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Posted Date: 4 February 2025

doi: 10.20944/preprints202502.0190.v1

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Review

Emerging Biochemical Conversion for Plastic Waste Management: A Review

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Abstract: In recent years, vast amounts of plastic waste have been released into the environment worldwide, posing a severe threat to human health and ecosystems. Despite the partial success of traditional plastic waste management technologies, their limitations underscore the need for innovative approaches. This review provides a comprehensive overview of recent advancements in chemical and biological technologies for converting and utilizing plastic waste. Key topics include the technical parameters, characteristics, processes, and reaction mechanisms underlying these emerging technologies. Additionally, the review highlights the importance of conducting economic analyses and life cycle assessments of these emerging technologies, offering valuable insights and establishing a robust foundation for future research. By leveraging literature from the past five years, this review explores innovative chemical approaches, such as hydrolysis, hydrogenolysis, alcoholysis, ammonolysis, pyrolysis, and photolysis, which break down high-molecular-weight macromolecules into oligomers or small molecules by cracking or depolymerizing specific chemical groups within plastic molecules. It also examines innovative biological methods, including microbial enzymatic degradation, which employs microorganisms or enzymes to convert high molecular-weight macromolecules into oligomers or small molecules through degradation and assimilation mechanisms. The review concludes by discussing future research directions focused on addressing the technological, economic, and scalability challenges of emerging plastic waste management technologies, with a strong commitment to promoting sustainable solutions and achieving lasting environmental impact.

Keywords: Plastic waste; Conversion; Catalyst; Mechanism; Circular economy

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1. Introduction

Plastic products have permeated nearly every aspect of human life due to their numerous advantages, such as corrosion resistance, lightweight properties, antibacterial features, ease of processing, and low cost. Plastics are generally categorized into two main types based on their physical and chemical properties: thermosetting plastics and thermoplastics. Thermosetting plastics include phenolic resin (PF), urea-formaldehyde resin (UF), melamine resin (MF), unsaturated polyester resin (UPR), epoxy resin (EP), silicone resin (SI), and polyurethane (PU). These plastics undergo chemical reactions and harden after being heated, pressurized, or combined with hardeners for some time.

Conversely, thermoplastics, which are plastics that retain plasticity at certain temperatures, include polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), poly-styrene

doi:10.20944/preprints202502.0190.v1

(PS), polyoxymethylene (POM), polycarbonate (PC), polyamide (PA), acrylic resin (PSA), polyethylene terephthalate (PET), polysulfone (PSF), acrylonitrile butadiene styrene copolymer (ABS), and polyphenylene ether (PPE). From 1950 to 2020, the global annual plastic production skyrocketed, rising from 1.7 × 10^6 t to an astonishing 3.7 × 10^8 t [1]. This rapid growth was notably amplified in 2020, fueled by the sharp increase in the production and widespread use of medical protective equipment rich in plastics in re-sponse to the COVID-19 pandemic [2]. According to statistics, about half of the world's plastic products become waste and enter the environment annually [3].

Plastic waste is notoriously resistant to degradation and can remain in the natural environment for extended periods. Untreated plastic waste can adversely impact water, air, and soil ecosystems. Over time, physical, chemical, or microbial interactions can de-grade plastic waste into smaller particles, including microplastics (< 5 mm) and nano-plastics (< 1 μm) which exhibit biological toxicity to organisms [4–6]. In addition, micro-plastic and nanoplastic particles have a large specific surface area and strong adsorptionaffinity, enabling them to act as carriers for heavy metals and persistent organic pollu-tants [7–11]. These characteristics make them particularly harmful to humans and eco-systems [7,8,10,11]. Therefore, the effective conversion and reuse of plastic waste havebecome an urgent global priority.

Landfill and incineration are the traditional technologies for treating plastic waste[12,13]. To a certain extent, traditional technologies can solve the problem of plastic pol-lution. However, landfill and incineration also have many drawbacks to treating plasticwaste. For example, landfill methods require extensive land resources and prolongeddegradation periods [14]. The incineration method, on the other hand, emits smoke con-taining toxic and harmful substances such as heavy metals, organic compounds, acidicgases, and particulate matter [14]. Additionally, the slag and fly ash generated by incin-eration contain heavy metals, and fly ash also contains dioxins and a large number ofsalts, which are classified as hazardous waste [14]. Moreover, these conventional meth-ods fail to recover valuable resources effectively from plastic waste, emphasizing theneed for innovative alternatives. Emerging technologies for plastic waste treatment arethus essential to overcome the limitations of traditional approaches.

This review aims to provide a comprehensive overview of the technical parameters,characteristics, processes, and reaction mechanisms of different emerging technologies,focusing on chemical and biological methods for converting and utilizing plastic waste.Additionally, the review includes an economic analysis and life cycle assessment of thesetechnologies, offering valuable insights and guidance for future research and develop-ment. Recent literature (especially in the past five years) in various databases has beenreferenced, and the review summarizes the latest research progress on conversion andutilization of various types of plastic waste comprehensively. The review covers a widerange of contents on various types of technologies. More types of technologies are in-troduced in the review compared to other related reviews. Economic analysis and lifecycle assessment of the latest technologies is innovative in the review compared to someother related reviews, emphasizing the importance of sustainability and long-term im-pact.

2. Emerging Technologies

The technologies for converting or recycling plastic waste typically include physical, chemical, and biological methods. However, in recent years, research has increasingly focused on chemical and biological technologies as these methods demonstrate superior efficiency and sustainability in tackling the challenges of plastic waste management [14–16].

2.1. Chemical Methods

The principle of chemical methods is to break down high-molecular-weight macromolecules in plastics into smaller oligomers or monomers through cracking or depolymerizing chemical groups within the plastic polymers. Not only does this processreduce

doi:10.20944/preprints202502.0190.v1

plastic waste, but it also generates valuable chemicals that can be repurposed forvarious applications. Typically, the reactions of this process occur under specific condi-tions, such as the presence of additional reactants or catalysts, controlled temperature,reaction medium, or illumination.

Recent advancements in chemical recycling technologies of plastic waste have incorporated various devices, including tank reactors, electrolyzers, autoclaves, reactionvessels, fluidized-bed reactors, furnaces, fixed bed reactors, tube reactors, pyrolyzers,microwave ovens, fluidized bed gasifiers, and tar -cracking reactors, to optimize theconversion process (Table 1). Most researchers have used thermal chemical methods (e.g.,pyrolysis, gasification, hydrothermal gasification) to treat plastic waste, so the conversionprocess of plastic waste often occurs under high temperatures (usually at 200-850 °C)(Table 1). In general, pyrolysis needs to be carried out under inert gases (e.g., N_2, Ar) andgasification can be conducted under inert or non-inert gases (Table 1) [54]. Furthermore,hydrothermal gasification often occurs in the presence of supercritical water when thetemperature and pressure of water rise above the critical point (Table 1) [54].

Non-thermal chemical methods, in contrast, operate at lower temperatures, typicallybelow 150 °C and involve direct reactions between plastic waste and reactants such asmethanol or other chemical agents, reducing energy requirements (Table 1). Some bio-mass (e.g., *Enteromorpha clathrata*, cellulose, cooking oil, lignin, rice straw, sugarcane ba-gasse, pine wood) and plastic waste are pyrolyzed and they can react together (Table 1).Additionally, treating plastic waste by photochemical methods generally does not re-quire high temperatures, but it needs sunlight or ultraviolet (UV) (Table 1). As seen fromTable 1, $Pt/\gamma\text{-}Al_2O_3$, $MTO/Cl{-}Al_2O_3$, electrocatalyst, choline chloride-2urea (ChCl-2Urea),stannous octoate, Pt@S-1, $Pt/SrTiO_3$, $Ir\text{-}^{tBu}POCOP$, $[PdP(^tBu)_3(m\text{-}Br)]_2$, commercial ben-tonite (CB), kaoline, silica gel , activated charcoal, composites with alumina-substitutedKeggin tungstoborate (KAB) and kaolin, four Ni-Fe catalysts, MgO, Fe/Al_2O_3, HZSM-5zeolite, Y-zeolite with transition metals, waste refinery catalyst, zeolite beta composite,CeO2-supported Ru, Ru-modified zeolite, ZSM-5, Seawater, CaO/Fe_2O_3 oxygen carrier,Nb_2O_5, tetrabutylammonium decatungstate (TBADT) or Grubbs Catalyst M_20_2 are utilized as catalysts in the conversion process of plastic waste. The products include solids,liquids or gases such as potassium diformate, terephthalic acid, H_2, bisphenol A, PU,naphtha hydrocarbons, alkyl aromatics, C_2–C_4 olefins, 1,3-butadiene, C_4–C_{60} *n*-paraffins,isoparaffins, mono-olefins, paraffins, naphthenes, aromatics, char, carbon nanotubes(Table 1).

Table 1. Technical parameters of chemical methods for converting or recycling plastic waste.

Plastic waste	Device	Reactant	Catalyst	Temperature	Reaction medium	Illumination	Product	Reference
PE	Tank reactor	C_2H_4	Pt/γ-Al_2O_3, MTO/Cl–Al_2O_3	100 °C	Atmospheric C_2H_4	/	Propylene	[17]
PET	Electrolyzer	H_2O	Electrocatalyst	60 °C	KOH aqueous solution	/	Potassium diformate, terephthalic acid, H_2	[18]
PC	Autoclave	Methanol	ChCl-2Urea	130 °C	Autogenous pressure	/	Bisphenol A	[19]
PC	Reaction vessel	C_6HN, $C_8HN_2O_2$	Stannous octoate	70-75 °C		/	PU	[20]
PE	Autoclave	/	Pt@S-1	250 °C	Anisole	/	Naphtha hydrocarbons	[21]
PE	Autoclave	/	Pt/$SrTiO_3$	300 °C	3 MPa of H_2	/	Fuel oil	[22]
PE	Reaction vessel	C_2H_4	Ir-^{tBu}POCOP, [PdP(^{t}Bu)3(m-Br)]2	130-350 °C	170 Pa of H_2	/	Propylene	[23]
PE	Autoclave		Pt/γ-Al_2O_3	280 °C	/	/	Alkylaromatics, alkylnaphthenes	[24]
PE	Furnace	/		295 °C	/	/	Fuel oil, syngas	[25]
Plastic mixture	Fixed bed reactor	/	KAB/kaolin composites	500 °C	N_2	/	Carbon nanotubes	[26]

Plastic mixture	Tube reactor	/	Four Ni-Fe catalysts	430-571 °C	N2	/	Jet fuel, H2-enriched gases	[27]
		/	Activated carbon		N2			
Low-density PE	Fixed bed reactor	/	Activated carbon, MgO	450-600 °C	N2	/	Jet fuel, H2-enriched gases	[28]
PP	Fixed bed reactor	/	Fe/Al2O3	500 °C	N2	/	H2, liquid fuels, carbon nanotubes	[29]
PE	Fixed bed reactor	/	Fe/Al2O3	500 °C	N2	/	H2, liquid fuels, carbon nanotubes	[29]
PS	Fixed bed reactor	/	Fe/Al2O3	500 °C		/	H2, liquid fuels, carbon nanotubes	[29]
PVC	Fixed bed reactor	EC	/	550 °C	N2	/	Bio-oil, bio-char, non-condensable gas	[30]
High-density PE	Fixed bed reactor	/	Y-zeolite with transition metals	600 °C	N2	/	Aromatic fuel oils, H2	[31]
PP	Autoclave	/	Waste refinery catalyst	100-450 °C	N2	/	Methylbenzenes, alkanes	[32]
PET	Horizontal furnace	/		600-1000 °C		/	Porous carbon	[33]
	Tube furnace	/	/	900 °C	/	/	Porous carbon materials	[34]
Medical masks		/	/	360-400 °C	N2	/		[35]

Plastic mixture	Autoclave		Zeolite beta composite		Ar		Gasoline	
Low-density PE	Autoclave	/	CeO$_2$-supported Ru	200 °C	20 bar of H_2	/	Liquid fuels, waxes	[36]
Plastic mixture	Autoclave	/	Ru-modified zeolite	300 °C	2 MPa of of H_2	/	CH_4	[37]
Plastic mixture	Microwave oven	Cooking oil	/	400-550 °C	50 bar of H_2	/	Liquid fuel	[38]
Low-density PE	Microwave oven	Lignin	/	550 °C	Negative pressure	/	Hydrocarbon rich bio-oil	[39]
Plastic mixture	Microwave oven	/	/	450-500 °C	N_2	/	Fuel oil	[40]
PE, PP	Microwave oven	/	ZSM-5	500-740 °C	/	/	Fuel oil	[41]
PE, PC, PP, ABS	Autoclave	Soda lignin	/	500-750 °C	/	/	Syngas	[42]
PS	Tube reactor	/	/	500-800 °C	Supercritical water	/	H_2, CH_4, CO_2	[43]
PP	Tube reactor	/	Seawater	500-800 °C	Supercritical water	/	H_2, CH_4, CO_2	[44]

PE	Fixed bed reactor	Pine wood	CaO/Fe_2O_3 oxygen carrier	750-850 °C	Supercritical water	/	Syngas with high H_2/CO ratio	[45]
Plastic mixture	Reaction vessel	/	Nb_2O_5	RT	N_2	Sunlight	C_2 fuels	[46]
PE	Autoclave	Br_2, ethylene	Grubbs Catalyst M202	30-105 °C	/	400–410 nm UV	α,ω-divinyl-functionalized oligomer	[47]
PE	Fluidized-bed reactor	/	/	500-600 °C	2.7 bar of ethylene	/	H_2, C_1–C_4 paraffins, C_2–C_4 olefins, 1,3-butadiene, C_4–C_{60} *n*-paraffins, isoparaffins, mono-olefins, cycloalkanes/alkadienes, aromatics	[48]
Low-density PE	Autoclave	/	CB, kaoline, silica gel, activated charcoal	550-650 °C	N_2	/	Parafns, isoparafns, olefns, naphthenes, aromatics,	[49]
PE	Pyrolyzer	Cellulose	HZSM-5 zeolite	650 °C	/	/	char, syngas Oxygenated chemicals, olefins,	[50]

					N2		alkanes, and aromatics	
PP, PS	Microwave oven	Rice straw, sugarcane bagasse	HZSM-5	500 °C	N2	/	Bio-oil, biochar, gas	[51]
PE	Fluidized bed gasifier, tar-cracking reactor	/	Active carbon	790-840 °C	Air or oxygen	/	Syngas, tar	[52]
PE	Reaction vessel	DIAD	TBADT	110 °C	/	Sunlight	Low molecular weight PE with tunable polarity	[53]

ChCl-2Urea: choline chloride-2urea; KAB: alumina-substituted Keggin tungstoborate; EC: *Enteromorpha clathrata*; RT: room temperature; UV: ultraviolet; CB: commercial bentonite; DIAD: diisopropyl azodicarboxylate; TBADT: tetrabutylammonium decatungstate.

Hydrolysis, hydrogenolysis, alcoholysis, ammonolysis, pyrolysis, and photolysis are the basic reactions for the chemical conversion of plastic waste (Figure 1). These reactions break specific chemical bonds in polymers, such as carbon-carbon (C-C) or car-bon-oxygen (C-O) bonds, to produce oligomers, monomers, or other small molecules (Fig.1). For example, hydrolysis and hydrogenolysis can target carbonyl groups in PC, whilealcoholysis and ammonolysis primarily act on ester bonds (Figure 1) [20,55]. According tothe study by some researchers, C=C bonds were introduced from C_2H_4 to dehydrogenatePE [17,23]. For the pyrolysis process, the stability of molecular groups in plastic polymersvaries across different temperature ranges, leading to the formation of diverse moleculargroups and a wide variety of products. During the photolysis of plastic waste, phot o-catalysts absorb light energy and undergo electron transitions, forming electron-holepairs. These pairs react with hydroxide ions to generate hydroxyl radicals with strongoxidizing properties, which subsequently oxidize the plastic waste into inorganic substances (Figure 1). However, radicals may be different in different research processes. Theresult obtained by Kong et al. [53] showed that the electron-hole pairs could abstract ahydrogen atom from C-H bonds of PE to produce a long-chain alkyl radical, and itformed an aminyl radical under the addition of DIAD. In a different approach, Zeng et al.[47] used UV light to promote the bromination of PE instead of its direct photolysis,presenting an alternative light-driven strategy.

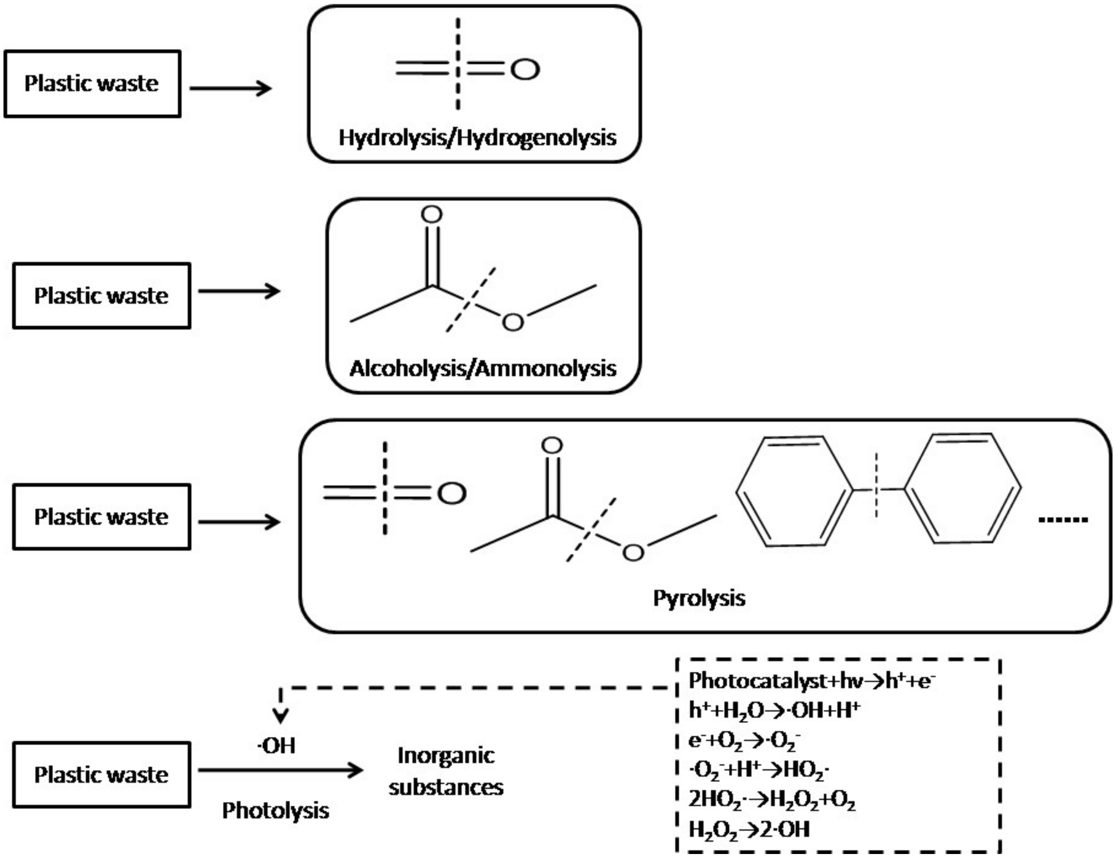


Figure 1. The mechanism of chemical conversion of plastic waste.

Catalysts play a pivotal role in the chemical conversion of plastic waste, facilitatingits efficient transformation into hydrocarbons with a narrow distribution by altering ac-tivation energy and regulating reaction kinetics. The pore structure and pH of the cata-lysts can significantly affect the catalytic performance. During pyrolysis, for instance,carbon-positive ions are generated through acid catalysis, thereby promoting the cleav-age of C-C bonds in plastic polymers (Figure 2) [56]. Among various catalysts, zeolite mo-lecular sieves, i.e., solid acid catalysts composed of Si/Al with well-ordered pores, exhibitunique catalytic activity towards C-C bond cleavage. During pyrolysis, long-chain hy-drocarbons are initially produced, followed by β-fracture of the long polymer chainsunder the action of acidic sites in zeolite molecular sieves or other carbocations (Figure 2),ultimately yielding gas and liquid products with specific carbon distributions. Some re-searchers found that smaller zeolite molecular sieves could increase the heat transfer rate,reaction rate, and oil yield [57]. Furthermore, Xie et al. [58] reported that the microporousstructure was conducive to forming small molecule gas products such as ethylene andpropylene, and the mesoporous structure was conducive to generating macromolecularproducts such as aromatics. For the pH of zeolite molecular sieves, it was reported thatthe acidity of the catalyst was higher when the ratio of silicon and aluminum was lower,leading to higher yields of light gaseous hydrocarbons and liquid aromatic hydrocarbons[58]. Activated carbon, another effective catalyst, also relies on its acidity for catalytic ac-tivity. During its production, functional groups such as C=O and -OH are generated,forming Brønsted acid sites that facilitate the cleavage of C-C and C- H bonds, resulting inlighter hydrocarbons [56]. Simultaneously, dehydrogenation at Lewis sites promotes thearomatization of products [56]. Alkali metal oxides and transition metal oxides can alsocatalyze the pyrolysis process. They possess active alkaline sites that attack hydrogenatoms on polymer chains, forming carbon negative ions, which then undergo β -fractureto produce light hydrocarbons (Figure 2). Besides, metal carbonates, which decompose intometal oxides with active alkaline sites upon heating, have been used to catalyze the py-rolysis of plastic polymers, enabling depolymerization through catalytic pyrolysis [59–62].However, the pyrolysis of plastic waste often produces harmful aromatic compoundssuch as benzene, aniline, and their derivatives. To address this issue, some researchershave used nickel catalysts to convert the hazardous chemicals produced from pyrolysisinto value-added syngas [58].

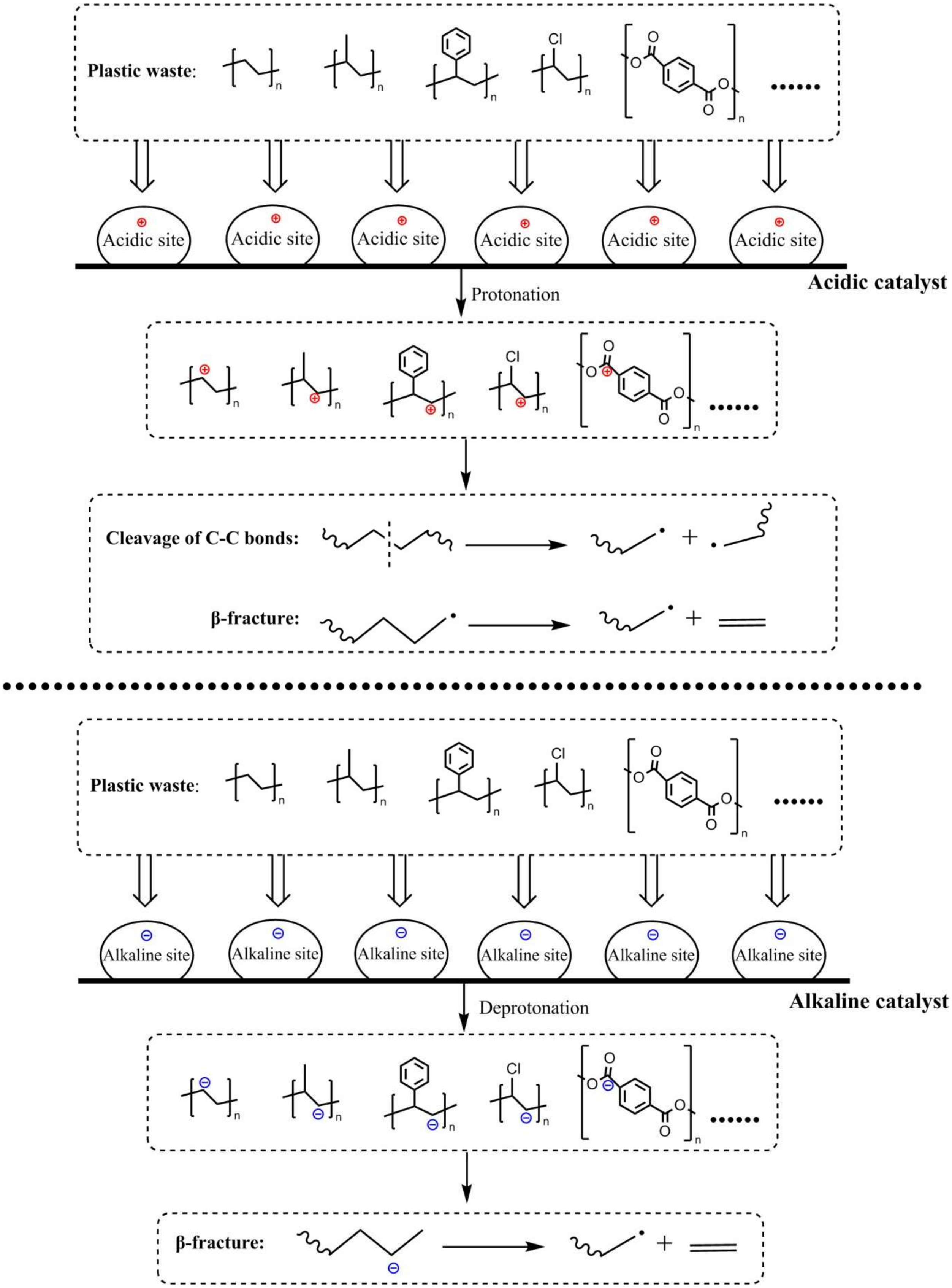


Figure 2. The catalytic mechanism of acidic and alkaline catalysts in the pyrolysis process.

Building on these advancements, recent studies have focused on addressing chal-lenges such as carbonization and sintering, which significantly reduce catalyst lifespanand performance. The introduction of hydrogen into catalytic cracking has proven to bean effective solution for mitigating carbon deposition in catalysts while simultaneouslyenhancing the yield and selectivity of gasoline and diesel fractions [56]. Hydrogenationpyrolysis usually employs bifunctional catalysts composed of metal and acidic sites (Fig.3) [58]. The metal active center promotes the dissociation of hydrogen molecules into ac-tive hydrogen atoms, while acidic sites facilitate the cleavage of C-C bonds (Figure 3). Thiscombined effect enables the decomposition of plastic polymers into stable small moleculehydrocarbons. Moreover, the addition of hydrogen reduces the required pyrolysis tem-perature compared to non-hydrogenated systems (Table 1). Bifunctional catalysts aremainly divided into precious metal (Rh, Ru, Pt) and non-precious metal (Ni, Cu, Fe, Co,W) catalysts [58]. Some researchers reported that the cleavage of C-C bonds, theβ-scission of alkylcarbenium ions and skeletal rearrangements occurred with the assis-tance of strong Brønstedacidity of Rh/Nb_2O_5, promoting the one-step solvent-free cata-lytic hydrogenolysis and isomerization of plastic polymers [63]. Additionally, reactionpressure plays a crucial role in the hydrogenation pyrolysis of plastic waste [58]. In-creasing hydrogen pressure in the reaction system enhances the coverage of active hy-drogen on catalyst surfaces, facilitating the hydrogenation saturation of intermediateproducts and their subsequent desorption from the catalyst surface. This process not onlyaccelerates the reaction rate but also helps prevent excessive depolymerization and theoverproduction of small molecule gases, while improving the overall release of productsfrom the catalyst surface.

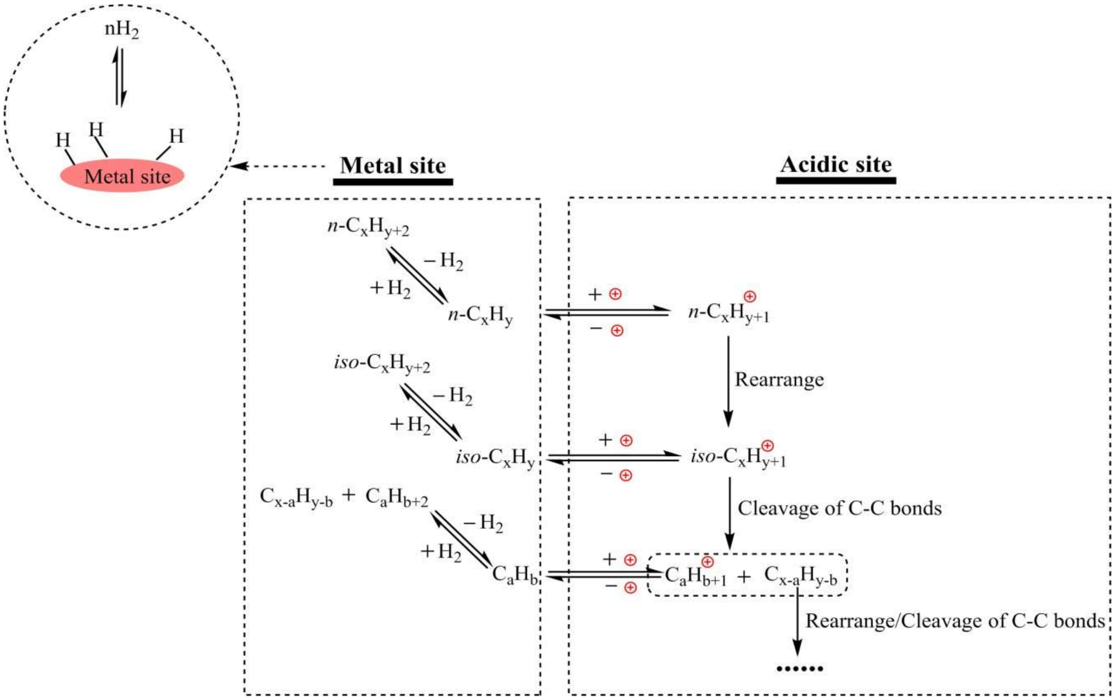


Figure 3. The catalytic mechanism of bifunctional catalysts in the pyrolysis process.

2.2. Biological Methods

Biological methods for pollution control include plant remediation, animal remedi-ation, and microbial remediation [64–66]. However, most research focuses on utilizingmicroorganisms to degrade plastic waste. These methods, commonly known as biodeg-radation, employ microorganisms or enzymes to convert high molecular weight mac-romolecules into oligomers or small molecules. Biodegradation typically involves eitherthe assimilation of microorganisms or direct enzymatic degradation, which disrupts thestructure of plastic polymers, reducing their molecular weight [67,68]. The biodegrada-bility of plastic waste is strongly influenced by its physical and chemical properties. Bi-odegradable and environmentally friendly plastic waste degrades more easily [69–72].Critical factors such as crystallinity, hydrophilicity, molecular weight, and toughnesshave a decisive impact on the biodegradability of plastic waste [16]. Plastic waste withhigher crystallinity is more resistant to biodegradation than those with lower crystallinity[16]. The presence of functional groups in plastic polymers increases their hydrophilicity,thus enhancing their biodegradability [73]. Higher molecular weight plastics are lesssusceptible to degradation [16], and softer plastics degrade more quickly than harderones [73]. Additionally, environmental factors such as moisture content, temperature,and pH influence microbial activity and enzyme efficiency, thus affecting biodegradation[74].

The biodegradation of plastic waste involves two main mechanisms: degradationand assimilation (Figure 4). Microbial enzymes, either extracellular or intracellular, pro-duced by microorganisms such as algae, bacteria, fungi, and actinomycetes are respon-sible for depolymerizing or decomposing plastic waste [75]. Among these enzymes, hy-drolases play a crucial role by cleaving chemical bonds in the presence of water. Whenhydrolase acts on a product (A-B), the reaction typically follows Eq. (1). Plastics found inthe environment are generally hydrophobic [76]. The breakdown of plastic waste by hy-drolases occurs in two steps. First, extracellular microbial enzymes adhere to the surfaceof plastic waste via hydrophobic interactions (Figure 4). The hydrophobic clefts in the activesites of these enzymes interact with hydrophobic groups on the plastic, improving theaccessibility of the enzyme to the material. In the second step, the enzyme's active siteshydrolyze specific chemical bonds within the plastic polymers, breaking them down intooligomers or small molecules that microorganisms can utilize as a carbon source (Figure 4).

$$A - B + H_2O \rightarrow A - OH + B - H \quad (1)$$

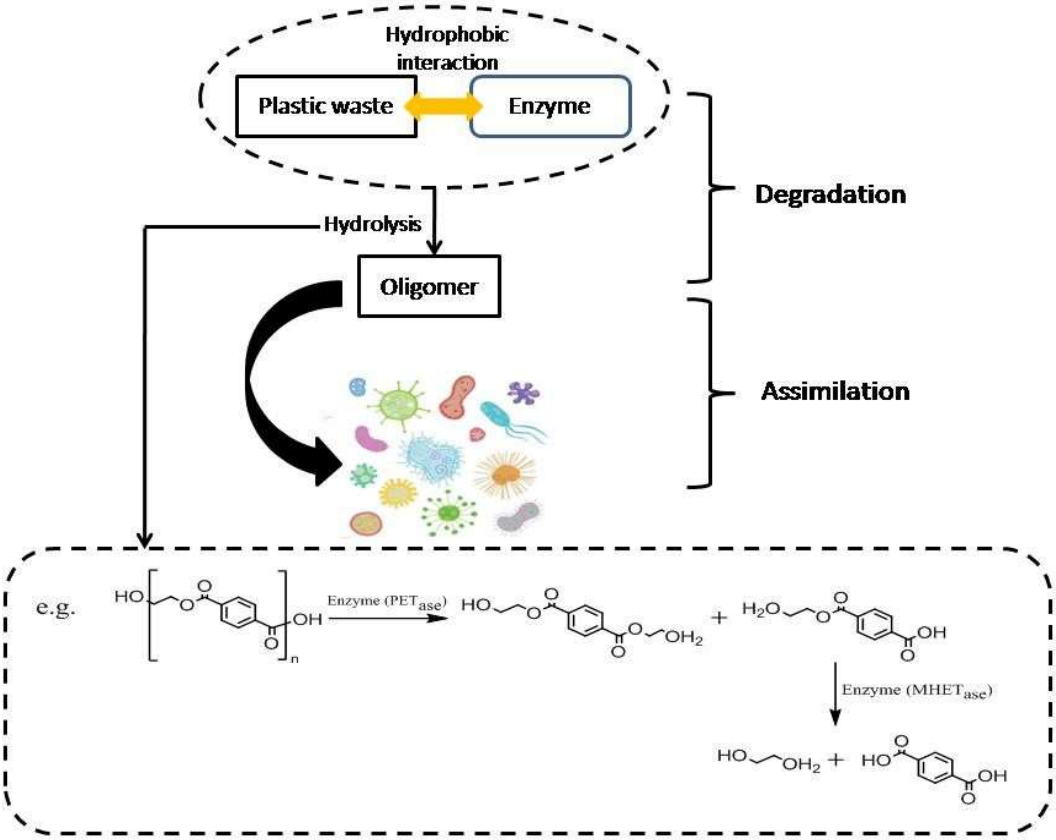


Figure 4. The mechanism of biodegradation of plastic waste.

Recently, some research has focused on the discovery of novel plastic-degradingmicroorganisms. Some microbial species (e.g., *Thermobifida fusca* , *Serratia plymuthica* strainIV-11-34, *Pseudomonas aestusnigri*, *Pichia pastoris*, *Rhococcus sp. SSM1*, *Streptomyces scabies*,*Clostridium thermocellum*, *Pseudomonas citronellolis*, *Bacillus flexus*, *Aspergillus flavus*,*Cobetia sp.*, *Halomonas sp.*, *Exiguobacterium sp.*, *Alcanivorax sp.*, *Aspergillus flavus*, *Fusariumfalciforme*, *Fusarium oxysporum*, *Purpureocillium l ilacinum*, *Uronema africanum* Borge,*Stenotrophomonas* sp., *Achromobacter* sp., *Bacillus* spp., *Pseudomonas* spp., *Paenibacillus* sp.,*Bacillus* sp., *Arthrobacter* sp., *Streptomyces* sp., *Sterigmatomyces halophilus*, *Meyerozymaguilliermondii*, *Meyerozyma caribbica* , *Enterobacter*, *Pseudomonas*, *Alcanivorax*, *Marinobacter*,*Arenibacter*, *Bacillus* spp., *Spirulina* sp., *Streptomyces* sp., *Phaeodactylum tricornutum*,*Chaetomium globosum*, and anaerobic marine consortia) have been found to degradeplastic waste effectively (Table 2). Plastic-degrading microorganisms are capable ofproducing hydrolases such as cutinase, lipase, esterase, and alkane monooxygenase,which can break down plastic polymers into smaller molecules (Table 2). The biologicalconversion of plastic waste generally occurs at lower temperatures than chemicalmethods (Table 1; Table 2) because high temperatures can deactivate the enzymes.However, the biological process often requires longer processing times (Table 2).Additionally, the hydrophobic nature of plastic polymers, attributed to theirhydrocarbon chain structures, can hinder microbial activity during biodegradation. As asolution, thermal or UV pre-treatment is frequently applied to polyolefin plastics,making them more amenable to biodegradation [76].

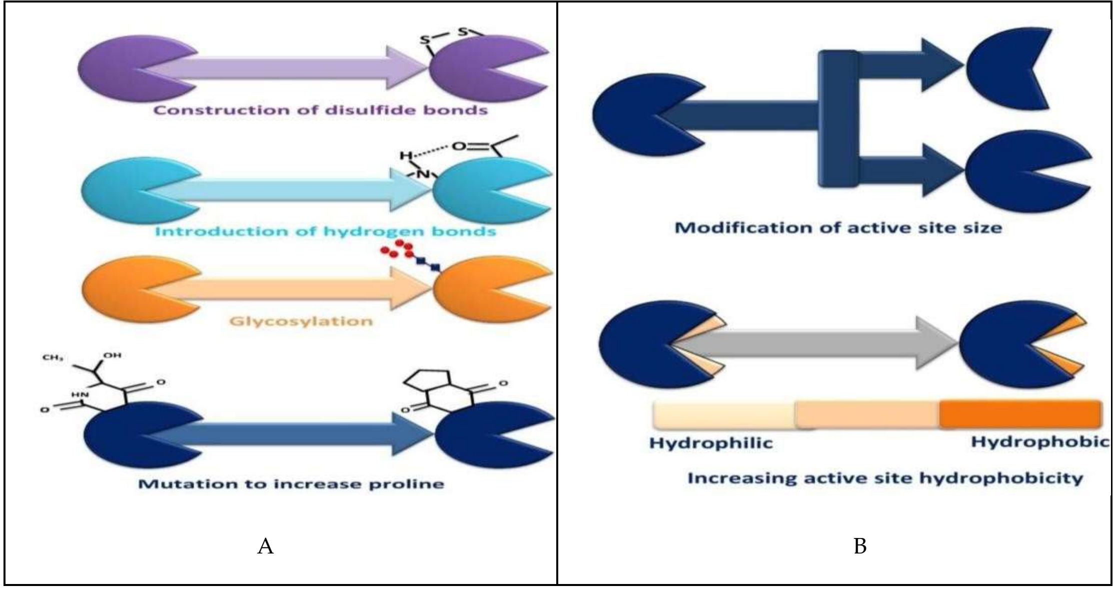
Table 2. Technical parameters of biological methods for converting or recycling plastic waste.

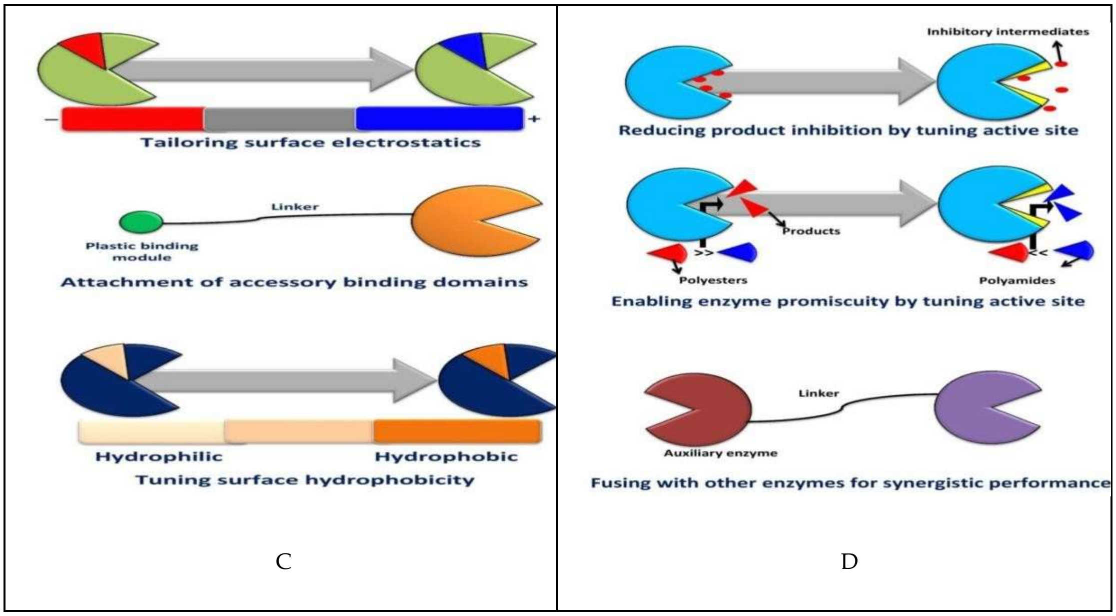
Plastic waste	Microorganism / Enzyme	Reaction condition	Product	Reference
PET	*Thermobifida fusca* / Cutinase (TfCut2)	1000 r/min, 70 °C, 96 h	Ethylene glycol, terephthalic acid	[77]
PET	*Serratia plymuthica* strain IV-11-34 / Synthase	26 °C, 30 d	Small molecules	[78]
PET		30 °C, 48 h	Bis(2-hydroxyethyl) terephthalate, mono(2-hydroxyethyl) terephthalate	[79]
PET	*Pseudomonas aestusnigri* / Carboxylic ester hydrolase	30 °C, 18 h		[80]
PET	*Pichia pastoris* / PETase	34 °C, pH 8.5	Small molecules	[81]
PET	*Rhococcus sp. SSM1* / PETase	37 °C, 20 d	Small molecules	[82]
PET	*Streptomyces scabies* / Protein Sub1	Anaerobically, 60 °C, 14 d	Terephthalic acid	[83]
PET			Small molecules	[84]
PET	*Clostridium thermocellum* / thermophilic cutinase	120 rpm, 28 °C, 18 d	Small molecules	[85]

PET	*Streptomyces* sp.	21-30 °C, 180 d	Terephthalic acid, mono(2-hydroxyethyl) terephthalic acid	[86]
PET	*Phaeodactylum tricornutum* / PETase	65°C, 14 h, pH 8	Small molecules	[87]
	LCC – ICCG variant / Depolymerase	37 °C, pH 7	Small molecules	
	Bacillus subtilis HR29 / BhrPETase			
PVC	*Pseudomonas citronellolis, Bacillus flexus*	Aerobically, 30 d	Small molecules	[88]
PVC	*Chaetomium globosum*	28 °C, 28 d	Small molecules	[89]
PVC	Anaerobic marine consortia	Anaerobically, 20 °C, 2 a	Small molecules	[90]
PP	*Aspergillus* sp., *Penicillium* sp.	29 °C, 30 d	Small molecules	[91]
PE	*Aspergillus flavus* / AFLA_006190, AFLA_053930	28 d	Small molecules	[92]
PE			Small molecules	[93]
PE	*Cobetia sp., Halomonas sp., Exiguobacterium sp., Alcanivorax sp.*	30-90 d	Small molecules	[94]
PE		30 d	Small molecules	[95]
PE	*Aspergillus flavus, Fusarium falciforme, Fusarium oxysporum, Purpureocillium lilacinum*	30 d	Small molecules	[96]
PE	*Uronema africanum* Borge	Aerobically, 150 rpm, 30 °C, 45 d	Small molecules	[97]
PE	*Stenotrophomonas* sp., *Achromobacter* sp. / Cutinase, lipase, esterase, alkane monooxygenase	30 °C, 30 d	Small molecules	[98]
PE		30 °C, 60 d	Small molecules	[99]
PE	*Bacillus* spp., *Pseudomonas* spp.	120 r/min, 25 °C, 90 d	Small molecules	[100]
PE	*Paenibacillus* sp., *Bacillus* sp.		Small molecules	[101]

	Arthrobacter sp., *Streptomyces* sp.	30 °C, 45 d		
	Sterigmatomyces halophilus, *Meyerozyma guilliermondii*, *Meyerozyma caribbica* / MnP, Lac, LiP	30 °C, 45 d		
	Enterobacter cloacae AKS7			
PE	PE-degrading bacteria, PHA-synthesizing bacteria	30 °C, 21 d	Small molecules	[102]
PE, PP	*Enterobacter*, *Pseudomonas*	37 °C, 160 d	Small molecules	[103]
PE, PET	*Alcanivorax*, *Marinobacter*, *Arenibacter*	30 °C, 80 d	Small molecules	[104]
PE, PVC	*Bacillus* spp.	180 rpm, 30 °C, 90 d	Small molecules	[105]
PP, PET	*Spirulina* sp.	112 d	Small molecules	[106]

Plastic waste can be enzymatically degraded via cell-free or whole-cell biocatalysis [76]. This process begins with microbial fermentation under optimal conditions, including precise temperature control, oxygen levels, pH, and nutrients [76]. Then the microbial cells must be disrupted in the cell-free process and plastic waste is incubated with microorganisms at high cell densities in the whole-cell process [76]. The performance of plastic-degrading enzymes can be improved via protein engineering and synthetic biology. Improvements primarily focus on four main areas: 1) enhancing the thermal stability of enzymes; 2) improving the attachment of plastic waste to the active sites of enzymes; 3) strengthening the interactions between plastic waste and the surface of enzymes; 4) refining additional functions of enzymes (Figure 5). The thermal stability of plastic-degrading enzymes can be promoted via adding disulfide bonds or salt bridges (Figure 5A) [107]. Enzymes depend on disulfide bonds or salt bridges to fold into a local or global shape, which is beneficial for improving heat resistance. Another strategy to enhance the thermal stability of enzymes is to engineer the creation of hydrogen bonds in the region (Figure 5A) [108], which can preserve higher-order protein structures of enzymes and make the structure of enzymes more stable. Additionally, glycosylation enhances the thermal stability of enzymes by strengthening the thermodynamic stabilization of enzymes and preventing the thermal aggregations of enzymes (Figure 5A) [109]. Furthermore, the cyclic structure of the proline side chain can reduce the conformational entropy opposing protein folding, which can make the structural rigidity higher. Therefore, introducing more proline residues is beneficial to enhance the thermal stability of enzymes (Figure 5A). A common strategy to improve the attachment of plastic waste to the active sites of enzymes is creating a wider opening of the active sites to increase the accessibility of plastic substrate (Figure 5B). However, a wider opening of the active sites does not always show improved catalytic performance, as an overly enlarged active site may lead to weaker substrate affinity because of reduced binding ability [109]. In certain situations, modifying the active site with a narrower space is favorable (Figure 5B). Also, the hydrophobicity of the enzyme binding groove of active sites is a potential engineering target (Figure 5B). Increasing the hydrophobicity can be conducive to plastic binding resulting from higher affinity. The substrate binding process is affected by electrostatic and hydrophobic interactions between plastic polymers and amino acid residues on the surface of enzymes. Hence, tailoring surface electrostatics and tuning surface hydrophobicity are common strategies (Figure 5C). Specifically, making the surface of enzymes electrically neutral can reduce electrostatic repulsion between plastic waste and enzymes, thus promoting the degradation efficiency of plastic waste. Another method to enhance the interaction between plastic waste and the surface of enzymes is the attachment of accessory binding domains to the surface of enzymes (Figure 5C). This approach is inspired by the fact that some enzymes show an auxiliary binding domain specialized in substrate adhesion. Therefore, plastic-degrading enzymes' absence of such function can be fused with heterologous binding modules to promote the interaction with plastic waste. Efforts in optimizing the performance of enzymes have also been made in other aspects such as reducing product inhibition by tuning active sites, enabling enzyme promiscuity, and creating multifunctional biocatalysts (Figure 5 D). First, intermediates or products in the degradation of plastic waste can inhibit the activity of enzymes, and such inhibition can be mitigated by tuning the active site architecture [109]. Besides, enabling enzyme promiscuity by tuning active sites is a meaningful approach to expand the degradation capacity of enzymes, especially for plastic waste that few known enzymes can efficiently degrade [109]. In addition, fusing with other enzymes for synergistic performance has been exploited to create bifunctional biocatalysts which can degrade plastic waste more efficiently [109]. The research about protein engineering mainly focused on PET-degrading enzymes, and the enzymes that can degrade other plastic waste efficiently are yet to be identified [110].





C

D

Figure 5. The mechanism of improving the performance of plastic-degrading enzymes (A: enhancing the thermal stability of enzymes; B: enhancing the attachment of plastic waste to the active sites of enzymes; C: enhancing the interaction between plastic waste and the surface of enzymes; D: refining additional functions of enzymes) (Modified from [76]).

3. Economic Analysis and Life Cycle Assessment of Emerging Technologies

Economic analysis (EA) involves evaluating, comparing, and demonstrating the financial benefits of different technologies [111]. The costs associated with emerging technologies for treating plastic waste include raw materials, labor, equipment, and operations. For instance, Chhabra et al. [112] reported that the total cost of the pyrolysis equipment was $6.62 million, with reactors accounting for 48% of the total cost. According to the report by Hu et al. [14], the cost of thermal chemical methods is higher than other emerging methods. Promoting the valorization of organic waste, including plastic waste, is essential for fostering a circular economy [113–116]. Products derived from plastic waste treatment, such as bio-oil, biochar, and syngas, can be reused as energy sources [117–119]. For instance, bio-oil, biochar, and syngas can be reused as energy sources. For example, in a plant processing 200 tons of municipal solid waste daily, including PET, PE, and PP, bio-oil contributed 86.8% of the total annual revenues of $11.53 million [112]. Additional products, like carbon nanotubes, have been used to produce transparent, conductive thin films. Similarly, terephthalic acid produced from the biological conversion of PET has been utilized to synthesize PET bottles with mechanical properties comparable to petrochemical-derived versions [86]. Such reuse of products not only offsets costs but also generates economic profits.

Life cycle assessment (LCA) is a method of summarizing and evaluating all inputs and outputs of a system throughout its lifecycle, as well as their potential impact on the environment [120]. Chhabra et al. [112] reported that the impact categories of oil production from plastic waste include acidification, climate change, freshwater ecotoxicity, freshwater eutrophication, human toxicity, land use, marine eutrophication, ozone depletion, and resource depletion. The potential impact on the environment (E_{pot}) is the difference between the net environmental impacts of the benchmark waste treatment ($EI_{WT,\ net}$) and ideal waste recycling ($EI_{WR,\ ideal,\ net}$) [120]. The net environmental impacts of the benchmark waste treatment ($EI_{WT,\ net}$) are defined as direct environmental impacts of the benchmark waste treatment ($EI_{WT,\ direct}$) minus the credit for avoided products (EI_{avP}). The net environmental impacts of ideal waste recycling ($EI_{WR,\ ideal,\ net}$) are defined as direct environmental impacts of ideal waste recycling ($EI_{WR,\ ideal,\ direct}$) minus the credit for avoided

doi:10.20944/preprints202502.0190.v1

chemicals (EI_{avC}) [120]. The direct environmental impact of the benchmark waste treatment ($EI_{WT, direct}$) consists of all environmental impacts required to treat 1 kg of plastic waste. Avoided environmental impacts (EI_{avP}) include the credit for avoided products. Waste recycling converts 1 kg of treated plastic waste into m_j kg of chemicals. These chemicals substitute their conventional production and corresponding environmental impacts (EI_j), leading to the credit for avoided chemicals (EI_{avC}) [120]. Environmental impacts (EI_j) are based on data from the LCA database. A method based on stoichiometry and thermodynamic data can be used to calculate $EI_{WR, ideal, direct}$ [120].

The method contains reactants ($\sum^{I} EI_i m_i$), residual waste ($\sum^{k} EI_k m_k$), and thermal energy ($EI_H Q_H$). m_i and m_k represent the mass of reactants and residual waste. EI_i and EI_k quantify the environmental impacts per kilogram, with EI_i representing the impact of reactant production and EI_k corresponding to the impact of residual waste treatment. EI_H represents the environmental impact of providing 1 MJ of energy using natural gas as fuel. Q_H represents the minimal energy demand for complete recycling per 1 kg of plastic waste. The relevant calculation formulas are as follows.

$$E_{pot} = EI_{WT, net} - EI_{WR, ideal, net} \quad (2)$$

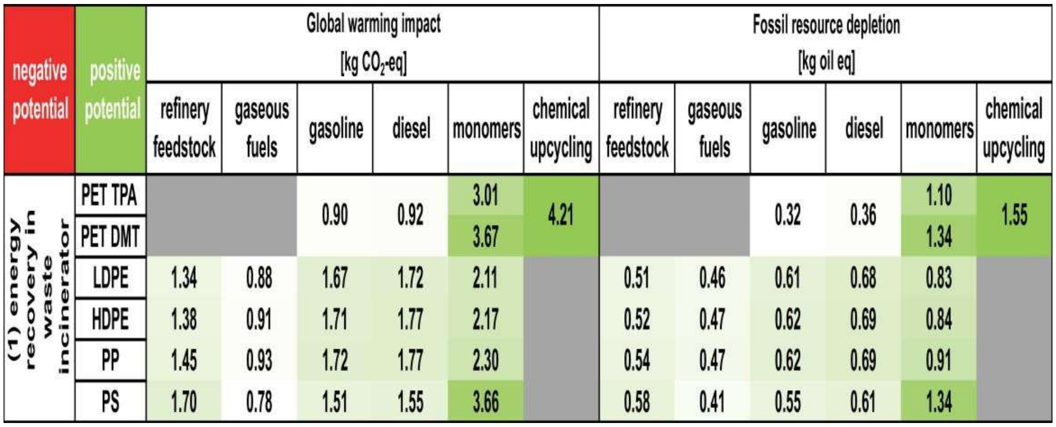
$$EI_{WT, net} = EI_{WT, direct} - EI_{avP} \quad (3)$$

$$EI_{WR, ideal, net} = EI_{WR, ideal, direct} - EI_{avC} \quad (4)$$

$$EI_{avC} = \sum EI_j m_j \ {}_1(5)$$

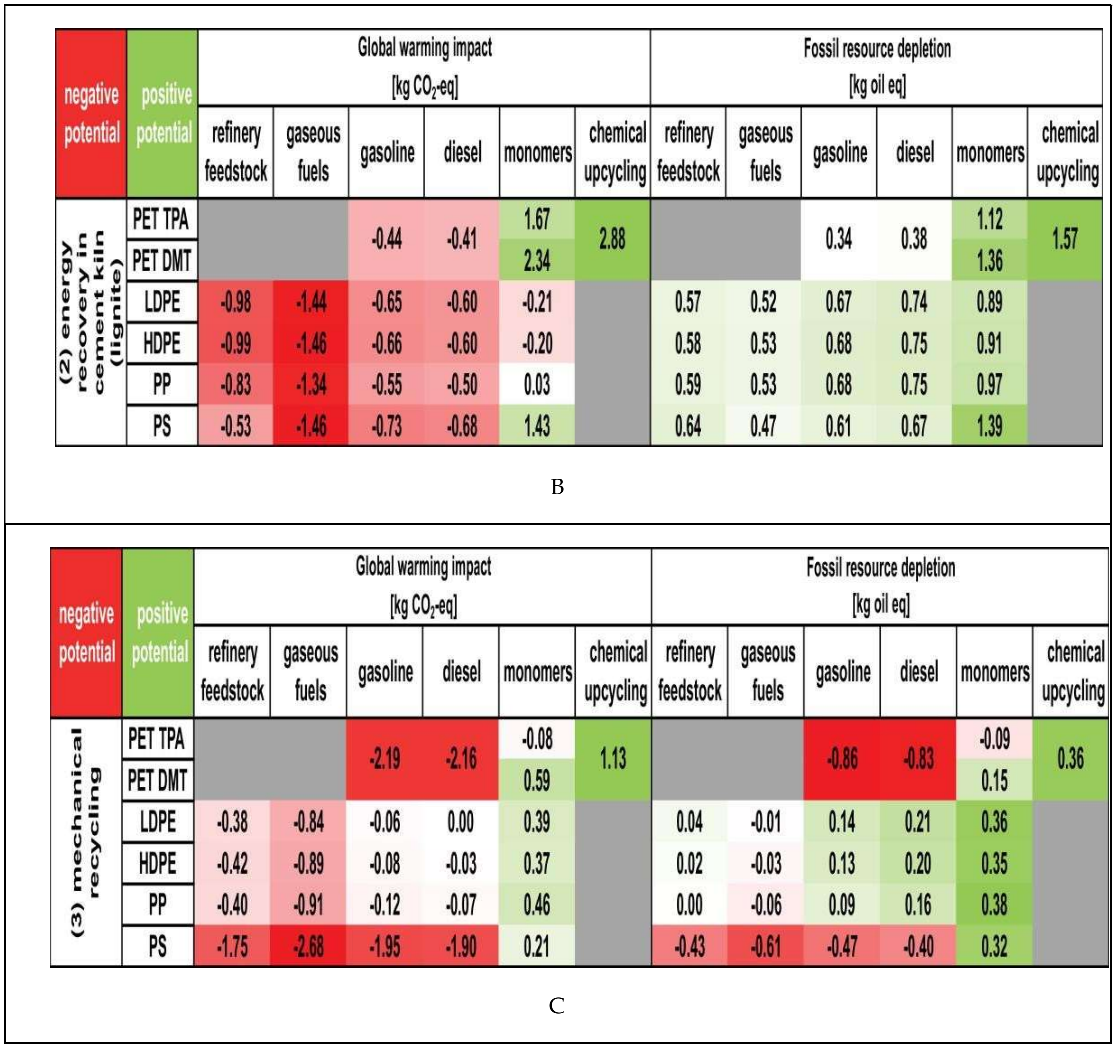
$$EI_{WR, ideal, direct} = \sum EI_i m_i + \sum EI_k m_k + EI_H Q_H \quad (6)$$

According to Meys et al. [120], PET, PE, PP, and PS should not be chemically recycled into refinery feedstock or fuel products. Instead, mechanical recycling or utilization in cement kilns is recommended to reduce global warming impacts. Conversely, chemical recycling into monomers or value-added products could potentially reduce global warming impacts compared to energy recovery in municipal solid waste incinerators, energy recovery in cement kilns, and mechanical recycling (Figure 6). The environmental potential for global warming varies, ranging from 0.78 kg CO_2-eq for producing gaseous fuels from PS to 4.21 kg CO_2-eq for the chemical upcycling of PET (Figure 6A). Recycling plastic waste to refinery feedstock and fuels shows a negative environmental potential, from -1.46 kg CO_2-eq for producing gaseous fuels from HDPE or PS to -0.44 kg CO_2-eq for producing gasoline from PET (Figure 6B). Additionally, the environmental potential for PET and PS is negative in Figure 6C.



negative potential	positive potential	Global warming impact [kg CO_2-eq]						Fossil resource depletion [kg oil eq]					
		refinery feedstock	gaseous fuels	gasoline	diesel	monomers	chemical upcycling	refinery feedstock	gaseous fuels	gasoline	diesel	monomers	chemical upcycling
(1) energy recovery in waste incinerator	PET TPA			0.90	0.92	3.01	4.21			0.32	0.36	1.10	1.55
	PET DMT					3.67						1.34	
	LDPE	1.34	0.88	1.67	1.72	2.11		0.51	0.46	0.61	0.68	0.83	
	HDPE	1.38	0.91	1.71	1.77	2.17		0.52	0.47	0.62	0.69	0.84	
	PP	1.45	0.93	1.72	1.77	2.30		0.54	0.47	0.62	0.69	0.91	
	PS	1.70	0.78	1.51	1.55	3.66		0.58	0.41	0.55	0.61	1.34	

A



negative potential	positive potential	Global warming impact [kg CO_2-eq]						Fossil resource depletion [kg oil eq]					
		refinery feedstock	gaseous fuels	gasoline	diesel	monomers	chemical upcycling	refinery feedstock	gaseous fuels	gasoline	diesel	monomers	chemical upcycling
(2) energy recovery in cement kiln (lignite)	PET TPA			-0.44	-0.41	1.67	2.88			0.34	0.38	1.12	1.57
	PET DMT					2.34						1.36	
	LDPE	-0.98	-1.44	-0.65	-0.60	-0.21		0.57	0.52	0.67	0.74	0.89	
	HDPE	-0.99	-1.46	-0.66	-0.60	-0.20		0.58	0.53	0.68	0.75	0.91	
	PP	-0.83	-1.34	-0.55	-0.50	0.03		0.59	0.53	0.68	0.75	0.97	
	PS	-0.53	-1.46	-0.73	-0.68	1.43		0.64	0.47	0.61	0.67	1.39	

B

negative potential	positive potential	Global warming impact [kg CO_2-eq]						Fossil resource depletion [kg oil eq]					
		refinery feedstock	gaseous fuels	gasoline	diesel	monomers	chemical upcycling	refinery feedstock	gaseous fuels	gasoline	diesel	monomers	chemical upcycling
(3) mechanical recycling	PET TPA			-2.19	-2.16	-0.08	1.13			-0.86	-0.83	-0.09	0.36
	PET DMT					0.59						0.15	
	LDPE	-0.38	-0.84	-0.06	0.00	0.39		0.04	-0.01	0.14	0.21	0.36	
	HDPE	-0.42	-0.89	-0.08	-0.03	0.37		0.02	-0.03	0.13	0.20	0.35	
	PP	-0.40	-0.91	-0.12	-0.07	0.46		0.00	-0.06	0.09	0.16	0.38	
	PS	-1.75	-2.68	-1.95	-1.90	0.21		-0.43	-0.61	-0.47	-0.40	0.32	

C

Figure 6. Comparison of the environmental potential of chemical recycling and other recycling methods (A: energy recovery in municipal solid waste incinerators; B: energy recovery in cement kilns; C: mechanical recycling) (Modified from [120]). Red represents negative environmental potential. Green represents positive environmental potential. White represents values equal to zero. Grey represents that chemical recycling has been omitted.

4. Future Perspectives

The use and implementation of emerging technologies for treating plastic waste face several significant challenges, including technological limitations, economic feasibility, scalability, environmental impacts, and regulatory constraints, which significantly impede their practical implementation and widespread adoption. The plastic waste feedstock is often complex, which makes the theoretical technical parameters of various emerging technologies not applicable. Fast catalyst deactivation caused by undesirable reactions is not conducive to engineering applications. The lack of sufficient research on the economic analysis and life cycle assessment of actual engineering is a problem. Additionally, contaminants (e.g., benzene, aniline and their derivatives, chlorine, bromine, sulfur, nitrogen) in plastic oil and its quality standardization) are often produced in the thermal chemical conversion of plastic waste. In addition, financial barriers, uncompetitive marketing strategies, limited availability of quality plastic waste, gaps in plastic waste supply and demand, inefficient and costly plastic waste segregation technologies, and lack of local expertise in plastic waste recycling and ambiguous legislations also impede the large-scale commercial implementation of treating plastic waste by emerging technologies.

Currently, most research mainly uses a single method (chemical or biological) to treat plastic waste. However, emerging chemical and biological methods have their advantages and disadvantages. The combined use of emerging chemical and biological methods to treat plastic waste may achieve complementary effects, which is worth studying in the future. Laboratory-scale studies primarily focus on single-type plastic waste, but real-world scenarios often involve mixed plastic waste alongside other household waste. Therefore, future research should prioritize the treatment of mixed waste streams using emerging technologies, with particular attention to how non-plastic waste impacts the treatment process. Additionally, the technical parameters of various emerging technologies ought to be thoroughly validated for practical engineering applications to ensure their effectiveness and scalability. A core aspect of the technical parameters is the catalyst, and identifying high-performance catalysts is essential and urgent. While most researchers have focused on pyrolysis, gasification, and hydrothermal gasification for treating plastic waste, limited studies have explored hydrothermal carbonization and hydrothermal liquefaction. Hydrothermal carbonization or hydrothermal liquefaction of plastic waste is a future research direction, because hydrothermal carbonization or hydrothermal liquefaction can be carried out under relatively mild temperature conditions compared to pyrolysis, gasification, and hydrothermal gasification. Similarly, the photolysis of plastic waste remains underexplored, and further efforts are needed to advance this area. The mechanism underlying the hydrothermal modification of plastic waste also warrants deeper investigation. In biodegradation studies, microorganisms are predominantly used to treat plastic waste. In addition to microorganisms, plants and small animals are often used to absorb some pollutants. Whether plants or small animals can be used to treat plastic waste is a research hotspot in the future. Understanding the mechanisms involved and assessing the adverse impact of plastic waste on these organisms are crucial research priorities. At present, the research about protein engineering mainly focuses on PET-degrading enzymes, and the enzymes which can degrade other plastic waste efficiently are yet to be identified. Furthermore, studies about the EA and LCA of emerging technologies for treating plastic waste are not sufficient. More specific research cases about the EA and LCA of emerging technologies are needed in the future. Additionally, further research is needed on the applicability of the calculation formulas of LCA of emerging technologies in engineering applications. While many products derived from emerging plastic waste treatment technologies hold potential for reuse, additional research is necessary to validate their practical applications. Advancing these areas of study will be key to addressing the challenges in plastic waste management and unlocking the full potential of these technologies.

5. Conclusions

Emerging technologies for converting and utilizing plastic waste mainly include chemical and biological technologies. Chemical methods focus on breaking down high molecular weight macromolecules into oligomers or small molecules by cracking or depolymerizing chemical bonds in plastic polymers. Key reactions for chemical conversion include hydrolysis, hydrogenolysis, alcoholysis, ammonolysis, pyrolysis, and photolysis, which cleave specific bonds in plastic polymers to produce oligomeric products. Catalysts are crucial in these processes, as they lower activation energy, regulate reaction kinetics, and facilitate the conversion of plastic waste into hydrocarbons with narrow distributions. Factors such as pore structure and pH of catalysts can significantly affect their performance. However, issues like carbonization and sintering can reduce catalyst efficiency and lifespan. Introducing hydrogen into catalytic cracking can not only effectively solve the problem of carbon deposition in catalysts, but also improve the yield and selectivity of gasoline and diesel fractions. Biological methods generally involve biodegradation, where microorganisms or enzymes break down macromolecules into oligomers or small molecules. The mechanism of biodegradation of plastic waste is degradation and assimilation. Economic analysis of emerging plastic waste treatment technologies for treating plastic waste refers to the calculation, comparison, and demonstration of various technologies, and is an important means of selecting various technologies based on economic benefits. Life cycle assessment evaluates the inputs, outputs, and potential environmental impacts of emerging plastic waste treatment technologies across the entire lifecycle of a system, guiding sustainable decision-making and process optimization. In summary, significant research is necessary to address the challenges and optimize the conversion and utilization of plastic waste through emerging technologies, ensuring their scalability, efficiency, and sustainability.

Author Contributions: Conceptualization, Z.L. and M.G.M; methodology, Z.L.; writing—original draft preparation, Z.L.; writing—review and editing, S.H.C. and M.G.M. All authors have read and agreed to the published version of the manuscript."

Funding: This research received no external funding. **Institutional Review Board Statement:** Not applicable. **Informed Consent Statement:** Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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