



Review

Plastic waste upcycling toward a circular economy



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ABSTRACT

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Large amounts of plastics are discarded worldwide each year, leading to a significant mass of waste in landfills and pollution to soil, air, and waterways. Upcycling is an efficient way to transform plastic waste into high-value products and can significantly lessen the environmental impact of plastic production/consumption. In this article, current advances and future directions in plastic waste upcycling technologies are discussed. In particular, this review focuses on the production of high-value materials from plastic waste conversion methods, including pyrolysis, gasification, photoreforming, and mechanical reprocessing. Plastic waste compositions, conversion products, reaction mechanisms, catalyst selection, conversion efficiencies, polymer design, and polymer modification are also explored. The main challenges facing the adoption and scale-up of these technologies are highlighted. Suggestions are given for focusing future research and development to increase the efficiency of upcycling practices.

1. Introduction

There are large amounts of solid wastes in the world, including plastics, tires, food, animal manure, woody biomass, and their mixtures. Among these solid wastes, plastic receives a great and increasing emphasis because of its production scale and environmental impact [1]. Plastics are commonly used for packaging because of their light weight, low cost, processability, and high performance [2–4]. Polyethylene (PE) and polypropylene (PP) are some of the most commonly used plastics in multilayer film packaging, among other applications. However, the high durability of plastics causes large amounts of waste accumulation in landfills and oceans because most synthetic polymers are designed for longevity and performance rather than recyclability and degradability [2,5].

The single-use applications of plastics for sterile packaging, storage, transportation, and disposable medical parts play a significant role in its contribution to global waste. Approximately 380 million tons of plastics are produced annually worldwide, and <20% is typically recycled,

resulting in huge contributions to global waste and environmental pollution. Recycling is often difficult because post-consumer plastic waste often consists of mixed plastics of unknown composition and frequently contains various contaminants, including organic (e.g., food remains) and inorganic (e.g., inks) ones. Most of this plastic waste is either incinerated in power plants or discarded to landfills or oceans, resulting in a low or lost value [1]. Single-use multilayer flexible packaging is a typical example of such non-recyclable waste that ends up in landfills and, eventually, in natural habitats. Approximately 8 million tons of plastics find their way into oceans annually, and the plastic pollution in oceans is predicted to outweigh the marine fish by 2050. One-third of all plastic produced worldwide is too complex (e.g., complex structures, complex mixture of different polymers) or small to recover or recycle in a practical and cost-effective manner [6]. Since plastic waste is largely chemically inert, estimates suggest that existing material would require around 250–500 years to completely degrade. Furthermore, the constituents of plastic waste can enter the human food chain through crops and animals. For example, crops might absorb and accumulate nanoplastics (e.g., dimensions < 6 nm), which can permeate

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Abbreviations and nomenclature

Abbreviation or nomenclature	Full name
PLA	Polylactic acid
ABS	Acrylonitrile butadiene styrene
PP	Polypropylene
PC	Polycarbonate
iPP	Isotactic polypropylene
PE	Polyethylene
LDPE	Low density polyethylene
HDPE	High density polyethylene
PET	Polyethylene terephthalate
PHB	Poly(3-hydroxybutyrate)
PS	Polystyrene
PVC	Polyvinyl chloride
PUR	Polyurethane
PTE	Polythioester
HHV	Higher heating value
LHV	Lower heating value

the cell wall of crops (e.g., root). Microplastics in chickens can derive from the consumption of earthworms that ingest microplastics. This poses a serious health threat, the extent of which is unknown [5,7,8].

Numerous technologies such as pyrolysis, incineration, and landfilling, have been developed to address plastic waste. Additionally, newer technologies including microwave-assisted conversion, photo-reforming, compatibilization, and sustainable polymer design are in development [1,2,6,9,10]. Particular technologies are better suited for certain types of polymers or mixtures. The research is ongoing to increase the conversion efficiency (the ratio of the feed consumption amount to the total feed amount) and selectivity (the ratio of conversion of the feed to a specific product to the overall conversion of the feed). Among conventional conversion technologies, landfilling and mechanical reprocessing are currently the most common and simplest to implement on a large scale. Landfilling is typically based on anaerobic degradation of waste (with bottom liner and top soil cover) that can generate landfill gas and leachate [11]. However, landfilling has the limitation of space use, emits undesirable gases including CH₄ and CO₂, and contaminates the aquifer [12]. Additionally, mechanical reprocessing presents a recycling limit issue because the mechanical stability of materials typically decreases with each cycle. Incineration gives rise to environmental issues such as CO₂ and toxic pollutant (e.g., dioxin) emissions [9].

Thermochemical conversion of plastic waste to high-value products is a promising technique from environmental and economic perspectives [9]. Pyrolysis is a type of chemically driven value recovery technique in which plastic waste is thermally decomposed at elevated temperatures in an inert atmosphere. Pyrolysis is often combined with in-line catalytic decomposition, in which polymers are thermally decomposed to produce carbon precursors. This is followed by a chemical vapor deposition pathway, in which a substrate is exposed to volatile precursors that react and/or decompose on the substrate surface, depositing carbon nanomaterials. Combining these processes gives the advantages of producing relatively pure H₂ and high value-added carbon nanomaterials [9]. Gasification is another thermochemical conversion technology in which plastic waste is brought to even higher temperatures than those used in pyrolysis in an oxygen-containing atmosphere. Valuable gas mixtures — often referred to as syngas — are produced, which can be used to produce fuel or can be directly incinerated to produce energy. Gasification offers wide flexibility in that the composition of the atmosphere or gasifying agent can be used to tailor the composition of the product. However, it is very sensitive to contaminants. New developments in gasification strategies, such as using utilizing steam or plasma, are being

explored and optimized to mitigate the effects of contamination and control heating during gasification [13].

To reduce the cost of plastic waste upcycling, new technologies such as compatibilization have emerged. Compatibilizers are typically multicomponent polymers of various architectures, such as graft, block, and random copolymers, that have tailored thermodynamic interactions with immiscible plastics in a given mixture [14]. The process of compatibilization comprises the addition of a substance (the compatibilizer) that is tailored to an immiscible blend of plastics or materials to increase their compatibility and stability [10,14]. Compatibilizers have potential for converting plastics to high-value products with lower costs, and this technique can be used to recycle mixed plastics into equal- or higher-value products [10].

Another new technology for plastic waste upcycling is depolymerization. Because the majority of monomers used for plastic production are derived from fossil fuels [15], developing selective catalysts to depolymerize plastics into monomers or building blocks for producing new polymers can be a solution to address plastic waste issues [2]. Depolymerization can aid in reducing plastic waste, but the economic viability of the pathway should be considered in the long term because depolymerization has not yet been demonstrated on a large, industrial scale [2,5].

A final strategy to address the end-of-life issue of packaging plastics is to use biodegradable polymers such as poly(3-hydroxybutyrate) (PHB), which can result in an environmentally closed circular ecosystem [2]. Some efforts have been made to develop biodegradable plastics, but the mechanical and other physical properties of these plastics are currently insufficient to completely replace conventional plastics. For example, PHB has poorer mechanical properties and lower chemical recyclability (both recycling efficiency and selectivity) than many commercial polymers such as polyethylene. Therefore, some non-biodegradable chemically recyclable polymers such as polycarbonates (PCs), polyurethanes (PURs), and polyesters are commonly used [2,16]. However, the effect of differing physicochemical properties in plastic waste streams has not been systematically studied. Overall, the current strategies of plastic waste recycling and upcycling have not yet been thoroughly analyzed to determine the most promising strategies. Considering the complexity of the products to be recycled/upcycled, there will not be a single best strategy but rather, a strategy tailored to the specific case.

This review evaluates current advances and future directions of the conversion of plastic waste to high-value products. The novelty and originality of the present work are a comparison of primary conventional and emerging conversion strategies, and a concept of designing polymers for subsequent conversion of plastic waste. In particular, this work assesses the state-of-the-art of conventional thermochemical upcycling methods such as pyrolysis and gasification, which are of significant interest with regard to their economic viability, current use in Europe, and relatively minor environmental impacts. Comparisons among various plastic wastes (e.g., PE, PP, polyethylene terephthalate [PET]) and conversion technologies are made. Common reaction mechanisms and catalysts used in the conversion of plastic waste are examined, as well as their resulting products (i.e., liquid fuel, H₂, carbon nanomaterial, lubricant, wax, and composites) and conversion efficiencies. Polymer design and modification for subsequent conversion of plastic waste are investigated. The main challenges facing the adoption and scale-up of these technologies are discussed. Suggestions for focusing future research and development are given.

1.1. Plastic waste types and compositions

Common plastic wastes mainly include PE, polystyrene (PS), polyvinyl chloride (PVC), PET, high-density PE (HDPE), and PP. >60% of municipal solid plastic waste is composed of polyolefins, mainly low-density PE (LDPE), linear LDPE, HDPE, and PP [15]. Table 1 shows the proximate analysis and properties of different plastic wastes. The

Table 1

Proximate analysis and properties of different plastic wastes. A low moisture content ($\leq 0.6\%$) indicates a fast process of plastic waste drying; a high ash content could negatively impact the pyrolysis performance; a higher fixed carbon content could typically result in a higher biochar yield during thermochemical processes; high mechanical strength and chemical resistance of plastic cause difficulty for waste upcycling.

Waste type	Moisture (%)	Ash (%)	Volatile (%)	Fixed carbon (%)	Other	Ref.
PE	0.17	–	99.8	0.02	Favorable impact strength/chemical resistance/ductility; Effective moisture barrier; Easily heat sealed	[17,18]
PS	0.45	0.04	99.1	0.39	–	[17]
PVC	0.16	–	94.8	5.06	Low cost; Good durability/chemical resistance/machinability	[17,19]
PET	0.38	0.09	90.1	9.43	Superior oxygen barrier/mechanical strength; High modulus/thermal stability (up to 350 °C)	[17,18]
Waste electrical and electronic equipment (mainly ABS and HIPS)	–	1.9	97.0	1.7	LHV: 37.7 MJ/kg;	[20]
Plastics (PS, PE, PVC, PP, or PET)	–	0–0.2	90.4–100	0–9.5	Waste composition (wt%): ABS (64), HIPS (33), PBT (3)	[21]
Municipal plastic waste	0.6	13.3	85.7	0.4	HHV: 20.8–46.5 MJ/kg	[22]
Municipal solid waste	–	39.9	49.0	11.1	–	[23]
Municipal solid waste	–	7.6	77.5	14.9	MSW composition (wt%): wood (2.9), paper (8.5), textile (3.2), plastic (11.2), rubber (0.8), food (55.9), other (17.5)	[24]
Fiber waste from paper recycling mill (containing plastic)	–	5.3–10.8	74.5–85.1	7.5–10.8	MSW composition (wt%): food and fruit (46.4), wood (4.7), paper (18.2), PVC (30.7)	[25]
HDPE	–	–	100	–	Calorific value: 38.7 MJ/kg	[26]
Combustible solid waste (containing PVC)	–	7.6	77.5	14.9	Combustible solid waste includes 31 wt% PVC	[27]
PP	0	0.4	99.6	0	–	[28]

Notes: acrylonitrile butadiene styrene (ABS); high-impact polystyrene (HIPS); polybutylene terephthalate (PBT); higher heating value (HHV); lower heating value (LHV).

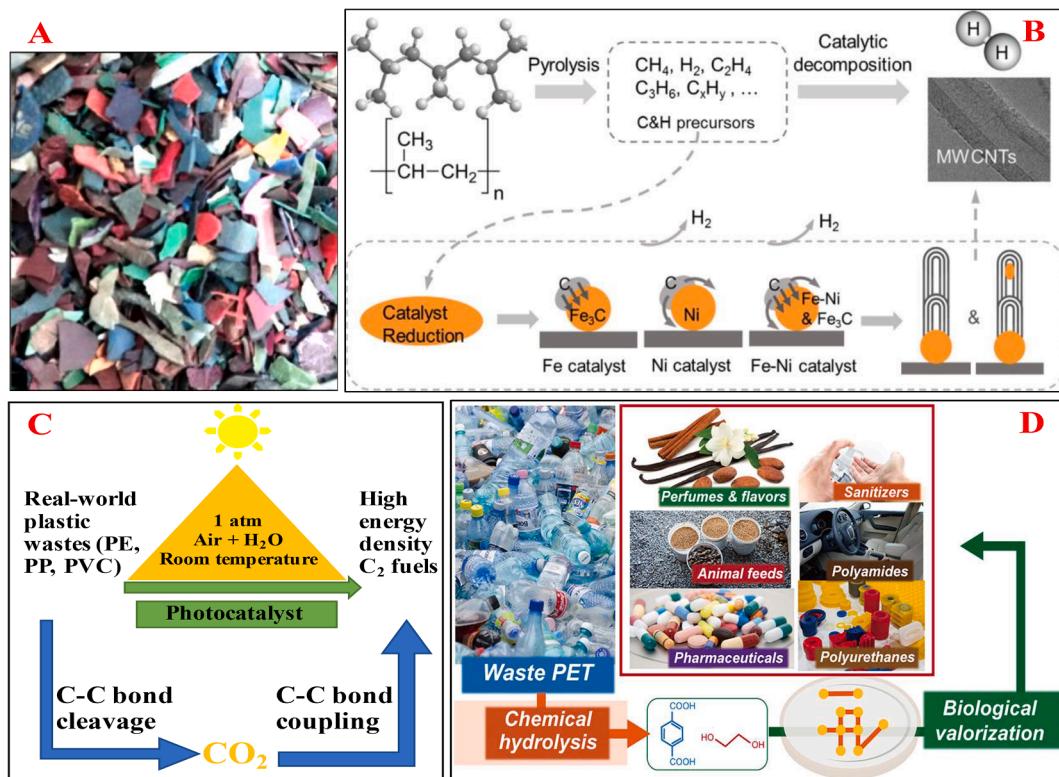


Fig. 1. Plastic waste conversion to high-value products. (A) The shredded and sieved municipal plastic waste sample (size range: 1–3 cm). Reproduced with permission from [22]. Copyright © 2016 Elsevier Ltd. (B) Schematic description of pyrolysis and catalytic decomposition of PP for H₂ and carbon nanotubes over Fe/Ni catalysts (MWCNTs: multi-walled carbon nanotubes). Reproduced with permission from [9]. Copyright © 2020 Elsevier Ltd. (C) Schematic illustration for converting plastic wastes to C₂ fuels by a two-step pathway over a photocatalyst under simulated natural environment conditions: plastic degraded into CO₂ by a photooxidative C-C bond cleavage and the produced CO₂ reduced into valuable C₂ fuels by a photoinduced C-C bond coupling. Reproduced with permission from [5]. Copyright © 2020 John Wiley and Sons. (D) Scheme for the PET waste upcycling: PET was chemically hydrolyzed to terephthalic acid and ethylene glycol, which were converted to higher-value products than PET. Reproduced with permission from [31]. Copyright © 2019 American Chemical Society.

moisture content of plastic waste is typically < 1%, but this seemingly low level of moisture is problematic for plastic manufacturing since it can degrade the polymers significantly. The ash content of plastic waste typically varies between 0% and 39.9%. Excessive ash in plastic waste needs to be removed because a high ash content could have a negative impact on the pyrolysis performance based on bio-oil yield. The fixed carbon content (solid carbon in the material that remains in the biochar after devolatilization) of plastic waste typically varies between 0% and 32%. Biochar is a carbon-rich porous material that is widely used for heat generation and soil remediation. Determining the fixed carbon content often aids the selection of appropriate conversion pathway and conditions, as it can affect the gasification rate and yield. Additionally, plastic waste usually has a high volatile content, >48%. The volatile content may be important for thermochemical processing because the volatile matter can produce tar, which can be detrimental to reactors. The variation in composition of plastic wastes underscores the complex nature of polymer recycling.

Plastic waste is typically cut into small pieces and cleaned to remove organic and other impurities from the surface of the material prior to conversions. In one study, HDPE waste collected from city landfills in Chennai, India was cut into 0.5–1.0 cm² pieces [29]. The impurities in the obtained plastic chips were removed by repeated washing and subsequently dried in an oven, which aided in maximizing the pyrolysis yield of bio-oil [29]. Furthermore, washing plastic waste can remove organic residue [14]. Fig. 1A shows a shredded and sieved municipal plastic waste sample (size range: 1–3 cm). The municipal solid waste (MSW) collected from a landfill in a further study by Liu et al. [30] was oven dried at 105 °C for 5 h, and milled. Then, MSW was sieved into particles under 200 µm in size and placed in a micro rotary mixer for 2 h to homogenize the materials before pyrolysis [30]. The final municipal plastic waste size selection depends on the conversion type because an optimum feedstock size (e.g., approximately 0.3 cm) can minimize the heat and mass transfer limitation during the thermal-chemical process. For example, we have previously [4] found that the biomass feedstock size had an impact on the bio-oil yield during pyrolysis. The smaller biomass feedstock (e.g., <0.05 cm) may have a higher heat transfer rate, causing a lower bio-oil yield because of more thorough breakdown of biomass to gases. The larger biomass feedstock (e.g., >0.4 cm) may have a lower heat transfer rate, causing a lower bio-oil yield because of more char generation [4].

The varied elemental content of different plastic wastes presents a challenge for converting plastics to high value-added products, as the C/H molar ratio in feedstock significantly affects the pyrolysis yields of products [32]. For example, a higher C/H molar ratio could result in a higher biochar yield and a lower tar yield. Balancing the elemental contents of plastic waste by adding in biomass or presorting might be a solution to resolve this issue. Table 2 shows an ultimate analysis of different wastes, indicating that plastic wastes mainly consist of C, H, O, and N. The C/H ratio of a material affects the thermochemical

conversion performance metrics such as composition and overall yield of products. Mixed plastic waste containing both degradable and non-degradable plastic components presents another challenge. A seemingly infinite number of different polymer structures exist, and even similar structures can exhibit vastly different properties. For example, PE contains secondary carbons that are resistant to oxidation from exposure to ultraviolet radiation or heat [15]. However, PE, as with many commodity polymers, can be engineered to display significantly different properties with an array of applications all the way from plastic sandwich bags, bottles, and garbage cans to hip implants. More thoroughly understanding the relationships between a polymer's chemical structure/composition and its degradability is important in developing tailored recycling processes.

1.2. Plastic waste recycling and upcycling technologies

Plastic waste recycling encompasses any method in which plastic waste is reused rather than discarded. Plastic waste is said to be downcycled when it is reused, but the recycled material does not retain the properties of the original material. Plastic waste is upcycled, on the other hand, when it can be reused without degrading its value or performance for the next use. Identifying processes for plastic waste recycling and upcycling can help reduce waste buildup in landfills and oceans, greenhouse gas emissions, and the dependence on non-renewable petroleum resources for polymer production, all while recovering the economic value of the material [14]. Different plastic waste recycling and upcycling pathways, shown in Fig. 2, need to be applied for specific plastic wastes because of their particular advantages and disadvantages. Pyrolysis, incineration, landfilling, and other pathways were developed to manage all waste streams. However, plastic waste is the main waste resource discussed in this review.

2. Advances in plastic waste conversion technologies

2.1. Pyrolysis

2.1.1. Conventional pyrolysis

Plastic waste pyrolysis is typically carried out in the absence of oxygen at 400–800 °C and atmospheric pressure over various catalysts, as shown in Table 3. High temperatures are usually required to carry out the thermochemical reactions. Maintaining these temperatures during the entire pyrolysis process is a challenge, so catalysts are typically used for completing the process at lower temperatures [29]. The pyrolysis products mainly contain gas, biochar, and bio-oil. The product yields are typically in the range of 2–47% of gas, 0–16% of biochar, and 31–91% of bio-oil. Bio-oil, being upgraded to jet fuel, can be considered as a high-value product, which is worth more to customers and returns a higher profit to the owner than a commodity product. Pyrolysis gas used for heat generation can be considered as a relatively low-value product

Table 2

Analysis of different wastes. The C/H ratio of waste is typically in the range of 5–15, and a high C/H ratio could result in a high biochar yield during pyrolysis. A low O content might be beneficial for producing hydrocarbons with an easy removal of O. The existence of S indicates H₂S might be generated during thermochemical processes.

Waste type	C (%)	H (%)	O (%)	N (%)	Other (%)	Ref.
PE	86.0	11.2	2.4	0.2	S: 0.2	[17]
PS	86.1	6.3	1.7	0.3	S: 0.2	[17,33]
PVC	38.3	4.5	—	0.2	S: 0.6, Cl: 56.4	[17]
PET	62.9	4.3	32.6	0.04	S: 0.1	[17]
Waste electrical and electronic equipment (mainly ABS and HIPS)	85.3	7.8	0.98	3.4	Cl: 0.02, Br: 0.13	[20]
Plastics (PS, PE, PVC, PP or PET)	38.3–86.1	4.3–12.7	1.9–57.0	0.04–5.7	S: 0–0.1	[21]
Municipal plastic waste	79.8	15.5	2.0	2.8	—	[22]
Municipal solid waste	29.9–45.3	4.6–6.1	22.0–39.5	1.3–2.3	S: 0.2–1.5	[23,24]
Fiber waste from paper recycling mill (containing plastic)	47.5–67.0	6.7–11.2	21.6–45.6	—	—	[25]
HDPE	85.4	14.2	0.15	0.08	—	[26]
Combustible solid waste (containing PVC)	45.3	6.1	39.5	1.28	S: 0.23	[27]
PP	86.9	12.5	0.32	0.28	S: 0.03	[28]



Fig. 2. Plastic waste conversion strategies. A comparison of primary conventional and emerging strategies for plastic waste recycling and upcycling.

Table 3

The product fraction of the pyrolysis of various wastes. Polycyclic aromatic hydrocarbons generated from the pyrolysis of PE may derive from Diels–Alder type reactions [17]. PS is well suited for pyrolysis because of its high bio-oil yield. Catalysts can help cracking large molecules during pyrolysis, and HZSM-5 is a promising catalyst for the pyrolysis of plastic waste.

Waste type	Catalyst	Conditions	Main product yield (%)	Ref.
PE	Without	800 °C, heat rate: ~350 °C/min, carrier gas: N ₂ , fixed bed reactor	Gas: 46 Bio-oil: ~43 Biochar: 0	[17]
PS			Gas: 6 Bio-oil: ~84 Biochar: ~2	[17]
PVC			Gas: 44 Bio-oil: ~31 Biochar: ~16	[17]
PET			Gas: 47 Bio-oil: ~38 Biochar: ~5	[17]
Municipal plastic waste	Without	500 °C, 2 bar, heat rate: 20 °C/min, carrier gas: N ₂ , batch reactor	Gas: 10 Bio-oil: 80.5 Biochar: 9.5	[22]
		550 °C, 2 bar, heat rate: 20 °C/min, carrier gas: N ₂ , batch reactor	Gas: ~11 Bio-oil: 82 Biochar: ~6	[22]
		600 °C, 2 bar, heat rate: 20 °C/min, carrier gas: N ₂ , batch reactor	Gas: ~12 Bio-oil: 84 Biochar: ~4	[22]
Waste electrical and electronic equipment	Without	400 °C, carrier gas: N ₂ , semi-batch reactor	Gas: 3 Bio-oil: 86 Biochar: 11	[20]
	HUSY		Gas: 3 Bio-oil: 83 Biochar: 13	[20]
	HZSM-5		Gas: 2 Bio-oil: 91 Biochar: 7	[20]

because of its modest heating value [34]. The composition of the product is affected by various factors including the operation temperature, pressure, space velocity (a ratio of the gas flow rate to the reactor volume), heating rate, reactor configuration, catalyst property, and catalyst bed material, among others. For example, 500–600 °C [35] can

be considered as an optimum reaction temperature range for the pyrolysis of waste. The catalysts (e.g., HZSM-5) with high surface areas can promote the waste conversion. For example, the use of the HZSM-5 catalyst (surface area of > 300 m²/g) can lead to a significant decrease (~34%) in the decomposition temperature of plastic waste, which is likely attributed to the cracking reactions facilitated by the acid sites on the catalyst surface [36]. Pyrolysis of plastic waste (containing ABS) over the HZSM-5 catalyst can likely follow a degradation mechanism of thermal cracking via a scission of C–C bonds of polystyrene chains [20].

Many researchers have focused on the production of high-quality bio-oil from the pyrolysis of plastic waste. The temperature, feedstock, heating rate, and reaction time all influence the pyrolysis performance. For example, Kalargaris et al. [37] obtained high-quality bio-oil, exhibiting similar properties to diesel fuel, via the pyrolysis of mixed plastic waste (mainly styrene butadiene and polyester) at two different temperatures (700 °C and 900 °C). The bio-oil produced at 700 °C exhibited higher brake thermal efficiency (break power of a heat engine regarding the thermal input from the bio-oil) and lower emissions of CO, CO₂, and NO_x, compared with that produced at 900 °C [37]. LDPE, HDPE, and PP were used in another study to produce bio-oil via slow pyrolysis at 300–400 °C in a semi-batch reactor. This study also found that changing the pyrolysis temperature directly affected the composition and properties of the produced bio-oil [38]. The pyrolysis degradation mechanism of plastics likely contributes from three general polymer chain reactions: polymer chain scission, side group, and recombination reactions [38]. Bio-oil produced from the pyrolysis of the mixed plastic waste (PE, PP, PET, PS, PVC, and others) in a further study by Singh et al. exhibited properties similar to those of diesel, and the bio-oil obtained at higher heating rates (20 °C/min) had higher density than that obtained at lower heating rates (10 °C/min) [39]. Miidad et al. found that raising the pyrolysis temperature from 400 °C to 450 °C increased the bio-oil yield from PS waste in a small pilot-scale batch pyrolysis reactor, and the optimum reaction time to achieve the highest bio-oil yield at 450 °C was 75 min (compared with 60 or 120 min) [40]. Different types of plastic wastes (PS, PP, and PE) were pyrolyzed at 450 °C and 75 min of reaction time, resulting in different bio-oil yields and qualities [41].

Dealing with pyrolysis byproducts is often challenging, as the byproducts consist of solid and gas phases that are potential to be useful in other applications. For example, biochar, a common byproduct, could

potentially be used to produce activated carbon or carbon nanotubes. Oginni et al. [42] used biochar (derived from pyrolysis of switchgrass) to produce activated carbon, which exhibited a high surface area of 698 m²/g and total pore volume of 0.6 cm³/g. Hidalgo et al. [43] utilized a microwave irradiation technology to convert a mixture of biochar and ferrocene to carbon nanotubes. The produced carbon nanotubes exhibited a high intensity ratio of 1.4, indicating a high degree of wall graphitization and material quality [43]. The gas product mainly consists of H₂, CO, CO₂, and CH₄, but varies significantly as a function of pyrolysis conditions. The proposed mechanism includes producing CO via decarbonylation reactions, CO₂ via decarboxylation reactions, H₂ via dehydrogenation reactions, and CH₄ via the intergradation of H radical with CH₃ radical [32]. The gas could potentially be used to produce liquid hydrocarbon fuel, natural gas, ethanol, or ethylene (for PE production). We [44] successfully converted biogas (mainly CH₄ and CO₂) to H₂ and CO, which were then converted to liquid hydrocarbon fuel via a novel technology of combining tri-reforming and Fischer-Tropsch synthesis. A preliminary economic analysis of the process of landfill gas conversion to liquid fuel on a commercial scale indicated that the breakeven cost of diesel generated was estimated as \$2.7 per gal if the landfill gas was free of cost. Additional credits (e.g., renewable fuel credits) can make this process more economically attractive. This process has been applied by T2C-Energy, LLC, and the pilot-scale test was demonstrated to be successful in 2019 [44].

Some researchers have focused on other high-value products from plastic waste pyrolysis beyond high-quality bio-oil by combining pyrolysis with other conversion techniques. For example, pyrolysis has been combined with subsequent in-line catalytic steam reforming. The performance of this combined process has been assessed in the H₂ production from various plastic wastes such as PP, PE, PET, PS, and their mixtures [45]. Yao and Wang [9] used the pyrolysis and in-line catalytic decomposition technique to convert polypropylene to H₂ and carbon nanomaterials using sol-gel-prepared Ni-Fe bimetallic catalysts. These catalysts are highly active because of their uniform mesoporous structure, high dispersion of active metals, and high reducibility. The majority of the carbon nanomaterials obtained from reacting PP over the Ni-Fe catalysts were in the form of carbon nanotubes, a high-value product. One proposed mechanism for the bamboo-like multi-walled carbon nanotube formation was vapor-liquid-solid: first, the hydrocarbon adsorption and decomposition on the catalyst surface to generate elementary carbon atoms; second, the dissolution and diffusion of carbon as liquid metastable carbides; and last, the carbon precipitation to grow a nanotube [9]. However, the thermal and thermo-catalytic methods for producing carbonaceous fuels can limit their practical applications because they usually require high temperatures (e.g., up to 400 °C) and precious metal catalysts to improve the product selectivity and narrow the product distribution [5].

In another study, clean H₂ and high-value carbon nanotubes were produced from the pyrolysis of mixed plastic waste (mainly PE and PP), with other byproducts such as a small amount of biochar (~0.1 wt%) and bio-oil (<15 wt% obtained over catalysts) [46]. Carbon nanotubes are cylindrical graphene sheets capped with spherical fullerene molecules [47] that exhibit highly desirable properties such as superior electrical conductivity, thermal stability, and high tensile strength. The potential for converting plastic waste to carbon nanotubes and other high value-added carbon nanomaterials (e.g., porous carbon nano-sheets) that can uptake CO₂ has made these conversion strategies a very active area of research. Panahi et al. [47] pyrolyzed different polymers at 800 °C and passed the gaseous intermediates through catalysts to synthesize carbon nanotubes via chemical vapor deposition. The catalyst type (stainless-steel wire cloths, including SS-304, SS-316, and SS-316L), catalyst pretreatment method (acid wash and heating at 800 °C), and polymer type (PET, PE, PS, and PP) all influenced the yield and physical properties of the carbon nanotubes. The SS-316 catalyst with PP polymer achieved the highest yield of carbon nanotubes [47].

One major challenge for efficient decomposition of plastic pyrolysis

hydrocarbons or volatiles to produce carbon nanotubes is the design of appropriate catalysts [9]. The formation mechanism of carbon nanotubes from polypropylene is shown in Fig. 1B. Designing catalysts with sufficient thermal stability is also difficult, as coke (carbonaceous material) deposition and metal sintering occur at high operation temperatures [9]. Including appropriate promoters (substances added to a catalyst to improve its performance in chemical reactions, such as Mg and Mo) in the catalyst could prevent coke deposition because of their oxygen storage capability and contribution to improving active metal dispersion.

Co-pyrolysis of biomass and plastic waste is a promising pathway toward efficient plastic recycling, as a possible synergistic effect between the processes can improve the bio-oil's property and yield [33]. Co-feeding with plastic is helpful for the biomass pyrolysis toward bio-oil quality. Plastic waste is known to have a high hydrogen content. Biomass can be added to the mixture to rebalance its C/H ratio and increase the process selectivity and overall value of the conversion products [33]. In one study, PVC and soybean protein were co-pyrolyzed, and their interaction accelerated the reaction (the maximum reaction rate was 12–16% higher compared with calculation of linear combination of individual pyrolysis results) [48]. Fang et al. [49] investigated the co-pyrolysis of MSW and paper mill sludge, finding a significant interaction between the MSW and paper mill sludge at high temperatures (e.g., 700 °C) that decreased the initial temperature (compared with paper mill sludge). This interaction was favorable for the pyrolysis process. The study found that a mass ratio of MSW to paper mill sludge at 9:1 was suitable for the co-pyrolysis [49]. Finding a suitable mass ratio of plastic waste to other components is crucial to optimize the co-pyrolysis process. While scaling-up the co-pyrolysis process, finding alternatives to replace valuable nutrients/food sources (e.g., soybean protein) to upcycle plastic waste will be critical. Furthermore, precise control or selection of the molecular weight of the polymers being upcycled might be helpful to improve the products of their following conversion.

Catalytic cracking (i.e., thermal reduction of the molecular weight of molecules by a catalyst) can reduce the energy demand for plastic waste upcycling, compared with the cracking without a catalyst. Various catalysts including zeolites and other metal oxides have been recently explored and developed to improve pyrolysis performance. For example, the effect of Ni-Fe bimetallic catalysts on the pyrolysis of the plastic waste was studied in a two-stage fixed bed reactor system [46]. The catalyst with more Fe resulted in more deposited carbon and hydrogen. This was attributed to its higher cracking ability and a relatively lower interaction between the support and active sites. The presence of Ni on the catalyst improved the graphitization degree of the produced carbons and the thermal stability [46]. Ni-Co-Al catalysts used in a further study significantly improved the syngas production during the conversion of plastic waste via a two-stage reactor: the first stage pyrolyzed the plastic, and the second stage consisted of dry reforming of the produced pyrolysis gases [50].

Muhammad et al. used zeolite catalysts to pyrolyze plastic waste collected from waste electrical and electronic equipment to produce gasoline range aromatic bio-oil in a two-stage reactor system [51]. While, Miidad et al. used natural and synthetic zeolite catalysts to pyrolyze various plastic wastes such as PP, PS, PE, and their mixtures to high-quality liquid bio-oil at 450 °C and 75 min of reaction time [52]. In these studies, the zeolite catalysts increased the conversion selectivity, resulting in bio-oil of a higher quality than that obtained without catalysts. Different catalysts such as HZSM-5, BNH₄ZSM-5, and USY (ultra-stable Y zeolite) were used in another study for the pyrolysis of urban plastic waste (mixture of PE and PP) [53]. BNH₄ZSM-5 was an excellent pyrolysis catalyst, as its high specific area and pore volume resulted in ~33 wt% of bio-oil and negligible biochar [53]. These studies suggest that the addition of catalysts, especially Ni-based catalysts, can help improve the plastic waste conversion selectivity. For example, Shi et al. [54] studied the co-pyrolysis of cellulose and PP over MCM-41 and Ni/MCM-

41 catalysts. The loading of 25 wt% of Ni effectively modulated the properties of MCM-41, which led to a 36% increase in the relative total amount of olefins and aromatics. The high catalytic performance of the Ni/MCM-41 catalyst can be attributed to its proper physical structural property, high metal dispersion, and strong metal-carrier interaction [54].

Other parameters have also been studied to evaluate the catalyst efficiency, such as the feedstock-catalyst contact mode (e.g., in-situ and ex-situ) and gas atmosphere (e.g., He and H₂). In an in-situ catalytic pyrolysis, the catalyst is mixed with the feedstock in one reactor; however, the catalyst is placed in a secondary reactor in an ex-situ catalytic pyrolysis. A study by Xue et al. [55] found the contact mode and atmosphere to influence the catalytic pyrolysis performance of plastic wastes (PET, PE, PS, and PP) as such: the in-situ and ex-situ catalytic pyrolysis occurred via different reaction mechanisms, and the H₂ carrier gas reduced solid residue in comparison to He carrier gas. One proposed mechanism for catalytic pyrolysis of PS consisted of the steps of primary cracking, chain attack, and cyclization. The free radical mechanism dominated the thermal decomposition of PS [55]. Lee et al. used CO₂ as a carrier gas for the pyrolysis of PET, which provided a novel pathway to enhance the energy recovery and reduce the acidic byproducts (e.g., benzoic acid) produced in typical pyrolysis in N₂ or He carrier gas [56].

In thermochemical plastic upcycling processes (e.g., pyrolysis and gasification), fixed-bed, batch, and fluidized reactors are most typically used. A fixed-bed reactor is typically a cylindrical tube filled with solid catalysts with reactants flowing through the bed; a batch reactor is typically a closed vessel with an agitator and heating system. A fluidized bed reactor is typically a device in which a fluid flows through solid catalysts at high enough speeds to suspend the catalysts. These reactors are designed to minimize operational problems such as coke formation and defluidization by incorporating features such as conical spouted or fluidized beds [45]. Fixed-bed reactors are easy to assemble and low-cost. However, coke can deposit inside the reactor tube, which may damage the reactor with time. Pyrolysis of plastic waste is typically investigated in a lab scale. For example, pyrolysis of hospital plastic waste (its minority is infectious, different from the plastic waste generated at home) was investigated using different fixed bed reactor scales (the sample mass increased from 0.05 g in a thermogravimetric analyzer to 600 g in a bench-scale reactor). Changing the reactor scale did not cause significant differences in the pyrolysis product distribution (lab scale: 70% of bio-oil and 17% of gas produced; bench scale: 83% of bio-oil and 17% of gas produced) [57].

To scale up the pyrolysis process in the future, some researchers have conducted the techno-economic assessments. For example, Fivga and Dimitriou [58] studied the pyrolysis of plastic waste for heavy fuel substitute production. They estimated that for the 10,000 kg/h plant capacity case, the facility needs to operate approximately one year to recover the capital investment. The fuel production cost can be reduced when the plastic waste cost decreases [58]. Bora et al. [59] calculated that pyrolysis has a better economic performance than gasification in terms of total net present value. Pyrolysis has the potential to reduce the environmental impact of plastic waste. The environmental impact categories mainly include climate change, human toxicity, water depletion, particulate matter formation, natural land transformation, and marine ecotoxicity. Pyrolysis has a lower overall greenhouse gas emission and better overall environmental performance than incineration and landfilling [59]. Gracida-Alvarez et al. [60] investigated that the pyrolysis-based refinery for the conversion of 500 t/day of waste HDPE can generate a net present value of \$367 million. The low taxes, low discount rates, and other positive incentives can help narrow the gap between the basic research and commercial applications.

Research carried out on catalytic degradation of PE by Jia et al. [15] determined that catalytic pyrolysis has disadvantages including a lack of product control and low energy efficiency. Pyrolysis temperatures typically range from 400 to 800 °C, and the products are complex, consisting of bio-oil, hydrocarbon gas, biochar, and wax. Additionally,

any contaminants in the plastic or mixed plastics can deactivate the catalysts or interfere with their activity. The catalytic activity depends on several factors including catalyst characteristics, plastic physico-chemical properties, and operating conditions. Conversion of plastic waste to high-value products will benefit greatly from the development of efficient methods to remove contaminants. Additionally, the development of low-temperature catalysts (e.g., NiFe₂O₄#SiO₂ and Pt-NiMg/Ce_{0.6}Zr_{0.4}O₂ catalysts) [12] could reduce the high energy consumption caused by high operation temperatures. So far, one promising catalyst used for plastic waste conversion could be a promoter-added, ZSM-5-based catalyst; its high specific area and pore volume lead to a high reactivity and efficiency. Of all common commodity plastics, PS is particularly well suited for pyrolysis because of its high bio-oil yield of 84 wt% [17], as compared with the 43 wt% bio-oil yield of PE.

Additives are almost inevitable in plastic waste, and researchers have investigated their effect on downstream recycling. For example, Yuan et al. [61] found that the additive (in the form of ash, 10% in PVC) in the PVC had a minor effect on the final dechlorination efficiency. The chlorine-containing PVC poses a threat to pyrolysis because highly corrosive HCl can be generated under the thermal degradation process [61]. Song et al. [62] investigated that the additive (in the form of iron oxide) increased H₂, CO and CO₂ production for the pyrolysis of MSW. However, more studies on the impact of additives on the downstream upcycling are lacking. Some attempts at commercial plastic waste upcycling have not been successful because of the presence of additives. The mechanism on whether some additives deactivate the downstream process catalysts or corrode the process equipment is not clear.

2.1.2. Microwave-assisted pyrolysis

Microwaves are usually referred to as electromagnetic waves [63]. Microwave-assisted heating has some advantages over conventional heating, such as the capability of non-contact volumetric heating and a higher energy efficiency [64]. Using microwave absorbents, known as susceptors, along with the feedstock during microwave-assisted pyrolysis can help reduce the feedstock processing time and improve the heating rate. The absorbents need to be high-loss tangent materials that convert microwave to heat energy [64]. Microwave-assisted heating can lead to a uniform heat distribution in some specific configurations and with specific feedstocks. For example, Zhu et al. [65] used a microwave cavity structure with a sliding base based on a phase-shifting heating strategy to heat a potato with dimensions approximately 60 × 40 × 9 mm³ (length × width × thickness). The phase-shifting heating strategy (moving the sliding base) was helpful to solve the problem of non-uniform heating during microwave-assisted heating. The coefficient of variation of the temperature for the potato was calculated as 0.5. When the phase-shifting heating strategy was applied to NaCl, the coefficient of variation of the temperature decreased to ~ 0.2 (~60% increase in the uniformity of heat distribution) [65]. Microwave-assisted pyrolysis is a new pyrolysis technique, in which microwave energy is transformed into heat inside the feedstock particle. Bio-oil is one common product of microwave-assisted pyrolysis of plastic waste. Fan et al. [66] studied the microwave-assisted pyrolysis of LDPE, finding that the obtained bio-oil contained 96% of gasoline. Rosi et al. [67] observed a rapid increase of temperature during the microwave-assisted pyrolysis of halogenated plastics. The obtained bio-oil had a higher heating value of 41 MJ/kg and was suitable for use as a fuel [67].

Microwave-assisted co-pyrolysis is often used to promote the synergistic effects between plastic components and the other materials or fillers. For example, researchers [68] found a synergistic effect between bamboo and PP during the microwave-assisted co-pyrolysis process, as the resulting mass of bio-oil exceeded the theoretical production mass. Suriapparao et al. [64] also found that the higher heating value of bio-oil obtained from microwave-assisted co-pyrolysis of PP and rice husk (42 MJ/kg) was much higher than that of the bio-oil (20 MJ/kg) obtained from the microwave-assisted pyrolysis of individual biomass sources. In addition, microwave-assisted co-pyrolysis has been shown to produce

bio-oil with a lower acidity and moisture content than those of bio-oil obtained from the microwave-assisted pyrolysis of individual biomass sources [64]. Microwave-assisted co-pyrolysis of biomass with plastic is a promising thermochemical pathway to convert mixed waste to bio-oil, but biomasses and plastics vary significantly regarding their elemental composition. Fodah et al. [63] also found that the yields of microwave-assisted pyrolysis products varied largely, depending on the feedstock type and pyrolysis conditions (e.g., heating rate and microwave power). One challenge is the further improvement of the microwave-assisted conversion process for easy acceptability and affordability. For the microwave heating mechanism, the electromagnetic energy is converted to thermal energy. The microwave penetrates into the material and is stored as energy, which is then converted to heat inside the material core [63]. A broader screening of biomasses and plastics (with different physicochemical properties) will contribute to building a database and optimize the microwave-assisted co-pyrolysis process.

The heating characteristics of microwave-assisted pyrolysis may lead to a narrower product distribution. Fan et al. [66] studied the ex-situ catalytic cracking of vapors from microwave-assisted pyrolysis of LDPE. Compared with in-situ catalytic cracking, ex-situ catalytic cracking has some advantages: the pyrolysis and catalytic cracking temperatures can be individually regulated, the vapors likely have more contact with the catalyst, and there is no need to separate the catalyst from the biochar produced (the catalyst can be regenerated for reuse). LDPE has poor dielectric properties, which makes it a poor absorber of microwave. Microwave absorbents can be added (mixed with LDPE) to increase the efficiency of microwave pyrolysis. In theory, bio-oil from pyrolysis of LDPE should exhibit no acid, no water, and a high calorific value owing to the absence of oxygen during the pyrolysis conversion process. The crude bio-oil is typically further upgraded via a catalytic process to enhance its selectivity and narrow the resulting product distribution for valuable chemical products. Fan et al. investigated the effects of the pyrolysis temperature (350–550 °C), catalytic reaction temperature (350–550 °C), and catalyst to reactant ratio (0–0.1) on the yield and chemical profile of products. A higher catalyst to reactant ratio, pyrolysis temperature, and catalytic reaction temperature favored gas production. The coke yield ranged from 0.1 to 1.9 wt% based on the reactant mass [66]. This indicates that catalysts need further exploration (e.g., adding promoter Mg to reduce the carbon deposition due to oxygen storage capability) [69] to minimize coke generation to further improve the catalytic performance during microwave-assisted pyrolysis or co-pyrolysis.

Along with bio-oil, other products are produced from the microwave-assisted conversion of plastic waste as well. For example, porous sulfonated carbon has been produced from LDPE plastic via sulfuric acid soaking through the microwave process [70]. Lithium-sulfur batteries have high energy density and have been explored as next-generation batteries. A porous sulfonated carbon layer can be used as an interlayer in lithium-sulfur batteries to improve the sulfur cathode capacity. This technique of functionalizing the LDPE plastic via microwave treatment can be extended to other polymers, unlike the pyrolysis of biomass waste to produce carbon materials [70]. In another study, terephthalic acid was produced from the depolymerization of PET waste via microwave-assisted neutral hydrolysis, a chemical process of decomposition performed under neutral conditions (not alkaline or acidic conditions). 2-pyrene-4, 6-dicarboxylic acid, a valuable monomer used to synthesize biodegradable polymers, was then produced from terephthalic acid via a comprehensive chemo-microbial hybrid process [71]. These studies prove microwaves can be utilized not only in pyrolysis, but also in neutral hydrolysis, based on the desired products such as bio-oil, porous carbon, and monomers.

2.2. Gasification

2.2.1. Conventional gasification

A second conversion technology, gasification, differs from pyrolysis.

Gasification typically occurs at higher temperatures (≥ 800 °C) with a gas carrier containing O₂ in partial combustion conditions, resulting in gas as the main product. Table 4 shows the conversion performance of various wastes via gasification and other thermo-chemical technologies. The gasification of plastic waste is typically carried out at the temperature of approximately 850 °C and atmospheric pressure over various catalysts. Gasification of MSW has a high overall efficiency and produces less particulate matter [72]. Different reactors, such as single-staged and multi-staged, have been developed for gasification. The multi-staged

Table 4

The conversion of various wastes via gasification and other thermo-chemical conversion technologies. 800–900 °C is typically used for gasification, and the produced gas mainly contains H₂, CO, and CH₄.

Waste type	Catalyst	Conditions	Main product yield	Ref.
Municipal solid waste	Without	850 °C, MSW feed of 4.4 g/min, downdraft fixed-bed gasifier	Gas: 1.1 Nm ³ /kg	[75]
Municipal solid waste	Without	750 °C, MSW feed of 25 kg/h, steam gasification, fluidized bed reactor	Gas: ~1.5 Nm ³ /kg	[76]
Plastic waste	Without	900 °C, in-situ gasification chemical looping combustion	CO ₂ : 97%	[77]
MSW with plastic solid waste	Without	Plasma gasification, plasma gasifier	H ₂ : 61% CO: 32% CO ₂ : 7%	[78]
Pinewood with PP	Without	900 °C, steam gasification, semi-batch reactor	Gas: ~51 g	[79]
Pinewood with PET	Without	900 °C, steam gasification, semi-batch reactor	Gas: ~46 g	[79]
Artificial waste	Without	900 °C, fluidized-bed gasifier	Gas: 0.7 Nm ³ /kg	[80]
Waste electric and electronic equipment	Without	429 °C, carrier gas: N ₂ , 2.45 GHz, absorber: carbon, microwave multimode reactor	Gas: 10% Bio-oil: 64% Biochar: 26%	[67]
Mixed wood sawdust and PS	Without	Biomass/polymer mass ratio of 1:1, 450 W, microwave-assisted co-pyrolysis	Gas: 28% Bio-oil: 59% Biochar: 13%	[64]
Rice husk and PP	Without	Biomass/polymer mass ratio of 1:1, 450 W, microwave-assisted co-pyrolysis	Gas: 35% Bio-oil: 41% Biochar: 24%	[64]
MSW with coal	Coal char	550 °C (pyrolysis), 800 °C (oxidation), 800 °C (reduction), waste feed of 1.3 g/min, three-stage co-gasification, tubular reactor	Gas: 1.6 Nm ³ /kg	[81]
PE	CaO	800 °C, air gasification, bench-scale fixed reactor	H ₂ : 38% CO: 34% CH ₄ : 4% CO ₂ : 24%	[82]
Coconut shell mixed with HDPE waste	Nickel and dolomite	870 °C, steam gasification, fluidized and fixed bed gasifiers	Gas: 571 g/kg	[83]
LDPE	MgO	2.45 GHz, microwave-assisted pyrolysis	Gas: 25–73% Bio-oil: 24–39% Biochar: 1–50%	[66]
Bamboo and PP	HZSM-5	250 °C, feedstock/catalyst ratio of 2:1, bamboo/PP ratio of 1:2, 1,000 W, 2.45 GHz, microwave-assisted co-pyrolysis	Gas: ~34% Bio-oil: 62% Biochar: 3%	[68]

gasification allows the reactions to be optimized individually under appropriate operating conditions [73]. The primary challenge facing gasification of waste is that it is intrinsically related to the physico-chemical properties of the input material, making it very sensitive to impurities or contaminants [74]. The oxidizing agent used in gasification is usually oxygen, air, or steam [59]. Using air as an agent can cause a high N₂ content in the gas product, which dilutes the energy content and limits the application of the gas product. When steam is used as an agent, the reactions during gasification can include steam reforming, water-gas shift, and Boudouard reactions [59]. Different approaches such as steam and plasma have been developed to aid gasification by providing control of moisture content and a more efficient method of heating, respectively. The gasification product mainly contains gas in the form of H₂, CO, and CH₄. However, the gas yield can vary largely from 10 to 73% (other products are biochar and bio-oil) depending on the gasification conditions (e.g., reaction temperature, reactor configuration) and waste feed types.

Syngas, a valuable product, is a mixture of H₂ and CO that is used for liquid fuels and chemicals. When syngas is desired as a primary product from gasification, its yield and composition are crucial and can be adjusted through different process parameters. The effect of changing the equivalence ratio (ratio of the actual to stoichiometric fuel/air ratio; 0.2–0.8), reaction temperature (550–850 °C), and moisture content (9–52%) during MSW gasification was investigated in a fluidized bed reactor [84]. The syngas yield increased with an increase in the equivalence ratio, and a higher temperature broadened the syngas mass distribution. The H₂ production yield was promoted, but the energy conversion efficiency was inhibited with an increase in moisture content at 650 °C. The appropriate MSW moisture content for gasification was found to be < 20% [84]. In another study, the presence of NiO modified dolomite catalysts increased the gas yield dramatically, and the H₂ content increased up to 40% during the gasification of MSW [72]. To assist the gasification technology development, mathematical models such as computational fluid dynamics simulations can be developed, which could aid in linking the gasification process and related parameters with its resulting products [72].

For the techno-economic assessments of the gasification process, Ng and Phan [85] reported that using gasification (producing H₂) can potentially save \$2.26 million per year on waste disposal cost while diverting it from landfills. A large gasification system (e.g., >100 dry t/h of waste) is ideal to be competitive with the production cost of H₂ generated from conventional fossil-based systems [85]. Bora et al. [59] found that the fast pyrolysis and gasification of PP waste can generate total net present values of \$149 million and \$96 million, respectively. The waste price, discount rate, and plant life are the most critical factors for the economic performance of the thermochemical systems. For example, when the discount rate increases from 10% to 15%, the total net present value of gasification decreases from \$96 million to ~\$9 million [59].

Catalyst deactivation is a concern during gasification of plastic waste, which is largely a result of contamination of the feedstock sources. Developing methods (e.g., presorting and cleaning) to effectively remove the contamination from plastic waste before gasification will be important to preserve the catalyst activity. Additionally, utilizing the gaseous products of gasification such as H₂ and CO for liquid fuel production via Fischer-Tropsch synthesis, while utilizing solid products such as biochar for carbon nanotube production (previously discussed) at the same time can be a promising pathway to augment the value and implementation of gasification strategies for upcycling plastic waste.

2.2.2. Plasma- and supercritical water-assisted gasification

In addition to microwaves, plasma and supercritical water have been used to assist existing technologies to upcycle plastic waste. In plasma gasification, the heat is provided from thermal plasma that typically derives from direct current non-transferred arc plasma torches [78]. Plasma is known as the fourth state of matter, in which part of the

gaseous molecules or atoms are in the ionized form [86]. Plasma can enable charged particles to interact with neighboring particles. A plasma gasification facility can be based on a gasification reactor with a plasma torch and plasma cupola [86]. Compared with conventional gasification, thermal plasma gasification has some advantages such as higher syngas yield, lower tar content, and more efficient energy use [87]. Plasma processing can lead to high energy density and high reaction temperature (e.g., >1,000 °C), which can promote the interactions between excited ions and particles [87].

Yayalik et al. [88] studied the plasma gasification of MSW and proposed some reaction pathways. For example, the decomposition of MSW generates CO, H₂, CO₂, H₂O, and C. The formation reactions mainly include: C reacting with H₂O to produce CO and H₂, and C reacting with CO₂ to produce CO [88]. A two-stage fluid bed gasification-plasma process was used for the gasification of refuse derived fuel (containing plastic), finding that plasma is helpful to remove tar and purify syngas [74]. Tar can block reactor pipes and can be considered as a relatively low-value product. In another study, air and steam plasma gasification of household waste containing approximately 5 wt% of plastic was performed in a plasma reactor [13]. Calculations showed that the air and steam plasma gasification of household waste can produce a high-calorific syngas with concentrations of 82 and 95 vol%, respectively. Household waste often contains toxic substances, which are difficult to treat. However, plasma gasification reliably destroys highly toxic furans, dioxins, and benzo(a)pyrene, all substances that cannot be destroyed through conventional incineration [13].

Supercritical water has also emerged as a candidate for converting plastic waste through gasification. For the supercritical water gasification, supercritical water serves as a solvent to facilitate a homogeneous reaction [89]. In addition, supercritical water serves as a catalyst to improve the reaction rate, attributed to the H-radicals at high temperatures and high ion production near critical points. Furthermore, supercritical water can tolerate wet plastic waste without a drying pretreatment, and can reduce the coking in the reaction. In a quartz tube reactor, the amount of water added is determined by the reaction pressure, reaction temperature, and tube volume [89]. One proposed mechanism for H₂ formation is mainly from the CO formation, followed by the water-gas shift reaction [90]. In one study, the supercritical water gasification of refuse derived fuel was performed in a batch reactor at 450 °C with RuO₂/r-Al₂O₃ catalysts, finding that the carbon gasification efficiency was ~98% (compared with the non-catalytic test, ~42%). When other components of MSW such as waste textile and waste wood were gasified, the reactivity of the feedstock depended on its composition because the produced gas composition varied largely [90]. Peng et al. [91] proposed a supercritical water gasification mechanism of polymer-containing oily sludge. The reaction pathways included pyrolytic reaction of polymer-containing oily sludge, steam reforming reaction, coking reaction, water-gas shift reaction, and methanation reaction [91].

2.3. Other conventional conversion technologies

Compared with pyrolysis and gasification, incineration of MSW has a greater environmental impact resulting from CO₂ and particulate matter emissions [92]. Incineration is an exothermic process that involves the combustion of waste. The discharge of the flue gas and ash can cause heat loss [92]. However, the incineration of MSW can be improved by more sufficient utilization of the byproducts [93]. Modern incineration equipment, designed with effective flue gas cleaning, ash recycling, and use of combined power and heat cycles, can benefit in the area of environmental sustainability [92]. Improving the energy efficiency, efficiently managing the residues, enhancing the plastic waste quality (e.g., presorting and cleaning) [92], and developing new plastic waste collection technologies are promising pathways for future expansion and adoption of incineration as a plastic recycling technique.

Mechanical reprocessing, including precleaning sorting and melt

extrusion, can be used to remanufacture plastic waste [47]. Mechanical reprocessing mainly consists of shredding, melting, and remolding plastic [14]. However, there are some limitations to mechanical reprocessing. For example, thermosets cannot be reprocessed via conventional mechanical reprocessing methods [14]. Additionally, mechanical reprocessing of plastic waste typically produces lower-value products with degraded properties [1]. Physical presorting of components for mixed plastic waste streams prior to mechanical reprocessing is necessary but comes at a high cost [18]. Contamination from unwanted polymers and fillers is another challenge in mechanical reprocessing [1]. The development of decontamination technologies for fast cleaning of the plastic waste and efficient presorting of the plastic mixtures will significantly increase the yield of high-purity polymers [14]. A potential pathway being explored by some researchers for plastic presorting uses the melting points of plastics to presort thermosets and thermoplastics. This concept and other improvements to mechanical recycling warrant future study.

Conventional incineration of plastic waste has higher CO₂ emissions than mechanical recycling [94]. Incineration of plastic waste emits CO₂, but some of the embodied energy of the MSW can be recovered. As with other recycling methods, high costs are involved in collection, separation, sorting and recycling for mechanical melting recycling [94]. Different polymer molecular weights and phase separation can inhibit the interfacial adhesion of plastic mixtures, which is detrimental to their mechanical performance. Incineration is inexpensive and convenient for mixed plastic waste since it can avoid the need for presorting. However, starting components cannot be recovered and reused once burned [14]. Incineration can be utilized when the mixed plastic waste cannot be sorted or other recycling methods are too expensive.

Landfilling has been widely utilized as a method to store plastic wastes. The waste degradation process in a bioreactor landfill is microbially accomplished to achieve an extensive and fast stabilization of waste [11]. The recirculation of the collected leachate mainly contributes to this process [11]. Large amounts of plastic waste go to landfills globally, but space availability and environmental pollution are significant issues in landfilling [47]. Most plastics are chemically stable and durable, and as previously discussed will not fully degrade for hundreds of years. However, some plastics do have components that break down quickly which can lead to air, soil and aquifer pollution from placing their waste in a landfill [47]; microplastics become a huge issue because they end up in human food chain. The landfill gas formation involves a variety of reactions such as hydrolysis, aerobic and anaerobic digestion, fermentation, and methanogenesis [95]. To reduce harmful gas emissions, we [12,44] demonstrated conversion of landfill gas from landfills to liquid fuels. This conversion of landfill gas to liquid fuels is a highly promising technology (integration of tri-reforming and Fischer-Tropsch synthesis) for expansion and commercialization.

Biochemical conversion such as anaerobic digestion of biodegradable plastic waste via micro-organisms has emerged as another promising technology for upcycling [47]. For example, researchers [96] reported that wax-worm caterpillars may degrade PE into ethylene glycol, a chemical which could be upcycled into the supply chains for producing polyester fibers and antifreeze, although the exact degradation mechanism and products are still being uncovered. Other researchers [97] indicated that the gut bacterium of mealworms can consume polystyrene to produce CO₂ and other products. Researchers [98] have also developed bacteria that degrades low- or high-crystallinity PET into CO₂ or even into its monomers. The PET hydrolysis reaction took place in this process [98]. Although biochemical conversion is an exciting upcycling technology with high potential, this type of polymer degradation has significant limitations. The process is currently very costly and time-consuming. Additionally, biochemical conversion can produce small-chain polymers or microplastics which can cause significant harm to aquatic life. Limiting or reducing the cost, speed, and harmful byproducts of biochemical conversion of plastic waste is crucial to make it a viable technology for widespread use in the

future.

2.4. Emerging conversion technologies

2.4.1. Photoreforming

Another promising recycling technology is photoreforming, a simple and low-energy method to convert plastic waste to H₂ or other chemicals such as acetic acid (CH₃COOH) using sunlight, water, and a photocatalyst [6]. Photoreforming of plastic waste under mild conditions (e.g., ambient temperature and pressure) typically results in a low selectivity and product yield, but recent research has begun to address this issue. In one study, plastic waste (e.g., PET, polylactic acid [PLA], and polyester microfibers) was successfully photo-reformed to H₂ and other chemicals at ambient temperature over CN_x/Ni₂P catalysts, which are inexpensive and nontoxic [99]. Ambient-temperature photoreforming is a simple and low-energy technology, but it has only been performed on very small scales. Uekert et al. were able to upscale the process from 2 to 120 mL, but were unable to produce larger yields [99]. In another study, visible light-driven oxygenation of C–C bonds of PE (which is non-biodegradable) was conducted to produce fuels and chemicals over a vanadium photocatalyst under mild conditions. This methodology could be used to recycle a broader range of polymers as well [100]. PE has also been completely photodegraded via C–C cleavage into CO₂, which can be further photo-reduced to C₂ fuel such as acetic acid via C–C coupling over Nb₂O₅ photocatalysts at the conditions of natural environments—atmospheric pressure, room temperature, water, air, and simulated one-sun irradiation—as shown in Fig. 1C [5]. Based on the above proposed photoconversion mechanism, this technology can highly selectively convert various plastic wastes (PE, PVC, and PP) to C₂ fuels. However, the current acetic acid yield from this process is relatively low, at ~ 0.1 mg/g_{cat} (g_{cat} refers to grams of catalyst). Designing two-component photocatalysts (one for C–C cleavage and the other one for C–C coupling) could increase the yield [5]. In addition, other new technologies such as 3D printing can be applied to synthesize customized photocatalysts (with better heat/mass transfer) to improve the CO₂ reduction efficiency. The photoreforming system needs to be upscaled further (e.g., much > 120 mL) to be a viable conversion technology for global plastic waste. 3D printing technology is a class of computer-aided manufacturing, facilitating the production of parts with complicated geometries [4,101]. For example, Thakkar et al. [102] 3D-printed zeolite monolith catalysts (outside diameter ~ 8 mm) for CO₂ removal from an enclosed environment.

>50 million tons of H₂ are produced worldwide each year for use in pharmaceutical, chemical, and agricultural industries. 96% of the H₂ supply in the world is generated through the reforming of fossil fuels [6]. Plastic waste pyrolysis into H₂ requires a high energy input and releases large amounts of greenhouse gases (approximately 12 g CO₂ per 1 g H₂) [6]. Therefore, photoreforming has become a potential alternative to convert plastic waste to H₂ for industrial use. In one study, three commonly used polymers – PLA, PET, and PUR – were successfully photo-reformed to produce H₂ over inexpensive CdS/CdOx quantum dots catalysts at ambient pressure and temperature [6]. Other polymers, such as polyethylene glycol, PVC, polyvinyl pyrrolidone, PS, PE, polymethyl methacrylate and PC, have also been photo-reformed to produce H₂. Furthermore, PET water bottles were photo-reformed into H₂. Plastic waste is a freely available substrate, but challenges for its photoreforming include its low water solubility, complex structure, and general non-biodegradability [6].

2.4.2. Other emerging conversion technologies

Numerous other technologies have been developed to convert plastic wastes. For example, hydrogenolysis (a chemical reaction in which a carbon–carbon or carbon–heteroatom single bond is cleaved by H₂) has been used to convert plastic waste (such as polyesters and PCs) to value-added diols over a molecular ruthenium catalyst [103]. Glycolysis (a process that degrades polymers by glycols) has been used to convert PET

to bis(2-hydroxyethyl)terephthalate over the $\text{Fe}_3\text{O}_4@\text{SiO}_2@(\text{mim})[\text{FeCl}_4]$ catalyst, which provided nearly 100% yield and selectivity [104]. Chemical hydrolysis was utilized in one study to convert PET waste to two monomers (terephthalic acid and ethylene glycol), which were then converted to higher-value products than PET, as shown in Fig. 1D [31]. A two-step method (methanolysis and hydrodeoxygenation) was used in a further study to convert PC waste to jet fuel range high density polycycloalkanes under mild conditions [105]. The gasoline and jet fuel range C₇–C₈ aromatics and cycloalkanes were produced by the alcoholysis of the PET waste (methanol is highly reactive for the alcoholysis of PET), followed by solvent-free hydrogenation and hydrodeoxygenation [106].

A catalytic processing of polyoxymethylene polymer waste combined with biomass-derived diols was conducted at low temperatures (e.g., 100 °C) by Beydoun and Klankermayer to produce value-added cyclic acetals, as shown in Fig. 3A. Cyclic acetals can be applied as fuel additives, solvents, pharmaceutical intermediates, and monomers for polymerization reactions [107]. PET was upcycled by researchers in combination with a bio-based monomer into higher-value and long-lifetime composites (e.g., fiber reinforced plastic) [108]. The growing market size and high selling price of fiber reinforced plastics make them ideal applications in which to use bio-based, sustainably sourced monomers [108]. Additionally, commodity polymer waste, bisphenol A based polycarbonate, has been upcycled via an organocatalytic depolymerization procedure into high-value added functionalized cyclic carbonate. Cyclic carbonate is an attractive monomer also used to synthesize PURs or PCs for various applications [109]. A proposed mechanism for this depolymerization is the ring-closure of the carbonate [109]. These emerging technologies showcase researchers' great interest in the upcycling of plastic wastes.

Recently, researchers from Rice University [111] has developed a flash graphene technology to convert plastic waste to graphene that exhibited turbostratic arrangement between the stacked graphene layers. Flash graphene technology is a flash Joule heating process in which amorphous conductive carbon powders are compressed inside a ceramic or quartz tube between two electrodes. High-voltage electric discharge can bring the carbon source to temperatures higher than 2,500 °C in <100 ms, converting the amorphous carbon to flash graphene [111]. In another study, a solid-state chemical vapor deposition method was used to convert plastic waste (PET, PVC, PE, PS, PP, and polymethylmethacrylate) to graphene foil at a large scale [112]. The obtained graphene foil exhibited a much higher electrical conductivity than conventional free-standing graphene film obtained at extremely

high temperatures (2,200–2,500 °C). In addition, graphene foil can act as various flexible components in a lithium-ion battery, which opens new application possibilities for graphene in a variety of fields [112]. This technology has also shown the ability to produce carbon nanotubes from plastic wastes, as discussed previously.

The treatment of PVC waste is particularly challenging [19]. In thermal treatments such as pyrolysis and gasification, the chlorine in PVC is converted to large quantities of HCl that can cause serious corrosion to process equipment at a wide range of temperatures. Based on these issues, PVC was used as a hydrogen source by Lu et al. to reduce hydrogen carbonate to formate under hydrothermal conditions via a green approach. The authors found that PVC could be completely dechlorinated at 300 °C [19]. This research suggests that PVC is not suitable for pyrolysis but can be utilized via other processes such as dichlorination.

The chemical inertness of PE owing to its strong single C–H and C–C bonds makes it difficult to degrade through low-energy processes [15]. Therefore, researchers developed a tandem catalytic cross alkane metathesis method to efficiently degrade PE to liquid fuels and waxes under mild conditions, as shown in Fig. 3B with a proposed degradation mechanism. Alkane metathesis is a technology in which alkanes are rearranged covalently to create products with a new distribution of alkanes. Readily available and inexpensive light alkanes (e.g., petroleum ether) were used as the reagents in this study. This method exhibited superior selectivity for linear alkane formation and allowed for different types of PEs with a variety of molecular weights to be completely converted to liquid fuels and waxes. The distribution of these products can be controlled by the reaction time and catalyst structure. The catalyst is compatible with various polyolefin additives, indicating common plastic waste, such as PE bags, bottles, and films, can be converted to high-value chemicals without any pretreatment [15]. In the future, the governing process mechanism needs further study to apply it to the degradation of other polymers such as PVC and polyoxymethylene.

2.5. Summary of conventional and emerging conversion technology

Based on all the discussed plastic waste conversion technologies (conventional and emerging), co-pyrolysis of plastic waste and biomass is a promising technology to achieve products with high quality and yield. Photoreforming is currently an emerging technology that can convert plastic waste to H₂ and chemicals under mild conditions, but the process should be scaled up. Designing polymers that can easily be modified and recycled in the future is also critical to recover value from

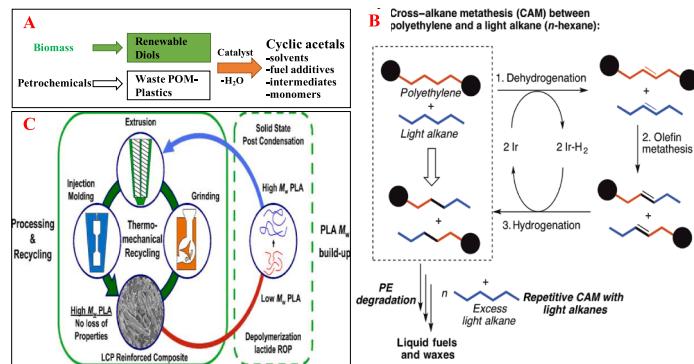


Fig. 3. Some emerging technologies for plastic waste conversion. (A) An efficient pathway for upcycling the polyoxymethylene plastic in combination with biomass-derived diols into versatile cyclic acetals. Reproduced with permission from [107]. Copyright © 2020 John Wiley and Sons. (B) Proposed degradation of PE through cross-alkane metathesis with light alkanes (e.g., n-hexane). Dehydrogenation of PE and light alkane generates unsaturated olefins. Cross olefin metathesis followed by hydrogenation results in breakdown of PE chain into shorter chains. Repeating the tandem reaction in multiple cycles degrades PE into short alkanes appropriate for transportation fuel use. Reproduced with permission from [15]. Copyright © 2016 American Association for

the Advancement of Science. <https://doi.org/10.1126/sciadv.1501591>. Further permission related to the material excerpted should be directed to the American Association for the Advancement of Science. (C) Strategies for reprocessing and increasing the molecular weight of PLA, which provide a route toward closed-loop recycling of liquid crystalline polymer-reinforced composites. The PLA phase can be chemically recycled for many times without loss of mechanical properties. Reproduced with permission from [110]. Copyright © 2019 American Chemical Society. <https://pubs.acs.org/doi/10.1021/acssuschemeng.9b06305>. Further permission related to the material excerpted should be directed to the American Chemical Society.

plastic wastes. Strategies for simplifying processing and integrating upcycled products into existing supply chains for industries, as well as the potential demand for upcycled products, all warrant further study. Additionally, the cost involved in energy consumption, presorting of plastic mixtures, chemical additives, and product separation should be considered and analyzed in future studies. For example, phenolic compounds are valuable chemicals, but separating them from bio-oil is an expensive process [113]. A gas purification process is typically used after the gasification to clean the syngas generated. AlMohamadi [114] studied the steam gasification of MSW for gasoline production. The plant's capital investment was largely affected by the MSW pretreatment, gas purification (\$26 million cost), and steam cycle.

All the described technologies are highly beneficial for the environment because they can reduce plastic waste, but the environmental impact (e.g., gas product emission and compatibilizer synthesis) involved in those processes also needs to be controlled and minimized. The distributed nature of plastic waste presents a major challenge as well, as it has led to small-scale, sparse conversion infrastructure. Finally, various states in the United States having different balances between sustainable and fossil fuel energy can influence the decision making in funding research and the construction or expansion of recycling facilities. Regarding future plastic waste management, the integration of multiple technologies is promising. For example, co-pyrolysis of plastic waste and biomass residue can be applied to produce bio-oil, biochar, and gas. Fossil fuel-based plastics can be replaced with bio-based ones for contributing to the environmental sustainability. Bio-oil can be upgraded to transportation fuel over Ni-based zeolite catalysts. Biochar can be used to generate carbon nanotube via microwave irradiation technology. Gas can be converted to syngas via a methane reforming technology, which is then converted via Fischer-Tropsch synthesis to liquid hydrocarbon fuel.

3. Polymer design and modification for subsequent conversion of plastic waste

Chemically recyclable polymers have been designed and developed in recent years as a method to manage plastic at the end of its usable life. Mechanical reprocessing, as described previously, can degrade the polymer's quality and cause residual impurities after multiple cycles of reuse [115]. However, chemical recycling can recover the precursor building blocks via depolymerization [116]. Nevertheless, polymers that can be selectively and easily depolymerized back to monomers usually require low-temperature (e.g., -40 °C) polymerization pathways and lack the mechanical/physical properties required for practical use. Additionally, the depolymerization of chemically recyclable polymers typically has low selectivity, meaning depolymerization can produce a mixture of many products which require substantial separation and purification. This low selectivity makes it difficult to attain a circular monomer-polymer-monomer cycle in which a polymer can be depolymerized and subsequently polymerized to the original product. There are also often trade-offs between a polymer's ability to depolymerize and its properties. This means that chemically recyclable polymers often suffer poor performance and are not as widely useful as many virgin (or chemically non-recyclable) polymers [116]. Furthermore, monomer recovery is usually costly, energy-intensive, and incompatible with complex mixtures. Depolymerizing plastics in a short reaction time at low temperatures and with high tolerance to additives is challenging [115]. However, these challenges have inspired researchers to look for possible solutions.

To overcome some of the obstacles in the development of chemically recyclable polymers, Zhu et al. [116] designed a polymer system based on γ -butyrolactone via a *trans*-ring fusion with repeatable chemical recyclability, and the polymer can be synthesized at room temperature under solvent-free conditions. Kort et al. [110] developed liquid crystalline polymer-PLA composites that can be recycled several times without a decrease in mechanical properties via maintaining the

molecular weight of polymer PLA, as shown in Fig. 3C. Christensen et al. [115] found that plastics polymerized via dynamic (reversible) covalent diketoenamine bonds can be used to recover the monomers from common additives, even in mixed plastic waste streams. Recovered monomers can subsequently be used to produce the same polymer formulation with the same performance as well as other polymer formulations with differentiated properties. This poly(diketoenamine) plastic can be produced, used, recycled, and re-used without a loss of value. Such a closed-loop polymer life cycle is crucial to sustainability efforts. These dynamic covalent polymers have the potential to replace non-recyclable thermoset materials [115].

A vitrimerization approach [117] has also been used to reprocess thermoset waste such as polyurethanes via dynamic chemistry. In vitrimerization, permanent networks are changed to dynamic ones over an appropriate catalyst solution, which turns them into vitrimers. This process has two requirements: a solvent for swelling the thermoset waste and a catalyst that is either miscible or soluble in the solvent for facilitating the dynamic reactions. Transesterification reactions allow dynamic bond exchange between hydroxyl and ester groups within the thermoset network. Yue et al. found that even though the mechanical performance of the reprocessed PUR was diminished, adding carbon nanostructures to the newly formed vitrimer (vitrimerized PUR) allowed it to resemble or even exceed the properties of the original material. By optimizing parameters of the vitrimerization process such as the catalyst species, catalyst concentration, and temperature, this methodology could be very promising for the upcycling of thermoset waste [117]. The described research indicates that polymer properties can be maintained during mechanical reprocessing when combined with chemical strategies such as vitrimerization and maintenance of a polymer's molecular weight (via solid state post condensation or depolymerization/polymerization).

Ring-opening polymerization/depolymerization of biosourced polythioesters (PTEs) has the potential to produce high-value materials, such as self-immolative polymers, optical/photochemical plastics, and degradable biomaterials, which can be easily reused [118]. The design of sustainable or "green" polymers has received much attention in recent years, particularly because of their renewable feedstock/monomers, high recyclability, material durability, and/or cost-effective synthesis under environmental-friendly conditions. However, manifesting all these qualities in a single polymer is difficult. Extreme conditions and expensive catalysts are usually required in the monomer-polymer-monomer processing cycle, which can cause a low depolymerization selectivity. Ring-opening polymerization and depolymerization of PTEs under mild conditions has been a recent breakthrough in this field so far. PTEs can be easily polymerized and recycled because of their susceptibility to nucleophiles. However, further improvement to optimize thermolysis and reduce cost (e.g., developing renewable bio-based catalysts) is needed for the commercialization of PTEs [118].

Another major challenge for upcycling mixed plastic waste is that many plastics are immiscible with each other, leading to phase separated materials with degraded properties [14]. Even a small amount of contamination of another type of plastic can drastically change the properties of the recycled materials. The compatibilization of mixed plastics can prevent the need for presorting, and a compatibilizer can control the phase behavior of the polymer mixture. A compatibilizer is similar to surfactants developed for stabilizing immiscible water/oil mixtures. Compatibilizers can also be tailored to a given plastic waste composition. In the future, advanced computational modeling and data analysis for developing novel compatibilizers, catalysts, and polymers will be helpful for upcycling polymer mixtures [14]. Particularly, developing a few common compatibilizers for a wide range of plastic mixtures would be of significant interest, as mixed plastic waste with different compositions currently requires different compatibilizers. Finally, providing more education to the public on the importance of waste sorting and good recycling practices will help tremendously in addressing mixed plastic waste in the future.

Numerous different multiblock copolymers have been developed recently for use in compatibilization of mixed plastic waste. For example, a multiblock copolymer was synthesized by Eagan et al. [10] for compatibilization of PE and isotactic polypropylene (iPP). The copolymer was added to improve the performance of a mixture of recycled PE and iPP, two of the most common plastics in the world. These blends are shown in Fig. 4A–C. PE and iPP have similar hydrocarbon makeup, but they do not blend or adhere, leading to fragile interfaces and phase separation. Recycling of polyethylene and iPP traditionally results in lower-value products due to degraded properties and sorting expenses, and approximately 95% of the material value (or economic value) is lost while recycling these commodity plastics. However, combining polyethylene and iPP using a multiblock copolymer as a compatibilizer has significant potential to affect the economic viability (e.g., eliminating the sorting expenses) and sustainability of recycling their waste [10]. Multilayer films consisting of two or more polymers are typically produced to combine the advantages of each component and improve the overall performance in food packaging application [18]. PET and PE are recyclable in the neat form, but a PET/PE multilayer film is difficult to recycle because one component cannot be physically separated from the other component due to the adhesion promoted by the tie layer. Therefore, the PET – PE multiblock copolymers were synthesized by Nomura et al. and introduced to PET/PE blends as an adhesive layer and compatibilizer additive. Then, the mixture was melt-reprocessed and exhibited superior mechanical properties compared with the blends processed without compatibilizers. This same strategy can be used for mixed waste combinations, such as PET/PP. However, the compatibilizer needs to be designed

appropriately to reduce the interfacial energy and improve the interfacial adhesion between immiscible polymer blends [18]. Some multiblock copolymers such as PE-PLA and PE-PP copolymers have been commercialized but at high prices, indicating the processing cost of multiblock copolymer compatibilizers needs to be further reduced before they are widely implemented.

The use of renewable resources as feedstock typically does not resolve all the end-of-use issues that plastics currently face. Biochemical recycling of biodegradable polymers can fail to recover valuable building block chemicals and cause potential environmental pollution [116]. However, developing the biodegradable polymers to have higher selectivity can be one potential method for the future plastic waste upcycling. For example, mulch films are produced for single-use agricultural applications to secure crops and suppress weed growth, but they are typically composed of nonbiodegradable PE [119]. The accumulations of these plastic wastes have negative economic and ecological impacts, as previously discussed. Biodegradable polymers such as poly (butylene adipate-co-terephthalate) could replace the nonbiodegradable PE because poly(butylene adipate-co-terephthalate) can degrade into soil, producing CO₂ and microbial biomass [119]. The generated CO₂ can be captured for methane tri-reforming use to produce syngas [69]. In addition, a strategy to replace fossil fuel-based plastics with bio-based plastics (e.g., making PLA from biomass such as corn) [120] can help the reduction of greenhouse gas emissions from plastics.

4. Conclusions

4.1. Summary

Upcycling of plastic waste has recently gained increased attention. The state of the art in polymer design for end-of-use, waste conversion technologies, reaction mechanisms, resulting product types/value, and efficiencies was systematically studied in this review. Plastic waste has great potential for conversion to high-value products such as liquid fuel, H₂, carbon nanotubes, and monomers. Each existing conversion technology has specific applications and types of plastic waste with which it can be optimally applied. The integration and scale-up of multiple technologies should be developed to address the enormous amount of plastic waste around the world.

The ability to convert plastic waste to an equal- or higher-value product is affected by several factors, including the plastic composition, processing history, reaction temperature, catalyst activity, and many other factors depending on the target application. For example, raising the reaction temperature from 400 °C to 450 °C can increase the bio-oil yield for PS pyrolysis, and raising the temperature from 550 °C to 850 °C can expand the syngas mass distribution for MSW gasification. Co-pyrolysis of plastic waste and biomass was found to be a promising technology because of the processes' synergism, resulting in a high product yield and quality. A promoter-added zeolite-based catalyst was identified as a promising catalyst in plastic waste pyrolysis because of its high specific area, pore volume, and metal dispersion.

The design and modification of virgin polymers play a crucial role in their upcycling after their end of use. Designing polymers with recycling or upcycling in mind can help reduce plastic waste considerably. Chemically recyclable polymers that can be depolymerized back to monomers after their typical end of use have been developed. Two such systems identified in this review were a polymer system based on γ-butyrolactone and a polymer system that was polymerized via dynamic covalent diketoenamine bonds. Finally, multiblock copolymers were used as an adhesive layer and compatibilizer additive for immiscible plastic mixtures such as PE/iPP and PE/PET.

4.2. Challenges and future directions

The primary challenges facing wide-scale implementation of plastic waste conversion include high cost (e.g., because of high energy

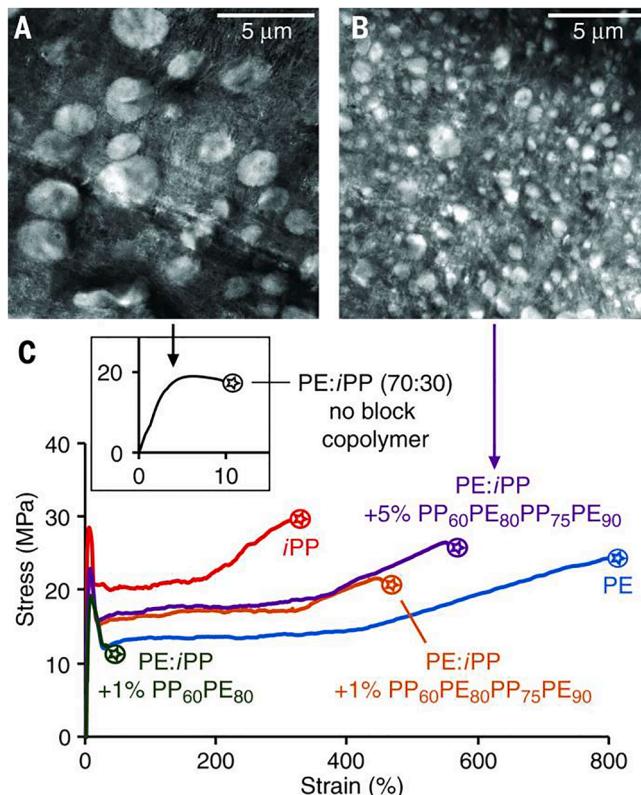


Fig. 4. Tensile properties of PE/iPP materials and blends. (A) transmission electron microscopy (TEM) images of PE/iPP blends without block copolymer showing droplet morphology; (B) TEM images of PE/iPP blends with 5 wt% tetrablock copolymers showing droplet morphology; (C) materials were melt-blended without block copolymer or with 1 wt% diblock (green), 1 wt% tetrablock (orange), or 5 wt% tetrablock copolymers. Reproduced with permission from [10]. Copyright © 2017 American Association for the Advancement of Science.

consumption and the need for presorting of plastics), time demand, a wide variability in plastic composition (especially for plastic mixtures), and the presence of contaminants and non-polymer species in most waste streams (indicating the need for presorting).

- 1) Economical and advanced catalysts with higher activity need to be explored and developed to further improve the plastic waste conversion efficiency and selectivity. Conventional catalysts used in thermal conversions tend to deactivate due to metal sintering and coke formation.
- 2) Systematic experimental process development and condition optimization are needed to further improve conversion efficiencies. The heating rate in pyrolysis and gasification as well as the mild conditions (e.g., sunlight, water, pressure and temperature) in photo-reforming need to be optimized.
- 3) Research interest in polymer design to enhance upcycling should continue to grow. Compatibilizers can be developed to minimize or even eliminate the need for presorting plastic mixtures. This would allow for more widespread conversion at a much lower cost. More effective catalysts to enhance the depolymerization efficiency and selectivity to monomers are also needed. Additionally, a long-term solution is to design polymers for reuse (i.e., polymer chains that break down to oligomers when triggered at the end of life).
- 4) More research is needed on upcycling of thermosets. The vast majority of current conversion technologies focus on thermoplastics. Finally, one significant implementation strategy to reduce plastic waste is to reduce the growth rate of the global plastics demand and spread knowledge about plastic reuse.

CRediT authorship contribution statement

Xianhui Zhao: Conceptualization, Writing - original draft. **Matthew Korey:** . **Kai Li:** . **Katie Copenhaver:** . **Halil Tekinalp:** . **Serdar Celik:** . **Kyriaki Kalaitzidou:** . **Roger Ruan:** . **Arthur J. Ragauskas:** . **Soydan Ozcan:** Conceptualization, Supervision, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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