) (Czajczyńska et al., 2017; Ragaert et al., 2017).

Industrial pyrolysis processes for the thermal treatment of municipal waste have not been able to gain importance due to the significantly lower technology readiness level compared to waste incineration and the higher treatment costs caused by the more complex technical design (Gleis et al., 2018). New developments in legislation make pyrolysis an interesting pre-treatment of specific waste fractions to yield a condensate providing access to a carbon source suitable for further processing. In terms of circular economy, chemical recycling with pyrolysis as pre-treatment could prove to be a method of closing the gap for plastics that cannot be mechanically recycled due to their respective molecular structure, *e.g.*, thermosets. Again, the viable end-of-life scenarios have to take into account the already implemented value chains, thereby evaluating the replacement potentials (Meys et al., 2020). Additionally, pyrolysis could be a possibility to use specific waste fractions as raw material and generate valuable chemicals and precursors for biotechnological upcycling and subsequent use in various industrial and commercial applications.

3. Monomers as substrates for microbes

The previously described methods for plastic depolymerization are effective ways for making plastics accessible for microbial digestion. In many microbes, we can exploit or engineer the bow-tie structure of metabolism (Fig. 1 (Sudarsan et al., 2014; Becker and Wittmann, 2020; Jovanovic et al., 2021),) that enables the use of alternative substrates to fuel the central carbon metabolism, while finally producing, besides biomass, a single product of choice. In the following, we describe metabolic pathways and microbes capable of metabolizing the main monomers identified above. While some monomers (such as SA and octanoic acids) are catabolized in common central carbon metabolic pathways, others require highly specific routes and enzymes, which are not available ubiquitously. To reduce the high number of monomers emanating from the above enumerated depolymerization methods, we focus on the compounds specified in Table 4. For some monomers, we identified more generic proxies, as also stated in the table. In the following, the monomers are sorted by their assimilation into central carbon metabolism (upper glycolysis, β-oxidation, TCA cycle, aromatics degradation pathways).

One specific microbe shown to feature high potential for valorization of many monomers from plastic depolymerization is *P. putida*. This Gram-negative gamma proteobacterium has a very versatile

Table 3
Possible compounds of pyrolysis condensate by thermal degradation.

Plastic polymer	Compounds of pyrolysis condensate	Refs
Polyethylene low density	BTX aromatics, mono- & dimethylbenzene, trimethylbenzene, indane, indene, methylidenes, naphthalene, alkylated naphthalene, acenaphthylene, acenaphthene, fluorene, C4–C60 hydrocarbon: 1-alkenes (>C4) and others	Williams and Williams, 1999; Wampler, 1989
Polyethylene high density	BTX aromatics, cyclohexene, methyl cyclopentene, C4–C60 hydrocarbon: 1-alkenes (>C4) and others (mainly oligomers, with additional amounts of C_{10+4x} oligomers)	Wampler, 1989; Jung et al., 2010b
Polypropylene	BTX aromatics, 2-methyl-1-pentene, 3-methylcyclopentene, higher yield of C4–C13 hydrocarbons (mainly branched), lower yield of >C13 hydrocarbon (mainly branched), Ethylbenzenes, Indene, Biphenyl	Wampler, 1989; Jung et al., 2010b
Polystyrene	Styrene, ethylbenzene, cumene, propylbenzene, 2-ethyltoluene, naphthalene, diphenylmethane, anthracene, 1,2-diphenylethane, 2,2-diphenylpropane, 1,3-diphenylpropane, phenylnaphthalene, diphenylbenzene, triphenylbenzene, BTX aromatics	Onwudili et al., 2009
Polycarbonate	Phenol, 4-methyl-phenol, 2-methyl-phenol, 4-ethyl-phenol, 4-(1-methylethyl)-phenol, 4-isopropenyl-phenol, 4-(1-methyl-1-phenylethyl)-phenol, 4,4'-(1-ethylidene)bis-phenol, 4,4'-(1-methylethylidene)bis-phenol, aromatic and aliphatic hydrocarbons	Antonakou et al., 2014
Polymethyl methacrylate	Methyl methacrylate (>92 wt%)	Panda et al., 2010; Punkkinen et al., 2017
Polyamide 6	Caprolactam (up to 100 wt%)	Lehrle et al., 2000; Punkkinen et al., 2017

Table 4
Monomers arising from plastic degradation and the respective polymers they are generated from. Some monomers are used as proxies for similar molecules in the subsequent section on microbial metabolization.

Representative monomers	Polymers	Proxy for
Ethylene glycol	PET, PEF, PUR	–
D-lactic acid	PLA	–
Styrene	PE, PP, PS, PC	Aromatics
3-Hydroxyoctanoic acid	PHA, PE, PP, PUR	3-Hydroxyalkanoic acids, C4–C13 hydrocarbons
Hexadecan(oat)e	PE, PP, PC	Aliphatics, >C14 hydrocarbons
2,4-Toluenediamine	PUR	4,4′-Methylene dianiline
Caprolactam	PA	6-Aminohexanoate, hexamethylenediamine
Adipic acid	PBAT, PUR, PA	Azelaic acid, Sebacic acid, Suberic acid
Methyl methacrylic acid	PMMA	–
1,4-Butanediol	PBS, PBAT, PUR	–
Succinic acid	PBS	–
2,5-Furandicarboxylic acid	PEF	–
Terephthalic acid	PBAT, PET	–
Phenol	PE, PP, PS, PC	Aromatics

metabolism, enabling the consumption of many different carbon sources. Pseudomonads have so far been engineered to metabolize the PET monomers EG (Li et al., 2019) and TPA (Kenny et al., 2012), as well as some PUR monomers such as AA (Ackermann et al., 2021), 1,4-BDO (Li et al., 2020), and even 2,4-toluenediamine (TDA) (Espinosa et al., 2020). With the example of *P. putida's* metabolic network, catabolic pathways of the here described monomers are shown in Fig. 2.

3.1. Ethylene glycol (EG)

EG was first synthesized in 1856 by Charles-Adolphe Wurtz (1856). Nowadays, EG is produced from ethylene, which in turn originates from petrochemical resources *via* steam cracking of ethane (Pang et al., 2016). A commercial bio-based route *via* ethanol has also been established (Harmsen et al., 2014). In 2019, about 42 Mt of EG were produced worldwide (Garside, 2020), with different applications in a wide range of polyesters (Yue et al., 2012).

So far, various organisms have been described that can use EG as the sole source of carbon and energy under both aerobic and anaerobic conditions (Fincher and Payne, 1962; Gaston and Stadtman, 1963). As has been demonstrated for a variety of different microbes, metabolization happens through the sequential oxidation of EG to glyoxylate (KEGG, R00476) *via* the intermediates glycolaldehyde (KEGG, R01781) and glycolate (KEGG, R01333) (Mückschel et al., 2012). In recent years, efficient metabolization of EG has been implemented in *P. putida*, either by metabolic engineering or by laboratory evolution (Li et al., 2019;

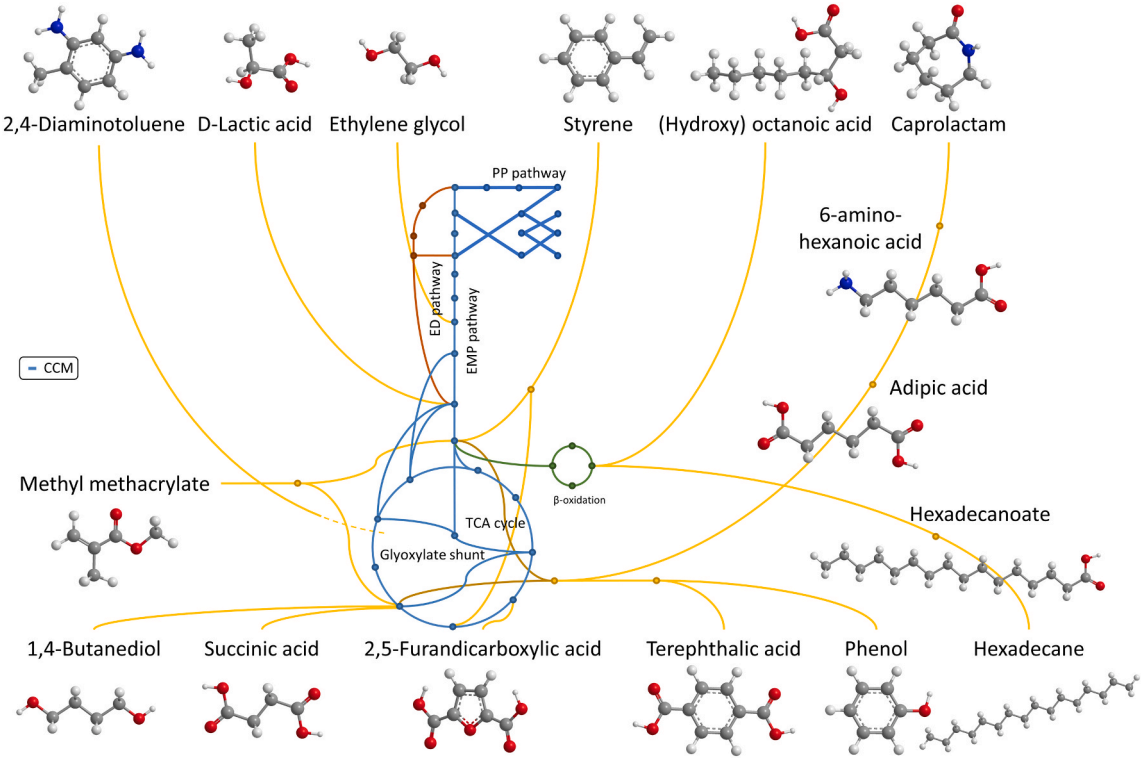

Fig. 2. Metabolization of monomers from plastic depolymerization. The metabolic network of *P. putida* is shown including central carbon metabolism (CCM, blue) as well as some secondary pathways (Entner Doudoroff pathway – brown, β-oxidation - green). The entry points of the metabolization routes of plastic monomers into the central carbon metabolism are shown in yellow. For some monomers, alternative routes exist (see supplementary information "SI Table" for details), but are not shown for a better overview.

Franden et al., 2018). A bottleneck in the above-described sequential oxidation was observed to be the final step from glycolate to glyoxylate. Overexpression of the gene coding for the membrane anchored oxidase GlcDEF removed this restriction. Further, the oxidation reactions should be balanced such that the toxic aldehyde intermediates glycolaldehyde and glyoxal do not accumulate. Another bacterium that has recently been engineered to utilize EG as carbon source was *Escherichia coli* (Pandit et al., 2021; Panda et al., 2021).

For further metabolization of glyoxylate as sole carbon source, two main options exist: 1) Routes only generating redox equivalent and CO_2 and 2) routes that allow the usage of glyoxylate as carbon source. The first being the utilization of glyoxylate by the AceA (KEGG, EC 4.1.3.1) or GlcB (KEGG, EC 2.3.3.9) enzymes involved in the glyoxylate shunt (Li et al., 2019). This route can, at least in part, enable utilization of glyoxylate as carbon source, but only if a co-substrate is provided. For the utilization as sole carbon source, it was discovered that *P. putida* KT2440 features the glyoxylate carboligase (Gcl) enzyme (KEGG, EC 4.1.1.47), converting two glyoxylate molecules into tartronate semialdehyde and CO_2 (KEGG, R00013). The former is converted to glycerate, either directly (KEGG, R01745) or *via* hydroxypyruvate (KEGG, R01394, R01388), and subsequently to the glycolysis intermediate 2-phosphoglycerate (KEGG, R08572) (Franden et al., 2018).

The described pathway from glyoxylate to a central carbon metabolite has a yield of 0.75 mol/mol, as one CO_2 molecule is released. An alternative pathway for EG assimilation without carbon loss has been described by Wiegant et al. (Wiegant and de Bont, 1980). Here, a diol dehydratase generates acetaldehyde from EG, which is converted to acetyl-CoA *via* acetate, but the feasibility of this reaction for metabolic engineering purposes is questionable. The dehydratase is oxygen sensitive, requires vitamin B12, and in its native host, it is part of a much larger context of accessory enzymes and a protein microcompartment that hinder its functional expression in other organisms (Crowley et al., 2010). In a more recent approach, Lu et al. (2019) used enzyme engineering to construct a synthetic pathway from C1 substrates to acetyl-CoA, which can also be utilized for 100% carbon-efficient EG metabolization. Glycolaldehyde is converted to acetyl-phosphate, which is transformed to acetyl-CoA. In a similar approach, Scheffen et al. (2021) enabled the conversion of glycolate and CO_2 to glycerate.

3.2. Lactic acid (LA)

LA has been discovered in history three times in different organisms. It was first isolated by Carl Wilhelm Scheele in 1780 from milk (Parks et al., 2020) and in 1808 discovered in muscles after exertion (Kompanje et al., 2007). Finally, in 1813, Henri Braconnot found out that LA was present in fermented media (Benninga, 1990). Today, an estimated 1.5 Mt of LA are produced (Rodrigues et al., 2017). About 90% is derived from microbial fermentations, traditionally using different *Lactobacillus* strains (Hofvendahl and Hahn–Hägerdal, 2000), while nowadays pH-tolerant bacteria and yeast are used for the production of both stereoisomers, of which L-lactate is dominating the market.

Metabolization of LA involves a single step to form the central metabolite pyruvate (KEGG, R00704) *via* the lactate dehydrogenase (LDH) (KEGG, EC 1.1.1.28). LDH is an enzyme found in nearly all living cells (Tang et al., 2017). However, in general, LDH are utilized for the synthesis of LA. The reverse reaction (*i.e.,* LA oxidation) is commonly considered to be only catalyzed by NAD-independent LDH (Garvie, 1980).

3.3. Styrene

Styrene is one of the few monomers for which the world production stagnates in some years, however at a huge 37 Mt per annum scale (HDIN Research, 2019). Styrene is mainly used for polymerization to polystyrene (PS, 60% of all styrene), followed by copolymer synthesis (like acrylonitrile butadiene styrene (ABS)), latex, and rubber manufacturing. Especially the PS application in single use plastics (*e.g.*, foam trays for food take away, super light, stable, and heat insolating) are coming under scrutiny and are banned in the EU from 2021 (Directive (EU) 2019/904), because PS is a highly recalcitrant plastic that survives for centuries in the environment.

Styrene is a common product in pyrolysis of recalcitrant polymers. For microbial degradation of styrene, three pathways are reported for aerobic degradation by microbes, while also anaerobic degradation is possible (Tischler, 2015). Very prominent is the specific styrene degradation pathway starting with the conversion of styrene to styrene oxide (KEGG, R05488) catalyzed by the styrene monooxygenase (KEGG, EC 1.14.14.11). The subsequent conversion *via* side-chain oxidation to phenylacetate (KEGG, R10697), ring activation, and finally ring cleavage yields acetyl-CoA and glutaryl-CoA. Direct ring cleavage of styrene is considered a side activity, as the dioxygenases from toluene degradation and others can catalyze this reaction. After ring activation, the ring opening can proceed *via* meta-cleavage for example, resulting in acetaldehyde, pyruvate and acrylate. A recently described pathway by Heine et al. (2018) proceeds after activation of the side chain by the styrene monooxygenase *via* glutathione activation of the side chain to phenylacetate, which is degraded to two acetyl-CoA and succinyl-CoA in *Gordonia rubripertincta* CWB2.

Styrene or phenylacetate as substrate for PHA production was presented by the group of O'Connor (Ward et al., 2005). They went on and used PS pyrolysis oil to convert 64 g of plastic waste into 6.4 g of PHA (Ward et al., 2006), which could be enhanced even further (Goff et al., 2007; Nikodinovic-Runic et al., 2011). This is remarkable as most microbes could not even grow or survive in the presence of a second phase of styrene (*i.e.*, at styrene concentrations above 2 mM). However, organic-solvent-tolerant *Pseudomonas* for example are equipped with the necessary machineries, especially solvent efflux pumps (Heipieper et al., 2007).

For the last 20 years or so, styrene biotransformation to styrene epoxide has been investigated in detail (Schwanemann et al., 2020). The latter molecule is interesting for polymer synthesis, but more importantly as substrate for pharmaceutical synthesis if the stereochemistry can be guaranteed. This biotransformation is optimized for rate, with sustained activities of 180 U/g_{CDW} or about 11 $mM_{styrene}/g_{CDW}/h$ using a mutant of *Pseudomonas taiwanensis* VLB120 (Volmer et al., 2019), a natural styrene degrader (Panke et al., 1998), a rate that exceeds glucose uptake under most conditions. Bühler et al. reported that the very high rate of aromatic uptake can only be explained by direct uptake from the organic phase (Bühler et al., 2006; Park et al., 2006), avoiding the transfer into and from the aqueous phase. Indeed, bacterial adherence to hydrocarbons is a common phenomenon (Rosenberg, 1984), and *Pseudomonas* and other bacteria that utilize hydrophobic substrates can be found on the surface of the organic phase droplets. The aspects of product toxicity, solubility, volatility, and mass transfer add additional challenges to the use of styrene and other plastic monomers as substrates for microbes. However, these challenges can be overcome with the right choice of host and with the opportunities of metabolic engineering and synthetic biology.

3.4. (Hydroxy)octanoic acid

The cleavage of the bioderived PHA yields 3-hydroxy fatty acids. Furthermore, pyrolytic degradation of polymers such as PE, PP, and PUR also yields medium chain length hydrocarbons for which we will use octanoic acid as proxy. Octanoic acid (or caprylic acid, from the Latin word for goat) is naturally produced by many mammals and also contained in coconut oil and palm kernel oil. Octanoic acid is a common molecule in chemical industry and produced from oxidation of octanal. It is used for the production of fragrances and dyes.

Free fatty acids are activated by acyl-CoA synthetase as described above. Promiscuity of this enzyme, accepting also hydroxy fatty acids, has been shown for 12-hydroxy-octadecenoic acid (Ichihara et al.,

1997). Subsequently, these molecules are degraded in β-oxidation.

3.5. Hexadecan(oat)e

Monomers that potentially result from cleavage of polyethylene are hydrocarbons including alkanes. Enzymatic activation by a monooxygenase or other means to introduce oxygen potentially results also in fatty acids. As proxies for microbial metabolization, we here consider hexadecane and hexadecanoate. Hexadecanoate or palmitic acid is the most widely distributed and abundant unsaturated fatty acid in nature (Stedman, 1995). As the name suggests, it has been discovered in palm oil in 1840 by Edmond Frémy (1842). It is now widely used in a variety of fields, ranging from cosmetics, foods, and even military applications. The global palmitic acid market has been 202,653 Mt in 2016 (Absolute Reports: Global, 2019).

Metabolization of the alkane (hexadecane) starts by activation through a (long-chain length) alkane monooxygenase (KEGG, EC 1.14.14.28), forming a primary alcohol, which is oxidized to the respective aldehyde and further to the fatty acid hexadecanoate. By action of a long-chain length-acyl-CoA synthetase (KEGG, EC 6.2.1.3) the fatty acid is activated by attachment of a CoA group and introduced into the β-oxidation (KEGG, map00071) for further degradation and formation of acetyl-CoA. Microbial conversion of products from PE and PP pyrolysis has been shown before using bacteria such as *Pseudomonas aeruginosa* (Guzik et al., 2014) and *Ralstonia eutropha* (Johnston et al., 2017, 2019; Radecka et al., 2016) as well as fungi such as *Yarrowia lipolytica* (Mihreteab et al., 2019).

3.6. 2,4-Toluenediamine (TDA)

Diisocyanates like methylene diphenyl isocyanate (MDI) and toluene diisocyanate (TDI) are used for polyaddition reactions to form PUR. Due to their highly reactive nature (Gama et al., 2018) the products from a depolymerization are the respective diamines, 4,4′-methylenedianiline (MDA) and TDA (Magnin et al., 2019b; Marchant et al., 1987; Matsumiya et al., 2010; Cregut et al., 2013). These diamines are both toxic for microorganisms and highly valuable (they serve as precursors for the production of the diisocyanates). Hence, separation of the diamines after plastic hydrolysis is discussed to increase the economy of the upcycling process (Utomo et al., 2020).

So far, microbial metabolization of TDA as sole carbon source in pure cultures has only been shown by a few isolates (Espinosa et al., 2020; Kim et al., 2002). Espinosa et al. (2020) isolated a *Pseudomonas* sp. Strain from a site rich in brittle plastic waste, capable of using TDA as sole source of energy, carbon, and nitrogen. The proposed pathway consists of various deoxygenation, decarboxylation, and deamination steps, a ring cleavage, and the homoprotocatechuate meta-pathway. While the details of the pathway are under investigation, it relies on a high promiscuity of the involved enzymes regarding their substrate specificity. Espinosa et al. speculate that the degradation of TDA leads to metabolites of the tricarboxylic acid (TCA) cycle or amino acid metabolism.

3.7. Caprolactam

Caprolactam was first synthesized in 1899 by Siegmund Gabriel und Theodor A. Maass (Gabriel and Maass, 1899). Some chemical methods have been developed for its industrial production, which has been kickstarted in 1938, when polycaprolactam has been invented as alternative for PA 6. Pyrolysis of PA 6 yields caprolactam, while its enzymatic depolymerization yields 6-aminohexanoate.

Microbes able to degrade caprolactam have been isolated from PA 6 production sites, *e.g.,* a strain of *Pseudomonas jessenii* (Kulkarni and Kanekar, 1998). Caprolactam is metabolized in a series of reactions to AA *via* 6-aminohexanoate (KEGG, R05356) and 6-oxohexanoate (KEGG, R05507) catalyzed by the caprolactamase, the 6-aminohexanoate aminotransferase (KEGG, EC 2.6.1.116, NylD), and the 6-oxohexanoate dehydrogenase (KEGG, EC 1.2.1.63, NylE) (Otzen et al., 2018; Esikova et al., 2012; Takehara et al., 2018). The resulting AA is metabolized as described above. Hexamethylenediamine, originating from PA 6.6, is likely degraded *via* the same pathway after transamination to ε-aminohexylaldehyde and subsequent oxidation to 6-aminohexanoate.

3.8. Adipic acid (AA)

AA is an important dicarboxylic acid in the chemical industry (Musser, 2005). The global production was 3.9 Mt in 2018 of which the large majority were used as (co)-monomer for PA 6,6 (with hexamethylene diamine) and PA 6 production (PCI Research GmbH, 2011). Biotechnological production of AA mainly focuses on the microbial conversion of lignin aromatics to AA precursors like glucaric acid or muconic acid and subsequent chemical hydrogenation (Kruyer and Peralta-Yahya, 2017; Polen et al., 2013). Wittmann et al. (van Duuren et al., 2020) estimate that a lignin monomer-based biocatalytic production of muconic acid and subsequent chemocatalytic step to AA would reduce the CO_2 carbon footprint by 58%, while being cost-competitive to the established fossil-based production routes. Microbial production of AA has been shown in 2014 when an *E. coli* strain able to produce AA directly from glucose was developed. The metabolic production pathway was adapted from degradation routes, similar to the one from *Acinetobacter baylyi* (Yu et al., 2014), which was first reported by Parke et al. (2001).

AA degradation starts with an activation to adipyl-CoA by an adipate-CoA ligase (KEGG, R06944). In three subsequent steps, 3-oxoadipyl-CoA is formed *via* 2,3-dehydroadipyl-CoA and 3-hydroxyadipyl-CoA (KEGG, R06943, R06942, R06941), catalyzed by the acyl-CoA dehydrogenase DcaA, the enoyl-CoA hydratase DcaE (KEGG, EC 4.2.1.17), and the 3-hydroxyacyl-CoA dehydrogenase DcaH (KEGG, EC 1.1.1.35). Finally, catalyzed by the thiolase DcaF (KEGG, EC 2.3.1.174), succinyl-CoA and acetyl-CoA are formed and introduced into the TCA cycle (KEGG, R00829). The responsible genes are clustered in two operons in *A. baylyi* (Parke et al., 2001). While enzymes for transport (DcaK and DcaP), CoA transferase subunits (DcaIJ), and an acyl-CoA dehydrogenase (DcaA) are encoded in one operon, the other operon consists of enzymes related to β-oxidation (enoyl-CoA hydratase, ketoacyl-CoA reductase, 3-hydroxyacyl-CoA dehydrogenase, and a thiolase within *dcaECHF*). Recently, adaptive laboratory evolution of *P. putida* KT2440 combined with chromosomal integration of the *dcaAKIJP* cluster resulted in efficient growth on AA (Ackermann et al., 2021). Furthermore, the engineered strain was able to grow on longer-chain dicarboxylates suberic, azelaic, and sebacic acid that might originate from PA degradation. AA was revealed as suitable substrate for the synthesis of PHA (Ackermann et al., 2021) or rhamnolipids (Utomo et al., 2020) by *P. putida*.

3.9. Methyl methacrylate

Polyacrylates are a polymer class with a wide spectrum of applications, as many monomers or co-monomers can be used to tailor the resulting material for the envisaged applications. Indeed, this feature results in a massive use of 9,000,000 tonnes per annum, with the most prominent polymer being PMMA (more than 3 Mt (Gaytán et al., 2021),). Hence, we here exemplarily discuss the biochemical degradation of the PMMA monomer methyl methacrylate. Methyl methacrylate is still synthesized from fossil resources, while several synthesis routes from renewable resources exist. Indeed, methacrylate is mainly synthesized from acetone (Lebeau et al., 2020), another molecule that could readily be obtained from renewable carbon sources. Methacrylate can also be synthesized by decarboxylation of itaconate (Lebeau et al., 2020), a dicarboxylic acid produced commercially using *Aspergillus terreus* (Krull et al., 2017) and with also favorable titer and yield by *Ustilaginacea* (Hosseinpour Tehrani et al., 2019; Becker et al., 2021).

The biodegradation of methyl methacrylate likely starts with the hydrolysis of the methyl group by an esterase activity, followed by a CoA activation as seen for the biochemical conversion of many organic acids. The half-life of methyl methacrylate in soil was reported to be three weeks or considerably shorter (Jørgensen et al., 2008).

3.10. 1,4-Butanediol (BDO)

1,4-BDO is a commodity chemical used for the production of plastics and polyesters (Yim et al., 2011). Additionally, it is used to manufacture tetrahydrofuran and γ-butyrolactone (Grand View Research Inc.:, 2018). In 2020, more than 8 Mt of 1,4-BDO were produced worldwide (NextMCS, 2021), with tetrahydrofuran estimated to cover 50% of the 1, 4-butandiol market, *via* polytetrahydrofuran also named polytetramethylene ether glycol (PTMEG), the soft part of spandex fibers. One of the most important uses of 1,4-BDO is as chain extender in the production of PUR but it is also used as co-monomer in many polyesters such as polybutylene terephthalate (PBT) and PBAT.

While approaches for microbial synthesis of 1,4-BDO have been published (Yim et al., 2011) and are commercialized, so far, little is known about its microbial catabolism. Recently, *P. putida* KT2440 has been proposed as host organism for 1,4-BDO metabolization (Li et al., 2020). The wild-type strain is capable of very slow growth on 1,4-BDO, which facilitated an adaptive laboratory evolution approach after which several strains with significantly enhanced growth rate and biomass yield were obtained. The genomic and metabolic basis of efficient 1, 4-BDO metabolism was characterized using genome re-sequencing, proteomics, and reverse engineering of the evolved strains. In a first step, the alcohol dehydrogenases PedE (KEGG, PPC_2256) and PP_2049 (KEGG, PP_2049) catalyze oxidization of 1,4-BDO to 4-hydroxybutyrate. Further metabolization is unclear, as at least two pathways exist: oxidation to succinate or employing β-oxidation to yield glycolyl-CoA and acetyl-CoA.

3.11. Succinic acid (SA)

SA is a dicarboxylic acid with multiple biological functions. It has been discovered in amber in 1546 by Georgius Agricola and is now industrially produced from C2 to C4 compounds such as maleic acid, 1,4-BDO, and EG. In recent years, biotechnological production approaches using genetically engineered microorganisms have been developed (Cheng et al., 2013). The SA market was 47.5 kt in 2014 (Grand View Research, 2016). SA is directly incorporated in the TCA cycle (KEGG, map00020).

3.12. Terepththalic acid (TPA)

The production of TPA from fossil resources experienced strong growth in the last decades to a predicted 53 Mt in 2022 with the large majority reserved for polyester manufacturing, especially PET (GlobalData, 2019). Bio-based synthesis was reported using furfural as substrate for chemocatalysis (Tachibana et al., 2015), while also isobutanol, limonene, and *trans*,*trans*-muconic acid were proposed as bio-based substrates (Collias et al., 2014). Still, all TPA today originates from fossil resources.

TPA is aerobically degraded *via* the metabolic funnel of aromatics that requires few dedicated enzymes to convert the substrate to a common intermediate, here protocatechuate, and further to central carbon metabolism intermediates. The degradation of phthalates was investigated early on (Keyser et al., 1976), as their derivatives like esters used as plasticizers were found in the environment, with toxic effects on mammals (Giuliani et al., 2020). The microbial degradation pathway of TPA starts with an activation of the aromatic ring (KEGG, R05148) by a dioxygenase (KEGG, EC 1.14.12.15), followed by the reduction to hydroxyl groups in the *meta*- and *para*-positions to form protocatechuate (KEGG, R01633). The genetic inventory required is well documented for *Comamonas testosteroni*, a bacterium that can grow on TPA as sole carbon source. Besides the dioxygenase and the corresponding reductase, the dehydrogenase, a transporter and a regulator coding gene are located in the corresponding operon (Wang et al., 1995). The genetic inventory required for TPA utilization is discussed by Salvador et al. in a recent article (Salvador et al., 2019). The degradation of protocatechuate during growth on TPA seems species dependent, as *meta*- and *ortho*--cleavage pathway operations are reported and even the degradation *via* catechol was postulated (Hara et al., 2007). The usage of different degradation pathways influences directly the yield. When degrading *via* the ortho-cleavage pathway or catechol, as both proceed subsequently *via* the ketoadipate pathway to succinyl-CoA and acetyl-CoA 6 of the 8 carbon atoms are conserved. The degradation of TPA *via* meta-cleavage results in pyruvate and oxaloacetate, none-activated central carbon metabolites conserving 7 carbon atoms (MetaCyc, 3-oxoadipate degradation pathway, MetaCyc, protocatechuate degradation II (ortho-cleavage pathway), MetaCyc, protocatechuate degradation I (meta-cleavage pathway)).

Anaerobically, TPA is readily consumed by environmental consortia, in which some bacteria first decarboxylate it to benzoate, which is subsequently CoA activated and after a multi-enzyme cascade to 3-hydroxyl-pimeloyl-CoA funneled into β-oxidation, with methane and CO_2 as end products (Kleerebezem et al., 1999). While anaerobe processes are of great interest in industrial biotechnology, the rate of anaerobe TPA utilization is most likely too slow for any application, as it requires days rather than hours to utilize low millimolar concentrations.

Kenny et al. used TPA from pyrolysis of PET as sole carbon source (Kenny et al., 2008) and developed a fermentation for the production of medium chain length PHA from a mixture of TPA and glycerol (Kenny et al., 2012), contributing early to the vision of plastic monomer upcycling. The co-utilization of TPA and EG from enzymatic PET hydrolysis for the production of PHA and a rhamnolipid-derivative was recently reported using an engineered *Pseudomonas* sp. GO16 (Tiso et al., 2021). Apart from pseudomonads, other microorganisms have been engineered to metabolize TPA, *e.g.*, *Acinetobacter baylyi* (Pardo et al., 2020). Co-utilization of substrate mixtures will be required when contributing to the utilization of mixed-plastic fractions. Such a co-utilization is generally feasible as seen by the advances of utilizing lignin and lignocellulose monomer mixtures as carbon source for the production of valuable chemicals (Kohlstedt et al., 2018; Becker and Wittmann, 2019; Mohamed et al., 2020; Elmore et al., 2020).

3.13. 2,5-Furandicarboxylic acid (FDCA)

The difficulties in the synthesis of TPA from renewable carbon resources like sugars or CO_2 is one motivation for FDCA development, as this dicarboxylic acid can be readily synthesized using a hydroxymethylfurfural (HMF) oxidase from a *Cupriavidus basilensis* isolate in a recombinant *Pseudomonas* (Koopman et al., 2010a, 2010b). HMF can also be chemocatalytically synthesized from sugars, especially fructose (Kuster, 1990). Notably, despite these clear advantages in hand, still no commercial source of bulk FDCA from renewable carbon resources is on the market, mainly due to the combined challenge of providing high quality HMF (Galkin and Ananikov, 2019) and the conversion to the plastic monomer consistently at a competitive price. As substitute for TPA for the production of PEF instead of PET, the world market would be huge.

End-of-life of PEF can be seen in analogy to PET, with mechanical, chemical, and biotechnological upcycling feasible (Haernvall et al., 2017). The PEF monomer 2,5-furandicarboxylic acid can be readily used as carbon source *via* the HMF degradation pathway (Koopman et al., 2010a), converting it to alpha-ketoglutarate of the TCA cycle and CO_2. This pathway starts with the 2,5-furandicarboxylate decarboxylase, followed by the 2-furoyl-CoA synthetase (KEGG, EC 6.2.1.31), the furoyl-CoA dehydrogenase (KEGG, EC 1.3.99.8), and two hydrolases, forming 2-furoic acid (KEGG, R10213), 2-furoyl-CoA (KEGG, R02986),

5-hydroxy-2-furoyl-CoA (KEGG, R02987), and finally 2-oxoglutaryl--CoA (KEGG, R10211).

3.14. Phenol

Approximately 12 Mt of phenol were produced in 2020, being mainly utilized for production of bisphenol A as monomer of polycarbonates, caprolactam as monomer of PA 6, and phenolic resins (Bedford, 2019). An example for the latter is Bakelite, the first plastic ever made and commercialized from synthetic chemicals. Bakelite is a thermosetting phenol formaldehyde resin that degrades to its monomers for example under heat treatment. Phenolic resins have a market volume of an estimated 7 Mt and are often used in combination with other materials such as wood (*e.g.*, furniture and laminate) and other plastics, in which the weight percentage of phenol is rather low. Underivatized phenol from plastic degradation is hence rather rare. An alternative source might be pyrolysis of polycarbonates (Grause et al., 2010).

Biological phenol degradation was investigated early, as phenol was a prominent contaminant from coal and later petrol chemistry and was used as antiseptic. Phenol degradation starts with monohydroxylation in *ortho* position by the phenol hydroxylase to form catechol (KEGG, R10043). The ring-cleavage of catechol in *ortho*- or *meta*-position results in different stoichiometries of succinate and acetyl-CoA or pyruvate and acetaldehyde, respectively. Anaerobic degradation proceeds *via* carboxylation to 4-hydroxybenzoate (KEGG, R01238), which is, in analogy to anaerobic TPA degradation, again CoA activated and further degraded by β-oxidation (KEGG, map00071). While many reports exist for bioremediation of soil, water bodies, and waste water (*e.g.*, from coal gasification) or as minor component in lignin hydrolysates, reports using phenol as sole or main carbon source for producing valuable chemicals are rare (Maskow et al., 2004; Wosman et al., 2016). Zhang et al. reported PHA production from phenol, investigating growth medium compositions and importantly phenol toxicity using a mixed microbial culture (Zhang et al., 2018).

4. Monomers to products – what can be achieved?

Here, we quantify the potential of the envisaged upcycling pathways by assessing the maximum theoretical yields of target metabolites using plastic monomers as carbon source. This assessment builds on the capability of microbes to utilize the bow tie structure of metabolism, by which many different carbon sources can be funneled to a few central metabolites as building blocks for many different biosynthetic products. The yield of a targeted product on a targeted substrate depends on the host's metabolic network and the nature of its catabolic and anabolic pathways. Here, we evaluate the theoretical yields of valuable products synthesized from plastic monomers using the metabolically versatile microbial species *P. putida* (Wilkes and Aristilde, 2017), which is described in detail by the stoichiometric metabolic model *i*JN1462 (Nogales et al., 2019).

Table 5
Monomers and proxies used in the metabolic modeling for the polymers. For the first seven polymers, microbial degradation has been added to the model, while the lower five polymers have to be depolymerized previously (either enzymatically or *via* pyrolysis). For these polymers, proxies are used for modeling.

Plastic polymers		Monomers/Proxies
Biological degradation	PHA	(*R*)-3-hydroxyalkanoic acid
	PBS	1,4-Butanediol, succinic acid
	PUR	Ethylene glycol, 2,4-toluenediamine, 1,4-butanediol, adipic acid
	PBAT	1,4-Butanediol, adipic acid, terephthalic acid
	PET	Ethylene glycol, terephthalic acid
	PEF	Ethylene glycol, 2,5-furandicarboxylic acid
	PLA	D-lactic acid
Prior degradation	PP	Hexadecane
	PE	Hexadecanoate
	PA 6	6-Aminohexanoate
	PS	Styrene
	PC	Phenol

A total of twelve different plastics were used as hypothetical feedstock, including fossil and bio-based polymers (Table 5). Known microbial degradation pathways for PET, PLA, PBS, PBAT and PHA were added to the model. In the case of non-biodegradable plastics, main monomers produced by pyrolysis or enzymatic cleavage of each plastic were used instead (Table 5). In order to provide a complete overview of the potential of biological networks for the upcycling of plastic waste, we analyzed the theoretical yields of a large array of interesting metabolites covering a broad chemical space. We here focused on added-value compounds for industrial applications, such as the United States Department of Energy (2004) top 12 chemicals (Werpy and Petersen, 2004) and other related compounds, including also monomers for plastic production (Table 6, Fig. 3). We also included rhamnolipids, which are biosurfactants and glycolipids of industrial interest (Tiso et al., 2017a, 2017b, 2020a) and its aglycon precursor hydroxyalkanoyloxy alkanoate (HAA), which can be used as intermediate in the chemical industry (Tiso et al., 2020b, 2021; Mensah et al., 2020; Meyers et al., 2019). Further, building blocks for biomass and important central metabolites were investigated (Table 7, Fig. 3). To do so, it was required to expand the metabolic model by the respective biosynthetic pathways for those analyzed metabolites not produced naturally by *P. putida*. Overall, the model was expanded with 177 new reactions and 122 not-unique metabolites (see supplementary information "SI Table").

The model-based computation of theoretical maximal yields of 43 metabolites returned significant differences, of up to 30%, depending on the type of plastic used as carbon source. PLA stands out as the most suited plastic in terms of yield ($Cmol_{product}/Cmol_{substrate}$) in stark contrast with PEF and PET, which supported rather low yields. Overall, three major substrate groups could be identified: i) high-yield plastic PLA with mean theoretical yields above 0.78, ii) medium-yield plastics PP, PE, PHA, PA 6, PS, PBS, PU, PC, and PBAT with mean theoretical yields ranging from 0.6 to 0.78 and iii) low-yield plastics PET and PEF with mean theoretical yields below 0.6. Noteworthy, yields with PLA were predicted to be similar to those estimated using glucose as carbon source. In fact, these two carbon sources clustered together using Euclidean clustering (Fig. 3). These high yields were not so much due to the degree of reduction of these compounds, but rather to their common catabolism *via* pyruvate, which can be easily used as chemical scaffold for fixing a CO_2 molecule *via* pyruvate carboxylase, thus synthesizing oxaloacetate. Corroborating this hypothesis, high fluxes through pyruvate carboxylase were predicted when using glucose and LA as carbon sources (data not shown). The difference in theoretical yields using other polymers seems to be more related to the carbon chain length and the level of reduction of the monomers. Thus, while the medium-yield group comprised medium and long carbon-chain fatty acids and highly reduced aromatic compounds, the low-yield group was characterized by more oxidized monomers including substituted aromatics and heterocycles (Table 6, Fig. 3).

Interestingly, the mean theoretical yields estimated for high and medium-yield plastics were comparable to those computed using glucose, a carbon source used across the globe in biotechnological applications (Table 6, Fig. 3). This finding suggests that these plastic-waste feedstocks are promising carbon sources for biotechnological purposes. Since the upcycling of plastics will seldom start off with a single type of plastic and instead is likely to entail mixtures of several types, the computational identification of these different groups becomes interesting for tailoring the mix of plastics to the production of a particular target product.

Finally, it is noteworthy to highlight the burden on yield due the transport to the intracellular space of the different monomers. We corroborated that transport is not a negligible impact. Interestingly, we found that the magnitude of the burden significantly depends on the chemical nature of the metabolite being transported. For instance, the

Table 6
Theoretical yields for chemicals of industrial interest. The yields were computed by using the genome scale metabolic model iJN1462. The table shows the maximal theoretical yields for the biological production of the products (left column) from the monomers (or respective proxies) of the plastic polymers shown in the top row. The products are subcategorized into compounds from the US Department of Energy list (Werpy and Petersen, 2004), which can be produced microbially (top eleven entries) and compounds with microbial production routes of general interest for the chemical industry. The value of the yield is presented with shaded cells according to the legend at the bottom. The green shaded entries represent higher yields, while the grey entries show medium yields, and the remaining entries (shaded orange) are low yields. For 'trivial cases' (see text) the numbers are printed in red.

		Feedstock												
		High Yield		Medium Yield									Low Yield	
	Products	Glucose	PLA	PP	PE	PHA	PA 6	PS	PBS	PUR	PC	PBAT	PET	PEF
Compounds from DOE list	3-Hydroxybutyrolactone	0.81	0.80	1.00	1.00	1.00	0.93	0.83	0.81	0.83	0.70	0.74	0.67	0.63
	3-Hydroxypropanoate	0.73	0.72	0.75	0.75	0.75	0.75	0.73	0.75	0.71	0.60	0.67	0.56	0.50
	Aspartic acid	1.16	1.15	1.00	1.00	1.00	1.00	1.00	1.00	0.95	0.96	0.89	0.80	0.79
	Fumaric acid	1.16	1.15	1.00	1.00	1.00	1.00	1.00	1.00	0.95	0.96	0.89	0.80	0.79
	Glucaric acid	0.96	0.82	0.75	0.75	0.75	0.75	0.75	0.75	0.71	0.68	0.67	0.60	0.57
	Glutamic acid	0.92	0.92	0.83	0.83	0.83	0.83	0.83	0.83	0.79	0.83	0.74	0.67	0.68
	Glycerol	0.74	0.71	0.75	0.75	0.75	0.75	0.73	0.75	0.71	0.59	0.67	0.56	0.49
	Itaconic acid	0.92	0.92	0.83	0.83	0.83	0.83	0.83	0.83	0.79	0.83	0.74	0.67	0.68
	Malic acid	1.16	1.15	1.00	1.00	1.00	1.00	1.00	1.00	0.95	0.96	0.89	0.80	0.79
	Sorbitol	0.84	0.73	0.75	0.75	0.75	0.75	0.74	0.75	0.71	0.61	0.67	0.57	0.51
	Succinic acid	0.98	0.97	1.00	1.00	1.00	1.00	1.00	1.00	0.95	0.89	0.89	0.80	0.72
Compounds of industrial interest	1,4-Butanediol	0.60	0.67	0.67	0.67	0.67	0.67	0.61	0.74	0.65	0.49	0.61	0.46	0.40
	Adipic acid	0.69	0.64	0.64	0.64	0.64	1.00	0.64	0.64	0.72	0.73	0.81	0.66	0.45
	Caprolactam	0.61	0.61	0.60	0.60	0.60	0.60	0.60	0.58	0.57	0.55	0.53	0.46	0.46
	D-Lactic acid	0.97	0.96	0.75	0.75	0.75	0.75	0.75	0.75	0.71	0.75	0.67	0.60	0.62
	Ethylene glycol	0.59	0.56	0.50	0.50	0.50	0.50	0.50	0.50	0.53	0.46	0.44	0.50	0.48
	Hexadecanoic acid	0.64	0.63	0.80	0.97	0.82	0.72	0.62	0.61	0.61	0.52	0.57	0.47	0.41
	Phenol	0.68	0.62	0.64	0.64	0.64	0.64	0.64	0.64	0.61	0.97	0.57	0.49	0.44
	Styrene	0.68	0.63	0.60	0.60	0.60	0.60	0.97	0.60	0.57	0.53	0.53	0.48	0.44
	1,3-Propanediol	0.66	0.64	0.75	0.75	0.75	0.75	0.65	0.69	0.66	0.53	0.60	0.49	0.44
	Ethanol	0.66	0.66	0.76	0.80	0.77	0.71	0.65	0.62	0.62	0.54	0.57	0.47	0.42
	Ethylene	0.31	0.31	0.29	0.29	0.29	0.29	0.29	0.29	0.27	0.28	0.25	0.23	0.24
	Isobutanol	0.66	0.66	0.50	0.50	0.50	0.50	0.50	0.50	0.47	0.50	0.44	0.40	0.42
	Isoprene	0.64	0.61	0.63	0.63	0.63	0.63	0.60	0.63	0.59	0.50	0.56	0.46	0.41
	Propylene glycol	0.65	0.62	0.75	0.75	0.75	0.75	0.63	0.69	0.64	0.51	0.60	0.48	0.42
	di-Rhamnolipids	0.71	0.67	0.85	0.86	0.86	0.78	0.67	0.66	0.67	0.55	0.63	0.51	0.44
	HAAs	0.67	0.67	0.87	0.97	0.90	0.74	0.66	0.63	0.64	0.55	0.60	0.50	0.43
	PHA	0.69	0.68	0.91	0.97	0.96	0.76	0.68	0.64	0.65	0.57	0.61	0.51	0.45

Legend	1.20	1.10	1.00	0.90	0.80	0.70	0.60	0.50	0.40	0.30	0.20
Yield (Cmol/Cmol)											

decrease in yield using glucose was about 3.5% irrespective of ATP or proton-driven glucose transport. Similar results were found using phenol (as proxy for polycarbonate), a highly oxidized compound (see supplementary information "SI Table"). However, we predicted a much more negligible impact due to transport using the compounds 6-aminocaproate and 3-hydroxyalkanoic acid for more reduced polymers, such as PA 6 or PHA, respectively, strongly suggesting that the excess of electrons of these compounds largely mitigates the metabolic burden of the transport.

Clearly, ethylene was the compound rendering the lowest yields irrespective of the carbon source used. However, this highly inefficient production is not attributable to the intrinsic chemical nature of ethylene but to its biosynthetic pathway, where 3.5 mol of CO_2 are produced per mol of ethylene being produced (Fukuda et al., 1992). Some table entries are included for completeness, rather than as possible options. These 'trivial cases' are molecules derived from plastic hydrolysis rather than synthesized from monomers using microbes (*e.g.*, EG and TPA from PET degradation, or 1,4-BDO and AA from PUR degradation) (those 'trivial cases' are marked in red in Table 6).

Regarding the central metabolites (Table 7), overall, we found that the reduction state and carbon chain length of the produced molecules largely conditioned the theoretical yield. High yields were computed for short carbon chains metabolites with low reduction state and *vice versa* including several carboxylic acids involved in the TCA cycle and related compounds (Fig. 3). It is worth noting the higher yields predicted for oxaloacetate, which were above 1 using both high and medium-yield plastics as carbon sources. As anticipated above, this finding can be attributed to the fact that excess electrons from such feedstock promote a significant CO_2 reduction and, ultimately, carbon fixation *via* pyruvate carboxylase. This anaplerotic activity drives the high yields computed for TCA cycle-metabolites and gluconeogenic intermediates. Lower yields were computed for more reduced compounds such as sugars and fatty acid derivatives. Depending on the plastic used as carbon source these exhibited yields ranging from 0.4 to 1.0.

Overall, the stoichiometric-based analysis clearly shows the feasibility of plastic-derived monomers as promising carbon sources for

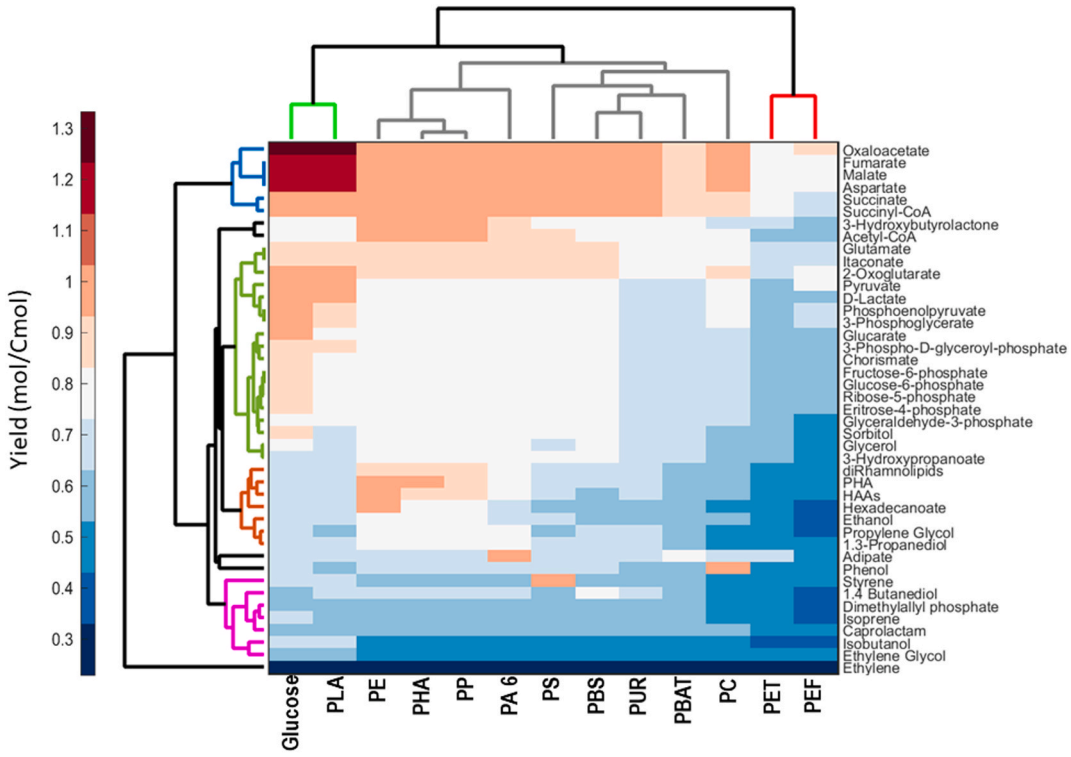

Fig. 3. A clustered heat map of maximum theoretical yields of selected added-value metabolites from twelve fossil-based and bio-based plastic monomers computed for *P. putida* using iJN1462. Theoretical yields were computed as moles of carbon produced per moles of carbon consumed. The twelve plastics analyzed in this study clustered in three different groups, high-yield in light green, medium-yield in grey, and low-yield in red. For analysis, the model was expanded by adding the degradation pathways for several plastic-derived monomers such as TPA, styrene, phenol, 6-aminocapronate, 2,5-furandicarboxylic acid, AA, hexane, and TDA (Table 5, supplementary information "SI Table"). Similarly, it was required to equip the model with the missing metabolic pathways responsible for the biosynthesis of metabolites that were non-native to *P. putida*. Overall, the model was updated with a total 174 new reactions and 122 non-unique metabolites (see supplementary information "SI Table"). Maximum theoretical yields were computed by using flux balance analysis in the absence of growth but accounting for non-growth associated maintenance. Carbon uptakes were normalized in order to provide identical Cmol substrate.

biotechnological processes. The theoretical yields we found are on par with those reported for traditional feedstocks such as glucose. In fact, high-yield plastics returned similar values. In addition, even the cost-effective revalorization of low-yield plastics might be achieved by implementing bioprocesses based on mixtures of high and low-yield plastics as carbon source. This scenario seems most realistic given how plastic upcycling is currently managed. It should, however, be noted that these yield estimates do not account for the metabolic or economic burden of the depolymerization, which can be a significant factor that varies widely for the different plastics in terms of metabolic (enzyme production) or energetic (pyrolysis) costs. Also, in this respect, the highest-yield substrate PLA stands out positively as it is readily biodegradable.

5. Metabolic upcycling of plastics - how much CO_2 can we avoid?

(Bio)chemical upcycling is often intuitively regarded as environmentally beneficial. However, waste treatment processes are complex and may lead to unwanted environmental consequences (Geyer et al., 2017). In particular, chemical recycling of plastics may actually increase environmental impacts compared to alternative waste treatment, such as mechanical recycling or combustion in a cement kiln (Meys et al., 2020). Thus, to identify potentially advantageous biochemical upcycling routes, we compared the environmental impacts to alternative waste treatment options. Our focus is on the global warming impact (GWI) as environmental indicator.

Waste treatment in general and recycling/upcycling specifically serve two functions: the primary function, eliminating waste, and secondary, producing valuable products from waste (Fig. 4). These valuable products could be chemicals from biochemical upcycling, polymers from mechanical recycling, or heat and electricity from waste incineration. If the production *via* waste treatment avoids these products' conventional production, waste treatment leads to an environmental benefit. Conventional production is defined as the most practiced production route for a given chemical. Currently, these production routes are primarily based on fossil-based resources. Thus, the net global warming impact GWI_{net} of waste treatment is the difference between the benefit of avoided production GWI_{avP} and the impact of the waste treatment GWI_{WT}.

The potential GWI_{pot} of biochemical upcycling compared to alternative waste treatment options is then obtained by subtracting the net impact of the alternative recycling technology $GWI_{\text{net,WT}}$ from the net impact of biochemical upcycling $GWI_{\text{net, BC}}$ (Fig. 4):

$$GWI_{\text{pot}} = GWI_{\text{net,BC}} - GWI_{\text{net,WT}} = (GWI_{\text{avP,BC}} - GWI_{\text{BC}}) - (GWI_{\text{avP,WT}} - GWI_{\text{WT}}). \quad (1)$$

Table 7
Theoretical yields for metabolites from the central carbon metabolism. The yields were computed by using the genome scale metabolic model iJN1462. The table shows the maximal theoretical yields of common biochemical pathways (left column) from the monomers (or respective proxies) of the plastic polymers shown in the top row. The value of the yield is presented with shaded cells according to the legend at the bottom. The green shaded entries represent higher yields, while the grey entries show medium yields, and the remaining entries (shaded orange) are low yields.

	Feedstock												
	High Yield		Medium Yield									Low Yield	
Metabolites	Glucose	PLA	PP	PE	PHA	PA 6	PS	PBS	PUR	PC	PBAT	PET	PEF
2-Oxoglutaric acid	0.97	0.97	0.83	0.83	0.83	0.83	0.83	0.83	0.79	0.83	0.74	0.67	0.76
3-Phospho-D-glyceroyl-phosphate	0.90	0.85	0.75	0.75	0.75	0.75	0.75	0.75	0.71	0.71	0.67	0.60	0.60
3-Phosphoglycerate	0.97	0.92	0.75	0.75	0.75	0.75	0.75	0.75	0.71	0.75	0.67	0.60	0.65
Acetyl-CoA	0.82	0.81	1.00	1.00	1.00	0.91	0.86	0.78	0.78	0.73	0.74	0.62	0.57
Chorismate	0.88	0.81	0.75	0.75	0.75	0.75	0.75	0.75	0.71	0.68	0.67	0.60	0.57
Dimethylallyl phosphate	0.61	0.59	0.63	0.63	0.63	0.63	0.58	0.63	0.59	0.48	0.55	0.45	0.39
Erythrose-4-phosphate	0.85	0.76	0.75	0.75	0.75	0.75	0.75	0.75	0.71	0.64	0.67	0.60	0.53
Fructose-6-phosphate	0.89	0.77	0.75	0.75	0.75	0.75	0.75	0.75	0.71	0.64	0.67	0.60	0.54
Glucose-6-phosphate	0.89	0.77	0.75	0.75	0.75	0.75	0.75	0.75	0.71	0.64	0.67	0.60	0.54
Glyceraldehyde-3-phosphate	0.80	0.76	0.75	0.75	0.75	0.75	0.75	0.75	0.71	0.63	0.67	0.60	0.53
Oxaloacetate	1.33	1.33	1.00	1.00	1.00	1.00	1.00	1.00	0.95	1.00	0.89	0.80	0.91
Phosphoenolpyruvate	0.97	0.92	0.75	0.75	0.75	0.75	0.75	0.75	0.71	0.75	0.67	0.60	0.65
Pyruvate	1.00	1.00	0.75	0.75	0.75	0.75	0.75	0.75	0.71	0.75	0.67	0.60	0.73
Ribose-5-phosphate	0.88	0.76	0.75	0.75	0.75	0.75	0.75	0.75	0.71	0.64	0.67	0.60	0.53
Succinyl-CoA	0.95	0.94	1.00	1.00	1.00	1.00	1.00	1.00	0.95	0.84	0.89	0.77	0.69

Legend	1.40	1.30	1.20	1.10	1.00	0.90	0.80	0.70	0.60	0.50	0.40
	Yield (Cmol/Cmol)										

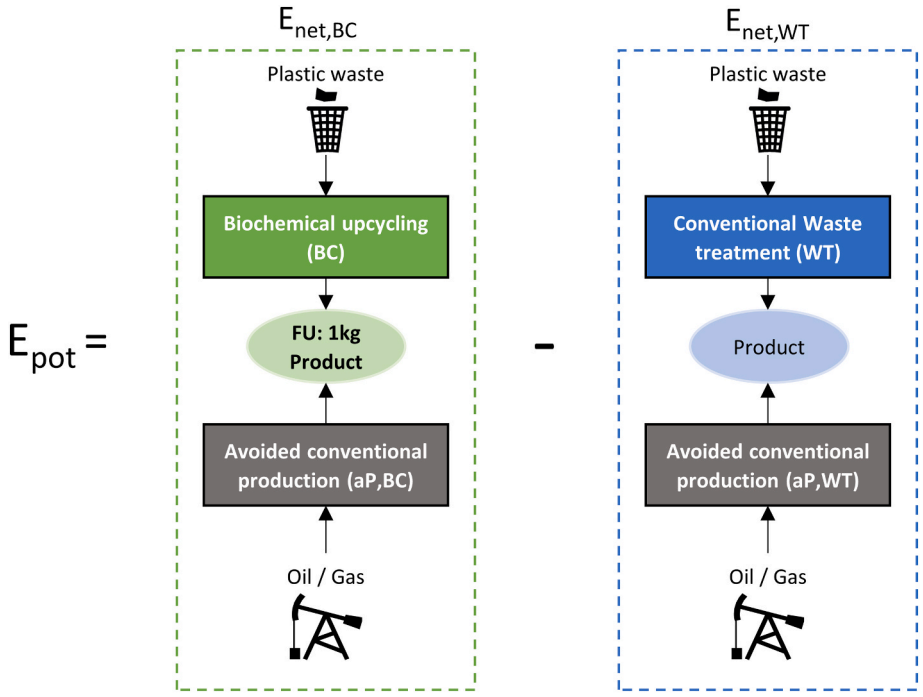

Fig. 4. System boundaries for calculating the potential environmental impact reduction E_{pot} of biochemical recycling (BC) as difference of its net impact $E_{net,BC}$ and $E_{net,WT}$ of competing conventional waste treatment (WT). Both biochemical recycling and conventional waste treatment yield a product that avoids its conventional production.

Table 9
List of the chemicals included in the assessment of the environmental potential of biochemical upcycling. If no conventional fossil-based production is available, a functional substitute has been identified. Functional substitution is assumed on a mass basis if not stated otherwise. (LHV, lower heating value).

Name	Functional substitute
1,3-Propanediol	–
1,4-Butanediol (1,4-BDO)	–
Adipic acid (AA)	–
Caprolactam	–
Ethanol	Gasoline based on LHV
Ethylene	–
Ethylene glycol (EG)	–
Hexadecanoate	Diesel based on LHV
Isobutanol	–
Isoprene	–
Itaconic acid	Acrylic acid
Lactic acid (LA)	Polyethylene terephthalate
Malic acid	–
PHA	Polyethylene terephthalate
Phenol	–
Propylene glycol	–
Styrene	–
Succinic acid (SA)	Adipic acid

This study uses 1 kg chemical product produced *via* biochemical upcycling as functional unit. The theoretical product yield on substrate computed in section 4 from the metabolic network is assumed as the yield of biochemical upcycling and thus determines the required amount of waste for the production of the 1 kg product. The alternative waste treatment technology treats the same amount of waste.

5.1. Biochemical upcycling

For now, biochemical upcycling is mostly hypothetical, and many possible routes are still under investigation. Thus, a detailed assessment of the environmental impacts of biochemical upcycling is not possible today. Here, we aim at guiding further development by estimating the maximum potential for environmental impact reductions of various bio-based upcycling routes. The maximum potential is calculated by employing best-case assumptions for biochemical upcycling, whereas real data is used for the competing alternative waste treatment (Meys et al., 2020). As a result, if the maximum potential GWI_{pot} is below zero, this biochemical route would increase environmental impacts compared to the current waste treatment, even in the best case. Thus, we would certainly not expect benefits in a real-world setting for pathways with a negative GWI_{pot}. In contrast, biochemical upcycling technologies with a high maximum potential should be more robust towards real-world impacts and thus be of particular interest for further research. To calculate the maximum potential, the impact of biochemical upcycling GWI_{BC} should be as small as possible and should require the least amount of waste input. As best-case assumption for biochemical upcycling, we assume the impact of biochemical upcycling GWI_{BC} to be equal to the stoichiometric CO_2 emissions from the fermentation and the maximum theoretical yield reported in Fig. 3 and Tables 6 and 7.

Most of the metabolites discussed previously in this review do not have a fossil-based counterpart. Here, we limit the analysis to chemicals that either have a chemically identical fossil-based counterpart or that can provide functional substitution of a fossil-based counterpart, *i.e.*, the metabolite is not chemically identical but it provides the same function as the fossil-based counterpart (Table 9). Examples of such functional substitution are, *e.g.*, succinic acid (SA) replacing adipic acid (AA) due to their similar structure and di-acid functionality (Cok et al., 2014) or ethanol replacing gasoline based on heating value. This preselection ensures a sound comparison of the environmental impacts between biochemical recycling and fossil-based production since the functional unit provides the established basis for environmental assessments according to the ISO-standard on LCA (Iso.org:O 14040:2006, 2006).

To assess the environmental impact of biochemical upcycling, we use cradle-to-grave system boundaries. Cradle-to-grave system boundaries are required since functionally substituted chemicals do not have the same carbon content. As a result, neglecting the end-of-life stage would favor chemicals with high carbon content. Here, we assume that all chemicals are eventually combusted or degraded, and their carbon is thus released to the environment. The chemical's use phase can be neglected since we assume functionally equivalent products.

To calculate the environmental impact of the chemical production avoided by biochemical upcycling $GWI_{avP,BC}$, LCA databases or industrial data of established production is employed (see supplementary information "Supplement").

5.2. Alternative waste treatment

Currently, waste treatment employs three main pathways: landfilling, incineration, and mechanical recycling (Geyer et al., 2017). These pathways could serve as alternatives to biochemical upcycling. However, although landfilling of plastics is currently still the main mode of waste disposal (Ellen MacArthur Foundatio, 2021; Hundertmark et al., 2018b), it is increasingly falling out of favor and is already banned in several countries (PlasticsEurope, 2018). We thus do not consider landfilling as a viable long-term waste treatment option. Mechanical recycling requires highly sorted waste and is only available for certain types of plastic. Mechanical recycling is currently only feasible for four plastics considered in this study: PE, PP, PS, and PET. Thus, we discuss waste incineration as the main alternative waste treatment option for all polymers and then discuss mechanical recycling for these four plastics separately.

To calculate the maximum potential $GWI_{net,WT}$, we adopt data on waste incineration and mechanical recycling from Meys et al. (2020). For waste incineration, an efficiency η_{inc} of 0.45 and heat-to-electricity ratio of 0.75 is assumed, based on the average efficiencies for municipal solid waste incinerators in Europe (Eriksson and Finnveden, 2009; Flamme et al., 2018). For mechanical recycling, state-of-the-art processes are considered, and performance loss due to downcycling is reflected by a substitution factor of virgin-to-recycled polymer of 0.7 for PE and PP, 0.9 for PS, and 1 for PET.

5.3. Global warming reduction potential of biochemical upcycling

Fig. 5 shows the potential maximum reduction in global warming impacts GWI_{pot} (Eq. (1)) of biochemical upcycling. Nearly all biochemical upcycling routes have a maximum reduction potential greater than zero when compared to waste incineration. The only exception is the production of ethylene by recycling polycarbonate as waste feedstock due to its very poor yield (cf. Section 4, Table 6).

The maximum potential of biochemical upcycling strongly correlates with the impact of the fossil-based reference product. This strong correlation is due to the smaller impact of the alternative waste treatment technology (0.3–3.1 kg CO_2 eq/kg product, excluding ethylene) compared to the impact of fossil-based production (2.3–10.9 kg CO_2 eq/kg product). Thus, climate benefits are most likely achieved by aiming upcycling towards chemicals with high climate impacts from current fossil production such as 1,3-propanediol, caprolactam, SA/AA or isoprene rather than chemicals with a very high theoretical yield such as malic acid.

In addition to the high potential to reduce global warming impacts, high impact chemicals also tend to have a higher market price than low impact chemicals, making the economic viability of chemical upcycling more likely. However, high impact and expensive chemicals often have a smaller market size.

The values for the maximum potential can be compared to previous environmental assessments of fermentation processes. For a wide range of products, fermentation and product separation lead to global warming impacts from 0.3 to 4.6 kg CO_2 eq/kg product (Winter et al., 2021).

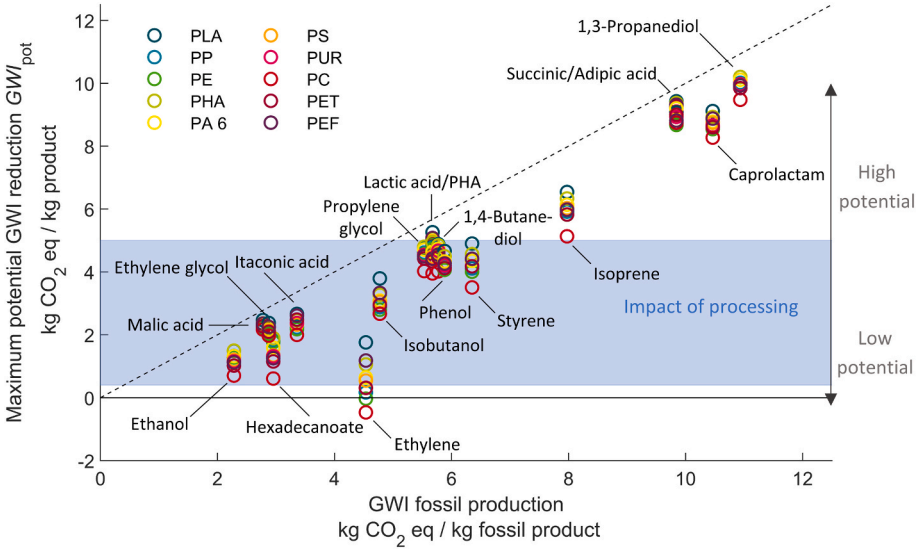

Fig. 5. Maximum potential GWI_{pot} for reduction of global warming impacts from biochemical upcycling as function of impact of the fossil reference product. Incineration is considered as alternative waste treatment. While the colored circles represent the polymers as substrate, the compounds in the diagram represent the products. The dashed line represents the maximum achievable reduction if upcycling has zero impact. The shaded areas represent the gate-to-gate global warming impact of published fermentation processes.

Thus, biochemical upcycling routes with a maximum reduction potential greater than 4.6 kg CO_2 eq/kg product can be seen as very likely to reduce global warming impacts in the real world. These promising routes produce 1,3-propanediol, caprolactam, SA/AA and isoprene. In contrast, biochemical upcycling routes with a maximum potential lower than 0.3 kg CO_2 eq/kg product should be expected to increase global warming impacts in an actual process.

Most chemicals have a maximum reduction potential within the expected range of the fermentation process's impact. For these processes, a detailed assessment is required to quantify actual reductions of climate impacts. Sufficient data is available for ethanol, isobutanol, and LA where either production is established, or process designs have been proposed. Thus, knowledge from these processes can be transferred to biochemical upcycling. The impact of separation is around 0.3 kg CO_2 eq/kg for ethanol based on Moncada et al. (2018), 1.4 kg CO_2 eq/kg for isobutanol based on Adome et al. (Adom et al., 2014), 2.0 kg CO_2 eq/kg itaconic acid based on Nieder-Heitmann (Nieder-Heitmann et al., 2018), and 2.2 kg CO_2 eq/kg for LA separation and reaction to PLA based on Papong et al. (2014). Assuming the separation in a biochemical upcycling process does not differ significantly from the separation during

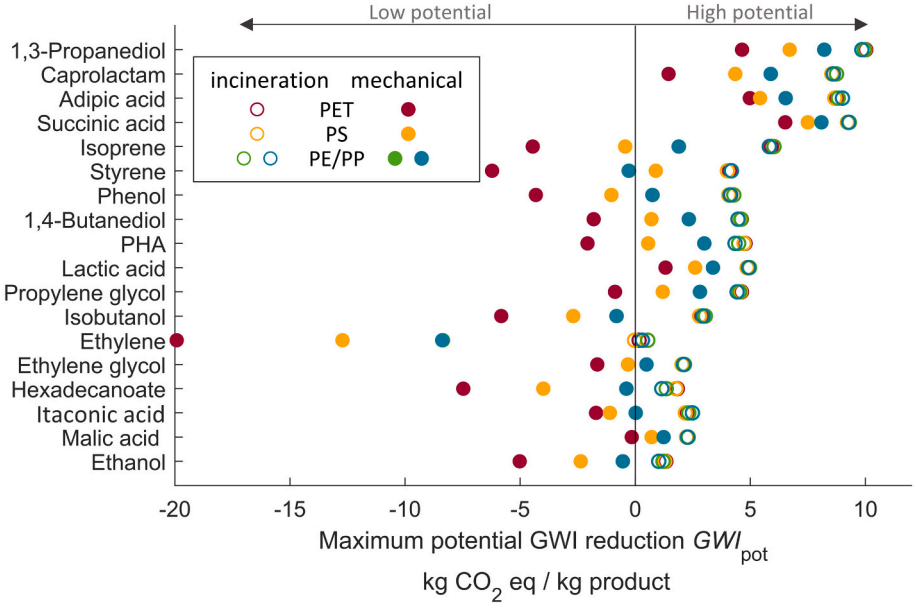

Fig. 6. Potential reduction in the global warming impact of biochemical upcycling compared to incineration and mechanical recycling. Mechanical recycling for PP and PE leads to nearly the same results, and thus, the markers overlap. A negative potential indicates that biochemical upcycling is not advantageous.

fermentation from glucose, all four products would reduce global warming impacts compared to waste treatment by incineration. However, the impacts of fermentation from glucose are only relevant if comparable titers are achieved, and no additional separation challenges are introduced by plastic waste.

To our knowledge, life cycle assessments are not available for the separation of styrene, hexadecanoic acid, and PHA from fermentation broths. In our view, these chemicals might be of particular interest, as they do not mix well with water and might thus be separated with little effort and impact. For the other chemicals, a complete process design is required to quantify the reduction potential of biochemical upcycling more precisely.

For some chemicals, such as malate, itaconate, propylene glycol, 1,3-propanediol, and 1,4-BDO, the maximum reduction potential is very insensitive to the plastic waste feedstock. Since all plastic types as feedstock lead to similar global warming impacts, these products could be of particular interest when unsorted plastic waste is recycled, as a high potential can be expected from all parts of the unsorted waste.

In contrast to waste incineration, mechanical recycling requires cleaned and sorted waste as input. If applicable, mechanical recycling generally achieves a much higher environmental benefit than waste incineration. Thus, the potential for biochemical upcycling is much lower if compared to mechanical recycling instead of incineration (Fig. 6).

For the three plastic types currently suited for mechanical recycling (PET, PS, and PE/PP), polyethylene and polypropylene retain the largest potential for biochemical upcycling due to the rather small benefit of mechanically recycling polyethylene/polypropylene. The potential maximum reduction is still above the expected impact of fermentation processes for the high-impact products 1,3-propanediol, caprolactam, adipic acid, and succinic acid. PS also still has a significant potential for biochemical upcycling compared to mechanical recycling for several chemicals. For PET, however, mechanical recycling seems to be the superior option in almost every case. Only very few chemicals could be produced by biochemical upcycling of PET and have the potential to reduce global warming impacts compared to mechanical recycling. Nevertheless, the use of mechanically recycled PET in materials with food contact currently faces regulatory barriers. Thus, some PET waste streams might be unsuitable for mechanical recycling and available for biochemical upcycling (De Tandt et al., 2021).

Additionally, the yield is more critical when biochemical upcycling is compared to mechanical recycling, rather than to waste incineration, due to the higher net global warming benefit $GWI_{net,WT}$ of mechanical recycling. For instance, isoprene has a theoretical yield of 0.30 kg isoprene/kg PET and thus requires 3.3 kg of PET per kg of isoprene. Combusting this amount of PET in a waste incineration facility would only result in a benefit of 2.4 kg CO_2 eq/kg isoprene for the generated heat and electricity. However, mechanically recycling this PET waste and thus avoiding the production of virgin PET and the combustion of the polymer would result in a benefit of 12.5 kg CO_2 eq/kg isoprene. This effect is much less pronounced for chemicals with a high yield, such as succinic acid.

The presented analysis assesses the environmental reduction potential of various biochemical upcycling routes. The main factor for biochemical upcycling's environmental potential is shown to be not the theoretical yield of the fermentation but the environmental impact of the fossil-based reference product. This result highlights the need to focus future research on high-impact chemicals rather than high-yield ones. Still, the analysis is based on the theoretical yields. Thus, achieving yields close to the theoretical yield is still essential as processes with much lower yields will perform significantly worse.

Additionally, the fermentation process and following separation tasks introduce a large uncertainty into our assessment of the environmental potential. While some chemicals still show promise even for high separation impacts, it is unclear for the majority of chemicals whether an actual biochemical upcycling processs will reduce climate impacts. Thus, future efforts should quantify the impact of separation for biochemical upcycling to refine the estimate of potential environmental benefits. Promising methods for separation synthesis have been developed based on superstructure optimization (Wu et al., 2017).

The type of plastic waste feedstock only had a secondary effect on the impact of biochemical upcycling. In particular, some chemicals show a particularly narrow distribution of feedstock impact, indicating that these products could be of particular interest when mixed waste is recycled. However, the type of plastic waste feedstock could play a larger role when the impact of plastic depolymerization is additionally considered. Here, polymers that can be depolymerized *via* enzymatic hydrolysis could outperform polymers depolymerized by more energy-intensive pyrolysis.

However, while biochemical upcycling compares favorably to waste incineration, it is often unfavorable compared to mechanical recycling. Thus, biochemical upcycling should focus on plastic types and waste fractions that cannot be recycled mechanically, in line with current waste treatment hierarchies.

6. Conclusions

With the ever-increasing amounts of plastics produced, recycling strategies, rather than landfilling and incineration, have to move in focus. Biotechnological plastic degradation is promising for polyesters, with the prominent example PET. In addition, pyrolysis oils can also be utilized as microbial substrates. The evaluation of theoretical maximal yields of valuable chemicals from plastic monomers are shown to differ substantially. However, the assessment of replacing common recycling strategies by a biotechnological route highlighted that the product yield on carbon is less a determinant of the theoretical maximal yields than the resource efficiency of the established chemical synthesis route. Hence, this work contributes to guide the focus of biotechnological plastic waste valorization to products like isoprene, 1,4-BDO, caprolactam, and succinic/adipic acid. Further, potential climate benefits for the investigated products malate, itaconate, propylene glycol, 1,3-propanediol, and 1,4-BDO are insensitive to the plastic substrate used and are likely a good choice for mixed plastic fraction valorization. As mechanical recycling, which is already very competitive for some plastics and chemical recycling will improve and mature quickly, the biochemical upcycling route should focus on plastic types and plastic mixtures that cannot be used with these technologies. *Vice versa*, this work also provides guidance for the development of biobased plastic products specifically for biochemical upcycling as end-of-life solution.

This assessment aims to target the development of biochemical upcycling and thereby maximize its contribution to address the vast amount of plastic today and the increasing needs for future technical solutions. Overall, we hope that our analysis can guide research of biochemical upcycling towards the most sustainable paths, identifying numerous opportunities for metabolic engineering.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ymben.2021.12.006.

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