MANTECH Publications

Journal of Research in Applied Chemistry
Volume 1, Issue 1, January- June 2018

Chemical Recycling and Upcycling of Polymers

Suresh Sharma[1], Sangita Verma[2], Anil D. Pawar[3], Subham Choudhury[4]

Associate Professor[1], Assistant Professor[2, 3, 4]

Department of Applied Chemistry

Greenfield Research College, Haryana, India

Email ID : *sureshsharmai3i@yahoo.com[1], sangita.verma0002@gmail.com[2], subhamchaudharyeie@rediffmail.com[3]*

Abstract

The rapid growth of polymer production over the last five decades has transformed modern society, enabling lightweight materials, affordable consumer goods, and advanced technologies. However, this success has also resulted in severe environmental challenges related to plastic waste accumulation, limited recyclability, and dependence on fossil resources. Conventional mechanical recycling suffers from degradation of material properties and limited applicability to mixed or contaminated waste streams. In this context, chemical recycling and polymer upcycling have emerged as promising strategies to close the materials loop by converting waste polymers back into monomers, fuels, or higher-value chemicals. This review paper discusses the fundamental principles, recent developments, and technological challenges associated with chemical recycling and upcycling of polymers. Major chemical recycling routes such as pyrolysis, gasification, solvolysis, and depolymerization are critically reviewed with respect to reaction mechanisms, catalysts, process conditions, and product selectivity. In addition, emerging upcycling approaches that transform plastic waste into functional materials, specialty chemicals, and advanced carbon products are highlighted. Environmental and economic considerations, including life cycle assessment and scalability, are also addressed. The paper aims to provide a comprehensive overview of current research trends while identifying key

knowledge gaps that must be addressed for large-scale implementation of chemical recycling and upcycling technologies.

Keywords: *Chemical recycling, polymer waste, plastic upcycling, depolymerization, circular economy*

INTRODUCTION

Synthetic polymers such as polyethylene (PE), polypropylene (PP), polystyrene (PS), poly(ethylene terephthalate) (PET), and polyvinyl chloride (PVC) are integral to daily life due to their durability, versatility, and low cost. Global plastic production has increased dramatically, exceeding hundreds of millions of tonnes per year. Unfortunately, the same durability that makes polymers useful also leads to persistent environmental pollution. A significant fraction of plastic waste ends up in landfills or the natural environment, causing ecological and health concerns.

Mechanical recycling has been the dominant recycling strategy for decades, but it is limited by polymer contamination, additive complexity, and property degradation after repeated processing. As a result, only a small percentage of plastics are effectively recycled into high-quality products. Chemical recycling offers an alternative approach by breaking down polymer chains into smaller molecules, enabling recovery of monomers or other valuable chemicals. When properly designed, chemical recycling can handle mixed and contaminated waste streams, which are unsuitable for mechanical recycling.

In parallel, the concept of polymer upcycling has gained attention. Unlike traditional recycling, which often leads to materials of lower value, upcycling aims to convert waste polymers into products with enhanced functionality or higher economic value. This review focuses on both chemical recycling and upcycling pathways, emphasizing their role in achieving a circular economy for plastics.

Classification of Polymer Recycling Approaches

Polymer recycling strategies are generally divided into four major categories—primary, secondary, tertiary, and quaternary recycling—based on the degree of material transformation and the nature of the final products. This classification helps in understanding the technological complexity, environmental impact, and value recovery potential of different recycling routes.

Primary recycling refers to the direct reprocessing of uncontaminated and single-type polymer waste into products with properties similar to the original material. This method is typically applied to clean industrial scrap generated during manufacturing, such as off-cuts or rejected components. Since the polymer structure remains largely unchanged, primary recycling preserves material quality. However, its applicability is limited because it requires highly sorted and clean waste streams, which are rarely available in post-consumer plastic waste.

Secondary recycling, often grouped together with primary recycling as mechanical recycling, involves physical processing steps such as sorting, washing, shredding, melting, and remolding of plastic waste. In this case, the polymer undergoes thermal and mechanical stress, which can lead to chain scission, oxidation, and degradation of additives. As a result, the recycled product usually exhibits inferior mechanical and thermal properties compared to virgin plastics. Secondary recycling is widely used for common polymers such as polyethylene, polypropylene, and PET, but repeated recycling cycles typically result in downcycling, where the material is used in lower-value applications.

Tertiary recycling encompasses chemical recycling processes in which polymers are chemically transformed into monomers, oligomers, fuels, or other valuable chemicals. Unlike mechanical recycling, tertiary recycling alters the polymer's molecular structure, allowing recovery of basic building blocks that can be reused for polymer synthesis or chemical production. This category includes thermal processes such as pyrolysis and gasification, as well as catalytic depolymerization and solvent-based treatments like hydrolysis, glycolysis, and methanolysis. Tertiary recycling is particularly attractive for mixed, contaminated, or multi-layer plastics that are unsuitable for

mechanical recycling. However, challenges such as high energy consumption, catalyst deactivation, and process economics still limit large-scale deployment.

Quaternary recycling involves energy recovery from plastic waste through controlled combustion or co-processing in industrial furnaces. In this approach, plastics are used as an alternative fuel source due to their high calorific value. While quaternary recycling reduces waste volume and recovers energy, it does not preserve material value and is often associated with greenhouse gas emissions and potential release of toxic compounds if not properly managed. Consequently, it is generally considered the least favorable option in the waste management hierarchy.

Within this framework, **chemical recycling** is a key component of tertiary recycling and represents a bridge between waste management and chemical production. It offers the possibility of closing the materials loop by converting plastic waste back into feedstock chemicals. **Polymer upcycling** can be viewed as an advanced or refined form of tertiary recycling, as it goes beyond simple feedstock recovery. Upcycling intentionally targets the conversion of waste polymers into products of higher economic or functional value, such as specialty chemicals, advanced carbon materials, or functional polymers. By increasing the value of recycled outputs, upcycling has the potential to improve the overall sustainability and economic attractiveness of polymer recycling systems.

Table 1: Comparison of Polymer Recycling Strategies

Recycling Method	**Process Nature**	**Feedstock Quality**	**Product Value**	**Limitations**
Mechanical recycling	Physical reprocessing	Clean, sorted	Low to moderate	Property degradation
Chemical recycling	Chemical conversion	Mixed, contaminated	Moderate to high	High energy demand
Upcycling	Chemical/functional transformation	Mixed polymers	High	Process complexity

Thermal Chemical Recycling Processes

Thermal chemical recycling processes rely on the application of high temperatures to break down polymer chains into smaller molecular fragments. These approaches are particularly attractive for treating mixed and contaminated plastic waste streams that are difficult to recycle mechanically. Among the various thermal methods, pyrolysis and gasification are the most extensively studied and technologically developed routes.

Pyrolysis

Pyrolysis is a thermal decomposition process carried out in the absence of oxygen, typically at temperatures ranging from 400 to 800 °C. Under these conditions, long polymer chains undergo random scission, leading to the formation of smaller hydrocarbons. The product distribution usually consists of three main fractions: non-condensable gases (such as hydrogen, methane, and light hydrocarbons), condensable liquids known as pyrolysis oil, and solid residues in the form of char.

Polyolefins such as polyethylene (PE) and polypropylene (PP) are particularly well suited for pyrolysis due to their simple hydrocarbon backbones and high hydrogen content. Pyrolysis oils derived from these polymers can resemble petroleum fractions and may be used directly as fuels or further refined into chemical feedstocks. In contrast, polymers containing heteroatoms, such as PVC or PET, pose additional challenges due to the formation of corrosive or oxygenated compounds.

Catalytic pyrolysis has gained significant attention as a means to improve product selectivity, lower reaction temperatures, and enhance process efficiency. Catalysts such as zeolites (e.g., ZSM-5), metal oxides, and supported metal catalysts promote cracking, isomerization, and aromatization reactions. Zeolite-based catalysts, in particular, favor the formation of aromatic hydrocarbons and light olefins, which are valuable chemical intermediates. However, catalyst deactivation due to coke formation and contamination remains a major issue.

Another important challenge in pyrolysis is the management of impurities in mixed plastic waste. For example, PVC releases hydrogen chloride during thermal decomposition, which can corrode equipment and poison catalysts. Effective pretreatment, dechlorination strategies, and robust reactor materials are therefore essential for practical implementation. Despite these challenges, pyrolysis remains one of the most mature thermal recycling technologies and is already being explored at pilot and commercial scales in several regions.

Gasification

Gasification is a high-temperature thermochemical process in which polymer waste is converted into synthesis gas (syngas), primarily composed of carbon monoxide (CO) and hydrogen (H_2). Unlike pyrolysis, gasification is conducted in the presence of a controlled amount of oxygen, air, or steam, typically at temperatures above 800 °C. Under these conditions, organic polymers are almost completely converted into gaseous products, with minimal formation of liquid hydrocarbons.

The syngas produced through gasification serves as a versatile intermediate that can be transformed into fuels and chemicals via established industrial processes such as Fischer–Tropsch synthesis, methanol synthesis, or hydrogen separation. This flexibility makes gasification attractive from a systems integration perspective, as it allows plastic waste to be incorporated into existing chemical and energy infrastructures.

One of the key advantages of gasification is its tolerance toward heterogeneous and contaminated feedstocks. Mixed plastics, composite materials, and even plastic waste combined with biomass or municipal solid waste can be processed in a single gasification unit. However, this flexibility comes at the cost of high capital investment and operational complexity. Advanced gas cleaning systems are required to remove particulates, tar, acid gases, and trace contaminants before syngas utilization.

From an environmental standpoint, gasification can achieve high carbon conversion efficiencies and lower emissions compared to direct incineration, provided that proper control and cleanup

technologies are employed. Nevertheless, the economic feasibility of plastic gasification remains strongly dependent on scale, syngas utilization pathways, and policy incentives. As a result, gasification is currently more common in integrated waste-to-energy or waste-to-chemicals concepts rather than standalone plastic recycling facilities.

Solvolysis and Depolymerization Methods

Solvolysis and depolymerization methods represent an important class of chemical recycling technologies in which polymers are chemically cleaved in the presence of suitable solvents and, in many cases, catalysts. Unlike thermal processes that rely on high temperatures, solvolysis-based approaches typically operate under relatively milder conditions and offer better control over product composition. These methods are especially attractive for condensation polymers, whose backbone contains hydrolysable functional groups.

Solvolysis refers to reactions in which polymer chains are broken down by interaction with a solvent such as water, alcohols, glycols, or amines. The solvent acts both as a reaction medium and as a reactant, participating directly in bond cleavage. Poly(ethylene terephthalate) (PET) has been the most extensively studied polymer in this context due to its widespread use in packaging and textiles, as well as its well-defined ester linkages.

PET solvolysis can be carried out through several routes, including hydrolysis, glycolysis, and methanolysis. **Hydrolysis** involves the reaction of PET with water, either under acidic, alkaline, or neutral conditions, leading to the formation of terephthalic acid and ethylene glycol. Alkaline hydrolysis is particularly effective but generates large volumes of wastewater, which must be treated before disposal. **Glycolysis**, one of the most commercially attractive routes, uses excess ethylene glycol to depolymerize PET into bis(2-hydroxyethyl) terephthalate (BHET). This process operates at moderate temperatures and pressures and produces monomers that can be directly reused for PET synthesis. **Methanolysis**, on the other hand, employs methanol to produce dimethyl terephthalate and ethylene glycol, yielding highly pure products but requiring higher pressures and more complex separation steps.

Depolymerization reactions are often enhanced by the use of catalysts to reduce activation energy, accelerate reaction rates, and improve selectivity toward desired products. A wide range of catalytic systems has been reported, including metal acetates, metal oxides, ionic liquids, and organocatalysts. Metal salts such as zinc acetate are commonly used in PET glycolysis due to their high activity and low cost. Ionic liquids have attracted attention as both solvents and catalysts, offering tunable properties and the possibility of catalyst recycling, although their high cost and potential toxicity remain concerns. Organocatalysts provide a metal-free alternative and are considered more environmentally benign, but their long-term stability under industrial conditions is still under investigation.

Beyond PET, other condensation polymers are also suitable for solvolytic recycling. **Polyamides**, such as nylon-6 and nylon-6,6, can be depolymerized through hydrolysis or alcoholysis to recover monomers like caprolactam or diamines and diacids. **Polycarbonates** can undergo methanolysis or hydrolysis to yield bisphenol A and carbonate derivatives, which are valuable chemical feedstocks. These processes generally require careful control of temperature, pressure, and catalyst concentration to avoid side reactions and product degradation.

Overall, solvolysis and depolymerization methods offer high product purity and the potential for true closed-loop recycling. However, challenges related to solvent recovery, catalyst reuse, energy input, and scalability must be addressed before widespread industrial adoption. Continued research into greener solvents, more robust catalysts, and integrated process designs is expected to play a crucial role in advancing these technologies toward practical application.

Catalytic Chemical Recycling of Polyolefins

Polyolefins, mainly polyethylene (PE) and polypropylene (PP), account for the largest share of global plastic production and waste generation. Their widespread use in packaging, consumer goods, and industrial applications makes them a critical target for sustainable recycling strategies. However, polyolefins are composed almost entirely of strong, non-polar carbon–carbon and carbon–hydrogen bonds, which renders them chemically inert and highly resistant to conventional

depolymerization methods. This structural simplicity, while beneficial for durability, poses significant challenges for chemical recycling.

In recent years, catalytic chemical recycling has emerged as a promising approach to overcome these limitations. Research efforts have focused on developing catalysts capable of selectively activating and cleaving C–C bonds under relatively mild conditions compared to traditional thermal cracking. Among the various strategies explored, hydrogenolysis has attracted particular attention. In hydrogenolysis, polyolefin chains are reacted with hydrogen in the presence of supported metal catalysts, leading to controlled chain scission and formation of smaller hydrocarbon molecules.

Supported noble metal catalysts such as ruthenium (Ru), platinum (Pt), and palladium (Pd), as well as more abundant metals like nickel (Ni), have demonstrated significant activity in polyolefin hydrogenolysis. These catalysts can convert long polymer chains into a range of products, including lubricants, waxes, diesel-range hydrocarbons, and light fuels. By tuning catalyst composition, metal loading, and reaction conditions such as temperature and hydrogen pressure, it is possible to influence product selectivity and molecular weight distribution. This level of control distinguishes catalytic recycling from non-selective thermal processes.

Another emerging area within catalytic polyolefin recycling involves tandem or bifunctional catalytic systems. In such systems, metal sites facilitate hydrogenation and C–C bond cleavage, while acidic supports promote isomerization or cracking reactions. This synergistic behavior can enhance efficiency and broaden the spectrum of obtainable products. Nevertheless, maintaining catalyst performance over extended operating periods remains challenging, particularly due to coke formation and sintering of active metal particles.

Despite its potential, catalytic recycling of polyolefins is still largely confined to laboratory and pilot-scale studies. One major hurdle is catalyst stability in the presence of real-world plastic waste, which often contains additives, fillers, dyes, and trace contaminants. These impurities can poison

active sites or accelerate catalyst deactivation. Scalability is another concern, as continuous reactor designs and efficient heat and mass transfer are required for industrial implementation.

Overall, catalytic chemical recycling of polyolefins represents an important step toward achieving true circularity for the most abundant plastic materials. While significant progress has been made in catalyst development and mechanistic understanding, further research is needed to improve robustness, reduce costs, and integrate these processes into existing chemical manufacturing infrastructure. Continued advances in this area could enable the transformation of polyolefin waste from a persistent environmental problem into a valuable resource.

Polymer Upcycling Strategies

Upcycling aims to transform waste polymers into materials with higher value or functionality. One approach involves converting plastics into carbon-based materials such as carbon nanotubes, graphene, or activated carbon. These materials have applications in energy storage, catalysis, and environmental remediation.

Another strategy focuses on chemical functionalization of polymer chains to introduce new properties. For instance, waste polystyrene has been modified into ion-exchange resins or specialty polymers. Such approaches not only reduce waste but also create economic incentives for recycling.

Figure 1 illustrates a schematic overview of chemical recycling and upcycling pathways for common polymers.

Environmental and Economic Considerations

The sustainability of chemical recycling processes depends on their overall environmental impact and economic feasibility. Life cycle assessment studies indicate that chemical recycling can reduce greenhouse gas emissions compared to incineration, particularly when recovered products displace virgin materials. However, high energy requirements and solvent use may offset some benefits.

Economic viability is strongly influenced by feedstock availability, product value, and policy support. Upcycling processes that generate specialty chemicals or advanced materials may offer better profitability than fuel-oriented recycling routes.

Challenges and Future Perspectives

Despite significant progress, chemical recycling and upcycling technologies face several challenges. These include high capital costs, catalyst deactivation, feedstock heterogeneity, and lack of standardized waste streams. Moreover, integration of chemical recycling into existing waste management infrastructure remains limited.

Future research should focus on developing robust catalysts, energy-efficient processes, and modular reactor designs. Policy incentives, extended producer responsibility, and public awareness are also crucial for accelerating adoption. Collaboration between academia, industry, and government will play a key role in translating laboratory-scale innovations into commercial reality.

CONCLUSION

Chemical recycling and upcycling of polymers represent promising pathways toward sustainable plastic waste management and circular material flows. By enabling recovery of monomers, fuels, and high-value products from waste plastics, these approaches overcome many limitations of mechanical recycling. While technical and economic challenges persist, ongoing advances in catalysis, process design, and systems integration are steadily improving feasibility. Upcycling strategies, in particular, offer opportunities to transform plastic waste into valuable resources rather than treating it as an environmental burden. Continued research and supportive policy frameworks

will be essential to realize the full potential of chemical recycling and upcycling in the coming decades.

REFERENCES

1. Al-Sabagh, A. M., et al., *Egyptian Journal of Petroleum*, 2016, 25, 53–64.
2. Ragaert, K., Delva, L., Van Geem, K., *Waste Management*, 2017, 69, 24–58.
3. Garcia, J. M., Robertson, M. L., *Science*, 2017, 358, 870–872.
4. Jehanno, C., et al., *Nature*, 2022, 603, 803–814.
5. Vollmer, I., et al., *Angewandte Chemie International Edition*, 2020, 59, 15402–15423.
6. Coates, G. W., Getzler, Y. D. Y. L., *Nature Reviews Materials*, 2020, 5, 501–516.
7. Solis, M., Silveira, S., *Waste Management*, 2020, 105, 128–138.
8. Rahimi, A., García, J. M., *Nature Reviews Chemistry*, 2017, 1, 0046.
9. Fivga, A., Dimitriou, I., *Waste and Biomass Valorization*, 2018, 9, 207–220.
10. Kaminsky, W., *Journal of Analytical and Applied Pyrolysis*, 2021, 153, 104978.