

# Catalytic Chemical Recycling of Post-Consumer Plastics: A Review

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**ABSTRACT:** The objective of this paper is to provide a critical review of Catalytic Chemical Recycling of Post-Consumer Plastics using data from online and in-library resources. The adaptability of plastic has significantly contributed to numerous product innovations and everyday convenience and the waste poses a significant environmental challenge due to its durability and slow degradation rate. Catalytic chemical recycling seen as a promising approach by converting plastic waste into valuable products like fuels and monomers. This process involves breaking down plastic polymers into smaller molecules using catalysts, reducing the need for fossil fuelbased feedstocks. The study explored various catalytic methods, including microwave-assisted, plasma-assisted, supercritical water, and photocatalytic conversion, which can yield high-value products. By promoting catalytic chemical recycling, we can reduce plastic waste, conserve resources, and contribute to a more sustainable future.

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Plastics have become essential in modern society, finding use across numerous sectors such as consumer goods, construction, transportation, textiles, packaging, healthcare, and electronics (Millet *et al.*, 2019). Compared to traditional materials like wood, concrete, and metal, plastics are favoured for their adaptability, light weight, and cost-effective production. Their strength, durability, moldability, and chemical resistance make them integral to countless products that enhance comfort, convenience, and safety in daily life. Global plastic production has surged over the years, reaching approximately 400 million tonnes by 2022 (Plastics Europe, 2022), driven by economic growth and

population increases that have spurred higher demand.

However, the rising demand for plastics, combined with their advantageous properties such as light weight, durability, and low cost, also poses significant challenges for waste management. These attributes contribute to the accumulation of plastic solid waste (PSW), which occupies substantial space in the environment. Plastic waste poses serious environmental concerns as current disposal methods often result in health and ecological hazards, contributing to global warming, climate change, pollution, and the degradation of biodiversity and natural resources (Maria and Dwinanto, 2019). Single-use plastics, particularly those used for packaging and sheeting, are frequently discarded

after a single use and persist in the environment due to their durable nature (Hopewell *et al.*, 2009).

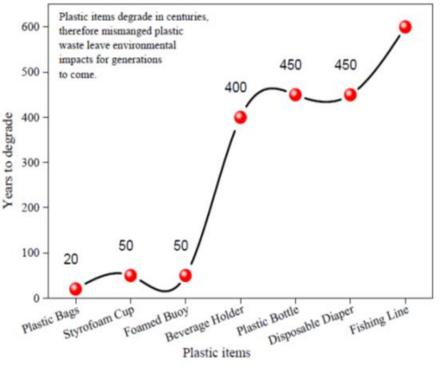


Fig.1: The degradation time of different types of plastic (Maitlo et al., 2022).

Nearly all plastics in use today are derived from nonrenewable fossil fuels, contributing significantly to a high carbon footprint, which includes the total emissions of greenhouse gases such as carbon dioxide (CO<sub>2</sub>) and methane throughout their lifecycle. Common household plastics include polyethylene terephthalate (PET), polyethylene (PE)—available in two main types: low-density polyethylene (LDPE) and high-density polyethylene (HDPE)—polyvinyl chloride (PVC), polypropylene (PP), polyurethane (PU), and polystyrene (PS) (Briassoulis *et al.*, 2019; Millet *et al.*, 2019). Typically, these plastics are used once and then disposed of in landfills.

According to Scott *et al.* (as cited in Miao *et al.*, 2021), packaging materials made from polyethylene, polypropylene, polystyrene, and polyvinyl chloride account for approximately 50%–70% of total plastic waste. Miao *et al.* (2021) further notes that polyethylene is the most prevalent type, constituting 69% of plastic waste, particularly from items like plastic bags, and representing 63% of packaging waste overall. Consequently, polyolefins such as PP, HDPE, and LDPE are the primary synthetic plastics requiring breakdown. The valorisation of plastic waste through catalytic chemical conversion into

reusable building blocks offers a potential solution for plastic waste management while providing a strategy to reduce the chemical industry's carbon footprint.

Plastic Wastes: The trend in plastic innovation and consumption all over the world keep increasing and this has led to the increase in plastic wastes and the difficulties for their management. Generally, plastic wastes (PW) are divided into two main groups: industrial plastic wastes (IPW) and municipal plastic wastes (MPW). These two main groups of PW have different qualities and properties, therefore, can be subjected to different management strategies. IPW are homogeneous and easily located and managed. On the other hand, MPW are post-consume residues generated after the use of plastic products and are usually found in municipal solid wastes (MSW), construction wastes and residues from electrical and electronic equipment. Plastics can be categorized into two classes: thermoplastic and thermosets. Thermoplastics have property that enable them to melt, mold and hence can be reheated and reshaped again which can be recycled easily while thermosets do not have such property due to their different kinds of chemical bonds and structural arrangements. Thermoplastic has different polymers including PET (polyethylene terephthalate), HDPE (high density polyethylene), PVC (polyvinyl chloride), LDPE (low density polyethylene), PP (polypropylene), PS (polystyrene) etc, with different properties and their uses.

Thermosets are plastics that can soften and melt but take shape only once. They are not suitable for repeated heat treatments; therefore, if heat is reapplied, they will not soften again but they stay permanently in the shape that they solidified into. Thermoset plastics pass through a series of physical and chemical transformations under specific conditions creating 3D linkage in bonding. This change is irreversible because, on heating, these arrangements of molecules in thermosets plastic cannot be reformed and remelted (Evode et al., 2021). Thermosets are widely used in electronics and automotive products. Thermoset plastics contain epoxy, ester, melamine formaldehyde, phenolic formaldehyde, silicon, urea formaldehyde, polyurethane, metalised and multilayer plastics etc. Of the total post-consumer plastics waste in the world, thermoplastics constitute more than 70% while the remaining correspond to thermosets.

*Common Types of Plastic:* Plastics are classified on the basis of the polymer from which they are made, therefore the variety of plastics are very extensive. The types of plastics that are most commonly reprocessed are polyethylene (PE), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET) and polyvinyl chloride (PVC).

Polyethylene (PE): Various types of PE exist. They are classified according to their density. The two main types of polyethylene are low-density polyethylene (LDPE) and high-density polyethylene (HDPE). LDPE is flexible, soft and easy to cut, with the feel of candle wax. It is transparent when thin; and milky white when thick, unless a colour pigment is added. LDPE is used in the manufacture of film sheeting, sacks and bags, blow-moulded bottles, food boxes, flexible piping and hosepipes, household articles such as toys, buckets and bowls, telephone cable sheaths, etc. HDPE is tougher and stiffer and milky white in colour. It is used for the manufacture of bags and industrial wrappings, soft drinks bottles, detergents and cosmetics containers, toys, crates, jerry cans, water tanks, dustbins and other household articles.

While being a valuable material for many uses, polyethylene persists in the environment and causes environmental pollution on an unprecedented scale. An estimated 80% of all virgin PE ever produced has accumulated in landfills and the natural environment (Geyer *et al.*, 2017) which may release toxic compounds dangerous to human health and the habitat.

*Polypropylene (PP:* Polypropylene is a more rigid type of plastic, that is easily formed in high temperature, flexible, hard, and resistant to fat. Because of the nature of this plastic, it is used for the production of high-quality home ware, chairs, housings for car batteries, home appliances, suitcases, crates, nursing bottles, pipes, fittings, wine barrels, rope, carpet backing, netting, woven sacking, surgical instruments, food containers and straws.

*Polyethylene terephthalate (PET):* Polyethylene terephthalate (PET) is composed of repeated units of polymerized ethylene terephthalate monomer  $(C_{10}H_8O_4)$ . It exists as an amorphous (transparent) and as a semi-crystalline (opaque and white) thermoplastic material. Generally, it has good resistance to mineral oils, solvents and acids but not to bases. The semi-crystalline PET has good strength, ductility, stiffness and hardness while the amorphous type has better ductility but less stiffness and hardness. PET is a lightweight plastic and has good barrier properties against oxygen and carbon dioxide. Therefore, it is utilized in packaging bottled water, soda, juice, cooking oil, and food. Other applications include food trays for oven use, roasting bags, audio/video tapes as well as mechanical components and synthetic fibres.

*Polystyrene (PS):* Polystyrene (PS) is a type of plastic that is brittle and usually transparent. It is easily formed in high temperatures and is very stiff at room temperature. PS is used for cheap, transparent kitchen ware, light fittings, bottles, toys, food containers, etc. This type of plastic is not favourable for use because it cannot be decomposed by the soil, and can release toxic gas when burned.

*Polyvinyl chloride (PVC):* One of the most commonly used thermoplastic material is PVC. PVC has a low commercial cost and inherent properties that make it a suitable plastic for the production of different products. In its natural form (i.e. unless plasticizers are added), polyvinyl chloride (PVC) is a hard, rigid material which is used for bottles, thin sheeting, transparent packaging materials, water and irrigation pipes, gutters, window frames, building panels, etc. If plasticisers are added, the product is known as plasticized polyvinyl chloride (PPVC), which is soft, flexible and rather weak, and is used to make inflatable articles such as raincoats, shower curtains, furniture coverings, bottles, hosepipes and

electrical cable coverings, shoes, flooring, automobile linings, etc. PVC is not recommended to be used as a food or beverage packaging because the substances contained in PVC can disrupt the digestive system.

Thus, as PVC is a highly demanded plastic, there is an increment on its production as well as a growth of PVC wastes. PVC contains around 60 wt.% of chlorine therefore, management of PVC wastes is not easy. When landfilled, it can easily be degraded by oxidation producing toxic halogenated compounds for the environment.

Other plastics extensively used in our daily lives are as follow:

- High Impact Polystyrene (HIPS) – used in fridge liners, food packaging, vending cups.

- Acrylonitrile butadiene styrene (ABS) – used in electronic equipment cases (e.g., computer monitors, printers, keyboards), drainage pipe.

- Polyester (PES) – used in fibres, textiles.

- Polyamides (PA) (Nylons) - used in fibres, toothbrush bristles, fishing line, under-the-hood car engine mouldings.

- Polyurethanes (PU) - used in cushioning foams, thermal insulation foams, surface coatings, printing rollers.

- Polycarbonates (PC) - used in CDs, eyeglasses, riot shields, security windows, traffic lights, lenses.

- Polycarbonate/Acrylonitrile Butadiene Styrene (PC/ABS) - A blend of PC and ABS that creates a stronger plastic. Used in car interior and exterior parts and mobile phone bodies.

*Recycling as An Innovative Approach:* Shahnawaz *et al.* (2019) pointed out that only 10 % of plastic waste is recycled all over the world. Recycling of plastics waste have a number of advantages. It reduces the demand of virgin materials and energy required to create new resources from nature, thus ultimately reduction of carbon footprints, reduces the load on landfilling, generates employment and save the fossil fuel reserves.

Although recycling is associated with some issues which includes difficulty in separation of plastic from non-plastics (no 'magnet' equivalent), breakage in polymer chains on recycling, varied composition of plastic resins that make them incompatible for particular recycling, degradation of quality of recycled polymer than virgin polymer, low market value of thin plastic film, identification of reuse and recycling opportunities, lack of infrastructure for recycling and low value of recovered plastics.

## MATERIALS AND METHODS

The methods of recycling Plastic wastes are classified into four main techniques: primary recycling, mechanical recycling (Secondary recycling), chemical recycling (Tertiary recycling) and energy recovery (also known as combustion or Quaternary Recycling) (Singh *et al.*, 2016; Chen *et al.*, 2018). Mechanical recycling (Sinha *et al.*, 2010) and chemical recycling (Wang *et al.*, 2015; Lamberti *et al.*, 2020) are the two main approaches used in order to recover pure polymers respectively.

*Primary recycling:* Primary Recycling is the most popular process method recycling due to its simplicity and low cost. This process refers to the reuse of products in their original structure. The disadvantage of this process is represented by the existence of a limit on the number of cycles for each material.

*Mechanical recycling:* Mechanical recycling refers to reprocessing of plastics by physical means, in which the plastic wastes will be formed by cutting, shredding or washing into granulates, flakes or pellets of appropriate quality for manufacturing, and then melted to make the new product by extrusion. The reprocessed material can also be blended with virgin material to obtain superior results. This process can only be used for thermoplastic polymers, because of their ability to be re-melted and reprocessed into end products. Mechanical recycling does not involve the alteration of the plastic polymer.

*Chemical recycling:* Among the above recycling methods, chemical recycling is the only technique acceptable according to the principles of sustainable development, because this method leads to the formation of the monomers from which the polymer is made (Francis, 2016; Karayannidis and Achilias, 2007; Al-Salem *et al.*, 2009).

In chemical recycling, plastic is chemically converted to monomers or partially depolymerized to oligomers through a chemical reaction leading to a change in the chemical structure of the polymers. This method is able to transform the PE into smaller molecules, suitable for use as feedstock material starting with monomers, oligomers, or mixtures of other hydrocarbon compounds (Francis, 2016; Olah *et al.*, 2008). The resulted monomers can be used for new polymerizations to reproduce the original or a related polymeric product.

The chemical reactions used for decomposition of polymers into monomers are:

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- Pyrolysis

- Thermal cracking
- Catalytic cracking and reforming
- Chemical depolymerization
- Hydrogenation
- Glycolysis
- Photodegradation
- Gasification
- Methanolysis
- Ultrasound degradation
- Degradation in microwave reactor.

*Energy recovery or quaternary recycling:* Energy recovery entails recovery of steam, heat and electricity from waste through combustion. This process is usually carried out for plastic waste that cannot be recycled. The most effective way to reduce the volume of organic materials which involves the recovery of energy is represented by incineration. Through this method, the energy content of the PW is recovered. Although this method generates considerable amount of energy from polymers, it is not ecologically acceptable because of the health risk from airborne toxic substances, for example,

#### **RESULTS AND DISCUSSION**

Although plastic is considered an indispensable commodity, one of the most pressing environmental issues today is plastic pollution, as the world's ability to deal with plastic wastes is challenged by the rapid accumulation caused by their slow degradation rate, the complexity of the plastic products, and most importantly, little driving force from society to manage this waste. Therefore, the rapid growth of the use and disposal of plastic materials has proven to be a burden to the environment and the ecosystem.

Converting waste plastics into liquid and gaseous fuels is considered a promising technique to eliminate the harm to the environment and decrease the dependence on fossil fuels. Recycling waste plastic by converting it into monomers is another effective solution to the plastic pollution problem.

One of the possible ways for efficient waste plastic utilization is catalytic chemical recycling. This method of recycling is used for processing various types of plastic waste (Briassoulis *et al.*, 2019). Catalysts have been widely used to improve recycling processes by: (1) reducing the reaction temperature drastically; (2) increasing the degradation rate and; (3) improving the product selectivity of the fuel and valuable chemicals produced.

The advantages of catalytic degradation of plastics over other methods of depolymerisation are (i) It breaks down plastics resulting in the production of lower hydrocarbons (ii) it lowers cracking temperature by lowering the activation energy thereby reducing the cracking time and lowering energy consumption drastically (iii) there is narrow product distribution with peaks at lighter hydrocarbons in the boiling point range of motor fuel (i.e. lower boiling point range) and a higher selectivity to liquid products. (iv) It inhibits the formation of undesirable products

Therefore, the energy costs for catalytic degradation compared to other methods e.g. thermal degradation is lower.

Catalytic chemical treatment is a method of recycling scheme that results in changing the chemical structure of the plastic material itself (Briassoulis *et al.*, 2019). It encompasses various treatment methods that result in high end value products from PW. Such methods include aminolysis (Goje *et al.*, 2004; Sinha *et al.*, 2010; Sadeghi *et al.*, 2011), hydrolysis (Campanelli *et al.*, 1993; Evans and Chum, 1991; Panda *et al.*, 2010), glycolysis (Simon *et al.*, 2014; 2015; Sharma and Bansal, 2016), gasification (Dou *et al.*, 2016; Wang and Zhao, 2016; Onwudilia and Williams, 2016), pyrolysis (Singh and Ruj, 2016; Abosede *et al.*, 2018; Shams *et al.*, 2021) and hydrogenation (Bockhorn *et al.*, 1999; Aznar *et al.*, 2006).

The use of a strong catalyst results in the production of lower hydrocarbons ranging between  $C_3$  and  $C_5$ . Catalysts are classified into homogeneous and heterogeneous. Homogeneous catalysts are usually in a single-phase liquid solution i.e. the reactants, products, and catalysts are in the same phase, while the heterogeneous catalysts exist in solid forms (Yansaneh and Zein, 2022). Some of the homogeneous catalysts for plastic recycling include potassium hydroxide (KOH), aluminum chloride (AlCl<sub>3</sub>), sodium methoxide (CH<sub>3</sub>ONa) and sodium hydroxide (NaOH). Commonly used acidic catalysts are hydrochloric, phosphoric, sulphuric, and organic sulphonic acids. Heterogeneous catalysts mostly exist in solid form, and can be added to solid, liquid or gaseous compounds in the mixture (Yansaneh and Zein, 2022). Heterogeneous catalysts are of more common use, because of their easy separation from the liquid product, which allows the catalyst to be reused and regenerated (Al-Salem et al., 2017). Another important advantage of heterogeneous catalysts over homogeneous ones is that they are noncorrosive. Most used catalysts are the following: zinc oxide, ZnO; magnesium oxide, MgO; calciumcarbonate, CaCO<sub>3</sub>; calcium carbide, CaC<sub>2</sub>; silicon dioxide, SiO<sub>2</sub>; aluminum oxide, Al<sub>2</sub>O<sub>3</sub>; silicon

dioxide alumina doped, SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>; zeolite Socony mobil-5, ZSM-5; zeolite; redmud; activated carbon and fluid catalytic cracking, FCC (Ratnasari *et al.*, 2017; Budsaereechai *et al.*, 2019).

Depolymerisation of PE by catalytic cracking into liquid fuels was recently reviewed (Abosede *et al.*, 2018). Most of these processes are promoted by heterogeneous acid catalysts (e.g., zeolites, alumina, silica) and are usually unselective, resulting in a broad distribution of gas ( $C_3$  and  $C_4$  hydrocarbons), liquids (cycloparaffins, oligomers, aromatics) and solid products (char, coke) as a consequence of the random scission of C–C bonds into radicals, which

leads to a complex mixture of olefinic and crosslinked compounds.

Abosede *et al.* (2018) reported the catalytic cracking (pyrolysis) of polyethylene plastic waste using synthesised zeolite Y from Nigerian kaolin deposit. After the analysis of the liquid fuel obtained, fifty compounds were identified which revealed the presence of mostly alkenes and aromatics in the hydrocarbons range of C  $_{8}$ -C $_{29}$ . This is made up of 56 % of gasoline fractions range of C $_{6}$ -C $_{12}$ , 26 % of diesel and kerosene fractions range C $_{13}$ -C $_{18}$ , and 10 % of fuel oil range C $_{18}$ -C $_{23}$ , while 8 % is residual fuel range greater than C $_{24}$ .

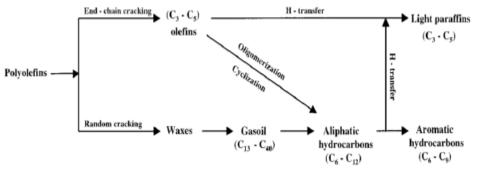


Fig.2: Reaction pathways for catalytic pyrolysis of polyolefins. (Aguado et al., 2001)

Shams *et al.* (2021) utilized the use of calcium hydroxide  $Ca(OH)_2$  as catalyst at 250-300°C for the thermal cracking of Polyethylene Terephthalate (PET) to Fuel. During the heat breakdown phase, PET decomposes to strong and solid non-biodegradable terephthalic acid and benzoic acid complexes.

In the same vein, Paula et al. (2022) carried out thermal and catalytic pyrolysis of PE, PP and PS plastic waste with ZSM-5 zeolites and modified mordenite (MOR). Mordenite was treated with NaOH in order to improve the pore size. By treatment with alkali, a mesoporous morphology can be produced in the catalyst, thus preserving its acidity. Mordenite has an irregular pore size, which could contribute to the occurrence of secondary reactions taking place on the catalyst surface. Reactions on the catalyst surface may contribute to bimolecular secondary processes and the production of aromatic compounds, which further lead to lower conversion rates and increase light fraction hydrocarbons. Low conversion rates can also be related to mono-dimensional channel systems and low mesoporosity, which limited the catalyst's access to polymer chains on the active sites. However, the treated ZSM-5 catalyst showed better performance in the catalytic processing of plastics compared to mordenite.

The catalytic Chemical Recycling of Polyethylene terephthalate (PET) using nano ZnO was performed by Alzuhairi et al. (2022). The catalytic activity of the catalyst was found to be high by reducing the reaction time until one hour instead of 7 hours without catalyst. The analysis of the thermograms has indicated the presence of various kinds of monomer, dimer and oligomers. Kamber et al. (2010) studied a potent organic catalyst, N- heterocyclic carbenes, generated insitu from an ionic liquid in the presence of a base and used for the transesterification reaction of PET with ethylene glycol in refluxing anhydrous tetrahydrofuran to generate bis(2-hydroxyethyl) terephthalate (BHET). The reaction time was shortened to 1 h and the relatively mild reaction conditions are attractive. Fukushima et al. (2011) developed an organic phase transfer catalyst, guanidine 1,5,7-Triazabicyclo [4.4.0] dec-5-ene (TBD), which is a potent neutral base and an efficient catalyst for the glycolysis of postconsumer PET (beverage bottles) to its monomer and about 78 % yield bis(2-hydroxyethyl) terephthalate (BHET) was isolated with 0.7 wt% of the catalyst and excess amount of ethylene glycol at 190°C for 3.5 h under atmospheric pressure. The recycling of the catalyst for more than five cycles was also demonstrated.

Nunes *et al.* (2014) successfully investigated the depolymerized of PET to diethylterephthalate (DET) under supercritical ethanol with 1-Butyl-3-methylimidazolium tetrafluoroborate as catalyst. A robust PET conversion of 98 wt% was obtained, and adding 1-Butyl-3-methylimidazolium tetrafluoroborate can reduce the reaction time from 6 h to 45 min.

Bernard *et al.* (2021) investigated the catalytic depolymerization of Low- and high-density polyethylene (LDPE/HDPE) without added H<sub>2</sub>, to  $C_2-C_{20+}$  alkanes and alkenes via energy-efficient radio frequency induction heating, coupled with dual-functional heterogeneous Fe<sub>3</sub>O<sub>4</sub> and Ni- or Pt-based catalysts. The initial results of the study also indicate that zeolite-based Ni catalysts are more selective to light olefins, while Ni supported on ceria catalysts are more selective to C<sub>7</sub>-C<sub>14</sub> alkanes and alkenes. Up to 94 % LDPE conversions were obtained with minimal aromatic, coke, or methane formation which are typically observed with thermal heating.

Emerging Technologies: Plastic waste conversion to value added products has gained extensive importance in alleviating environmental pollution and the energy crisis. Different types of plastics including polyvinyl chloride (PVC), polypropylene (PP), (PE), polystyrene (PS), polyethylene and polyethylene terephthalate (PET) can be converted through the application of alternative energy-driven catalytic processes into products such as H2, chemical feedstocks, newly functionalized polymers and other fuels. In this review, several approaches to plastic recycling have been discussed but due to the growing trends of environmental concerns, the use of emerging alternative technologies to supply energy such as mechanochemical approaches (Tze-Gang et al., 2023), photo-reforming (Gazi et al., 2019) as well as microwave (Esun et al., 2023; Myren et al., 2023) and plasma reactors have been considered for the depolymerization of plastics. The use of bio-inspired catalyst which include polymer digestion by enzymes and also the efforts to use alternative solvents, such as supercritical fluids (e.g. H<sub>2</sub>O and CO<sub>2</sub>), or ionic liquids (ILs) and deep eutectic solvents are approaches attempted to address problems encountered in conventional methods. Catalytic chemical recycling of plastics under microwave irradiation and in supercritical fluids often lead to more homogenous temperature profiles throughout the reactor. This can lead to faster heating rates and a more controlled and selective reaction, due to similar reaction rates at all locations of the reactor. Reactions are also faster in several reported cases. For example, microwave reactors can lead to shortened reaction times during solvolysis, but the use of a catalyst is required to achieve high selectivity to monomers.

Mechanochemical *approach:* Mechanochemistry uses mechanical energy during chemical and physicochemical transformations. Mechanochemical procedures are usually environmentally friendly. In the past, mechanochemistry did not attract much attention but recently it has been demonstrated that mechanochemistry has immense advantages over conventional plastic recycling methods Boldyrev and Tkacova (2000) pointed out some of the advantages of mechanochemical procedures over conventional processes: a simplified procedure, an ecologically safe method since its operations do not use solvents and a possibility of making a product in the metastable state. Different types of plastics are being used and discarded on a daily basis. To recycle these plastic waste materials using the conventional technology, they need to be sorted and separated according to type and colour which may be difficult to achieve and time consuming. A solid-state shear pulverization (S<sup>3</sup>P) technology can be used to recycle these various mixtures of waste plastics which ordinarily will not be compatible by a shear force in the S<sup>3</sup>P in a continuous one-step process that converts faked or pelletized plastics to powder of different sizes. Tze-Gang et al. (2023) investigated the depolymerization of Polymers with low ceiling temperatures  $(T_c)$ . They demonstrated the generation of a low-T<sub>c</sub> polymer, poly(2,5-dihydrofuran) (PDHF), from an unsaturated polyether that contains cyclobutane-fused tetrahydrofuran, THF in each repeat unit. Upon mechanically induced cycloreversion of cyclobutane, each repeat unit generated three repeat units of PDHF which completely depolymerizes into 2,5-dihydrofuran in the presence of a ruthenium catalyst. The concept of mechanochemically regulating the Tc of polymers can be applied to develop next-generation sustainable plastics.

*Photocatalysis:* Photo-reforming is one of the promising emerging photocatalytic technologies that has attracted attention due to its cleanness and high efficiency. Photocatalysis offers a novel approach by not only mitigating plastic waste but also generating valuable chemical products because of its ability to harvest solar energy and convert it to  $H_2$ , other fuels, chemical feedstocks, and newly functionalized polymers with a high energy density and zero carbon emission. It involves oxidative breakdown of polymers into lower molecular weight materials in the presence of ultraviolet (UV) radiation (sunlight) and a photocatalyst which dominates the conversion process to generate  $H_2$  from an organic substrate and

water. The substrate acts as an electron donor and is oxidized by the excited photocatalyst to other organic molecules. The photo-generated electrons are then transferred from the photocatalyst to a co-catalyst and reduce water to H<sub>2</sub>. Given its high demand for chemical, agricultural, pharmaceutical and renewable energy applications H<sub>2</sub> is a particularly valuable product. Photocatalyst such as CdS/CdO<sub>x</sub>, (Uekert et al., 2018) CN/Ni<sub>2</sub>P (Uekert et al., 2019) and TiO<sub>2</sub>/Pt have been applied in plastic photo reforming to produce hydrogen gas. Unlike existing technologies for the depolymerization of plastics that requires high thermal energy, photo reforming reactions can be conducted at ambient temperature and pressure, uses sunlight as its only energy input and produces fuelcell-grade H<sub>2</sub> with other valuable chemical products (Uekert et al., 2018, 2019; Gazi et al., 2019).

Microwave-Assisted Catalysis: Microwave-assisted conversion provides an efficient route for recycling

plastic waste compared to conventional strategies of plastic waste management (Bäckström et al., 2017). Microwave irradiation is a rapid, efficient, and environmentally procedure friendly that depolymerizes plastic wastes. This method of recycling waste plastics accelerates the chemical reactions by reducing the reaction time and reaction temperature, thus acquiring higher chemo-selectivity and production (Arias, 2021). Esun et al. (2023) implemented microwave heating in PET glycolysis using ZnO as catalyst. They demonstrated that ZnO catalysts are highly active and selective for the glycolysis of PET to produce bis(2-hydroxyethyl) terephthalate, achieving more than 95 % yield in less than 10 minutes. The ZnO-catalysed glycolysis have lower global warming potential than the conventional petrochemical-based production and homogeneouscatalysed glycolysis.

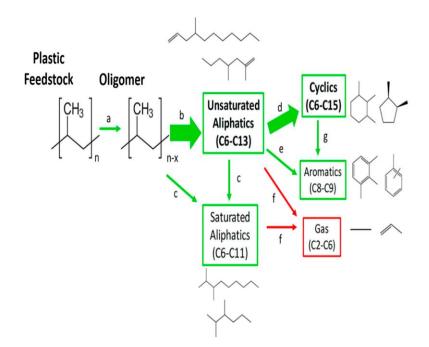


Fig.3: Potential reaction scheme of converting polypropylene via supercritical water depolymerization process. A green box represents oil phase products and a red box denotes gas products. The thickness of arrows represents the relative amounts of products (Chen *et al.*, 2019).

depolymerisation: *Supercritical* fluid Another method of waste depolymerization is plastic supercritical water depolymerization. It is a thermochemical process, which usually requires moderate temperatures (≥374.15 °C) and pressures (≥22.129 MPa) (Miao et al., 2021) since it does not involve a phase change. As the reaction conditions approach the critical point of water, its properties such as density, ionic strength, dielectric constant, and heat/mass transport coefficients are rapidly changed. Especially, the rapid change of density

correlates with other macroscopic properties to reflect changes at the molecular level, such as viscosity, molecular diffusivity, and solvation power (Peterson *et al.*, 2021). These significant changes enable the supercritical water to give rise to fast, selective, and efficient reactions to convert plastic wastes to monomers, as compared to conventional depolymerization methods (Kraft *et al.*, 2021). Watanabe *et al.* (1998) performed the conversion of low-density polyethylene (LDPE) using supercritical water. Polyethylene conversion was around 30% under the following reaction conditions: temperature of 400 °C, pressure of above 30 MPa, and reaction time of 30 min. Chen et al. (2019) recently converted polypropylene (PP) into oil using supercritical water (Fig 3). The experiments were carried out at: 380-500 °C and 23 MPa over a reaction time of 0.5-6 h, and up to 91 wt% of PP was converted into oil at 425 °C with a 2–4 h reaction time or at 450 °C with a 0.5– 1 h reaction time. Their investigation also claimed higher reaction temperatures (of > 450  $^{\circ}$ C) and longer reaction times (>4 h) leading to more gas products. The components of oil are about 80-90 wt% and have the same boiling point range as naphtha (C5-C11) with a heating value of 48-49 MJ/kg. The oil derived from PP has the potential to be used as gasoline blend stocks or feedstocks for other chemicals and the conversion procedure has a low greenhouse gas emission than conventional methods. Additionally, these researchers summarized the potential reaction pathways of major intermediates in the conversion process, as shown below. PP was quickly decomposed into oligomers at short times (<0.5 h) at the temperature of 425 °C. When the reaction time was further increased (from 0.5 to 4 h), majority of the unsaturated aliphatic were transformed into cyclic via cyclisation. During the same period, small amounts of unsaturated aliphatic (olefins) became saturated aliphatic (paraffins) and aromatics.

*Conclusions:* The utilization of plastic is increasing all over the world, and the problem of plastic waste generation is a growing concern but despite their problems, plastics provide benefits to our daily lives. However, plastic recycling presents a promising solution. Catalytic recycling, in particular, offers advantages such as increased yield, reduced reaction time, and narrower product distribution. In order to increase plastic recycling, strong infrastructure for separate waste collection and well-functioning markets for recycled plastics are essential. If recycling of these plastics is embraced and prioritise, we can mitigate environmental pollution, conserve resources, and promote sustainable development.

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*Data Availability Statement:* Data are available upon request from the first author or corresponding author or any of the other authors

### REFERENCES

Abosede, AA; James, A O; Vincent, EE (2018). Catalytic cracking of polyethylene plastic waste using synthesised zeolite Y from Nigerian kaolin deposit. Appl. Petr. Res., 8: 211–217. https://doi.org/10.1007/s13203-018-0216-7

- Aguado, J; Serrano, DP; Sotelo, JL; Van Grieken, R; Escola, JM (2001). Influence of the operating variables on the catalytic conversion of a polyolefin mixture over HMCM-41 and nanosized HZSM-5. *Ind. Eng. Chem. Res.*, 40: 5696–5704.
- Albertsson, AC; Hakkarainen, M (2017). Designed to degrade. *Sci.*, *358*, 872–873.
- Al-Salem, S; Lettieri, P; Baeyens, J (2009). Recycling and recovery routes of plastic solid waste (PSW): A review. *Waste Manage*. 29: 2625–2643.
- Al-Salem, SM; Antelava, A; Constantinou, A; Manos, G; Dutta, A (2017). A review on thermal and catalytic pyrolysis of plastic solid waste (PSW). J. Environ. Manag., 197: 177–198.
- Alzuhairi, MAH; Khalil, BI; Hadi, RS (2017). Nano ZnO catalyst for chemical recycling of polyethylene terephthalate (PET). *Eng. Technol. J.*, 35A(8): 831–837.
- Arias, JJR; Thielemans, W (2021). Instantaneous hydrolysis of PET bottles: An efficient pathway for the chemical recycling of condensation polymers. *Green Chem.*, 23: 9945–9956.
- Bäckström, E; Odelius, K; Hakkarainen, M (2017). Trash to treasure: Microwave-assisted conversion of polyethylene to functional chemicals. *Ind. Eng. Chem. Res.*, 56: 14814–14821.
- Bernard, W; da Silva, MN; Brooker, J; Wallace, S; Gunawan, K; Dickson, JA; MacLeod, KM (2021). Catalytic depolymerization of waste polyolefins by induction heating: Selective alkane/alkene production. *Ind. Eng. Chem. Res.*, 60: 15141– 15150.
- Briassoulis, D; Pikasi, A; Hiskakis, M (2019). Endof-waste life: Inventory of alternative end-of-use recirculation routes of bio-based plastics in the European Union context. *Crit. Rev. Environ. Sci. Technol*, 49(20): 1835–1892.
- Budsaereechai, S; Hunt, AJ; Ngernyen, Y (2019). Catalytic pyrolysis of plastic waste for the production of liquid fuels for engines. *RSC Advances*, 9: 5844–5857.

- Chen, D; Yin, L; Wang, H; He, P (2014). Pyrolysis technologies for municipal solid waste: A review. *Waste Manag.*, 34: 2466–2486.
- Chen, L; Nohair, B; Zhao, D; Kaliaguine, S (2018). Highly efficient glycerol acetalization over supported heteropoly acid catalysts. *Chem. Cat. Chem.*, 10: 1918–1925. https://doi.org/10.1002/cctc.201701656.
- Chen, WT; Jin, K; Wang, NHL (2019). Use of supercritical water for the liquefaction of polypropylene into oil. ACS Sus. Chem. Eng., 73749–3758.
- Estahbanati, MRK; Kong, XY; Eslami, A; Soo, HS (2021). Current developments in the chemical upcycling of waste plastics using alternative energy sources. *Chem. Sus. Chem.*, 14(19): 4152–4166. <u>https://doi.org/10.1002/cssc.202100874</u>.
- Esun, S; Yuquing, L; Maranthi, J; Raul, FL; Sionisious, GV (2023). Microwave-assisted depolymerization of PET over heterogeneous catalysts. *Cat. Today*, 418: 114124.
- Evode, N; Qamar, SA; Bilal, M; Barceló, D; Iqbal, HMN (2021). Plastic waste and its management strategies for environmental sustainability. *Case Stud. Chem. Environ. Eng.*, 4: 100142. https://doi.org/10.1016/j.cscee.2021.100142.
- Francis, R (2016). *Recycling of Polymers: Methods, Characterization and Applications*. John Wiley & Sons.
- Fukushima, K; Coulembier, O; Lecuyer, JM; Almegren, HA; Alabdulrahman, AM; Alsewailem, FD; McNeil, MA; Dubois, P; Waymouth, RM; Horn, HW. *et al.* (2011). Organocatalytic depolymerization of poly (ethylene terephthalate). *J. Polym. Sci., Part A: Polym. Chem.*, 49: 1273–1281.
- Gazi, S; Đokić, M; Chin, K. F; Ng, PR; Soo, HS (2019). Visible light-driven cascade carboncarbon bond scission for organic transformations and plastics recycling. *Adv. Sci.*, 6(24): 1902020.
- Geyer, R.; Jambeck, JR; Law, KL (2017). Production, use, and fate of all plastics ever made. *Sci. Adv.*, 3(7): e1700782.
- Hopewell, J; Dvorak, R; Kosior, E (2009). Plastics recycling: Challenges and opportunities. *Philos. Trans. R. Soc. B, Biol. Sci.*, 364: 2115–2126.

- Kamber, NE; Tsujii, Y; Keets, K; Waymouth, RM (2010). The depolymerization of polyethylene terephthalate (PET) using N-heterocyclic carbenes from ionic liquids. *Chem. Educ.* 87, 519–521.
- Karayannidis, GP; Achilias, DS (2007). Chemical recycling of poly(ethylene terephthalate). *Macromol. Mater. Eng.*, 292: 128–146.
- Kraft, S; Vogel, F (2017). Estimation of binary diffusion coefficients in supercritical water: Mini review. *Ind. Eng. Chem. Res.*, 56: 4847–4855.
- Lamberti, FM; Román-Ramírez, LA; Wood, J (2020). Recycling of bioplastics: Routes and benefits. J. Polym. Environ., 28: 2551–2571. https://doi.org/10.1007/s10924-020-01795-8.
- Maitlo, G; Ali, I; Maitlo, HA; Ali, S; Unar, IN; Ahmad, MB; Bhutto, DK; Karmani, RK; Naich, SUR; Sajjad, RU, *et al.* (2022). Plastic waste recycling, applications, and future prospects for a sustainable environment. *Sustainability*, 14, 11637.
- Miao, Y; von Jouanne, A; Yokochi, A (2021). Current technologies in depolymerization process and the road ahead. *Polymers*, *13*, 449. https://doi.org/10.3390/polym13030449.
- Millet, H; Vangheluwe, P; Block, C; Sevenster, A; Garcia, L; Antonopoulos, R (2019). The nature of plastics and their societal usage. In *Plast Environ* 1–20). Royal Society of Chemistry.
- Norbert, M; Chunfei, W; Paul, TW (2017). Pyrolysis of waste plastics using catalysts: Activated carbon, MCM-41, and HZSM-5. *IJCEA*, 8(1): 30– 34.
- Nunes, CS; Vieira da Silva, MJ; da Silva, D. C; dos Reis Freitas, A; Rosa, FA; Rubira, AF; Muniz, EC (2014). PET depolymerization in supercritical ethanol catalyzed by [Bmim][BF4]. *RSC Adv.*, 4, 20308.