

Turning Plastic Waste into Valuable Chemicals

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Submitted: 16-02-2026; Accepted: 22-05-2026; Published: 01-07-2026

Abstract

The rapid increase in plastic production and poor quality of its disposal have become one of the major environmental issues that cause serious contamination of water and land resources. Traditional methods of handling waste such as incineration and land filling are non-suitable because of their toxic environmental effect and low efficiency. Recently, transforming discarded plastic waste into valuable chemicals has come out as one of the potential and eco-friendly methods to deal with this growing challenge. This method decreases plastic accumulation as well as allows for the recovery of valuable chemicals which can play a part in closed loop production. There are many conversion techniques such as catalytic, thermal and chemical recycling methods are also studied to convert plastic waste into valuable products such as monomers, hydrocarbons and chemicals. Catalytic process is one the methods which gained attention because of their ability to perform function under milder conditions with increase selectivity and the low energy requirements.

Keywords: Plastic waste, catalytic pyrolysis, valuable chemicals, chemical recycling

Review article

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1. Introduction

According to reports, worldwide production of plastic in 2021 was 390.7 MT and predicting to reach 500 MT by 2050 [1]. The economic development and co-operation organization stated that the globally plastic waste has grown to be a significant environmental problem. Human health and ecosystem posing a major risk by the wastage of 70% plastic that are either leached as well as landfilled into the environment [2]. More than 4.9 trillion kg of plastic garbage are manufacture globally per year, hardly 9% is reuse [3]. The rapid increase in plastic garbage is a worldwide issue. Plastic is commonly used in construction, electronics and packaging due to their strength, effectiveness and affordability. This increase in development has resulted in the destruction of recycled plastic products being extremely difficult [4]. They release harmful compounds because of their poor degradability and retain long time to decompose also contaminate soil, air and groundwater. Some of the remaining material is burned, releasing dioxins as well as carbon dioxide that increase pollution in air and worldwide warming [5-6]. The four primary methods have been developed to reduce plastic waste. First is primary recycling techniques also called closed loop recycling, in this method directly reuse of clean plastic waste to create new products.

So, this technology is not used for plastic waste problems. Another type of mechanical re-cycling is

secondary recycling, that collects used plastics from several places which are contaminated. A unique type of secondary recycling is the dissolution of combined plastics in suitable organic solvents and subsequent deposition of various components with the addition of non-solvents constitutes [7]. Mechanical characteristics of plastics decline during this process are because of the decrease in weight of molecules or the contaminants of the existing matrix by different mixed polymers. Tertiary recycling also known as advanced recycling, which transforms plastics into useful chemicals thought the chemical process such as solvolysis, pyrolysis and gasification. The quaternary recycling is another type of technique in which energy recovers from burning of plastic and it is often used to manage extremely contaminated plastic waste that is difficult to get rid of in other way [8]. Chemical recycling is one of the potential processes to support closed-loop plastic waste management and circular economy. When handling plastic waste, the chemical breakdown and recycling process offers many benefits including speed and efficiency. These are degraded and fracture into tiny molecules with the application of electricity, heat, light and others chemical reactions [9]. Solvolysis and pyrolysis methods are most used for recycling plastic waste [10].

The importance of innovative approaches to lessen their ecological impact is highlighting by the fact that traditional-disposal techniques like incineration and

landfilling cannot sufficiently address the volume and environmental risks corresponding with plastic waste [11]. Plastic waste valorization provides a practical alternative to conventional disposal by converting waste plastics into useful resources [12]. Valorization techniques convert waste plastics from environmental liabilities into products with economic value by recovering materials, chemicals or energy. This approach reduces waste accumulation, lessens reliance on fossil fuels and advances the "Sustainable Development Goals of the United Nations" by converting into raw materials from the used plastics for new uses. Valorization also facilitate a sustainable supply of resource across industries by promoting a circular strategy that are reduce plastic waste as well as increase the plastics life cycle [13-14]. This review focused on advancement in chemical recycling. May technologies examined such as hydrolysis, catalytic, hydrogenolysis and others to convert plastic trash into the valuable chemicals and fuels with catalysts to decrease the contaminated plastics.

2. Pyrolysis

It is a commonly used technology. Chemical recycling is efficiently method of pyrolysis for plastic waste. When compared to incineration and landfills, pyrolysis can efficiently lower the emission of toxic gases. Pyrolysis is performed at specific pressure and temperature and free oxygen environment. Liquid oil is the most significant product of pyrolysis which can be used as direct fuel source. The remaining carbon can be utilized as adsorbent materials and fuels. Moreover, pyrolysis includes both catalytic pyrolysis and thermal pyrolysis [15-16].

2.1. Catalytic Pyrolysis

The breaking of polymer chains of molecules, catalytic pyrolysis utilizes a catalyst that controls the product distribution and process of reaction. The addition of a catalyst can decrease the required temperature for reaction, while at the same time lowering energy usage. To attain the beneficial effects of target products, it is also possible to optimize product distribution and reduce product varieties [17]. Zeolite molecular sieve catalysis has been the focus of extensive studies because of their selectivity as well as extremely effective catalyst selectivity in the context of catalytic combustion of pyrolysis. The most frequently used catalyst of zeolite molecular sieve HY, HZSM-5, ZSM-5 and Y-type molecular sieves. Furthermore, a variety of components such as clays, activated carbon, metals and terracotta have been thoroughly studies for their potential usages in the catalytic pyrolysis of plastic waste [18]. Light alkaline gasses (C_1 - C_4), light chain olefins (C_2 - C_4), aromatic hydrocarbons (C_5 - C_{11}), non-aromatic hydrocarbons (C_6 - C_{11}) and heavy hydrocarbons (more than 20) [19]. The tandem catalytic combustion technique incorporates in-situ as well as non-situ catalysis using two catalysts, such as HZSM-5 and MCM-41 [20]. It has been shown that the initial conversion of MCM-41 inhibits the production of aromatic poly-cyclic hydro-carbons increasing output of xylenes and reducing coke output [21]. The choice of suitable catalyst can reduce production of harmful by-products ecological and financial sustainability of catalytic combustion which provides an efficient method for the creative use of plastic waste.

3. Solvolysis

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It is a type of chemical recycling methods that split up resins into tiny monomers, molecules and monomers substitutes into reagents such as chemical and thermo or thermal catalysis treatments. Polyester plastic is typically recycled using this method and PET becoming the most common application. The treatment with ammonolysis, solvolysis and alcoholises may restore important chemical substances and cause less damage in environment [22]. In comparison to pyrolysis, it reduces the energy activation of reaction of recyclable plastic cracking process [23].

3.1. Alcoholises

The process of depolymerization of PET at certain pressure (1-25 atm) and temperature (110-270°C) is known as ammonolysis. The reaction mediums are ethylene glycol and propylene glycol. Most commonly medium is ethylene glycol [24]. Without catalyst, this process is extremely slow, and PET cannot completely break down into BHET. Moreover, many of catalysts that are commonly used such as ionic liquid, salts and zeolites have been suggested to serve as a solution to this problem [25]. Homogenous catalysts such as acetates of Mn, Pd, Zn and Co are commonly used because of affordability and significant catalytic activity of these chemicals. There are two catalysts which re commonly used such as magnesium acetate and zinc acetate [26]. A highly successful method for producing BHET in large quantities was the synergistic activation of ethylene glycol as well as carbonyl groups in the PET by anions and metal centres.

3.2. Ammonolysis

During this process, NH_3 is most frequently utilized reaction medium and temperature ranging in this process is (70-180°C) [27]. High pressure of reaction and catalyst are required for the speed of chemical reaction because ammonolysis process is much slower. This is an effective process for turning plastic waste into nitrogenous compounds such as acetonitrile, pyrroles, aromatic amines, pyridines and indoles [28]. This transforming process offers a supply of feedstock as well as increasing PET's chemical recovering efficiency. Furthermore, scientists have explored the recycling of post-consumer discarded PET using ammonolysis in this presence of several organo-catalyst and amino alcohols generate idol terephthalamides. Poly ester amides can be synthesized from idol terephthalamides, which can be used in several of industries such as coating, textiles and paper [29]. Furthermore, ammonolysis shows a promising method for converting discarded plastic into valuable chemicals but there are still many hurdles in practical applications.

4. Chemical Recycling Pathways

4.1. Glycolysis

In this reaction, polyethylene teraphthalene react with ethylene which produce bis (2-hydroxyethyl) terephthalate monomers and oligomers that can be repolymerized under the influence of Zn^{2+} / organic catalyst at 160-300 [30].

4.2. PET Methonolysis

In which ester linkage of PET transforms into ethylene glycol and dimethyl terephthalate by depolymerization of PET also gives intermediate is methyl ester, which are subsequently transformed to DMT. The

reaction parameter ranges from 25-280°C, when using ionic liquid and catalyst. The optimized studies revealed that the yields of DMT are 90-99% [31].

4.3. Hydrolysis

Ethylene glycol and terephthalic acid are yields of hydrolysis. For PET development, TPA can be directly utilized as monomer feedstock as well as require acid preparation or crystallization. The process can occur under acidic, neutral, basic and enzymatic conditions with various catalysts [32].

4.4. Hydrogenolysis

Reductive methods generate saturated hydrocarbons compounds. The functionality and carbon skeleton strongly relies on catalyst as well as conditions [33]. Moreover, based on the levels of de-oxygenation, PET hydrogenolysis produced ethylene glycol and terephthalic acid and under specific condition, small aromatic molecules. [34].

4.5. Catalytic Cracking

Complex mixtures such as coke, light-hydrocarbons and aromatic are produced by non-selective thermal processes (Table 1). HZSM-5 like catalyst shift distributions in favor of valuable aromatics. Less expensive catalyst such as mesoporous prefers aliphatic fractions. Product identities such as kerosene-range alkanes, waxes and BTX define market application of market for lubricants, chemical feedstock and fuel (Fig 1) [35].

5. Valorization Methods

Modern methods offer revolutionary promise for managing plastic waste more sustainably and value of plastic waste has drastically changed [36]. The use of catalysts has been essential and overcoming these challenges, improving efficiency and control. Catalytic processes like hydrocracking and hydrogenolysis also offer various ways to convert plastic waste into a variety of useful chemicals, including waxes, monomers, lubricants, monomers, fuels with low energy requirements and improved product selectivity. Thus, the interaction between multiple chemical processes and the complication of plastic waste has created numerous possibilities for valorization [37].

5.1. Advancement in Chemical Recycling

Recent advancement in solvent dependent depolymerization and controlled dissolution has significantly enhanced selectivity and monomer recovery. Polyethylene terephthalate of solvolysis now routinely yield more than 90% weight, recovery of Bis (2-hydroxyethyl) terephthalate using powerful heterogeneous catalyst, using about 20% less energy than traditional glycolysis. In just 24 hours, Tandem catalytic hydrogenous of polyethylene using single-site Molybdenum complexes transforms more than 70% of feedstock into oils and waxes at 175 degrees Celsius, opening doors to high value lubrications requiring significant post-processing. Furthermore, it is investigated in Sweden the potential for chemical recycling, where household plastic packing was less than 7% recycled and 93% was destroyed for energy

recovery. The feasibility of catalytic cracking, pyrolysis and gasification was investigated. Catalytic cracking and pyrolysis required more pilot-scale research prior to commercial deployment, while gasification was successful in producing intermediates for new plastics. To convert plastic waste into useful chemicals, examined variety of chemical recycling methods, especially hydrothermal liquefaction, pyrolysis and gasification. The result produced from this study is that recovery of monomer is 28% weight and emission output 34.25% weight (Fig 2) [38-39].

6. Comparisons between innovative and traditional approaches

Mechanical recycling is preferred because of its applicability and simplicity for properly organized plastic waste streams. Due to its low energy demand, this process is inexpensive and energy efficient [40-41]. Furthermore, it promotes a system with closed loop by converting plastic waste into products with intended application. Currently, mechanical methods represent more than 90% waste plastic efforts with main focus on polyethylene terephthalate and polyethylene. However, difficulties like degraded material qualities of recycled products as well as their inappropriateness for polluted waste still significant challenge [42-43]. Conventional chemical recycling techniques such as solvolysis, hydrocracking, gasification and pyrolysis that perform function in extreme environment. These procedures have advantages for different kinds of contaminated plastic because of their elevated operating temperature. This situation also allows the potential and high degradation rates for wide-spread industrial application.

The high energy requirements create environmental issues and limit their cost-effectiveness to situations with large volumes of plastic waste, even though they have been proven at a medium-industrial scale and are almost ready for widespread use. Additionally, high temperatures may cause random polymer dissociation which could lower product quality and selectivity (Fig 3). Solvolysis is a more cost-effective choice compared with chemical techniques because of its lesser operating temperature (between 50 and 300 °C), which lead to lower energy consumption [41-44]. Solvolysis is particularly useful for processing C-X-containing plastics, such as PET, which results in increased economic value and the selection of more suitable products. Electrochemistry, photo-catalysis and biotechnology are advanced technologies. These technologies are more sustainable and eco-friendly methods for plastic waste management. Due to eco-friendly and reduced energy usage, these technologies have great potential of plastic reuse in future (Table 2) [44].

7. Waste to chemicals

The aim of development in chemical valorization is to recover specialized compounds and monomers with minimal environmental effect and great selectivity. Selective dissolution, depolymerization and catalytic cracking that recover of valuable intermediate and monomers. These precursors can create new polymers, reducing dependence on raw material derived from fossil fuels.

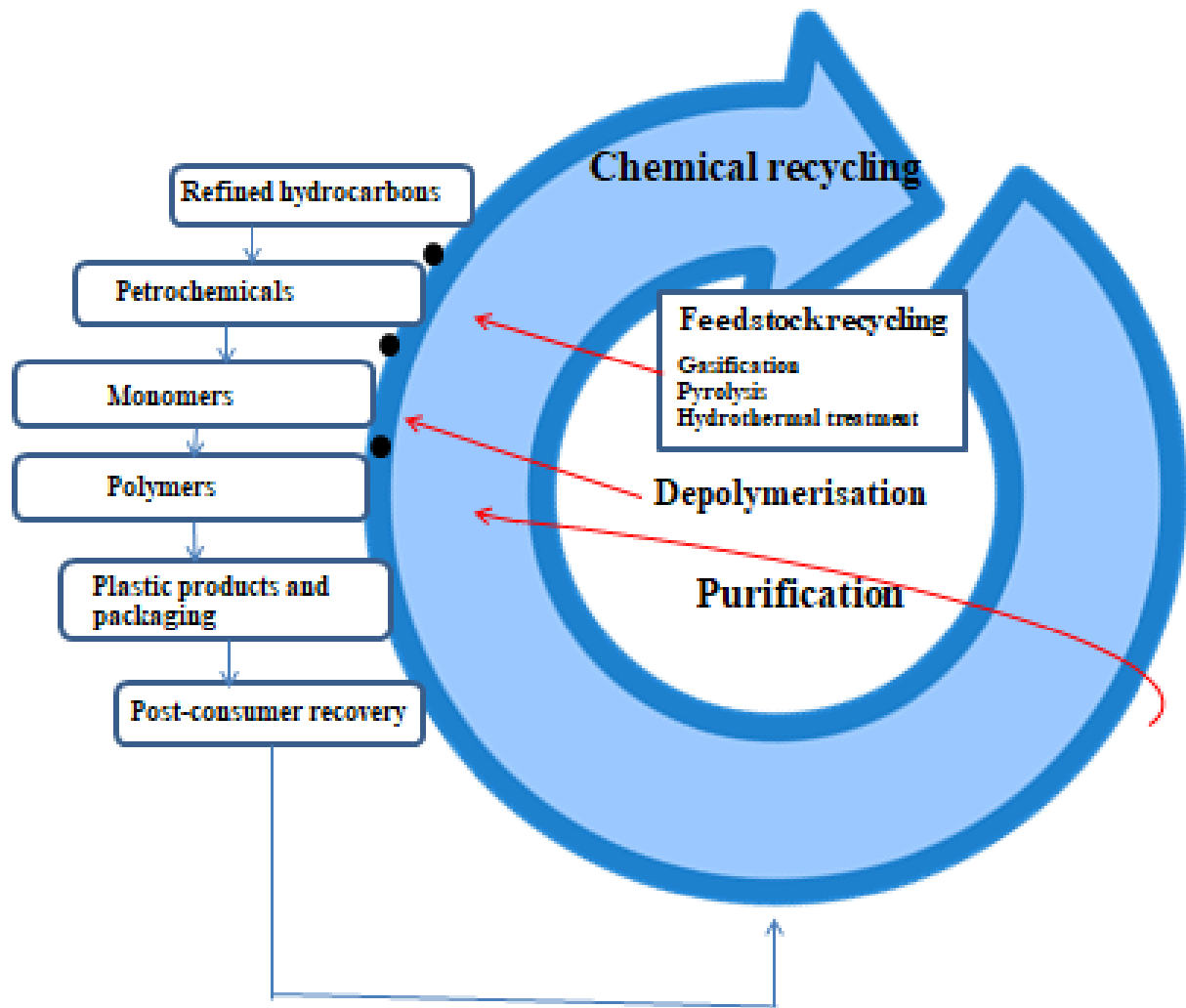


Figure 1: Schematic representation of chemical recycling process

Figure 1: Pathways of chemical recycling

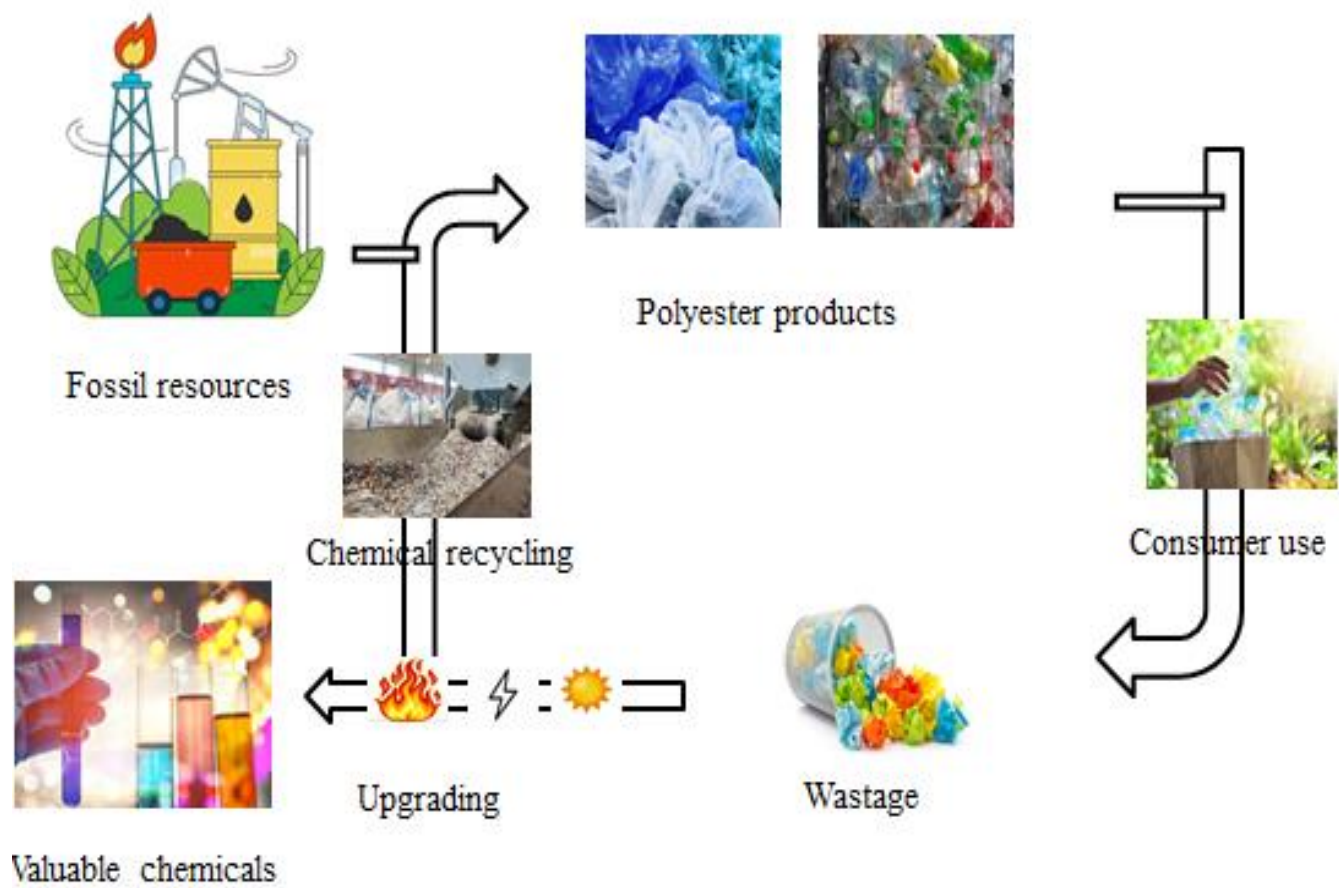


Figure 2: Valuable chemicals from recycling chemicals

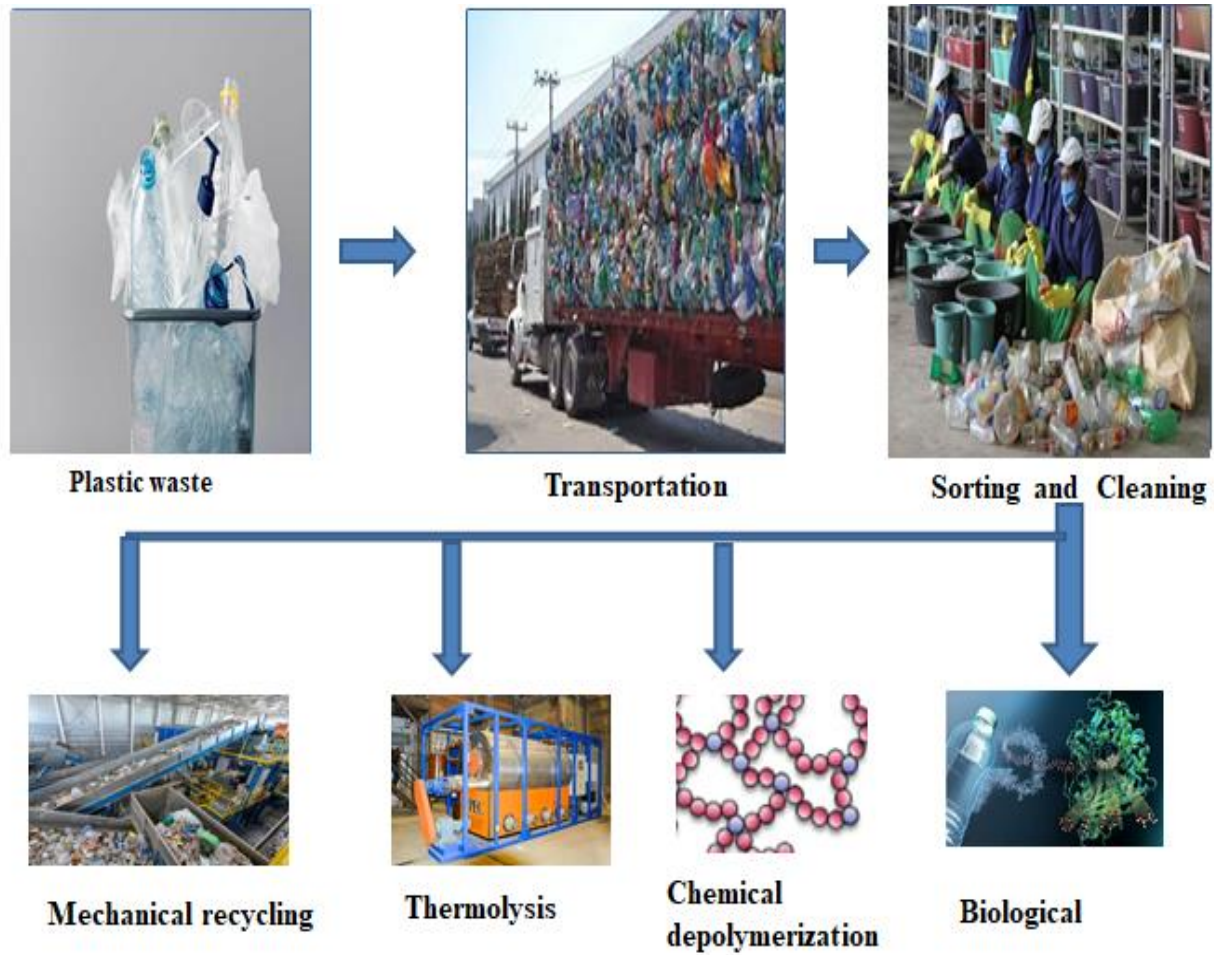


Figure 3: Up-cycling of plastic waste

Table 1: Processes of chemical recycling of plastic

Process	Parameters	Results	References
Pyrolysis	Without oxygen 400-700°C Continuous or batch reactor.	Char, liquid oil and gas. (C ₅ -C ₂₀)	[47]
Depolymerization	Catalysed by metal salt, acids or bases 180-280°C	Monomers such: Dimethyl terephthalate (DMT), Terephthalic acid (TPA) and Ethylene glycol (EG).	[30]
Solvolytic	Solvents such ethylene glycol, methanol and ethanol. Catalyst: Organ catalyst Zn acetate 150-250°C	Oligomers, BHET and DMT	[31]
Gasification	Incomplete oxidation 700-1200°C	Syngas for methanol production.	[48]
Catalytic pyrolysis	Catalyst: Stainless steel Zeolites Alumina (350-550°C)	Products are: H ₂ , aromatics, CNTs and alkanes.	[49]
Hydrogenolysis	Catalyst: RuPt C/Ru 250-350°C	Naphtha-range Hydrocarbons Liquid alkanes Fuels	[50]

Table 2: Comparison between chemical and mechanical recycling techniques

	Mechanical Method	Chemical Method
Operational principle	These are examples of physical processing melting, sorting and shredding. After valorization, the polymers are maintained structure of original polymer.	This involves breakdown of chemicals. These include: pyrolysis, gasification and de-polymerization. In which plastics transform into fuels, monomers and many other chemicals.
Input items	Includes single polymer Such as PP, PET and HDPE.	Contaminated, multi-layer and mixed plastics.
Output	Recycled fibre, plastic timber and pellets.	Monomers, oils, syngas, wax
Energy utilization	Low	High
Discharge	Minimal	Based on process
Advantages	Cheap	Create high value compounds
Disadvantages	Contaminated problems	Potential harmful by-product
Cost effectiveness	High	Intermediate

Companies like IBM and Garbo manufactured glycolysis apparatus that selectively breakdown into bis (hydroxyethyl) terephthalate from polyethylene terephthalate using more than 92% produced at 500 kpa and 200 degree celsius, decreasing consumption by approximately 15%, when compared to previous process. The almost full removal of multi-polymer process is now feasible using novel solvent system, producing monomers having purity more than 98% for recycling with solvent yield more than 90% [45]. Albor created composites of fibre reinforcement from reused polycarbonate and PET having tensile strength comparable of virgin substances. Moreover, current value of TRL is still at 5 because of expensive nature of composites production and solvent application [46].

8. Challenges

Although there is increasing interest in valorization of plastic waste, but it remains limited due to its applications such as economy, regulatory and technological barrier. Stakeholders are frequently discouraged from employing these processes by high operational expenses, initial capital expenditure and variable values of recycled materials. Recycling process such as pyrolysis and de-polymerization are less efficient than virgin plastic manufacture or typically re-cycling because they require expensive machinery and energy consuming processes [51]. Moreover, there is an inconsistent consumer demand for valorization of plastics because of recycled substances thought to be lower quality than virgin plastics. To reduce these problems, create subsidies, financial incentives and partnership between public and private sectors.

9. Future perspectives

Coordination efforts throughout the industries are necessary for promoting the valorization of discarded plastic with policy makers, industries and research institutions serving equal roles in scaling and development of innovative approaches. Research foundations provide fundamental research and scientific understanding required to create new raw substances and techniques for processing. Rapid technological development makes the future of plastic waste

valorization highly positive. Several new catalysts are also being development to enhance chemical recycling selectivity and decrease energy usage. These development points shift toward more scalable, effective and sustainable efficient management strategies. The technologies which are incorporated significantly reduce polluted environment, improve the prevention of resources and encouraging the sustainable plastic lifetime.

10. Conclusions

The rapid growth of discarded plastic has become significant environmental problem, and the creation of sustainable recycling methods is becoming more essential. The transformation of plastic waste into useful chemicals and this provides an effective solution to reduce environmental pollution at the same time retrieving useful resources. Recent advancements in chemical and thermal recycling, especially catalytic based processes, could be significantly converted into monomers, fuels and other useful chemicals. Such methods help in reducing plastic waste as well as fossil resources of virgin origin. Furthermore, there is still an issue regarding catalytic durability, mixed plastics streams, economic viability and process efficiency.

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