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**Sustainability spotlight**

The depletion of fossil feedstocks and the $CO_2$ emissions is turning the governments and the research community towards the upgrading the industrial processes to more eco-friendly chemo-biological based technologies. The use of plastic and biomass wastes as biorefinery feedstocks represents an unlimited and ubiquitous alternative that can be adapted to each country, region and climate's availability of renewable resources. In particular, the biobased valorization of mixed wastes such as, plastic and textiles, plastic and biomass, and food wastes and plastics, are emerging research fields that needs further development for industrial application.

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# Thermochemical and Chemo-biological Molecular Recycling of Plastic Waste and Plastic-Biomass Waste Mixtures: An Updated Revision

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Massive amounts of plastic and biomass waste is mismanaged worldwide, causing detrimental consequences to the human health and the environment. In fact, the disposal of residues through landfill without further processing and burning for household heating and cooking are common practices. Thermochemical processing such as pyrolysis, chemical depolymerization and bioprocessing, prove feasible for recovering valuable building block molecules from plastic residues. The main goal of pyrolysis is to obtain aliphatic hydrocarbons useful as fuel, while chemical processing conducts to constitutive molecules of the plastic (i.e., monomers and polyols) able to be repolymerized and reinserted in the market. On the other hand, the bioprocessing of plastic waste requires prior chemical depolymerization in order to unleash the building blocks. Chemo-enzymatic treatment of waste plastic-biomass mixtures is an open challenge due to the diverse composition of the residues, along with the presence of additives and contaminants. The few reports found in the literature regarding the bioprocessing of plastic residues with lignocellulosic biomass and paper, indicate that a chemical pretreatment cannot be avoided and that some substances present in the residues can act as fermentation inhibitors that affect waste bioprocessing.

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The depletion of fossil feedstocks and $CO_2$ emissions is turning the governments and the research community towards upgrading the industrial processes to more eco-friendly chemo-biological based technologies. The use of plastic and biomass wastes as biorefinery feedstocks represents an unlimited and ubiquitous alternative that can be adapted to each country, region and climate's availability of renewable resources. In particular, the biobased valorization of mixed wastes, such as plastic combined with textiles residues, biomass or food waste, are emerging research fields that needs further development for industrial application.

## 1. Motivation and outline of the review

The development of novel technology towards the conversion of wastes in valuable substances is at the cutting edge of the scientific community`s interest. Nevertheless, attempts to process complex mixtures of wastes have been assessed only recently. The most recent advances in the valorization of residues will be addressed in this review with special attention on the chemical, catalytic and biological treatment of mixtures of various types of plastics and mixtures of plastic and biomass wastes. This overview of cutting-edge processes for mixed waste valorization provides niches and opportunities for further advancement of the research devoted to solve the billions of tons of wastes that are dumped around the world.

Before discussing the more recent investigations concerning the valorization of plastics and plastic-biomass waste mixtures it is important to present fundamental aspects regarding the magnitude of the problem in terms of quantity of plastic waste, the end-of-life management and the emission of greenhouse gases (GHG) as equivalent carbon dioxide ($CO_2e$).

## 2. Global plastic residues generation, disposal and environmental impact

According to the reports of the International Energy Agency and the World Bank, 44% of the worldwide waste is composed of biodegradable type of residues, such as food leftovers, food industry residues (i.e., potato peel, waste cooking oil, etc.) and green waste that includes tree pruning, grass clippings, branches, wood chips, bark, wood, palm trees and branches, and weeds[1,2]. Then, 17% of the waste is paper and cardboard and 12% is of plastic origin. Nowadays, plastic residues get worldwide attention due to the debris found in the ocean along with the detection of microplastics in water streams. The Organization for Economic Cooperation and Development (OECD) estimated that this year around 23.5 million tons of macro and microplastic waste leaked to the environment around the world[3].

Recently, Cottom *et al.* published a global macroplastic pollution emissions data analysis[4]. Interestingly, the authors defined the term "*pollution emission*" as materials that have moved from the managed or mismanaged system (controlled or contained state) to the uncontrolled or uncontained state, that is released towards the environment. Somehow, this is important in the sense that the analysis is focused in the plastic waste management rather than the amount of plastic produced. The findings of Cottom *et al.* demonstrated that 52.1 million metric tons per year (Mt year$^{-1}$) of plastic debris are not adequately managed worldwide, that in turn would have an impact in the carbon and environmental footprints. India generates the largest amount of plastic pollution, accounting for 9.3 Mt year$^{-1}$, followed by Nigeria (3.5 Mt year$^{-1}$), Indonesia (3.4 Mt year$^{-1}$) and China (2.8 Mt year$^{-1}$).

Going deeply in the relevancy of proper management of plastic waste, Figure 1 shows the amount of plastic produced per capita and recycled in various countries; the percentage of recycled plastic based on the total amount of plastic wastes is indicated above each column[5]. In this context, South Korea possesses the highest percentage of plastic waste recycling (60%) followed by various European countries, such as Germany, Denmark, Belgium and Norway (48-35%). United States, the larger waste producer per capita (811 kg), recycles only 23%.

Landfilling, even though leads to long-term environmental contamination, is the end disposal of 40% of the global plastic waste, as depicted in Figure 2. In addition, 32% goes

directly to open non-regulated dump sites and only 8% is disposed of in sanitary landfills with

gas collection systems[2,6]. In fact, plastic management is directly related to the socio-economic

profile, since low-income countries dump 93% of their plastic (solid) waste. The non-regulated

dumping causes the pollution of waterways, that in turn generates marine litter as

microplastics, accounting for 11.6-21.1 Mt in the Atlantic Ocean in 2020[6]. In addition, non-

regulated dumping goes along with open burning of plastics within all type of solid garbage

and the emission of harmful gases and ashes[7]. For instance, bottles made of polyethylene

terephthalate (PET) release $CO_2$, methane, formaldehyde and polycyclic aromatic

hydrocarbons; grocery bags, made of high-density polyethylene (HDPE), produce olefins,

aldehydes, CO and aromatic compounds; foam cups of polystyrene (PS) generate styrene gas,

acrolein, hydrogen cyanide; and curtains, made of polyurethane (PU), release phosgene,

among others[7].

The waste-to-energy incineration (WtE) is the end disposal of 14% of plastic waste. This

method involves $CO_2$ emissions unless a technology for carbon capture and storage (CCS) or

carbon capture and utilization (CCU) is applied downwards. Nowadays, only the Netherlands

has three operational CCU facilities, one of large scale and two pilot plants[8]. The former has

the capability of processing 360.635 ton/year of waste with 60 kt/year of $CO_2$ capture through

absorption. Norway and Japan have also operational pilot WtE-CCU plants.

Rubio-Domingo and Halevi gathered and analyzed various reports of the GHG emissions

generated by the plastic end-of-life management option[9]. The authors concluded that

landfilling and mechanical recycling have the lowest GHG among the disposal methods. On

the other hand, incineration possesses the highest emissions with 1-2.5 kg $CO_2$e/kg for WtE

and 1.8-2.0 kg $CO_2$e/kg (per kg of plastic) for incineration without an energy conversion

associated process. The investigation of Rubio-Domingo and Halevi also considered that the

gasification (0.2-1.8 kg $CO_2$e/kg) and pyrolysis (almost zero emission) are low emission

methods. This last method will be further discussed in the following sections due to its low

environmental impact and high potential to generate valuable substances.

The term "$CO_2$e" means $CO_2$ equivalent, and is used to compare the emissions from various greenhouse gases GHG on the basis of their global-warming potential (GWP), by converting amounts of other gases to the equivalent amount of carbon dioxide with the same global warming potential. This concept is related with the carbon and environmental footprints of a product. The former is the total amount of GHG generated along the life cycle of a product. Moreover, the environmental footprint (called also Life Cycle Assessment) involves, not only the GHG emissions, but also the environmental impact caused by: particulate matter emission, human toxicity, ozone depletion, eutrophication, land use, resource depletion, among others.

Zheng and Suh[10] calculated an emission of 1.8 Gt $CO_2$e of fossil fuel-based plastics along their life cycle in 2015 (see Fig. 2). By 2020, that number raised to 2.2 Gt $CO_2$e and is projected to grow up 31% by the year 2030, unless mitigation actions took place[11]. The major contributors to GHG emissions at the resin production stage (most polluting one) are: polypropylene (PP), polyurethane (PU), low-density polyethylene (LDPE), high-density polyethylene (HDPE) and polyethylene terephthalate (PET)[10]. In this context, the various strategies of valorization of actual residues based on those type of plastics will be discussed in the following sections.

Carbon footprint is calculated considering that the life cycle of a plastic involves coal combustion for the resin-production stage, which includes all activities from cradle to polymer-production factory gate, accounting for 61% of the total emission. In addition, the conversion stage, which covers the manufacturing processes that turn polymers into final plastic products (30% of the global emission) and the end-of-life stage, which refers to the treatment and disposal processes of plastic waste with 9% of $CO_2$e emission. Zheng and Suh pointed out that further efforts towards bio-based plastics and renewable energy (wind power and biogas) sources, lowering the demand, and recycling, are the key to diminish the carbon footprint of plastics.

Currently, only 9% of all the plastic waste is recycled. This observation is a driving force towards the development of valorization processes applicable to large amount of plastic

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waste. In this context, the following sections discuss the various investigations of thermo- 130

chemical-biological strategies of plastic waste recycling towards valuable platform molecules. 131

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## 3. Strategies of valorization of plastic residues towards valuable products
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Nowadays, the mechanical processing is the main route for recycling waste plastics of various 135

sources[1,12]. This methodology involves the classification of the collected waste according to 136

the polymers´ nature and color. Then, it is washed and mechanically ground into a secondary 137

raw material in the form of plastic flakes[12]. Then, the flakes are melted (extrusion stage) and 138

filtered to remove impurities. This recyclate that is ready to be reuse in new plastic products 139

is generally of a lower quality than starting virgin-grade plastics mainly due to the changes in 140

the polymer structure during the melting process. 141

In contrast, the chemical and biological recycling pursues the breaking down of the 142

polymer into valuable molecules suitable to be converted into new materials. The so-called 143

tertiary recycling of plastics, comprises the pyrolysis and hydrolysis of the wastes[13,14]. Those 144

processes often involve a sequence of procedures that might begin with the mechanical 145

treatment, followed by a chemical (catalytic or not) process and further biotransformation of 146

the obtained molecules. 147

The biological upgrading of that building block molecules uses biocatalysts based on 148

enzymes or microorganisms. Microbial bioprocessing of plastics involves assimilation and 149

mineralization of the carbon degradation products to build more complex molecules. In 150

contrast, the enzymatic treatment produces substances that can be further valorized into 151

second generation products. 152

An efficient recycling and valorization of plastic waste is a challenge since there is a large 153

number of different plastics, many of them consisting of a combination of different polymers 154

as well as the presence of additives, such as plasticizers, fillers and reinforcements, thermal 155

stabilizers and antioxidants, colorants, metals, among others. The variety and complexity of 156

their composition is a drawback that traditionally involves multiple processing steps to be 157

overcome. 158

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### 3.1. Thermochemical (chemical and pyrolytic) based treatments: An overview

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Tables 1 to 4 shows a pick of the latest reports on thermochemical and chemical methods that use plastic residues as feedstocks. In particular, the nature of the process, operative conditions, yield, recovery, purification and valorization, have been addressed on the treatment of polyethylene terephthalate[14-22], polyethylene[23-30], polypropylene[31-38] and polyurethane[39-44] based wastes.

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In general, the *pyrolysis* is a thermochemical process carried under an inert gaseous environment (non-oxidative atmosphere) provided by argon or nitrogen. More recently, the use of carbon dioxide has also been investigated as will be discuss later on. The process involves the decomposition of a substrate through heating carried out either in a slow or fast mode, with or without a catalyst, in a batch, fluidized or spouted bed reactor.

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The pyrolysis generates a liquid fraction called oil or biooil (if comes from biomass), composed of organic molecules that are lighter than the ones of the feedstock; a non-condensable gaseous fraction and a solid phase composed of a carbonaceous material (char or biochar). It is somehow obvious that the nature of the products of pyrolysis is related primarily to the starving oxygen environment that suppresses the gasification and combustion, preserving the integrity of the organic molecules and avoiding the generation of non-condensable gases. Secondly, the abundance of the liquid, gaseous and solid fractions and their composition depends on the heating rate and the temperature. A slow heating (slow pyrolysis), high residence time of the inert gas with the substrate (5-60 min) and temperatures from 300 $^{\circ}$C to 650 $^{\circ}$C, conduct to a higher proportion of the solid fraction. Fast heating (fast and flash pyrolysis), low residence time (0.5-1.0 s) and temperatures in the range of 450-600 $^{\circ}$C, improve the yield of oil[33].

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In turn, the pyrolysis might use a catalytic material in order to direct the decomposition towards targeted reactions and products. For instance, the non-catalyzed pyrolysis of PET

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typically yields terephthalic acid, benzoic acid vinyl ester and acetophenone. However, the pyrolysis of PET waste carpet catalyzed with a basic material such as CaO with steam co-feeding, conducts to the deoxygenation of PET's oligomers towards benzene[14] (see Table 1, row 1).

The pyrolysis of low-density polyethylene (LDPE) waste in the presence of a HZSM-11 zeolite yields light aliphatic hydrocarbons in the $C_8$-$C_{21}$ range rather than the $C_{18}$-$C_{35}$ obtained in the non-catalyzed process[23]. The acidic material catalyzes not only the cracking of hydrocarbons, but also the dehydrogenation of propane towards propylene (see Table 2, row 1).

In this context, the typical heterogeneous catalysts used in pyrolysis are aluminosilicate materials such as, zeolites (ZSM-5, ZSM-11, Y, HY)[14, 23,25-27,33,34] and the commercial catalyst used in the fluid catalytic cracking (FCC) process of petroleum refinery[25,27,32,33] (see Table 2, rows 3 and 5; and Table 3, rows 2, 3 and 4) .

Recently, Kanattukara *et al.* published an extensive investigation of the influence of various catalysts, such as ZSM5, activated alumina, the FCC catalyst and a halloysite nanotube clay, in the pyrolysis of wastes containing polyethylene (HDPE and LDPE) and polypropylene (PP)[34] (see Table 3, row 4). The catalysts allowed diminishing the temperature of the pyrolysis from 470 °C to 450 °C, reaction time from 5h to 4h, and improved the yield of the oil fraction compared with the non-catalyzed pyrolysis. These observations were attributed to the acid property of the materials that catalyze the cracking of fragments initially produced in the pyrolysis to even lower molecular weight hydrocarbons. In general, 70-80% of the oil was composed of olefins, followed by 20% of paraffins and cycloalkanes and a minor content of aromatic compounds.

Overall, the catalytic pyrolysis is intended to improve the amount of the liquid fraction towards suitable hydrocarbons to be applied as fuels. More precisely, $C_5$-$C_{15}$ hydrocarbons containing olefins and aromatic compounds, are key pyrolytic products. This goal is achieved primarily in the catalytic pyrolysis of polyethylene wastes, as shown in Table 2[23-27]. In some cases, a tandem pyrolysis, that is two successive pyrolysis, and tandem pyrolysis-steam
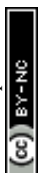
cracking was applied in order to further tuning the desired products[25,27] (Table 2, rows 3 and 5).

Typically, pyrolysis is carried out through conventional conduction heating, that is the feedstock is heating up at the surface and then the energy is conducted towards the inner part of the particles. Microwave assisted pyrolysis uses radiation that directly penetrates plastic material (of insulating nature) without absorption or is absorbed by dielectric materials (i.e., biomass) that are heated from the inside out. In this context, Table 2 (see row 4) shows that microwave pyrolysis of polyethylene (LDPE and HDPE) generates a high proportion of oil enriched in hydrocarbons that can be used as fuels[26].

Another non-conventional heating is plasma pyrolysis. This one provides extreme heat and high temperature (around 1200 °C) in a short period of time conducting to the generation of gases (i.e., CO, $H_2$ and hydrocarbons) and a low proportion of residues. This process is particularly indicated for the treatment of infectious medical plastic waste[31] (see Table 3, row 1).

The pyrolysis of polyurethane (PU) gives rise to harmful aromatic compounds, such as benzene, toluene, aniline, styrene, p-xylene, methylenedianiline (MDA), among others (Table 4, rows 1 and 2). Jung *et al.* reported the pyrolysis of waste PU catalyzed with 5 wt.% Ni/SiO$_2$ in a N$_2$/CO$_2$ environment to convert those chemicals in $H_2$ and CO (this gas mixture is known as syngas)[39]. The process was performed in a tandem mode through a pyrolytic reactor followed by a second one containing the catalyst. The slow pyrolysis was carried out between 100 °C to 700 °C at 10 °C/min, while the second reactor was set at 600 °C.

A similar approach was used to obtain syngas from the pyrolysis of disposable facemasks, composed of polypropylene, polyethylene and nylon[31] (see Table 3, row 1).

The non-catalyzed co-pyrolysis of PU with an epoxy resin also suppresses the decomposition of the methylene diphenyl diisocyanate monomer of PU towards HCN and aromatics (Table 4, row 2). In fact, the investigation of Wu *et al.* suggested that the acid sites of the epoxy resin catalyze the secondary cracking of those substances towards aliphatic hydrocarbons, alcohols, ethers and epoxides at temperatures above 500 °C[40].

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As observed in the Tables 1 to 4, the pyrolytic process is a commonality in plastic waste    246

treatment since it is suitable to be applied regardless of the nature of the polymeric matrix.    247

Nevertheless, less harsh processes for plastic waste depolymerization, such as hydrolysis,    248

glycolysis, methanolysis, aminolysis, hydrothermal degradation, hydrogenolysis and    249

hydrocracking, have also been investigated.    250

The *hydrolysis* is the reaction with water at high temperature that is performed under    251

acidic, alkaline or neutral conditions, with or without a catalyst[14]. The hydrolysis    252

depolymerizes the plastic waste towards the terephthalic acid (TPA) monomer of PET and    253

polyols in the case of PU. Table 1 (rows 2, 3 and 4) shows that the hydrolysis of waste bottles    254

of PET towards the monomer is highly effective to recover up to 100% of TPA[14-16]. Similarly,    255

the acidolysis of PU with dicarboxylic acids produces polyol, amine and esters (see Table 4,    256

row 4)[42].    257

Polyethylene is based on the polymerization of ethylene $C_2H_2$; therefore, the linear alkyl    258

chains of the polymer $(C_2H_4)_n$ do not have polar functions. In turn, PE is rather inert and not    259

suitable for hydrolysis. In the case of polypropylene, the hydrothermal degradation with    260

water in sub and supercritical conditions, at about 450 °C, in an inert gas at high pressure,    261

proved effective to degrade the PP waste towards an oil containing alkanes, alkenes, alcohols,    262

among others[36,37] (see Table 3, rows 6 and 7). The hydrolysis of ice cream packaging under    263

oxidative conditions, provided by hydrogen peroxide and $CO_2$, yields mostly acetic acid at a    264

lower temperature (150 °C vs 450 °C) than the process described before[35] (Table 3, row 5).    265

The *glycolysis* comprises the cleavage of the ester bonds of PET with ethylene glycol to    266

release oligomers, dimers and finally the 2-hydroxyethyl terephthalate (BHET)[20,21] (see Table    267

1, rows 8 and 9). Typically, heterogeneous catalysts, such as metal (Zn, Mn, Co and Pb) salts,    268

sulfated niobia, $ZnMn_2O_4$, g-$Fe_2O_3$, zeolites and silica nanoparticles, are used[13,20]. More    269

recently, deep eutectic solvents catalysts have been successfully used in the glycolysis of PET    270

waste with an important reduction of the temperature of reaction compared with the    271

heterogeneous catalyzed process[21] (Table 1, row 9). PU also undergoes glycolysis through the    272

reaction of the urethane group NHCOO with diethylene glycol, releasing a polyol and    273

carbamate compounds, $R_1NHCOOR_2$. The nature of these last ones depends on the isocyanate that was originally used for synthesizing the polymer. Most frequently, the isocyanate is diphenylmethane-4,4'-diisocianate, which provides the carcinogenic amine 4,4'-methylendianiline (MDA) upon PU glycolysis[41,43,44]. In this context, Donadini *et al.* studied the reaction of MDA with 2-ethylhexylglycidyl ether, acetic anhydride and ethylene carbonate in order to diminish its concentration in the reaction media[41]. The deaminated solution was then successfully used to synthesize new rigid PU foam (see Table 4, row 3). Microwave assisted glycolysis of rigid foams made of PU catalyzed with potassium acetate and stannous octoate proved far less time consuming and energy saving than the conventional heating (Table 4, row 5). The combination of the catalysts and diethylene glycol provided a dielectric media for an efficient heating that conducted to PU depolymerization towards polyols along with a low content of the harmful MDA[43].

The depolymerization of PET waste through *methanolysis* and *ethanolysis* implies the transesterification with methanol or ethanol at 70 °C to 200 °C, catalyzed with zinc acetate, potassium carbonate or biomass ashes[14,17-19]. The reaction yields dimethyl terephthalate and diethyl terephthalate, between other substituted monomers containing the terephthalate backbone (see Table 1, rows 5 and 6).

The *aminolysis* involves the reaction with an aqueous solution of a primary amine at 20-200 °C, under an inert environment with the presence of a catalyst or not [13,14]. This process was investigated in the depolymerization of PET [13,14,19] and PU[42]. The aminolysis of PET might be carried out with ethanolamine, ethylene diamine, allyl amine, hydrazine hydrate, hydroxylamine hydrochloride or alkyl amine, yielding bis(-2-hydroxyethyl) terephthalamide, bis(2-aminoethyl) terephthalamide; N,N'-diallyl terephthalamide, terephthalic dihydrazide, terephthalohydroxamic acid and N,N'-dialkyl terephthalamide, respectively[13]. In particular, the non-catalyzed solvent-free aminolysis of PET bottles waste, with 1,2-diaminopropane at 130 °C, provided a water-soluble amide of the monomer. This product is suitable to be condensed with salicylaldehyde towards a Schiff base[19] (see Table 1, row 7).

Table 4 (row 4) shows that the aminolysis of PU generates a biphasic system containing an upper phase with a polyol and a bottom one with disubstituted ureas. In this context, the polyols are easily recovered and reuse to synthesize new PU. In addition, the ureas might be further valorize through decomposition in amines and $CO_2$[42].

The *hydrogenolysis* is the selective scission of C-C and C-O bonds through reaction with 305
hydrogen. Typically, metal particles in acid or basic media are used as catalysts[45]. 306
Depolymerization of plastic through hydrogenolysis has gained attention since numerous 307
studies demonstrated that polyolefins are successfully converted to short-chain 308
hydrocarbons[46]. At 200-250 °C, liquid products are obtained from polyolefins and the 309
selective alkoxy C–O bond hydrogenolysis of polyesters drives to high yields of the 310
terephthalic acid (see Table 1, row 10). 311

Table 4 (row 6) shows that the hydrogenation of upholstery PU foam catalyzed with a Mn- 312
complex and t-BuOK, generates methylenedianiline, the corresponding formate and the 313
polyol[44]. 314

Hydrocracking is a process that converts heavy plastic molecules into lighter molecules by 315
breaking the long polymer chains in the presence of hydrogen with a bifunctional metal/acid 316
catalyst[46,47]. Zeolites are often used to catalyze these reactions due to their strong acidity, 317
high thermal and hydro-thermal stability and regeneration capacity. Furthermore, the 318
porosity of zeolites allows accessibility of certain reactants to the reaction sites, leading to 319
high selectivity[48]. Efficient hydrogen transfer from the hydrogen donors to the polyolefins is 320
crucial to this process. Typically, the reaction temperature is 150-450 °C and the hydrogen 321
pressure is between 20 and 100 bar. Hydrocracking of PE or PP with a bifunctional metal/acid 322
catalyst can achieve a liquid yield over 60% and the distribution of hydrocarbons in liquid fuels 323
will depend on the metal and acid sites of the catalyst[49,50] (see Table 2, rows 7 and 8 and Table 324
3, rows 8 and 9). 325

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### 3.2. Chemo-biological valorization of plastics residues

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The section above presented the investigations regarding the chemical and 329
thermochemical methods for the valorization of plastic wastes that were reported in the past 330
5 years. In comparison, biodegradation is a more environmentally friendly approach, since 331
bioprocesses use milder reaction conditions, such as room temperatures and mid-range pH. 332
More interesting, they avoid or minimize the use of biologically incompatible -toxic- reagents. 333
Interaction of bacteria and fungi with plastic waste has been successfully applied to degrade 334
the polymers into shorter low-molecular weight chains, either under aerobic or anaerobic 335
conditions[51,52]. Till today, three different strategies have been explored, including fungal, 336
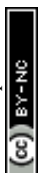
bacterial (isolates and consortia) and enzymatic biodegradation (native and bio-engineered isolated enzymes). Each of them is best suited to depolymerize different post-consumer plastics, as we will review in this section.

Combined strategies that valorize plastic waste through both chemical and biotechnological methods were designed to overcome the challenges of deconstructing highly crystalline polymers, such as PET or PU. Table 5 gathers reported tandem processes involved in the treatment of plastic wastes to recover valuable building block molecules. In addition, the biological and enzymatic based technologies developed for further valorization of the recovered substances are summarized and illustrated in the Figures 3A and 3B. Chemo-enzymatic treatment of textile waste based on polyesters was investigated by Quartinello *et al.*[53]. As a first step, the plastic waste was hydrolyzed in an aqueous environment at 250 °C and 40 bar (neutral hydrolysis), which depolymerized 85% of the PET fibers into terephthalic acid and oligomers (see Table 5, row 1, Fig. 3A). This energy-consuming pre-treatment was necessary to degrade highly crystalline fractions of PET into oligomers that enzymes can catabolize. These last ones were further hydrolyzed with 1-2 mg mL$^{-1}$ of *Humicola insolens* cutinase, an enzyme from the α/β hydrolase family, at pH 7, 50 °C, for 6 h. The overall process provides 97% of terephthalic acid (TPA).

Going even further in the biorefinery concept, Shingwekar *et al.* developed a two-step process for the depolymerization of post-consumer PET bottles to 92 wt% of bis(2-hydroxyethyl) terephthalate (BHET)[54]. The glycolysis performed at 190 °C for 1.5 h was catalyzed with ashes obtained from orange peel (Table 5, row 2, Fig. 3A), yielding a biocompatible mixture rich in BHET suitable for biological degradation, since the crystalline fraction of PET was eliminated. A native consortium of five bacteria strains, investigated previously by León-Zayas *et al.*, was isolated from soils polluted with petroleum products, taking advantage of the rapid adaptation and evolution capacities of bacteria[55]. Composed of *Bacillus thuringiensis* C15, *Bacillus albus*, *Pseudomonas* sp. B10, *Pseudomonas* sp. SWI36 and *Pseudomonas* sp. PFYNo1, the consortium uses more readily BHET than PET, synergistically degrading the glycolysis products by 62.63% in 2 weeks towards TPA and ethylene glycol (EG). The overall 2-step process stands as a sustainable methodology to valorize plastic waste without using toxic or costly reagents.
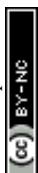
In a similar approach, Kim *et al.* investigated the chemical glycolysis and enzymatic hydrolysis of PET cup waste followed by the biological transformation of TPA towards catechol[56]. Altogether, the cascade-type process comprises the glycolysis of the polymer to BHET and mono(2-hydroxyethyl) terephthalate (MHET) with potassium carbonate $K_2CO_3$ catalyst, followed by the enzymatic degradation of BHET, MHET and oligomers to TPA (Table 5, row 3, Fig. 3A). Four commercial esterases from *Bacillus subtilis*, *Paenibacillus barcinonesis* and *Rhizopus oryzae*, *Methylobacterium populi* were assayed. This last one catalyzed a complete depolymerization of BHET at a loading of 41.8 μg mL$^{-1}$, 30 °C in 10 h. Finally, the biotransformation of terephthalic acid to catechol was achieved with a bioengineered strain of *Escherichia coli* at 30 °C for 20 h. Addressing the complete biorefinery concept, the authors proposed a PET upcycling using the catechol as a coating agent directly from the previous step, by simply removing *E. coli* cells without further purification. The catechol coating provided the scaffolding to further functionalization of different materials, with a broad range of applications.

Previous work of Yoshida *et al.*, reviewed by Blank *et al.*, supply the bases for more recent studies that engineer bacteria with a set of genes codifying PET-degrading enzymes[57]. The authors isolated the bacteria *Ideonella sakaiensis* 201-F6, capable to degrade PET and assimilate its monomers, and characterized the specific enzymes involved with that unusual feature, namely PETase and MHETase. The enzymes have the potential to be improved by genetic manipulation and to achieve PET depolymerization at milder temperatures and biologically relevant conditions.

A catalyzed glycolysis of model PET (not from a waste source) coupled with biological upgrading of BHET towards β-ketoadipic acid (β-KA, monomer of nylon 66) was reported by Werner *et al.*[58]. In this case, degrading enzymes from *I. sakaiensis* were used to transform *Pseudomonas putida* KT2440, obtaining a strain capable of harnessing EG by constitutive expression of native genes and BHET by heterologous expression of PETase, MHETase, TPA transporters and enzymes for TPA conversion to protocatechuate (PCA). The strain further converts BHET into the β-ketoadipic acid with a molar yield of 76% at 30 °C, pH 7 in 96 h of fermentation. This scheme of chemical depolymerization coupled with biodegradation proved to be yield-efficient, but improvement of biocompatibility of the glycolysis products is necessary to achieve process fluency and scaling. Valorizing the EG obtained as a by-product remains a future challenge, since β-KA represses EG utilization by bacteria[58].

The performance of *P. putida* KT2440 and engineered derivatives on post-consumer PET feedstocks is reviewed next. In this context, Sullivan *et al.* reported the chemical and biological processing of a mixture of high-density polyethylene, polystyrene, and poly(ethylene terephthalate) that are regular components of post-consumer plastics waste[59]. The authors used expanded polystyrene cups, milk containers made of polyethylene, and single-use beverage bottles (Table 5, row 4, Fig. 3A). At a first step, the mixture was subjected to auto-oxidization and depolymerization through a catalyzed process which conducts to a random type of chain scissoring. The process, carried out typically with manganese/copper containing catalysts and N-hydroxyphthalimide as oxidation promoter, was performed at 180-200 $^{\circ}$C for 5.5 h. As a result, benzoic acid, dicarboxylic acids and terephthalic acids were produced, with substantial energy consumption and need for wastewater treatment. An important observation highlighted by the authors was the fact that the catalytic treatment in an oxygen atmosphere, unlike a typical pyrolysis, generates a mixture of products with enhanced water solubility, suitable for biological fermentation. In this context, the authors used *P. putida* genetically engineered for the bioconversion of acetate, C4 to C17 dicarboxylates, benzoate, and terephthalate to polyhydroxyalkanoate, that is a natural polyester. In addition, these remarkable strains were designed to use acetate and dicarboxylates as a carbon source for cellular growth, while converting benzoate and terephthalate to β-ketoadipate, a monomer of polymers. The authors called that downstream valorization a "biological funneling", since the various molecules produced in the chemical treatment were bio-transformed to only two building block molecules. These approach enables the treatment of blends of plastic residues without previous sorting, which makes it cost-effective.

In the case of polyethylene (PE), it is interesting to discuss the investigation of Li *et al.* who isolated the marine bacteria *Microbulbifer hydrolyticus* IRE-31, capable to degrade the recalcitrant low-density polyethylene (LDPE)[60]. The bacteria, found in the wastewater of a lignin-rich pulp mill, were able to oxidize the surface of linear LDPE, monitored by scanning electron microscopy after 30 days of incubation. FTIR analysis brought insides of the unknown metabolic pathways of biodegradation of PE, revealing the formation of additional hydroxyl and carbonyl functional groups at the polymer surface, meaning that oxidative reactions may be the initial step for depolymerization. Nevertheless, the products of degradation were not informed.

A study by Shao *et al.* reports the biodegradation of un-treated PE with the native strain *Streptomyces albogriseolus* LBX-2 isolated from soil[61]. The authors highlight the importance of using microorganisms that can degrade virgin PE, avoiding the photo- and thermal pre-treatments. It has been proposed that the alkane hydrolase system, particularly alkane monooxygenase, is involved in PE degradation, supported by the similarities in the chemical structures of these substances. Arguing this hypothesis, the authors found 21 monooxygenase genes in the genome of *S. albogriseolus* LBX-2, while other bacterial genomes commonly harbor a few. Further genomic, transcriptomic and metabolic studies of the novel strain are needed to design rational biodegradation processes.

Gregory *et al.* reported the catalytic hydrogenolysis of waste polyolefins followed by biotransformation towards an ester wax and alcohols[62] (see Table 5, row 5, Fig. 3A). Interestingly, the authors isolated a consortium of bacteria (composed of two *Rhodococcus aetherivorans* strains) from LDPE debris found in the soil of a plastic recycling plant. Those bacteria were cultivated in a $C_{10}$-$C_{40}$ alkane mixture as a sole carbon source in order to enhance the bioconversion of the PE deconstruction mixture.

The investigations discussed above evidences that most of the research efforts are devoted to the treatment and valorization of PET based wastes. Nevertheless, this kind of plastics represents 10.2% of the global plastic production. But, what about the chemo-enzymatic treatment of more recalcitrant and by far less recycled plastics, such as polyurethane (PU)?

The diverse composition and variety of monomers of PU hinders the implementation of chemical depolymerization processes and requires the design of new recycling strategies. As described by Rossignolo *et al.*[63], degradation of PU takes place in three steps; namely, breaking of the polymer chains into oligomers; deeper depolymerization towards low-molecular weight species; and conversion to carbon dioxide and water (aerobic conditions) or, alternatively, to methane (anaerobic conditions).

In this context, an early investigation by Schmidt *et al.* demonstrated that enzymatic hydrolysis of model PU and thermoplastic polyester PU (TPU) with various strains of cutinases was achievable[64]. The authors cloned synthetic gene constructs corresponding to polyester hydrolases LC cutinase (LCC), TfCut2, Tcur1278 and Tcur0390 in *E. coli*, expressed and purified the recombinant enzymes that allowed the hydrolysis of solid polyurethane plastic. The

degradation, performed under incubation at 70 °C for 200 h, was concluded from surface 463
depletions and weight loss of PU, but the products of degradation were not reported. 464

Biological funneling for the upcycling of PU hydrolysates was proposed by Catur Utomo *et* 465
*al.*[65]. The researchers applied a defined microbial mixed culture composed of microorganisms 466
trained to use specific PU monomers and genetically engineered to yield rhamnolipids. The 467
advantage of this strategy relays in saving time and effort by developing various strains with 468
different metabolic capacities rather than a single strain with multiple biotransformation 469
events or multiple targeted features achieved by directed evolution. While three *P. putida* 470
KT2440 derivatives harboring different genetic optimizations enable the utilization of adipic 471
acid, 1,4-butanediol and EG, the addition of a fourth *Pseudomonas* sp. strain that degrades 472
2,4-toluene diamine (TDA) was not enough to reduce the inhibition caused by this isocyanate 473
by-product. To overcome the drawback, the authors proposed a chemical removal of TDA 474
from the PU hydrolysate prior to incubation with the microbial consortium. The scheme 475
allows the recovery of valuable TDA and the full utilization of other PU monomers originated 476
from a variety of PU wastes, but some issues regarding biocompatibility of the extractants 477
remains. 478

The review of Magnin *et al.* pointed out that there is only one investigation about the use 479
of oxidoreductases, such as laccase and a horseradish peroxidase, in the enzymatic 480
degradation of PU[66]. That review dates from the year 2021 and to our knowledge, there is not 481
additional publications on that matter. Magnin *et al.* discovered that the combination of an 482
amidase (E4143) and an esterase (E3576) was capable of hydrolyze model PU films towards 483
6-hydroxycaproic acid (HCA) and 4,4'-methylene dianiline (MDA)[67]. The researchers 484
developed an interesting strategy, using specifically designed TPU that allows to further 485
understand the molecular mechanisms of enzymatic catalysis. It was postulated a synergistic 486
two-discrete step degradation, by which esterase first attacks the polymer and releases water 487
soluble oligomers containing urethane bond, allowing amidase to better access and exert its 488
urethanase (hydrolase) activity. Finally, the efficient enzymatic system yielded 1 g/L of 6- 489
hydroxycaproic acid and 0.3 to 3 mg/L of MDA and MDA linked to caprolactone. As a 490
limitation, this time-consuming process requires boosting/replacement of the lost enzymatic 491
activity every two to three days during 51 days of incubation. 492

More recently, the same research group demonstrated that a commercial laccase from 493
*Trametes versicolor* fungi was active in the degradation of model foams, thermoplastic, 494
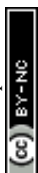
polyester and polyether-based PU incubated in 1-hydroxybenzotriazole at 37 °C for 18 days.[68] 495

Further investigation is needed to test if the combination of the prior studied esterase and 496

amidase with the novel laccase could create an efficient enzymatic system, suitable for 497

different kinds of PU. Moreover, the development of coupled schemes with physical (grinding 498

towards PU powder) or chemical (glycolysis) pre-treatments could enable full degradation of 499

the plastic. 500

It is worth noticing that the investigations discussed above used model materials which, 501

somehow, denotes the difficulty of the biological recycling of the actual PU waste towards 502

substances suitable for valorization, excepting for those motivated by basic research. In fact, 503

a very recent review by Rossignolo *et al.* pointed out that biodegradation is limited by the 504

number of microorganisms and enzymes able to degrade polyurethanes. In addition, the 505

various structures (polyester PU, polyether PU, among others) and forms (flexible and rigid 506

foams, elastomers, thermoplastic, etc.) would demand a previous PU waste separation to 507

enable an effective upcycling[63]. In this context, more research is needed to obtain engineered 508

microorganisms harboring the gene constructs necessary to overproduce genetically 509

optimized enzymes. The use of the metagenomic approach to find new enzymatic activities 510

among microorganisms belonging to degrading communities of PU and petroleum derivatives 511

seems to be the next step to overcome these issues. 512

Such strategy was used by Branson *et al.* in the only investigation that, to our knowledge, 513

reports the chemo-enzymatic recycling of an actual PU waste[69] (see Table 5, row 6, Fig. 3B). 514

The authors isolated DNA from soil largely exposed to PU residues and developed a 515

metagenome library. The screening for urethanase activity lead to the discovery of three new 516

enzymes, identified as: UMG-SP-1 to UMG-SP-3 with GenBank accession codes: OP972509, 517

OP972510, and OP972511. These enzymes converted 65% of the dicarbamates generated in 518

the glycolysis of polyether-polyurethane waste foam towards aromatic diamines under mild 519

conditions and at room temperature. 520

The development of tandem processes for plastic recycling is an ongoing effort that 521

requires a critical analysis of the technical feasibility, economic and environmental factors 522

before gone towards a scaling stage. In this sense, the need for waste sorting before 523

treatment is a bottle neck. Even though some bio-funneling strategies has been proposed to 524

overcome this drawback, the development of more integral waste processing approach to 525
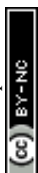
achieve circular economy goals is still a challenge. The few operative technologies that reached that stage of maturity will be further addressed in the section 4 of this review.

### 3.3. Valorization of plastic and biomass waste mixtures: a synergic effect exists?

The previous sections described the valorization of plastics waste of various sort. This section dives into the chemo-biological treatment of mixtures of plastic and biomass wastes and the effect of combining those major streams of residues. A detailed analysis has been published by Seath *et al.* regarding the synergistic effect of the co-pyrolysis of biomass and plastics to improve the yield and quality of biofuels[70]. In this context, the up-to-date reports (published in the past 5 years) on to the treatment of mixtures composed of plastic waste with textile fabrics (cotton based and synthetic)[71-76], waste food[77-79] and paper wastes[80] are discussed.

Table 6 summarizes the feedstocks, characteristics of the chemical pretreatment and the bioprocessing of the waste mixture, products obtained and further bioprocessing of them, if applied.

In the particular case of textiles containing PET (with the exception of those containing wool), grinding and a chemical pretreatment (i.e., alkaline hydrolysis) are required to increase the available sites for the biocatalytic saccharification with cellulases. Table 6 (see rows 1 and 2) shows that saccharification of cotton-based wastes is performed through a commercial cocktail of cellulases. This biocatalyst contains endoglucanases that randomly cut cotton cellulose chains; exoglucanases, that act at the ends of the cellulose chain yielding cellobiose; and β-glucosidases, that degrades cellobiose towards glucose[71,72]. Only one research presents the simultaneous depolymerization of PET and cotton biocatalyzed with cutinases and cellulases, giving rise to terephthalic acid and glucose[73] (Table 6, row 1). Unlike other methods, the work reported by Kaabel *et al.* uses the minimum amount of liquid just to provide enough moisture for the bioprocessing, but no pre-treatment is performed. Bioethanol is also produced through fermentation with *Saccharomyces cerevisiae* of carbohydrates obtained from textiles[72,76] (Table 6, rows 1 and 2).

Various types of plastics have also been recently addressed. These include PET microplastics; polyethylene, polypropylene and polystyrene found in films; plastics from disposable bags and food containers and, also, polylactic acid from biodegradable bags.

Particularly, complex mixtures of plastics with waste food and sewage sludge, have been 558
treated through anaerobic co-digestion both in mesophilic and thermophilic fashions with 559
bacteria and archaea microorganisms[77-79]. In this process, organic matter is degraded to form 560
biogas by the action of anaerobic bacteria at temperatures of 30 to 50 °C. The first stage 561
involves acid-forming bacteria that use carbohydrates as raw material. A second step 562
implicates the generation of acetic acid. The last stage comprises the bioconversion of acetic 563
acid, carbon monoxide, and hydrogen in biogas composed mainly of methane. 564

The mixture of wastes is frequently pretreated before the anerobic digestion. In this 565
context, Farghali *et al.* reported the pretreatment of 2 m$^3$ of a mixture of plastic films, waste 566
food and rice husks under subcritical water in a large-scale reactor at high temperature and 567
pressure[77] (see Table 6, row 3). A pretreatment was required to reduce the wastes to liquid 568
and solid fractions containing solubilized lignocellulose. In fact, volatile fatty acids released 569
from biomass through the hydrothermal process served as carbon-source for bacteria, 570
improving the biogas production. 571

In contrast with the positive effect of biomass-plastic mixture described above, the 572
investigations of Wang *et al.* regarding the co-digestion of PET microplastics with sewage 573
sludge and waste food was not synergistic[78]. In this case, the decomposition of PET into 574
diisobutyl phthalate and dibutyl phthalate resulted harmful to the microbial community of 575
the anerobic digestor (see Table 6, row 4). Indeed, those substances caused a decrease in the 576
amount of hydrolytic bacteria *Bacteroides vadin HA17* and the acidification performed by 577
*Clostridium* and *Sphaerochaeta*. 578

A similar outcome was obtained by Yu *et al.* in the co-digestion of food waste and 579
biodegradable plastic bags made of polybutylene adipate terephthalate (PBAT)/polylactic 580
acid (PLA)/starch[79]. The authors detected a decline in the biogas production at a 581
bioplastic/waste food ratio above 30% due to a detrimental effect on the bacterial community 582
diversity (see Table 6, row 5). The less effective anaerobic digestion under mesophilic 583
conditions and high plastic loading was attributed to the decrease of the *Synergistota* phylum 584
type of bacteria. Similarly, a decrease in the abundance of bacteria related to the hydrolysis 585
and acidification of organic substances (i.e., *Firmicutes* and *Bacteroidota*) was observed under 586
thermophilic conditions and high plastic loading. On the other hand, the composition of the 587
archaeal community (i.e., *Methanosarcina, Methanospirillum, Methanothermobacter* and 588
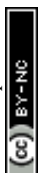
*unclassified_k_norank_d_Archaea*) was not influenced by the proportion of bioplastics mixed 589

with food waste. 590

Finally, Brown *et al.* investigated the co-fermentation of various plastics (PET, 591

polypropylene, low-density and high-density polyethylene, polystyrene, and polyvinyl 592

chloride) and paper waste through enzymatic hydrolysis with the commercial cellulase 593

CTec2® [80]. The authors demonstrated that the presence of acetic acid in the copy paper acts 594

as an enzymatic inhibitor of cellulases (Table 6, row 6). In this context, an alkaline pre- 595

treatment proved to be effective in removing contaminants and increasing the surface area 596

of the cellulose fibers that in turn, enhances the substrate-enzyme interaction. However, the 597

presence of plastic, ink, and stickies within the mixed paper stream, did not have an impact 598

on the enzymatic hydrolysis of cellulose towards glucose and xylose. 599

Figure 4 summarizes the synergistic and non-synergistic effect of mixing plastic and 600

biomass wastes. PET is one of the most common plastic wastes polluting the planet, and it is 601

also de most deeply studied in this section. Better yields in glucose and bioethanol production 602

were achieved employing cotton or wool combined with PET as biomass feedstock. 603

Nevertheless, the PET presence was detrimental when methane production from sewage 604

sludge-waste food or glucose generation from paper waste was studied. With regard to 605

polyethylene, polypropylene and polystyrene, there were analyzed combined with paper and 606

waste food, giving only synergistic effect in the anaerobic digestion of rice husks. Finally, 607

plastic residues from biodegradable bags did not present beneficial effect in the anaerobic 608

digestion studied with waste food as raw material. 609

610

**4. From lab bench to industry: actual high scale processes** 611

612

Previous sections discussed a variety of investigations dealing with thermochemical and 613

chemo-biological methods to treat plastic waste and mixtures of plastic-biomass waste, in 614

order to obtain valuable substances. This section presents the technologically mature and 615

cost-effective processes that scaled up towards industrial application and are effectively 616

applied to this day. 617

The report published by the capital investment firm called Closed Loop Partners and our 618

own search in the world wide web performed in January 2024, show that pyrolysis is the first 619

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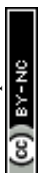
choice for plastic recycling with 36 companies all over the world. Chemical depolymerization 620

possesses the second place with 19 companies[81]. There is only one company called Carbios 621

(located in France) that applies chemo-biological methods. Carbios depolymerizes PET and 622

other polyesters from urban plastic and textile wastes through enzymatic hydrolysis. The 623

process uses an engineered cutinase where a divalent-metal-binding (formed by the side 624

chains of three acidic amino acid residues) site was replaced by a disulfide bridge to increase 625

the thermal stability of the hydrolase. The obtained TPA monomer is recycled to produce new 626

plastic[81-83]. 627

In addition, it is worth noticing that the startups: Scindo (London, UK), the University of 628

Portsmouth (USA) and Xampla (Cambridge, UK), developed biological based recycling 629

technologies that are currently at lab scale and moving towards large scale application[81]. 630

631

## 5. Conclusions and future perspectives 632

633

This review provides insights in the up-to-date research regarding the valorization of the 634

most common plastic type residues and plastic-biomass mixed wastes that account for the 635

major quantity of residues generated worldwide. 636

The valorization of waste-derived platform molecules for the production of refined 637

chemicals and commodities has been extensively explored in the last decades. Nowadays, 638

most of these compounds are originated from petroleum-based raw materials. However, the 639

depletion of fossil feedstocks and the GHG emissions associated to those energy sources is 640

turning the governments and research community into the obtention of bio-based building 641

blocks, upgrading the industrial processes to more eco-friendly ways. 642

The use of wastes as biorefinery feedstocks represents an unlimited and ubiquitous 643

alternative that can be adapted to each country, region and climate's availability of renewable 644

resources. Nevertheless, molecular recycling of mixtures of plastic and biomass residues is 645

not an easy task due to the variety of compositions and properties of those wastes, which in 646

turn might be either an advantage, as in the case of the pyrolysis of mixed plastic-biomass 647

residues, or a problem to overcome with an appropriate pretreatment. A remarkable fact is 648

that always a chemical or physical, or both treatments, are required for further application of 649

either an enzymatic or biological process in order to obtain valuable substances out of the
waste. In fact, multiple approaches of pretreatment have been investigated and novel, less
harsh ones are ongoing research.

The use of microorganisms as microscopic bioreactors for the production of commodities
has been largely exploited by humanity since early times. They have the complex metabolic
pathways and biologic machinery to synthesize all kind of biomolecules, including
biopolymers and its constituent building blocks. By this approach, with the appropriate
selection of the bacteria or fungi to be cultured, bulk mixtures enriched in target biomolecules
can be obtained.

This review clearly shows that there is a great deal of research to be done in order to
develop reliable chemo-enzymatic bioprocesses to treat and valorize mixtures of wastes. In
particular, the biobased valorization of mixed wastes, such as plastic and textiles, plastic and
biomass, and food wastes and plastics, are emerging research fields that needs further
development for industrial application. In fact, the cutting-edge investigations outlined in this
contribution shows a variety of vacancies and therefore, opportunities for the advancement
in the field.

## Author Contributions

The manuscript was written through contributions of all authors.

## Data availability

No primary research results, software or code have been included and no new data were
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## Conflicts of interest

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No primary research results, software or code have been included and no new data were generated or analysed as part of this review.