Review

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Recent Progress in Plastic Transformation and Depolymerization Techniques

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Review

Recent Progress in Plastic Transformation and Depolymerization Techniques

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Abstract: Plastic polymers derived from petroleum exhibit diverse physical properties, ranging from flexible to rigid, permeable to impermeable, and hydrophilic to hydrophobic. However, when discarded improperly, they become a significant problem. Plastic pollution poses a threat to the planet, affecting various ecosystems, including terrestrial environments, rivers, lakes, oceans, and underground freshwater sources. These ecosystems are polluted with ropes, fishing nets, syringes, plastic bottles, and garbage bags. This issue is closely linked to the incredible versatility of these materials, whose continuous growth in production is driven by their market value. The current linear production and consumption of plastics are unsustainable and result in excessive waste. This waste is poorly managed, leading to pollution and carbon dioxide emissions that undermine global climate goals and the Sustainable Development Goals (SDGs). While some macroplastics are mechanically recycled, others are incinerated, and a significant portion ends up in the environment. Strategies for transforming and depolymerizing plastics offer potential pathways for future reuse. In this article, we explore the latest alternatives for the transformation and depolymerization of macroplastics through processes such as pyrolysis and hydrogenolysis.

Keywords: Polymer; pyrolisis; sustainability; macroplastic; microplastic

1. Introduction

Plastics have been the great solution humanity found for more efficient materials. In nature, there is no solution that creates a problem, as they do not survive natural selection.

Macroplastic waste continues to accumulate in the environment and scientists are focused on finding ways to reuse it as a raw material for producing valuable chemical compounds for the materials and fuels industry. It's hard to disagree about the benefits provided by plastics when used and disposed of properly, yet citizens are dissatisfied with collection and recycling rates below 9% for macroplastics, short of the stipulated 30% target needed to achieve a circular economy. Industrial technologies for the mechanical and chemical recycling of plastics are cost-effective, sustainable, use abundant raw materials, have high economic yields and minimal waste. Whatever the method of reusing the huge amount of macroplastics scattered around the world, there is growing interest in recycling plastics or transforming them into chemical products that can be used in other reactions, as they are high added value waste [1]. From discarded waste, mechanically recycled and remanufactured plastics become new polymers for reuse, but mechanical recycling results in lower quality materials.

In 2019, IUPAC began to envision the future of chemistry and launched the series entitled "Top Ten Emerging Technologies in Chemistry", as part of an effort to widely promote the essential value of the chemical sciences and related fields, seeking to identify discoveries with the potential to transform our world [2]. The series continued and from 2020 to 2023 [3,4], there were suggestions and opinions, presenting several challenging ideas for the development of new technologies capable of significantly impacting our society. In 2023, for the first time, IUPAC selected two topics related to

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plastic recycling: "Biological recycling of PET" and "Depolymerization plastic waste" to produce reusable building blocks, which include monomers, oligomers or other value-added chemicals.

Many polymers are used in the manufacture of plastics, with the most common being used mainly in the production of parts and utensils (Figure 1). Monomers, the basic building blocks of polymers, after being grouped together and processed, usually using heat, are transformed into their final commercial form (e.g., packaging, furniture, parts, toys, household utensils, disposables, etc.). The most used polymers are polyethylene (PE) (**1**), polypropylene (PP) (**2**), polystyrene (PS) (**3**) and polyethylene terephthalate (PET) (**4**).

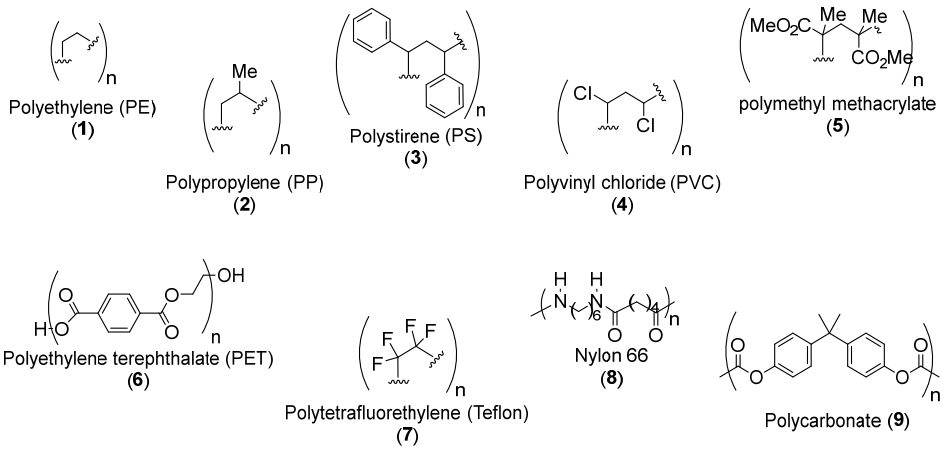

Figure 1. Main polymers used in plastics manufacturing.

Discarded macroplastics should not be considered waste, but valuable resources for new uses, such as the production of fuels, alcohols, aldehydes, surfactants, and detergents, among other possible materials [6]. This cycle of reuse is called the circular economy of plastics, and it generates high added value for these materials, reducing the consumption of oil derivatives and the environmental impacts of this industry through reuse, recycling, and chemical transformation into other products. It's important to note that not all plastics can be recycled and therefore end up losing economic value, awaiting the development of technologies for their recovery [7]. The recovery process and use of macroplastics includes the initial stages of collection, separation, processing, and marketing to prevent them from ending up in landfills, rivers, lakes, and oceans. These steps are essential parts of a city's waste management by both the public sector and civil society and are crucial for the success of any project aimed at recycling these materials that infest the environment. Figure 2 schematically shows the rates of recycling, dumping, and incineration of plastic waste consumed globally. [8].

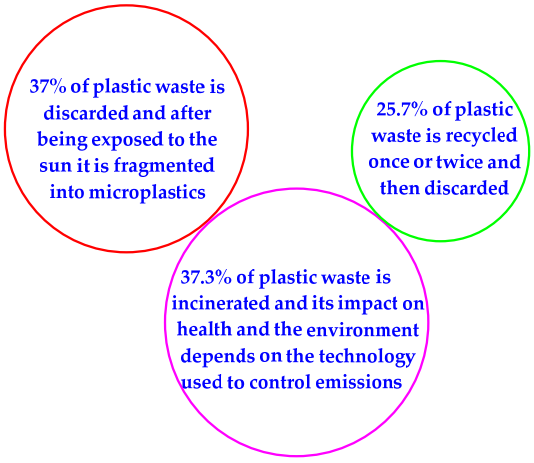

Figure 2. Options and rates for recycling, dumping, and incinerating plastic waste.

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An alternative to reducing the amount of macroplastics is to transform them into other valuable goods and services. For example, combustion can be used to produce thermal or electrical energy ('waste to energy'). [9]. Macroplastics are derived from oil and are therefore a valuable energy source compared to coal or other fossil fuels. In reality, much of the plastic discarded after use is incinerated in many countries to produce thermal or electrical energy using cement kilns or fluidized bed furnaces [10]. However, these processes contribute to an increase in atmospheric CO_2 and particulate matter in the air, as the plastic waste stream is mixed and heavily contaminated with other materials, including metals [11]. In addition, the combustion of plastics overlooks the fact that polymers could serve as raw materials for the production of other chemical materials with properties different from the originals [12].

Considering the future of the planet, we need to shift from a linear economy to a circular economy for plastics with zero waste, in other words, a carbon-neutral economy. The circular economy involves continuously reusing plastics, with various strategies for recovering macroplastics. (Figure 3).

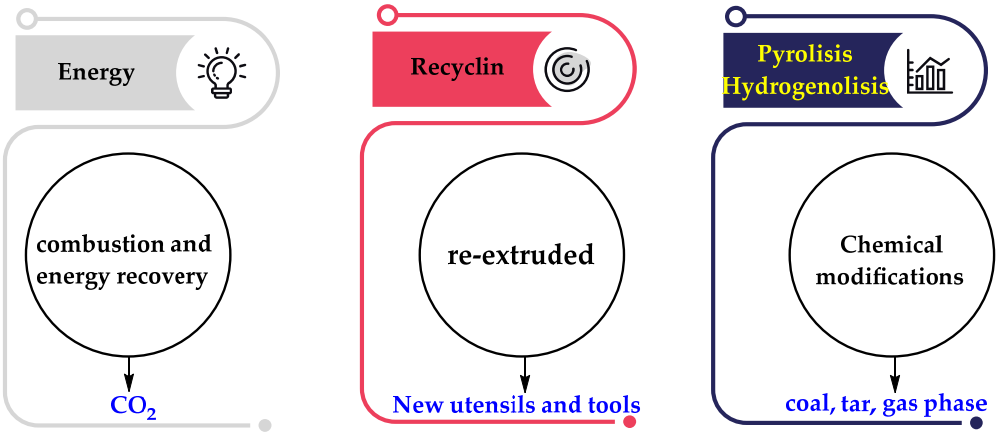

Figure 3. Strategies for the recovery of macroplastics.

Recycling, re-extrusion or mechanical recycling is a type of primary recycling that uses discarded macroplastics (mainly poly-α-olefins) [14]. This process stimulates the circular economy by keeping the polymers within their original carbon chain, allowing them to be reused in the manufacture of other products and reducing the pressure on oil production [15,16].

Chemical recycling, on the other hand, is appealing because it generates higher value-added products through various types of chemical conversions. Currently, chemical recycling is mostly limited to condensation polymers and requires large volumes of plastics to be profitable. Among the applicable methods, depolymerization, a process that began a few years ago, is gaining increasing prominence in the utilization of macroplastics [17], with the search for new procedures and new catalysts being expanded due to the crisis of environmental pollution by macro- and microplastics.

There are two alternatives for the chemical transformation or cracking of polyolefins: pyrolysis and hydrogenolysis. Both approaches promote the cleavage of polymeric chains and generate heterogeneous mixtures of polyolefins, and are carried out in reactors under pressure, heating, an inert atmosphere and using metal catalysts. It is important to note that the catalytic processes used in oil cracking and lignin breakdown can be extended to polyolefin depolymerization, including alkane dehydrogenation/aromatization, transfer hydrogenation, and hydrogen cogeneration, as well as opportunities to use the polymer itself as a hydrogen source [18]. Figure 4 summarizes what is expected from the pyrolysis and hydrogenolysis processes. These aspects will be discussed below.

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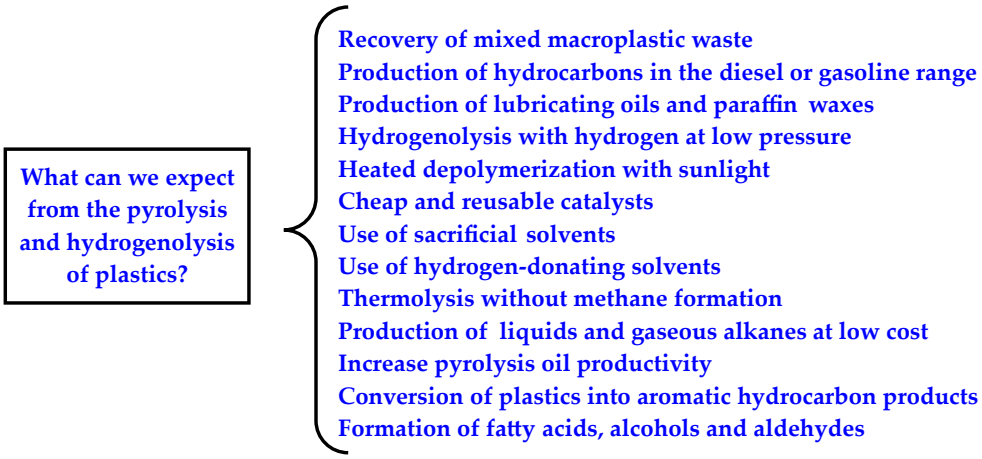

Figure 4. Objectives for depolymerization processes.

This article will only deal with chemical upgrading processes ("chemolysis") by pyrolysis and hydrogenolysis. It will not discuss the biochemical degradation of plastics or the production of biodegradable polymers.

2. Pyrolysis cracking

Pyrolysis is a thermochemical decomposition process that involves breaking down organic material at high temperatures (300-900 °C) in the absence of oxygen, with or without a catalyst, making it suitable for many waste products, including highly complex plastics. The removal of oxygen is crucial because its presence can lead to combustion rather than decomposition. Thermal pyrolysis involves simply heating plastics to induce the cleavage of their bonds and produce shorter-chain hydrocarbons, while catalytic pyrolysis is carried out with a catalyst to lower the temperature and reaction time. In general, pyrolysis offers the advantage of high degradation efficiency but has the disadvantages of high energy consumption, low product selectivity, and difficulty in studying the degradation mechanism. Both thermal and catalytic pyrolysis have been studied in various reactors (batch, semi-batch, fixed bed, fluidized bed, batch with fixed bed, rotary, etc.), using different materials that are important for the efficiency of plastic depolymerization processes [19].

Pyrolysis represents a promising technology for converting waste into renewable energy, aligning with sustainability objectives and the circular economy. It is being studied more extensively than hydrogenolysis due to its cost-effectiveness and practicality. The pyrolysis process is already used to convert organic biomass and various waste materials considered useless (such as agricultural waste, wood, plastics, and municipal solid waste) into biochar, bio-oil, and synthesis gas ('syngas'), thereby reducing the use of landfills and environmental pollution. Bio-oil can be refined to produce chemicals and other materials traditionally obtained from oil. However, it should be noted that pyrolysis has low efficiency for PVC [20]. The products obtained from the depolymerization of polyolefins, for example, vary according to the cracking conditions and the catalysts used (e.g., metal oxides, sulphated metal oxides, nanostructured zeolites, molecular sieves, metal carbonates, mesoporous materials, heterogeneous acids, zeolites, alumina, silica, etc.) [21]. The random splitting of C-C bonds into radicals generates complex mixtures of olefinic and cross-linked compounds.

In general, the pyrolysis depolymerization process produces three different phases, the proportion of which depends on the catalyst: a solid phase (coal or coke, 5-25% by weight), a liquid phase (tar, cycloparaffins, oligomers, aromatics, 10-45% by weight) and a gas phase (volatile alkanes and alkenes), all of which are used for various purposes. A problem in the recycling or chemical transformation of polymers is the contaminants (organic, inorganic, paper, halogens and metals) and various types of additives added to the plastics [22].

Polypropylene is very similar to polyethylene in that its structure only has C-H and C-C bonds. It is the second most used and discarded polymer and, therefore, the valorization of this material is extremely important to mitigate plastics in the environment.

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The concept of recycling and upgrading polyethylene, polypropylene, and other polymers into oils with low molecular masses and functional carbon chains has been studied by various research groups worldwide, yielding promising results for a future where plastics are valuable starting materials [23–27]. This idea has become increasingly urgent, as polyethylene waste accounts for approximately 30% of plastic waste. It is crucial to transform this waste into fuel oil, rich in alkanes, through catalytic hydrogenolysis of the C-C bond.

Thermocatalytic depolymerization of polyolefins is one of the most economically promising strategies for creating higher value-added products from plastic waste. As the chemical structures of polymers are very stable and have strong C-C bonds, it takes a lot of thermal energy, which is usually provided by pyrolysis above 300 °C under the influence of a catalyst and in the absence of air, to depolymerize them. Under these conditions, the polymers are fragmented into simpler units and this process can be applied to industrial and household plastic waste, transforming the polyolefins into gases, liquids and carbonized solid waste. The quality of the oil depends on the mixture of plastics, catalyst and the conditions used in the pyrolysis [28]. The oily liquids resulting from pyrolysis consist mainly of hydrocarbons in the diesel boiling point range (180-380 °C), amounting to approximately 50-55% by volume. However, these crude liquids are not suitable for use as diesel fuel, but if distilled in the diesel boiling point range they can be used in blends with conventional automotive diesel. In this way, the plastics can be reused in another form and no longer accumulate in the environment [29].

Ahmad et al. [30] obtained high selectivity for pyrolysis of high-density polyethylene (HDPE) in the liquid fraction using nanostructured $BaTiO_3$ doped with Pb at 350 °C, to provide alkanes (73.4%), olefins (22.5%) and naphthalene (4.1%). There are many other catalysts for hydrocracking polystyrene with high yields of oils, liquids and alkanes that can be used as lubricants, paraffin waxes or further processed into detergents and cosmetics [31]. Abbas-Abadi et al. [32] studied the continuous pyrolysis on a pilot scale of different raw materials at temperatures between 430-490 °C and pressures between 0.1 and 2.0 bar. At the lowest pressure, the yield of low-density polyethylene pyrolysis oil reached 95% conversion by weight and its composition was α-olefins (37-42%) and n-paraffins (32-35%). With polypropylene it was possible to form 84-91% iso-olefins (C9 and C15) and diolefins from oil. As for macroplastic waste, the pyrolysis oil yields were much lower and there was more char formation with metallic contamination. Whajah et al. [33] depolymerized polyethylene in high yields, induced by heating in the absence of hydrogen, at atmospheric pressure and with bifunctional catalysts based on zeolite containing dispersed Pt or Pt-Sn, obtaining hydrocarbons of up to 95% by weight after 2 h. The temperature of this process was 375 °C and the distribution of products ranged from light gas to hydrocarbons in the range of gasoline and diesel. Hafeez et al. [34] carried out the pyrolysis of plastics at a temperature range of 600-700 °C in a fluidized bed reactor on a Pt/Al_2O_3 catalyst, obtaining oils and waxes after 6-8 h. Conversion during hydrotreatment reduced the reactivity of the pyrolysis oil and promoted the production of diesel and kerosene.

Wang et al. [35] studied catalytic thermolysis associated with sunlight to transform a mixture of plastic waste using an abundant Ni-based catalyst. Solar energy can be an important source of radiation to produce sustainable and efficient plastic pyrolysis. The process used a mixture of plastic waste, containing five types of polyolefins, polyester, and polyvinyl chloride, converting them into methane with a carbon yield of 98% and HCl with a chlorine yield of 91%.

The catalytic pyrolysis process has thermodynamic limitations that hinder the adsorption of polymers to the catalysts to promote the cracking of the chains. Kang et al. tested catalytic reactions taking place inside mesoporous channels impregnated with Ru nanoparticles, allowing them to achieve an entropically more favorable stable transition state. This approach involves the synthesis of ruthenium catalysts distributed within mesoporous silica channels (SBA-15 <150 μm particle size, pore size 10 nm, hexagonal pore morphology). The design of the p-Ru/SBA-15 catalyst gave improved catalyst performance in the conversion of polyethylene into high-value liquid fuels, especially diesel. When the Ru/SiO_2 and Ru/C catalysts were evaluated, the mesoporous silica catalyst proved to be far superior in terms of solid conversion rate, providing a great opportunity for the chemical recycling of plastic waste [36].

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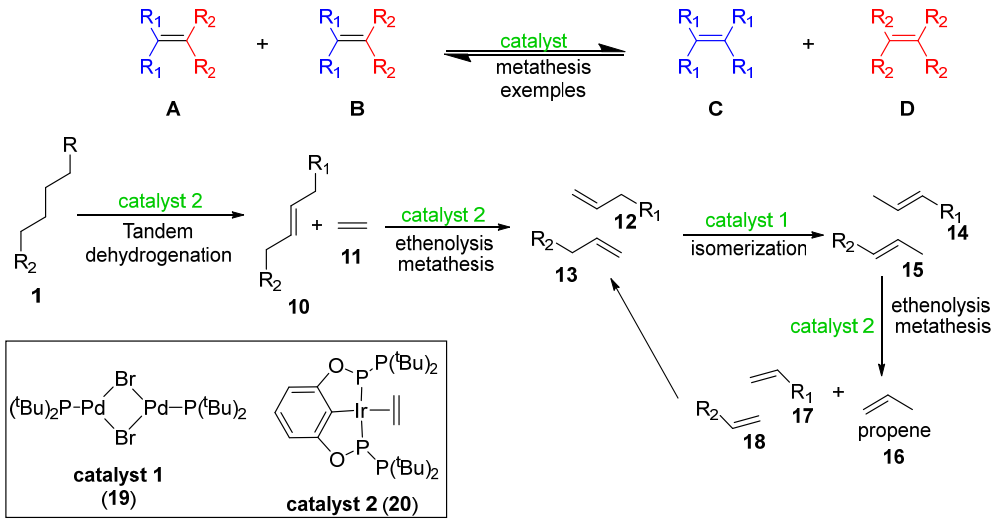
A very interesting strategy is the use of sacrificial solvents and co-fired hydrocarbons to cleave C-C bonds without the need to use hydrogen. In this field, Hancock and Rorrer carried out a very comprehensive review on the low-temperature depolymerization of polyolefins in the absence of hydrogen and the Tandem dehydrogenation and cross-metathesis of olefins for the depolymerization of polyethylene [37].

Cracking polyolefins in the presence of solvents provides benefits such as easier feeding of the reactants into the reactor and better heat and mass transfer. The presence of a hydrogen-donating solvent can improve the useful life of the catalyst and reduce the formation of coke residues. The catalytic cracking of polymers dissolved in solvents also allows higher value-added products to be obtained (e.g., tetralin, decalin, and methylcyclohexane) [38].

Wang et al. [39] developed an innovative strategy for the chemical conversion of polyethylene (**1**) via four catalytic reactions: dehydrogenation by Tandem reaction to introduce an unsaturation into the saturated polyethylene chain), ethenolysis (metathesis reaction [40] with ethene forming two terminal olefins), isomerization of the terminal olefin and new ethenolysis (new metathesis reaction with ethene forming propylene). In this method, which is detailed in Scheme 1, a large excess of ethylene is needed to achieve the ethenolysis events per polymer chain and shift the reaction equilibrium towards propylene. This recent experiment demonstrates that carrying out dehydrogenation, isomerization and ethenolysis simultaneously is a promising strategy for converting polyethylene plastic waste into propylene, a commodity with the second highest demand used as a raw material for the manufacture of polypropylene.



Scheme 1. Dehydrogenation/cross-metathesis/isomerization strategy to PE-PP conversion.

Xu et al. [41] reported a very relevant strategy for transforming polyethylene (**1**) and polypropylene (**2**) into fatty acids with an approximate conversion of 80% and average molar masses between 700 and 670 Daltons, respectively. The first stage is a temperature gradient pyrolysis that leads to the formation of waxes. The waxes are oxidized at the end of the chain with air and heating in the presence of manganese stearate, forming fatty acids (**21** and **22**) which can then be saponified to form soaps or surfactants (**23** and **24**) (Scheme 2). The authors point out that this process can be converted to an industrial scale with economic viability.

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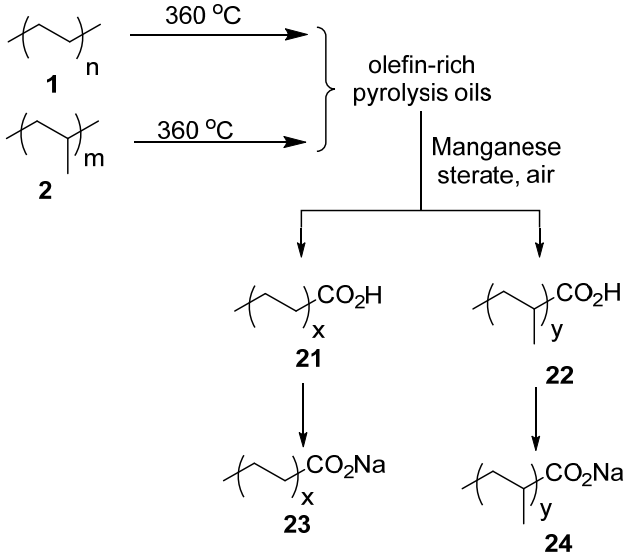
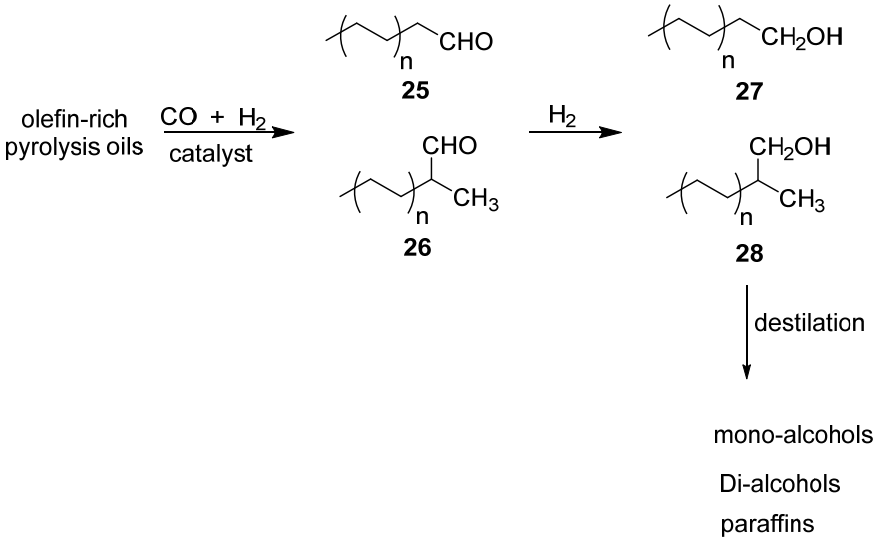


Scheme 2. Olefin-rich oil transformations from plastic pyrolysis.

As mentioned earlier, the pyrolysis of polyolefin waste used in plastic materials, in the absence of oxygen, can partially transform it into oils with high olefin concentrations. This oil can be a viable raw material for many new reactions. Considering that crude oil, natural gas, and naphtha have low olefin concentrations (3% by weight) these oils are relevant for fine chemicals. Within this context, Huber and collaborators prepared these pyrolysis oils with approximately 60% olefin by weight. This mixture was used to produce aldehydes through the hydroformylation reaction (Scheme 3) [42]. Briefly, the hydroformylation reaction involves the addition of synthesis gas ("syngas"), a mixture of CO and H_2, to olefins in the presence of a catalyst leading to the formation of aldehydes at carbon 1 (**25**) or carbon 2 (**26**) [43]. This reaction is very advantageous in terms of atomic economy, forming aldehydes on the terminal olefins selectively, valuable end products and intermediates in the synthesis of other chemical products such as alcohols, esters and amines. Regioselectivity can be controlled through the choice of catalyst and reaction conditions, making hydroformylation a versatile tool in synthetic organic chemistry. This route produces high value-added chemicals from post-consumer recycled polyethylene that can reduce greenhouse gas emissions. The aldehydes obtained from pyrolysis oils are abundant and are synthetic platforms to produce mono/dial alcohols by reduction or mono/dicarboxylic acids or mono/diamines by oxidative processes.



Scheme 3. Synthesis of alcohols from olefin-rich pyrolysis oils.

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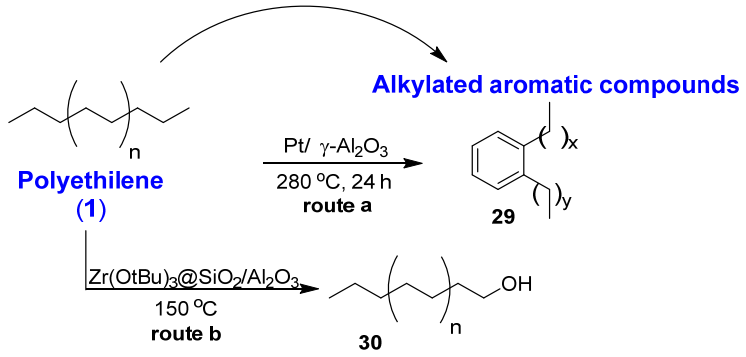
Zhang et al. [44] reported an innovative method in polyethylene cracking reactions: a one-pot low-temperature endothermic aromatization catalytic method. This method can convert polyethylene of different average molecular masses directly into liquid mixtures of valuable alkylated aromatic compounds (**29**) (Scheme 4, rote a). The heterogeneous catalyst used was Pt/Y-Al_2O_3 (0.200 g, containing 1.5% by weight of Pt dispersed as ~1 nm nanoparticles) at 280 °C (±5 °C). This method uses no solvent or H_2 and the liquid/waxy products reached 80% by mass and volatile hydrocarbons (15% by weight, approximately) demonstrating how waste polyolefins can be a viable raw material for generating aromatic hydrocarbons. Another innovative approach is the selective modification of the terminal methyl with hydrophilic groups on the carbon chains. This transformation can lead to many products for industrial applications. Zirconium-catalyzed reactions of saturated hydrocarbons with Zr(O*t*Bu)$_3$ lead to the formation of organoaluminium compounds that form alcohols when exposed to air. Kanbur et al. [45] showed that the Zr(O*t*Bu)$_3$@SiO_2/Al_2O_3 catalyst is capable of catalytically illuminating the terminal C-H bond of polyethylene at 150 °C followed by exposure to air to provide n-dodecanol (**30**) as the main product, revealing selectivity for activation of the methyl group without significant chain breakage, allowing C-H illumination of the methyl group of polyethylenes, polypropylene, polystyrene and poly-α-olefin oils. This reaction was tested with various polyolefins and yielded an oil with 68% of chains containing alcohol functionality after treatment of the reaction medium (Scheme 4, rote b).



Scheme 4. Transformation of polyethylene into polyalkylated aromatic compounds.

3. Cracking with Hydrogenolysis

In recent years there have been many publications exploring catalytic hydrogenolysis (pyrolysis under a hydrogen atmosphere) using various catalysts and which are the focus of large companies because it is a profitable investment and a solution to the serious plastics crisis [46,47]. Hydrogenolysis or hydrocracking is a reductive catalytic method for deconstructing polyolefin waste from plastics. It is a viable technology for recycling, especially for polyethylene and polypropylene. The issue lies in the yield of transforming these macroplastics into fuel oil with a high oil yield and preferably similar to diesel fuel (Scheme 5). Zheng et al. listed various types of catalysts used by 2022 in catalytic hydrogenolysis for various types of plastics. Most of the catalysts used zeolites as solid support (Ni/Co in montmorillonites, BaO, zeolite HZSM-5, Fe-modified with zeolite ZSM-5, zeolite Fe(3)-HY, zeolite, Fe/Al_2O_3 zeolite, ZnO zeolite, NiO/HY zeolite, SiC foam on ZSM-5, modified Mordenite, laboratory-synthesized ZSM-5 zeolite, ZAP USY zeolite, activated carbon) [48].

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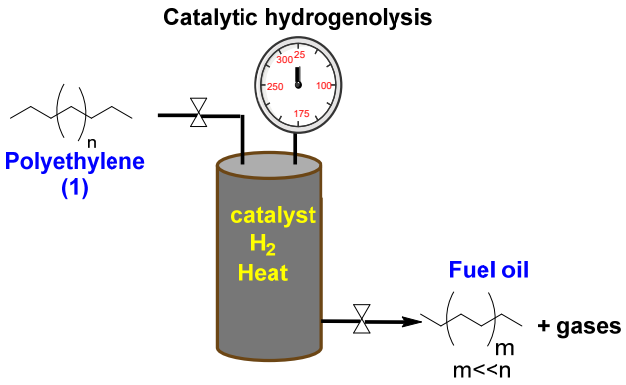

Scheme 5. General diagram of a polyethylene hydrogenolysis reactor.

More recently, other types of catalysts have been studied. The most recent catalysts and their performance in hydrogenolysis to recover plastic waste are presented below.

Celik et al. [49] studied the hydrogenolysis of polyethylene with H_2 at 170 psi and 300 °C catalyzed by Pt nanoparticles dispersed in ($Pt/SrTiO_3$) without solvent. Under these conditions, polyethylene (Mn = 8,000-158,000 Da) is converted into high-quality oil (Mn = 31,000 Da) that can be used as lubricants and waxes. Ruthenium is the metal used in the most active hydrogenolysis catalysts, but it is an expensive metal and produces a lot of methane. Wang et al. [50] explored the activity and economics of ruthenium-modulated tungsten zirconia (Ru-WZr) in the hydrogenolysis of low-density polyethylene and found that the deconstruction rate is fast and produces oil in the diesel range and under mild conditions (523 K and 50 bar H_2 for 2 h). The Ru-WZr catalyst significantly suppresses methane and produces a distribution of heavier carbon products that are valuable for fuel and wax/lubricant base oil. Catalytic hydrogenolysis has the potential to convert HDPE, which comprises around 30% of plastic waste, into valuable alkanes. Most research has focused on increasing the activity of laboratory-grade HDPEs that have a low molecular weight, with limited understanding of product distribution. No efficient catalysts are available for consumer products due to their lower reactivity. This study targets HDPE used in bottle caps; a waste product generated globally at a rate of approximately one million units per hour.

Ultrafine ruthenium particles (1 nm) supported on titania (anatase) achieved up to 80% conversion to light alkanes (C1-C45) under mild conditions (498 K, 20 bar H_2, 4 h) and were reused for three cycles. Small ruthenium nanoparticles were critical to achieving relevant conversions, as activity decreased dramatically with particle size.

Jaydev et al. [51] also studied the catalytic hydrogenolysis of high-density polyethylene with ruthenium nanoparticles supported on titanium oxide and achieved 80% conversion to light alkanes (C1-C45) under mild conditions (498 K, 20 bar H_2, 4 h) and with reuse of the catalyst for three cycles. In another study, Rorrer et al. [52] studied ruthenium nanoparticles supported on carbon (Ru/C) as a heterogeneous hydrogenolysis catalyst which proved to be highly active in converting polyethylene macroplastic waste into liquid and gaseous alkanes. The hydrogenolysis of polypropylene in the absence of solvent under mild conditions (200-250 °C, 20-50 bar of H_2).

Zhao et al. [53] carried out catalytic hydrogenolysis of polyethylene with heterogeneous nickel-based catalysts at 280°C and a cold hydrogen pressure of 3 MPa. The Ni/SiO_2 supported catalyst showed the highest activity with up to 81.18% of hydrocarbons (C4-C22). The result is comparable to catalysts using noble metals producing iso-alkane in the C5-C32 range with conversion above 68%. Du et al. [54] carried out one-step solvent-free hydrogenolysis with skeletal rearrangements promoted by a catalyst of polyolefin plastic waste in high-value gasoline, diesel and light lubricants with highly branched chains. The use of the bifunctional Rh/Nb_2O_5 catalyst takes place under mild conditions. The metallic Rh disperses in the Nb_2O_5 (strong Brønsted acid) which breaks the long carbon chains. The β-scission of the alkylcarbenium ions increases the catalytic hydrogenolysis and isomerization of the polyolefins. This technology is economically viable and could accelerate the circular economy of plastics.

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Xu et al. [55] have also shown that it is possible to obtain synthesis gas with solar irradiation with the help of water. For example, commercial plastic bags could be efficiently photoconverted into renewable synthesis gas using Co-Ga_2O_3 catalyst nanosheets, with hydrogen and carbon monoxide formation rates of 647.8 and 158.3 $\mu mol.g^{-1}.h^{-1}$, respectively. Water is photoreduced into hydrogen while plastics are photodegraded into carbon dioxide, which is further selectively photoreduced into carbon monoxide.

Ni_2Al_3-catalyzed pyrolysis of mixed polyolefin plastics for 5 to 120 min at 250–310 °C transforms these polymers into natural gas with carbon gas yields reaching 89.6% [56]. The gradual catalytic cleavage of the C-C bonds in polypropylene occurs preferentially at the terminal C-C bond in the side chain, with a low energy barrier. The gas generated was composed of 99.9% CH4 and 0.1% C2-C4 hydrocarbons and the catalyst have good recyclability. This process of catalytic production of natural gas with polyolefin plastic waste is a more economically competitive process based on the current price of natural gas.

One of the challenges of fragmentation in polyolefin chains is the formation of methane (usually > 20%) during hydrogenolysis. Overcoming this limitation brings economic benefits when it comes to producing liquid fuels. Chu et al. [57] solved this problem by using a Ru single-atom catalyst supported on CeO_2 and demonstrated its efficiency in producing only 2.2% methane and a liquid fuel yield of over 94.5% at 250 °C for 6 h. This remarkable catalytic activity and selectivity of the catalyst in the hydrogenolysis of polyolefins offers immense opportunities for plastic recycling. Tomer et al. [58] also studied the hydrogenolysis of polypropylene waste to form lighter liquid hydrocarbons with the Ru/CeO_2 catalyst. The catalyst was used in the proportion of 2% by weight of Ru/CeO_2, in the crystalline nanocube form, forming the liquid phase between 34-58% (220 °C, 16 h, 30 bar H_2). Brandon et al. [59] succeeded in hydrogenolysis of polyethylene using Ni supported on SiO_2. This reusable catalyst is very active at moderate temperatures and under H_2 pressure (300 °C, 30 bar H_2). Its performance is comparable to catalysts based on Ru and Pt, but with the advantage of having a much lower cost. The maximum yields of liquid products were 65% by weight (n-alkanes, iso-alkanes, cyclics, aromatics, etc.). The cleavage mechanism is sensitive to the size of the chain and the breaking point of the C-C bond of the polyolefin (polyethylene, polypropylene, and polystyrene). The advantage of this procedure is its ability to hydrolyze polyolefin mixtures. Cobalt was also immobilized on SiO_2 to produce liquid range hydrocarbons (C5-C30) at 200-300 °C, 20-40 bar H_2 for 2-36 h with high selectivity from polyethylene. The liquid product yield was 55%, comprising 75% non-solid products, with gas yields limited to 19% approximately [60].

The platinum complex nanoparticle catalyst (Pt(II) acetylacetonate or trimethyl(methylcyclopentadienyl)platinum) supported by chemical insertion of organometallics on the surface of $SrTiO_3$ nanocuboids was able to promote the hydrogenolysis of polypropylene to provide liquid products with a narrow range of molecular dispersion [61]. These catalysts were obtained by calcination and had Pt nanoparticles of 1.0-1.5 nm deposited on the $SrTiO_3$ nanocuboids. These catalysts hydrogenolyzed polypropylene into liquid products in >95% yield with average molecular weights of 200-300 Da at 300 °C and 180 psi H_2.

Many inorganic materials or waste can be used as catalysts. Red mud is a by-product generated during the Bayer process of extracting alumina (aluminum oxide) from bauxite. Rahman et al. used this material, after drying, as a catalyst to increase the productivity of hydrogenolysis conversion of various plastic materials. The results indicated that the conversion to oil ranged from 14-80% (w/w) depending on the type of polymer [62].

4. Conclusions

Some end-of-life macroplastic waste can be recycled through mechanical processes, but this accounts for only about 25%. This is a current reality. The recovery of plastics through chemical recycling into chemicals, fuels, lubricants, and paraffin waxes is still under investigation. Two technologies have emerged as the most studied: catalytic thermal pyrolysis and catalytic hydrogenolysis. Both have been extensively researched in recent years to determine the best reaction conditions, applicability to various types of polymers, and the most economical and efficient

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catalysts. These technologies also offer prospects for producing fine chemical compounds, such as acids, alcohols, and aldehydes. These are crucial steps, but without a reduction in production and improvements in the selective collection of macroplastics, no progress will be made in addressing the global plastics crisis.

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