

Chemical Recycling for Plastic Waste

Subjects: Polymer Science

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Plastics play an integral role in shaping our modern society and are ubiquitous in our daily lives. Their superior material characteristics, performance, and low production cost make them desirable for vast consumer and industrial applications. Chemical or feedstock recycling refers to any reprocessing technology directly affecting the formulation of polymeric waste or the polymer itself. The recycling plastic waste through chemical means are explored.

Keywords: plastics ; life cycle ; circular plastics ; circular economy ; circularity ; sustainability ; chemical recycling

1. Introduction

Chemical or feedstock recycling converts them into chemical substances and products, whether for the original or other purposes, excluding energy recovery ^[1]. Here, chemical substances and products include their constituents (e.g., monomers, oligomers), petrochemicals, and hydrocarbon mix ^{[2][3][4]}. All these can produce new plastic products of comparable quality to virgin plastics, thus eliminating downcycling ^{[5][6][7]}. Proponents believe it can complement mechanical recycling and valorize plastic waste it could not treat, thus increasing recycling rates and accelerating plastic circularity ^{[7][8][9][10]}. Conversely, critics still need to be convinced of its claimed environmental benefits, including the assumptions behind its life cycle assessments, and question its economic viability ^{[2][9][11][12]}.

Presently, chemical recycling routes include solvent-based purification, depolymerization, pyrolysis, catalytic cracking, and gasification. By 2030, it is forecasted that pyrolysis and depolymerization will be the dominant chemical recycling routes, jointly capable of recycling at least 5% of today's plastic waste volume, a considerable step up from the state-of-the-art ^{[8][13]}.

2. Solvent-Based Purification

Even if plastic waste is perfectly sorted by type, the material composition of each plastic piece may still be contaminated with foreign elements. Depending on their end-use application, Roosen, et al. ^[14] estimated that the degree of contamination within each plastic piece could range from 10 wt % to 45 wt %. These innate contaminants can be removed using established solvent-based purification (SBP) techniques such as (a) extraction and (b) dissolution with precipitation. For extraction, the target polymer is washed with an appropriate solvent that dissolves and extracts the contaminants. While the extraction process is relatively simple and straightforward, it is only effective for cases involving low molecular weight contaminants ^[15]. Dissolution with precipitation technologies is preferred for complex cases involving multiple contaminants of varying solvency properties, molecular weight, or insoluble materials. Instead of washing, the target polymer is dissolved at the highest concentration of a suitable solvent, leaving the contaminants left behind to be filtered away. Antisolvents are then added to reprecipitate the polymers in solvents to retrieve virgin-like polymers ^{[16][17][18]}.

SBP technologies for recycling various plastic types have been investigated for several decades. The fundamentals of recycling plastics with SBP techniques have remained unchanged since they were first established. Despite their heritage, authors noted inconsistency in their classification. Some works consider them a chemical recycling process ^{[19][20]}, while others do not ^{[3][21]}. The former argues that the processes constitute a chemical reaction and that fundamental chemistry knowledge is needed to comprehend and advance research in solvent–polymer interactions, their design, and recovery. Conversely, the latter argues that the chemical structure of the recovered polymers has not been significantly altered nor degraded during any SBP processes, which is a definitive feature of chemical recycling pathways ^[22]. Furthermore, plastic processing equipment can directly process the recovered polymers without further modifications ^[18].

Regardless of the scholarly debate, the merits of SBP techniques are that the recovered polymers are high quality and do not need further reform. As a result, SBP technologies score the highest in carbon dioxide avoidance (up to 6 tons of carbon dioxide avoided for each ton of plastic waste) compared to all other treatment methods ^[23]. However, researchers' review indicates that cost is the most significant drawback impeding their widespread adoption. Firstly, SBP technologies

use strong and hazardous organic solvents, which require certain technical and safety conditions to be satisfied before use [16][18][23]. Next, the unit cost of solvent is expensive and adds up when it is used on a commercial scale. Lastly, recovering solvent and antisolvent for subsequent reuse is energy-intensive, predominantly when the employed process operates at a high solvent/polymer ratio [15]. The removal of solvents must also be complete, as any residual solvent affects the target polymer's properties and, correspondingly, its resale value. These factors have led to the closure of some of the most established SBP facilities [24] and incidentally paved SBP's research direction.

Today, researchers are actively investigating alternatives to conventional solvents and antisolvents. Ideally, these emerging alternatives should be safe. They should be synergistic with their target polymer to optimize for (a) greater process efficiency during application and (b) recoverability and recyclability for subsequent use while not compromising on output quality [23]. Optimizing these conditions would lead to cost savings across the unit cost and associated recovery systems, paving the way to greater industry adoption and future developments. Green alternatives, such as supercritical fluids (e.g., dimethyl ether or carbon dioxide) and natural solvents (e.g., terpene oil), may enable these desired outcomes, leading to heightened research interest in their technical feasibility and unit economics for commercial implementations. Utilizing these green alternatives to purify enhanced recycled plastics (described in [Section 3.1](#)) for recycling has also emerged as an area of interest [17]. Beyond that, scholars are also actively investigating the optimal integration of SBP technologies with other treatment methods to separate mixed plastic waste more effectively and efficiently [16].

3. Depolymerization

Depolymerization refers to reversing a polymer to its monomer(s) or a polymer of lower relative molecular mass [25]. Methanolysis, glycolysis, and hydrolysis are several established depolymerization methods that are commercially available [26]. These methods correspond to the chemical agent that splits the plastics' functional ester groups at high temperatures to retrieve the target monomers. Methanolysis, glycolysis, and hydrolysis yield at least 65%, 50%, and 70% of the target monomers, respectively [27]. Known chemical agents include solvents, reagents, and catalysts such as glycol, methanol, water, manganese acetate [28], cobalt acetate [29], lithium hydroxide [30], n-butyl titanium oxide [31], acetic acid, sodium sulfate, and potassium sulfate.

Depolymerization is the only chemical recycling process capable of recovering an intermediate product (monomers), making it one of the most economically valuable approaches. It also uses less energy than the other chemical recycling processes [32] and can recycle cross-linked polymers [33]. After filtering out colorants and additives, the recovered monomers can be repolymerized into virgin-grade quality plastics, making them suitable for industrial applications where the plastics' purity is required [23][26]. However, depolymerization is only effective for homogeneous plastic waste and certain polymer types [3][21]. As a result, it is challenging for recyclers to acquire acceptable recyclates in high volumes to make the depolymerization process cost-effective and scalable [3].

Recent developments in depolymerization research aim to address these issues by widening its applicability. Researchers have successfully demonstrated selective depolymerization of targeted polymeric waste materials in nonhomogeneous plastic waste using hydrosilanes as reductants with organic [34], iridium(III) [35], aldehyde [36], ketones [36], and other catalysts. In their investigations, researchers observed that the effectiveness of the selective depolymerization process correlates with the reaction conditions, suggesting the need to optimize the recyclate–chemical agent pair and its associated reaction conditions to maximize the yield and output quality of the target monomers [37][38]. However, optimization increases the cost of the chemical agents, further diminishing the cost-effectiveness of the depolymerization process.

The cost of depolymerizing plastic waste is its most significant impediment, encouraging future researchers to pay attention to its commercial viability as they optimize the recyclate–chemical agent pair and its associated reaction conditions. Cost aside, the depolymerization process is also confronted with several technical issues that must be addressed before widespread adoption. They include the (a) small contact area between the chemical agent and the target polymer and (b) the challenges in recovering chemical agents in high purity after application [23].

4. Pyrolysis

Pyrolysis (or thermal cracking) refers to the irreversible chemical decomposition caused solely by a rise in temperature [25]. It is not incineration, as the plastic waste is thermochemically decomposed without oxygen [39]. Depending on the applied treatment method, pyrolysis occurs between 200 °C and 1300 °C. Pyrolyzing plastic waste at temperatures of 500 °C and lower produces liquid oil, while exceeding 500 °C produces more gaseous or char products such as gas, wax, and coke [40][41]. Pyrolyzing plastic waste in ideal conditions derives pyrolysis oil of similar performance to conventional diesel

oil, including its viscosity (up to 2.96 mm²/s), density (0.8 kg/m³), flash point (30.5 °C), cloud point (−18 °C), and energy density (41.58 MJ/kg), allowing it to be used as a fuel or a feedstock to manufacture other compounds [42]. With remarkable versatility, pyrolysis has emerged as the chemical recycling choice for major chemical companies [43], enabling it to reach commercial maturity [21]. Today, it is the most extensively studied chemical recycling technology, with the most research output and data available [2].

Pyrolysis, like all other processes, is not perfect. While it can directly treat mixed plastic waste, it is not highly encouraged. The recyclates should be first sorted and purified for pyrolysis to produce virgin feedstock of comparable quality [12]. If pretreatment steps are not undertaken, the quality of pyrolysis oil produced may be inferior and unfit for its intended purposes. For example, subjecting polyvinyl chloride (PVC) to pyrolysis causes it to release corrosive hydrochloric acid. Therefore, if PVC is not removed before pyrolyzing an incoming batch of mixed plastic waste, its presence, even in small amounts, can contaminate and destroy the entire batch of recyclates and corrode the reactor. Researchers tried pretreating the recyclates at 300 °C for 60 min to mitigate this problem, reducing the embodied chlorine content by ~75 wt% [44]. They also tried to remove hydrochloric acid from PVC by grinding it with a planetary ball mill before adding calcium oxide to react with the hydrochloric acid to produce calcium salts that can be washed away [45]. Recently, plasma pyrolysis (pyrolyzing plastic waste between 1730 °C and 9730 °C in less than a second) and hydrocracking (adding pressurized hydrogen to the pyrolysis) have also emerged as feasible alternatives due to their ability to remove or prevent the formation of hydrochloric acid [26]. All in all, researchers today are actively investigating practical pretreatment strategies for pyrolysis to treat mixed plastic waste effectively. They are experimenting with better methods and agents, including inhibitors that prevent hydrochloric acid and other plastics from diminishing the output [46].

Another significant drawback is that pyrolysis is energy-intensive, typically carried out at very high temperatures of 500 °C [43]. Even though it is commercially matured, techno-economic analyses suggest it is not an economically viable solution yet [10]. Hence, in addition to devising practical pretreatment strategies, researchers are investigating cost-effective and environmentally friendlier approaches for pyrolysis. Presently, catalytic cracking is the most promising solution. It involves adding complementary transition metal catalysts such as zeolites and silica–alumina to pyrolysis. These complementary catalysts enable pyrolysis to be more efficient at lower temperatures (300–350 °C) and use less energy [10]. It also facilitates the production of higher yield and better-quality pyrolysis oil. Both factors significantly improve its economic viability. However, unlike conventional pyrolysis, catalytic cracking is very sensitive to contaminants. Hence, the process cannot treat mixed plastic waste and is only suitable for pure polymers such as polyolefins and polystyrene. Plastic waste must also be pretreated before pyrolysis to achieve desired outcomes [47]. Adding catalysts and pretreatment processes increases the cost of pyrolysis. However, this is inevitable, as pyrolyzing polyolefins or polystyrene without catalysts produces pyrolysis oil of lower yield and quality to the extent that it requires further refining before use, resulting in an even higher processing cost [37]. Alternative solutions researchers explore today include microwave-assisted pyrolysis to lower energy consumption. In microwave-assisted pyrolysis, dielectric material or absorbents such as activated carbon, silicon dioxide, or graphene are introduced to absorb microwave energy. These absorbed microwave energies produce thermal energy that elevates the temperatures in the reactor, making it suitable for pyrolysis, thus reducing the energy supply needed to heat the reactor. However, microwave-assisted pyrolysis has several technical challenges, limiting it to laboratory and pilot scales only. These challenges include its inability to (a) uniformly heat the reactor and (b) precisely and consistently control the reactor's temperature with the absorbed microwave energies [26].

Other developments in improving its economic viability explore how to pyrolyze plastic waste to extract its high carbon content to produce other higher-valued materials. For example, Mohamed, et al. [48] co-pyrolyzed PET waste with zinc powder at 700 °C to create new carbon-based nanomaterials suitable for photocatalysis applications. On the other hand, Ko, et al. [49] valorized PET waste into synthetic graphite by first pyrolyzing the PET waste at 900 °C, followed by a boron-assisted catalytic graphitization at 2400 °C. Today, a kilogram of battery-grade synthetic graphite produces about 17 kgCO_{2e} [50] compared to a kilogram of virgin plastic at an average of 2.9 kgCO_{2e} [47]. Therefore, valorizing plastic waste into other higher-valued materials, such as synthetic graphite, helps offset the process cost and contributes more to lowering global emissions. However, this strategy does not accelerate plastic circularity. As such, authors encourage researchers to stay focused on returning plastic waste to plastics.

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