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CHEMICAL RECYCLING AND UPCYCLING OF PLASTIC WASTE: FROM LINEAR TO CIRCULAR ECONOMY

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ABSTRACT

The exponential growth of plastic production and the persistence of plastic waste in the environment have created a global pollution crisis. Currently, only 9% of plastic waste is recycled, predominantly through mechanical recycling that produces lower-quality materials. This review examines chemical recycling technologies that convert plastic waste back into monomers or valuable chemicals, enabling true circularity. Polyolefins (polyethylene, polypropylene), polyesters (PET), and mixed plastics are discussed. Recent advances in pyrolysis, solvolysis, and catalytic depolymerization are highlighted, along with upcycling strategies that transform waste plastics into higher-value products such as carbon nanotubes, lubricants, and surfactants. Industrial case studies and remaining challenges including feedstock heterogeneity, catalyst deactivation, and economic viability are addressed.

KEYWORDS: Plastic waste, Chemical recycling, Upcycling, Depolymerization, Circular economy.

1. INTRODUCTION

Plastics have transformed modern society. Since mass production began in the 1950s, over 8.3 billion metric tonnes of virgin plastics have been manufactured—equivalent to the weight of more than 80,000 aircraft carriers.[1] Packaging accounts for 40% of plastic use, followed by construction (20%) and consumer goods (15%). The longevity of plastics is both their advantage and their curse: a plastic bottle may be used for minutes but persists in the environment for centuries.[2]

The scale of plastic pollution is staggering. Approximately 6.3 billion tonnes of plastic waste had been generated by 2015, of which only 9% was recycled, 12% incinerated, and 79% accumulated in landfills or the natural environment.[1] Microplastics—particles smaller than 5 mm—have been found in Arctic sea ice, Mariana Trench sediments, human blood, and placental tissue.[3] The economic cost of plastic pollution, including cleanup efforts and ecosystem damage, exceeds $100 billion annually.[4]

Traditional mechanical recycling—washing, shredding, melting, and re-extruding—has fundamental limitations. Mechanical recycling degrades polymer chains (chain scission reduces molecular weight) and requires relatively clean, single-polymer streams. The resulting recyclate is typically downcycled into lower-value products (e.g., fleece jackets from bottles) that eventually reach their own end-of-life.[5]

Chemical recycling offers an alternative paradigm: polymers are depolymerized back to monomers or converted into valuable chemicals, enabling true closed-loop recycling. **Upcycling** goes further, transforming waste plastics into products of higher economic value than the original material.[6] This review covers chemical recycling and upcycling technologies for the three most abundant plastic waste streams: polyolefins (PE, PP), polyesters (PET), and mixed/heterogeneous waste.

2. Plastic Waste Landscape: Composition and Challenges

2.1 Major Plastic Types

Table 1 summarizes the most common plastics, their production volumes, and chemical structures.

Table 1: Major Plastics by Production Volume and Chemical Structure.

Polymer	Resin code	Annual production (Mt)	Repeating unit	C–C backbone?	Hydrolyzable bonds?
Polyethylene (PE)	2 (HDPE), 4 (LDPE)	110	-[CH_2 - CH_2]□-	Yes	No
Polypropylene (PP)	5	70	-[CH(CH_3)- CH_2]□-	Yes	No
Polyvinyl chloride (PVC)	3	45	-[CH_2 - CHCl]□-	Yes	No

Polystyrene (PS)	6	25	$-[CH(C_6H_5)-CH_2]$□-	Yes	No
Polyethylene terephthalate (PET)	1	30	$-[O-CH_2-CH_2-O-CO-C_6H_4-CO]$□-	No	Yes (esters)
Polyurethane (PUR)	7	25	-[O-R-NH-CO-NH-R'-]□-	No	Yes (urethanes)

The critical distinction for recycling is whether the polymer contains hydrolyzable bonds (esters, amides, urethanes). Condensation polymers (PET, polyamides, polyurethanes, polycarbonates) can be depolymerized by hydrolysis, alcoholysis, or aminolysis into monomers. Addition polymers (PE, PP, PS, PVC) have all-carbon backbones and require more energetic methods (pyrolysis, hydrogenolysis) to break C–C bonds.[7]

2.2 Challenges Specific to Plastic Waste Recycling

Feedstock heterogeneity: Municipal plastic waste is a mixture of PE, PP, PET, PS, PVC, paper labels, adhesives, and food residues. Sorting is technically challenging and expensive. Even after sorting, different grades of PE (HDPE vs. LDPE) are difficult to separate.[8]

Additives and contaminants: Plastics contain up to 20% by weight of additives—plasticizers (phthalates), flame retardants (brominated compounds), stabilizers (hindered amines, phenols), colorants, and fillers (talc, calcium carbonate).[9] These additives can poison catalysts, corrode reactors, and contaminate products. Phthalates in recycled PVC are a particular concern for food-contact applications.

Economic barriers: Virgin plastic is cheap ($800–1200/tonne for PE) due to low fossil fuel prices. Chemical recycling processes must compete with virgin production costs while coping with the expenses of collection, sorting, and purification.[10]

3. Chemical Recycling of Polyesters: PET as a Success Story

Polyethylene terephthalate (PET) is the most successfully chemically recycled plastic due to its hydrolyzable ester bonds. Global PET production is approximately 30 million tonnes annually, primarily for beverage bottles and polyester fibers.[11]

3.1 Glycolysis of PET

Glycolysis—reaction with excess ethylene glycol—depolymerizes PET to bis(2-hydroxyethyl) terephthalate (BHET), the monomer precursor. The reaction proceeds at 180–220 °C with a catalyst (zinc acetate, manganese acetate, or titanium alkoxides).[12]

Reaction

$PET + excess\ HO–CH_2–CH_2–OH \rightarrow BHET + oligomers$

BHET can be purified by recrystallization and repolymerized to virgin-grade PET. The glycolysis process has been commercialized by several companies. **PET4®** (France) operates a 20,000 tonne/year plant that converts post-consumer PET bottles to BHET with 95% yield.[13] A 2023 life-cycle assessment found that glycolysis-based recycling reduces greenhouse gas emissions by 70% compared to virgin PET production.[14]

3.2 Methanolysis and Hydrolysis

Methanolysis depolymerizes PET with methanol at 200 °C and 20–40 atm to produce dimethyl terephthalate (DMT) and ethylene glycol. DMT is a traditional monomer for PET production. **Eastman Chemical** has operated methanolysis plants since the 1980s. In 2022, Eastman announced a $250 million facility in Tennessee with 100,000 tonne/year capacity.[15]

Hydrolysis (with water at 250 °C, high pressure) produces terephthalic acid (TPA) and ethylene glycol. TPA is an alternative monomer to DMT. Hydrolysis is less common industrially because TPA purification is more difficult than DMT purification.[16]

3.3 Enzymatic PET Depolymerization

The discovery of PET-degrading enzymes has opened biological recycling routes. The bacterium *Ideonella sakaiensis*, isolated from a PET bottle recycling plant, produces two enzymes: PETase (hydrolyzes PET to MHET—mono(2-hydroxyethyl) terephthalate) and MHETase (hydrolyzes MHET to TPA and ethylene glycol).[17]

Directed evolution has produced PETase variants with dramatically improved activity. The **FAST-PETase** (functional, active, stable, and tolerant PETase) variant degrades 90% of amorphous PET in 10 hours at 50 °C.[18] A 2024 study reported a **turbo-PETase** that converts post-consumer PET bottles to TPA at 50 kg/m^3/day, sufficient for industrial feasibility.[19]

Carbios (France) has commercialized enzymatic PET recycling. Their process uses a proprietary PET hydrolase at 72 °C (above the glass transition temperature, allowing the enzyme to access amorphous regions). In 2023, Carbios opened a demonstration plant in Clermont-Ferrand with 5,000 tonne/year capacity, with plans for 50,000 tonne/year by 2026.[20] The process produces TPA and ethylene glycol that are indistinguishable from petrochemical-derived monomers and can be repolymerized into food-grade PET.

4. Chemical Recycling of Polyolefins: The C–C Challenge

Polyethylene (PE) and polypropylene (PP) constitute over 50% of plastic waste by mass but lack hydrolyzable bonds. Breaking the all-carbon backbone requires thermal or catalytic processes that are more energy-intensive than polyester depolymerisation.[21]

4.1 Pyrolysis

Pyrolysis—thermal decomposition in the absence of oxygen at 400–600 °C—converts polyolefins into a complex mixture of hydrocarbons: waxes (C_{20}–C_{50}), oils (C_5–C_{20}), and gases (C_1–C_4). Pyrolysis oil can be fractionated into naphtha (C_5–C_{12}) and fed to a steam cracker for olefin production (ethylene, propylene), closing the loop to virgin plastics.[22]

Limitations: Pyrolysis produces a broad product distribution, including aromatics and olefins that require hydrogenation before steam cracking. Heteroatoms (chlorine from PVC, nitrogen from polyamides, oxygen from PET residues) in the feedstock lead to HCl, HCN, and organic acids that corrode equipment.[23]

Industrial players: **Plastic Energy** (UK/Spain) operates pyrolysis plants in Spain (25,000 tonne/year) and the Netherlands (30,000 tonne/year), producing recycled naphtha for **SABIC** and **BASF.**[24] **Quantafuel** (Norway) has developed a catalytic pyrolysis process with integrated hydrotreatment to remove heteroatoms.[25]

4.2 Hydrogenolysis and Hydrocracking

Hydrogenolysis uses hydrogen gas and a metal catalyst (Pt, Ru, Ni on zeolites or carbon) to break C–C bonds at lower temperatures (200–300 °C) than pyrolysis. Products are alkanes (C_1–C_{60}) with narrow molecular weight distributions.[26]

A landmark 2020 study demonstrated hydrogenolysis of PE to liquid alkanes (C_6–C_{30}) using a $Pt/SrTiO_3$ catalyst at 300 °C and 20 bar H_2. The catalyst selectively cleaves internal C–C bonds rather than terminal bonds, producing a narrow distribution of mid-chain alkanes useful as lubricant base oils.[27]

Hydrocracking combines cracking (on acid sites of a zeolite) and hydrogenation (on metal sites). A bifunctional Pt/zeolite Y catalyst converts PE to C_4–C_{20} alkanes (gasoline and jet fuel range) with 80% yield at 250 °C.[28] The zeolite pores restrict access to long polymer chains, preventing over-cracking to methane.

Case study: Polypropylene hydrogenolysis: PP is more difficult than PE because each monomer unit contains a methyl branch. The tertiary C–H bond at the branch point is susceptible to β-scission, producing more low-molecular-weight gases (C_1–C_4). A 2024 study reported a Ni/SiO_2 catalyst that converts PP to C_6–C_{15} branched alkanes (high-octane gasoline blending components) with 85% selectivity at 280 °C.[29]

4.3 Tandem Catalytic Upgrading

Recent work has combined pyrolysis with downstream catalytic upgrading in a single reactor. A **tandem catalyst** system—a mesoporous zeolite (for pyrolysis/cracking) with embedded metal nanoparticles (for hydrogenation)—converts PE directly to C_5–C_{12} alkanes (gasoline) in one step.[30] The mesoporous pores accommodate long polymer chains, while micropores within the zeolite walls provide shape selectivity.

5. Upcycling: From Waste to Higher-Value Products

Upcycling transforms waste plastics into products with higher economic value than the original polymer, improving economic viability.

5.1 Upcycling PET to Carbon Nanotubes

PET is a carbon-rich feedstock (62.5 wt% carbon). Pyrolysis of PET with a ferrocene catalyst produces carbon nanotubes (CNTs) and terephthalic acid.[31]

A 2022 study processed post-consumer PET bottles with $Fe(acac)_3$ catalyst at 800 °C in a quartz tube reactor. The CNTs produced had diameters of 10–30 nm and lengths >10 μm. Residual terephthalic acid (80% recovery) was repolymerized to PET. The net carbon footprint was negative because the CNTs sequester carbon.[32]

5.2 Upcycling Polyolefins to Alkylaromatics

Alkylaromatics (linear alkylbenzenes, used in detergents) are normally produced by alkylation of benzene with long-chain olefins. Direct upcycling of polyolefins to alkylaromatics has been achieved using a Pt/zeolite catalyst at 280 °C.[33]

The mechanism: polyolefin hydrogenolysis produces long-chain alkanes; the alkane cyclizes and aromatizes on the zeolite acid sites; benzene (added as a co-feed) alkylates to form linear alkylbenzenes. A 2023 report achieved 70% conversion of PE to C_{10}–C_{14} alkylbenzenes—detergent precursors—with 90% linearity.[34]

5.3 Upcycling Mixed Plastics to Surfactants

Mixed plastic waste (PE, PP, PS, PET) is the most challenging feedstock. A 2024 study demonstrated a one-pot process using a hydroformylation catalyst [$Rh(acac)(CO)_2$ with a phosphine ligand] at 200 °C and 30 bar syngas (CO/H_2).[35]

The process proceeds in three stages: (1) thermal pyrolysis of mixed plastics to olefins (C_6–C_{20}), (2) hydroformylation to aldehydes, and (3) air oxidation to carboxylic acids. The resulting fatty acids are surfactants with similar properties to coconut-derived counterparts. A techno-economic analysis found that mixed plastic-derived surfactants could be profitable at crude oil prices >$60/barrel.[36]

6. Industrial Case Studies

6.1 Loop Industries (Canada/USA) – PET Depolymerization

Loop Industries has developed a low-temperature (100 °C) PET depolymerization process using a proprietary catalyst (non-disclosed, but believed to be an organocatalyst). The process depolymerizes low-quality PET (colored, contaminated, containing adhesives) that is unsuitable for mechanical recycling.[37]

The monomers (TPA and ethylene glycol) are purified by crystallization and distillation to 99.99% purity. The process has been validated at a pilot plant in Terrebonne, Quebec (2,000 tonne/year). In 2023, Loop announced a joint venture with **Suntory** (beverage company) to build a 100,000 tonne/year facility in France.[38]

6.2 Mura Technology (UK) – Hydrothermal Recycling

Mura's **HydroPRS™** (Hydrothermal Plastic Recycling Solution) process uses supercritical water (400 °C, 300 atm) to depolymerize polyolefins. Supercritical water acts as both a solvent and a reactant, promoting C–C bond cleavage while suppressing char formation.[39]

The product is a pyrolysis-like oil but with lower oxygen and chlorine content due to the hydrothermal environment. Mura has a 20,000 tonne/year demonstration plant in Teesside, UK, and has licensed the technology to **Mitsubishi Chemical** for a 100,000 tonne/year plant in Japan.[40]

6.3 Agilyx (USA) – Polystyrene Recycling

Polystyrene (PS) is difficult to recycle mechanically due to its low density (expanded polystyrene, EPS, is 98% air). Agilyx's process depolymerizes PS back to styrene monomer via thermal pyrolysis at 350–400 °C.[41]

The styrene monomer is recovered by fractional condensation and can be repolymerized to virgin PS. Agilyx operates a 10,000 tonne/year facility in Tigard, Oregon. In 2022, Agilyx and **INEOS Styrolution** (the world's largest PS producer) announced a joint venture to build a 100,000 tonne/year PS chemical recycling plant in Europe.[42]

7. Challenges and Future Directions

Feedstock heterogeneity remains the single largest challenge. Mixed waste containing PVC releases HCl, which corrodes reactors and poisons catalysts. Nitrogen-containing polymers (polyamides, polyurethanes) release NH_3 and HCN.[43] Advanced sorting technologies (near-infrared spectroscopy, X-ray fluorescence, triboelectric separation) are improving but remain expensive.

Catalyst deactivation by additives and contaminants. Halogenated flame retardants (brominated compounds) release HBr, which leaches active metals from catalysts. Antioxidants (hindered phenols, phosphites) adsorb onto catalyst surfaces, blocking active sites.[44] Development of poison-tolerant catalysts (e.g., using solid acid catalysts instead of noble metals) is an active area.

Economic viability: Chemical recycling is capital-intensive (typical plant costs 100–300million for 50,000tonne/yearcapacity). Lowoilprices(<100–300*millionfor* 50,000*tonne*/*yearcapacity*). *Lowoilprices*(<50/barrel) favor virgin plastic production. Carbon pricing (e.g., the EU Emissions Trading System) improves the economics of recycling by increasing the cost of incineration and virgin polymer production.[45]

Future directions

- **Microwave-assisted depolymerization**: Microwave heating reduces reaction times from hours to minutes and can be scaled continuously.[46]
- **Enzymatic polyolefin depolymerization**: The discovery of alkane-oxidizing enzymes (e.g., AlkB from *Pseudomonas putida*) is a first step toward biological PE recycling. Directed evolution may produce active P Eases within 5–10 years.[47]

- **Chemical recycling of PVC**: PVC is the most problematic plastic due to HCl release. Emerging processes use ionic liquids to extract plasticizers and degrade PVC at lower temperatures, leaving carbon char.[48]

- **Blockchain for plastic traceability**: Blockchain-enabled tracking of plastic waste from collection to chemical recycling can certify recycled content and enable premium pricing for recycled plastics.[49]

8. CONCLUSION

Chemical recycling and upcycling are essential for addressing the global plastic waste crisis. For polyesters like PET, commercial chemical recycling (glycolysis, methanolysis, enzymatic depolymerization) already produces virgin-quality monomers. For polyolefins, which lack hydrolyzable bonds, pyrolysis, hydrogenolysis, and hydrothermal processing are at varying stages of commercialization. Upcycling—transforming waste plastics into carbon nanotubes, alkylaromatics, and surfactants—offers a path to improved economic viability.

Industrial case studies from Loop Industries, Mura Technology, and Agilyx demonstrate that chemical recycling is moving beyond the pilot scale. However, feedstock heterogeneity, catalyst deactivation, and low oil prices remain barriers to widespread adoption. Policy interventions (mandated recycled content, extended producer responsibility, carbon pricing) are essential to level the playing field with virgin plastic production.

The transition from a linear take-make-dispose economy to a circular plastic economy is technologically feasible but requires coordinated action among chemists, engineers, waste management companies, brand owners, and policymakers. The next decade will determine whether chemical recycling becomes a cornerstone of sustainable materials management or remains a niche solution.

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