

Review

The Role of Catalysts in Waste Polymer Upcycling: Recent Developments and Future Trends

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Abstract: The increasing environmental burden of plastic and polymer waste necessitates transformative recycling strategies. This review explores the critical role of catalysts in enabling efficient chemical recycling and upcycling of synthetic and natural polymers with an emphasis on industrial innovations. Emphasizing catalytic depolymerization techniques—such as pyrolysis, gasification, oxidation, hydrocracking, hydrogenolysis, solvolysis, and enzymatic catalysis—the paper highlights recent advances in catalyst design and reactor technologies. This research highlights the interplay between polymer structure and catalyst selection, demonstrating how variations in backbone chemistry can shape catalytic pathways and ultimately affect material performance. Key developments include the use of metal-zeolite systems, metal-organic frameworks (MOFs), hybrid chemo-enzymatic pathways, and AI-optimized processes for selective and scalable conversion of plastic waste. The study outlines the potential of catalytic systems to enhance resource circularity by converting mixed or contaminated waste streams into valuable monomers, fuels, and chemicals. Emerging trends in AI-driven catalyst discovery and process optimization are also examined, positioning catalysis at the forefront of sustainable polymer waste management and circular economy innovation. Organized by depolymerization mechanism to highlight key catalytic pathways, this review integrates representative industrial applications to illustrate both recent breakthroughs and the varying technological maturity of scalable chemical recycling strategies for converting complex waste streams into valuable products.

Keywords: catalytic depolymerization; polymer upcycling; chemical recycling; circular economy; plastic waste valorisation; artificial intelligence

1. Introduction

The manufacture of chemicals and all of the countless articles of society that contain chemicals, faces a blizzard of issues from the desire to move away from non-renewable feedstocks, through the needs to make the chemical processing more efficient and less hazardous, to addressing the increasing environmental and societal pressures on many chemical products. Overall, the chemical industry needs to embrace the Circular Economy and minimise unsustainable inputs and unacceptable outputs. Polymers represent the largest volume use of chemicals, and as plastics, represent the greatest perceived threat of chemical products to the environment. Introducing circularity into the polymers and plastics sectors, is probably the best technical opportunity to demonstrate the potential for chemistry to drive a circular economy. We must find ways to minimise the harm caused by waste plastics, by maximising the reuse of waste polymers, and through chemical recycling we can simultaneously help alleviate the unsustainable demand for non-renewable (petroleum) feedstocks. Catalytic pyrolysis is one of the most important technologies for polymer waste valorisation. Catalytic gasification is one option to pyrolysis and is a relatively simple route to converting polymer wastes to chemical feedstocks. Oxidation is the most important chemical transformation for adding value to chemical feedstocks and its more



recent applications to polymer waste valorisation is an interesting development in the field. Catalytic hydrocracking and catalytic hydrogenolysis are also technologies in the area and are based on important basic chemistries with low costs and proven scalability. The best-established catalysts for many of the polymer waste valorisation technologies are zeolites although many other often heterogeneous catalysts are proving to be useful. Enzymes are less used by industry for chemical processes compared to chemical catalysts, but their natural status and their ability to achieve high selectivity in chemistry are increasingly important features and their use in waste polymer chemical valorisation is a promising development for the future. Some of the most recent and exciting developments in the catalytic chemical valorisation of waste polymers involve new catalysts and other process innovations. Waste is generally considered to be everything that no longer has a use or purpose and needs to be disposed. More formal definitions include “Any substance or object that the holder discards or intends or is required to discard” (UK Waste Framework Directive). To achieve end of waste status you require: (a) the substance or object is to be used for specific purposes; (b) a market or demand exists for such a substance or object; (c) the substance or object fulfils the technical requirements for the specific purposes and meets the existing legislation and standards applicable to products; (d) the use of the substance or object will not lead to overall adverse environmental or human health impacts.

Polymers can be either natural or synthetic and are created when small molecules, also known as monomers, combine chemically to form a larger network of connected molecules. The term is derived from the Greek prefix “poly-”, which means “many”, and the suffix “-mer”, which means “parts.” All plastics are polymers, but not all polymers are plastic. Plastic is a specific type of polymer. Plastics are synthetic and do not occur naturally. Most of the concerns associated with polymer waste are concerned with plastics but natural polymers can also end up as wastes. 0.3–0.4 billion tonnes of plastics are produced annually worldwide [1]. Plastics are a rapidly growing segment of almost all categories of municipal solid waste (MSW). The containers and packaging category has the most plastic tonnage including wraps, bags, and other packaging; polyethylene terephthalate (PET) bottles and jars; high-density polyethylene (HDPE) natural bottles; and other containers. Manufacturers also use plastic in durable goods, such as appliances, furniture, battery casings and other products. Plastics are present in non-durable goods other than packaging including disposable diapers, shower curtains, trash bags, single use (disposable) cups and cutlery [2]. The use of disposable plastic products increased rapidly as a result of COVID-19: in 2020 the global consumption of medical gloves and facemasks reached ca. 60 billion units per month [3]. The marine environment and its living organisms are particularly exposed to plastic waste contamination. Large and continuously increasing amounts of plastic products and debris are found in the open ocean, either on the surface or in the benthos of the deep seas, as well as in shorelines and living organisms [4]. Plastics alongside natural polymers are extensively used in clothing for example “Polycotton” is a mixture of cotton (natural polymer) and synthetic polyester. Textiles including clothing represent one of the greatest modern waste challenges but also present a significant opportunity in terms of chemical resource [5]. Globally 73% of the material that is used in clothing ends up in landfill or an incinerator with only 12% recycled. Those that are recycled are usually downgraded into cleaning cloths, mattress stuffing or insulation materials.

Challenges facing those seeking to valorise the polymers in waste textiles include: the wide range of garment types; the wide variety of materials in single garments (cotton, leather, metal, silk, as well as synthetic polymers); their flexibility, which makes pre-shredding that little bit more intensive compared to rigid plastics; the presence of large quantities of dyes and pigments; the complex composition of some fibres (i.e., polycotton being composed of PET and cotton); the chemical resistance of many fibres. Waste polymers both natural (cellulose) and synthetic (polyolefins) are major components of another major public waste stream, diapers. Disposable diapers are the third largest consumer waste in landfill and represent about 4% of total solid waste. In the US, ca. 4 million tons of diapers are disposed of every year with 80% going to landfill. The problem is worse in some countries where sanitary concerns lead to illegal dumping: in Indonesia for example, 21% of the waste in city waterways is diapers. The presence of chemical additives is a particular challenge here and include tributyltin (used as a biocide) which is toxic, dioxins (produced in the bleaching process) which are carcinogenic as well as adhesives, plasticizers and others [6]. Old carpets and rugs are another promising source of valuable polymeric materials notably wool, PET and other polyesters, and polypropylene although the strong glues used to bind the many components together can make separation very difficult. Some 2 million tons go to landfill every year [7]. Only 14% of plastic worldwide is recycled with the remaining incinerated (ca. 14%), landfilled (ca. 40%), or lost into the environment including marine pollution (32%) [8]. While over half of the polymers used today are polyolefins, they represent less than a half of the recycled polymers. Polyesters and especially PET, are by far the most recycled of all polymers (Figure 1):

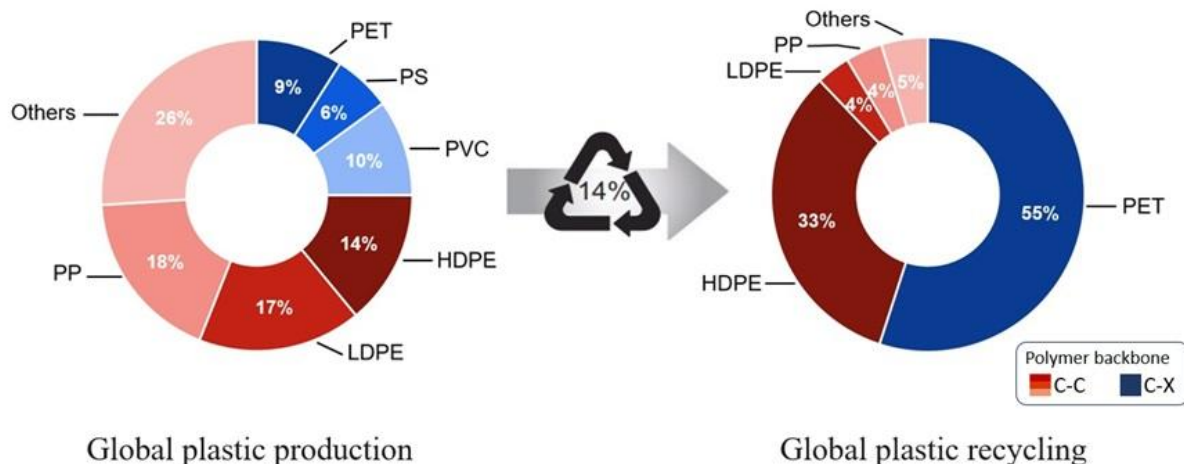


Figure 1. Global plastic production and recycling.

It is often cheaper to produce new polymers from virgin materials than to recycle and reuse existing materials especially given the difficulties in collecting and sorting often complex waste streams. Apart from the loss in resource, plastic waste is now considered to be a major environmental and likely health problem due to its ready conversion to microparticles that can easily migrate in the environment and can accumulate in living creatures including fish. The US EPA has a national strategy to prevent plastic pollution which has the Circular Economy concept at its heart. It has six main objectives: (1) Reduce Pollution from Plastic Production; (2) Innovate Material and Product Design; (3) Decrease Waste Generation; (4) Improve Waste Management; (5) Improve Capture and Removal of Plastic Pollution; (6) Minimize Loadings and Impacts to Waterways and the Ocean. Whereas in the Global North plastics production, use and recycling is regulated to varying degrees, in many developing countries plastic recycling is often not well controlled and environmental protection is poorly enforced, leading to major pollution and consequential health issues in places where exported waste is handled [9]. Uncontrolled recycling can also result in the transfer of potentially harmful substances into plastics for sensitive uses, such as children's toys and food contact materials.

In Europe, more plastics waste is destined for energy recovery (39.5%) (in EfW or via solid recovered fuels (SRF) recovered in cement kilns) than for recycling (29.7%). However, uncontrolled combustion of plastic waste and, in particular of those containing halogens such as, PVC, polytetrafluorethylene/Teflon, plastic containing brominated flame retardants, etc. can cause emissions of hazardous substances, e.g., acid gases and unintentional persistent organic pollutants (POPs) such as dioxins [10]. For the vast majority of plastic waste fractions including packaging, and from electronics, transport and construction sectors, labour or technology intensive sorting is needed in order to get a high quality recyclate [11]. In most cases secondary recycling applies, in which used plastics are cascaded into material applications different than the original, and often of less demanding material specifications (i.e., PET bottles into fleece and trainers). Chemical valorisation of plastic waste is a relatively immature field though growing in importance due to the increasing costs of virgin chemicals and thus the added value of recyclates. The economic viability of polymer waste recycling depends on whether the products obtained can offset the costs of recycling, sorting and processing [12]. This is made worse for physical recycling as the properties of most plastics are significantly compromised after several processing cycles. Chemical recycling gets around that problem if the problems of additives can be dealt with especially as some of these can reduce the catalyst lifetime by blocking active sites. In plastic materials used in most products the basic polymer is incorporated into a formulary (plastic compound) with different "additives", which are chemical compounds added to improve the performance (e.g., during shaping of the polymer, through injection moulding, extrusion, blow moulding, vacuum moulding), functionality and ageing properties of the polymer. The most commonly used additives in different types of polymeric packaging materials are plasticizers, flame retardants, antioxidants, acid scavengers, light and heat stabilizers, lubricants, pigments, antistatic agents, slip compounds and thermal stabilizers. Each of them plays a distinct role in delivering/enhancing the (final) functional properties of a plastic product. The company Neste is an example of a major company that have significantly increased their efforts in chemical recycling of plastic wastes. Their processing runs recently exceeded 2 kT for increased capacity to 150,000 T of liquefied plastic waste per year is planned with an ultimate target of 400 kT pa. They have processing stages are (i) pretreatment, (ii) upgrading and (iii) refining [13]. A new plant for chemically depolymerising various of plastics using supercritical water will process 23 kT pf waste

per annum with more capacity expected through new plants in countries including USA, Germany, Singapore and Japan [14]. Chemical technologies are emerging that can handle mixed plastic waste. Even plastic waste that is of such poor quality that is not suitable for mechanical recycling, can be used. This avoids downcycling to energy or the worst option of landfill and means less crude petroleum is needed for chemical manufacture. The Finnish research and innovation organisation VTT has licensed such technology to the US based Refinity and together they will work on optimising the technology to divert poor quality mixed plastics to chemical valorisation [15]. Natural polymers include polysaccharides and polypeptides. cellulose (i.e., cotton) and starch (i.e., cornmeal) are among the largest volume natural materials on earth. Natural polymers can also represent a large waste issue. While they are biodegradable, the presence of additives including dyes and the increasing use of cotton as part of fabric formulations such as “polycotton” as well as starches as part-components of food waste, means that these natural polymers can offer a waste valorisation opportunity. A global coalition of packaging and material companies is calling on UN Treaty makers to recognise natural polymer materials as a key tool in the fight against plastic pollution [16]. A real but largely unexploited opportunity is to valorise the polymer components of textile waste. This includes materials made solely from natural polymers, such as wool-based textiles, as well as those containing a mixture of natural and synthetic polymers, such as polycotton, which has become one of the most widely used materials in clothing. Most fabrics are composed of materials containing nearly 70% polyester, with PET being the most important. The total waste generated by the industry has been estimated at 92 million tons, with very little being upcycled into chemicals [17]. Used tyres are another enormous global waste problem that could be turned into a major chemical resource opportunity. Worldwide, around 1 billion vehicle tyres reach the end of their life in terms of performance and safety. Tyres are complex materials and typically contain natural and synthetic polymers as well as carbon black, silica, steel and numerous additives. While many regions have banned their disposal in landfills due to environmental and health risks, many are stockpiled and those that are valorised are downcycled to the production of rubber granulates for use in recreational areas. However, the growing concerns about microplastics will make such uses unacceptable. We desperately need innovative recycling solutions and in particular, we need to find cost-effective ways to recover the chemical value in waste tyres [18]. Like waste textiles, waste tyres are recognised as a major and growing environmental burden yet with the right technologies they could be transformed into circular resources that could substitute, vast quantities of virgin resources notably non-renewable petroleum.

Moreover, recent developments in artificial intelligence (AI) and machine learning (ML) are reshaping the landscape of catalyst discovery and process optimization. These tools enable high-throughput virtual screening of catalyst candidates, prediction of structure–activity relationships, and data-driven modelling of reaction kinetics. In the context of plastic depolymerization, AI can help identify optimal catalyst formulations based on polymer structure, simulate reaction pathways, and fine-tune process parameters to enhance selectivity and yield. By significantly reducing the time and cost associated with experimental trial-and-error approaches, AI-driven methodologies are accelerating the development of efficient, scalable, and sustainable catalytic systems tailored for diverse and complex waste streams.

2. Discussion

2.1. The Role of Catalysts in Recycling and Upcycling Waste Polymers

Chemical recovery (tertiary recycling), involves chemicals, e.g., raw materials such as monomers, being recovered or synthesised from the waste polymer (plastic). This can potentially be done by catalytic depolymerisation (Figure 2) or by pyrolysis usually with a catalyst to help control the process.

The choice of catalyst in most processes for the chemical recycling of polymers can have a fundamental effect not only on the efficiency and energy demands of the process, but also on the chemistry. Catalyst design for plastic depolymerization must consider the chemical structure of the target polymer, as differences in backbone composition and bond dissociation energies critically influence reactivity and catalyst choice. For example, polyolefins like PE and PP feature strong, non-polar C–C bonds, requiring metal catalysts (e.g., Ni, Ru) often supported on acidic oxides or zeolites to promote hydrogenolysis under elevated temperatures and pressures. In contrast, polyesters such as PET contain more labile C–O and ester bonds, which are more readily cleaved under milder solvolytic or hydrolytic conditions using acid/base or redox catalysts (e.g., Co/Mn, Zn(OAc)₂). PS, with its aromatic rings, benefits from catalysts that enable selective cleavage of side chains or de-aromatization, such as Pt-based systems. These differences highlight the importance of tailoring catalytic systems to match polymer bond types, with bifunctional or hybrid systems increasingly used to combine hydrogenolysis, hydrocracking, or solvolysis steps. Incorporating structural considerations into catalyst design allows for improved selectivity, lower reaction temperatures, and more efficient depolymerization across diverse

plastic feedstocks. Catalysts are designed to optimize bond cleavage mechanisms, enhance product specificity, and maximize reaction efficiency, while maintaining thermal and chemical stability under harsh or variable conditions, in alignment with the key design considerations outlined in Table 1:

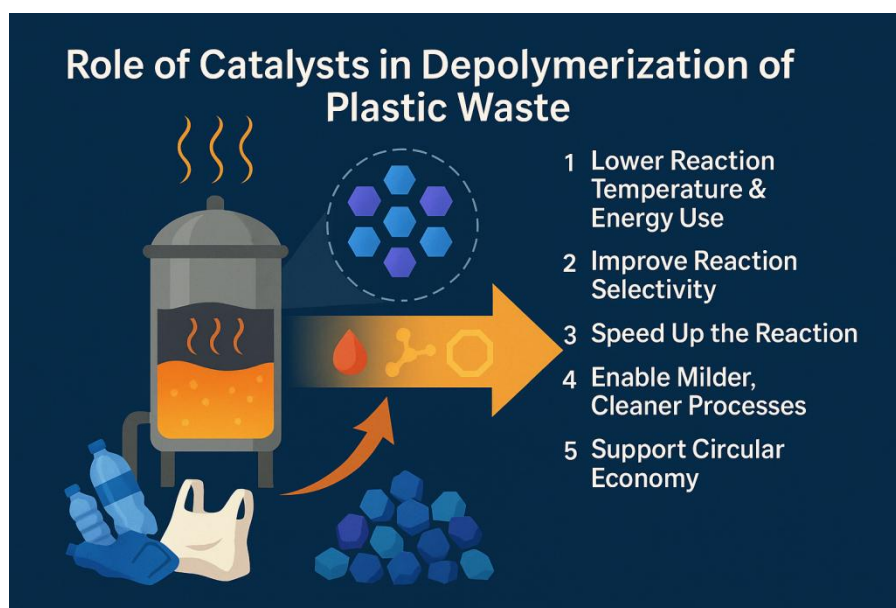


Figure 2. The role of catalysts in depolymerization of plastic waste. Image generated by the author using the AI tool ChatGPT (DALL·E).

Table 1. Typical catalyst systems used in the depolymerization of plastic waste, categorized by catalyst type. The table summarizes active components, support types, turnover frequency (TOF) ranges where available, and key notes on product selectivity and catalyst cyclic stability.

Catalyst Type	Active Components	Support Type	TOF (h^{-1})	Selectivity/Cyclic Stability
Zeolites	HZSM-5, Beta, Y-zeolite	Zeolite frameworks	Not typically reported	High selectivity to light hydrocarbons and aromatics; good stability
Metal Oxides	TiO_2 , CeO_2 , ZrO_2	Metal oxide matrices	Varies widely; often not reported	Moderate selectivity; high thermal stability
Transition Metals	Ru, Ni, Pt	Oxides, carbon, zeolites	$\sim 0.1\text{--}0.5$	High selectivity to specific monomers or fuels
Bimetallic Catalysts	Ni-Fe, Fe-Co, Ni-Cu	Oxides, carbon supports	$\sim 0.1\text{--}0.4$	Enhanced activity and selectivity due to synergy; moderate stability
Natural Catalysts	Montmorillonite, Kaolin	Naturally occurring minerals	Not defined	Moderate efficiency; environmentally benign
Carbon-Based Catalysts	Activated carbon, CNTs, graphene oxide	Carbon matrices or standalone	Not typically quantified	Good adsorption and cracking activity; recyclable
Acidic/Bifunctional Catalysts	Pt/ZSM-5, $\text{NiMo}/\text{Al}_2\text{O}_3$	Mixed oxide + zeolite	$\sim 0.2\text{--}0.5$	Good multifunctional selectivity; moderate cyclic stability
Ionic Liquids	[Bmim]Cl, cholinium ILs	Homogeneous phase	Not defined	Selective depolymerization (e.g., PET); not recyclable
Nanocomposites	Ni@SiO_2 , Fe@C, Ni-La-Pd	Inorganic/organic matrices	Varies; depends on composition	High dispersion and tailored activity; stable in some systems
Alkaline Earth Metals	MgO, CaO, K_2CO_3	Standalone or mixed supports	Not specified	Good basicity; moderate to high stability
MOFs	MIL-53, UiO-66, ZIF-8	Hybrid porous materials	Not typically reported	High surface area and tunability; variable stability

As shown in Table 1, the catalyst systems used for plastic waste depolymerization reflect a diverse range of materials and design strategies, each tailored to balance activity, selectivity, and stability under varying reaction conditions. Zeolites such as HZSM-5, Beta, and Y-type frameworks are widely recognized for their high selectivity toward light hydrocarbons and aromatic compounds, owing to their strong acidity and shape-selective microporosity, coupled with robust thermal stability. Metal oxides like TiO_2 , CeO_2 , and ZrO_2 provide versatile redox activity and high temperature resistance, offering moderate selectivity across various depolymerization pathways. Transition metals including Ru, Ni, and Pt, typically supported on oxides, carbon, or zeolites, achieve high selectivity toward specific monomers and fuel-range products, with reported turnover frequencies in the

range of 0.1–0.5 h⁻¹. Bimetallic catalysts such as Ni–Fe or Fe–Co leverage synergistic effects between metals to enhance activity and selectivity, though their stability may vary depending on the support and process environment. Natural mineral-based catalysts like montmorillonite and kaolin are environmentally benign and moderately effective, often serving as low-cost alternatives. Carbon-based catalysts, including activated carbon, carbon nanotubes, and graphene oxide, offer excellent adsorption and cracking activity, and can be reused due to their structural durability. Acidic and bifunctional systems—such as Pt/ZSM-5 and NiMo/Al₂O₃—combine hydrogenation and cracking functions, delivering broad chemical versatility with moderate cyclic stability. Ionic liquids such as [Bmim]Cl and cholinium-based solvents serve as effective homogeneous systems for PET solvolysis, though their recyclability remains limited. Nanocomposite catalysts, such as Ni@SiO₂ and Ni–La–Pd alloys, demonstrate high dispersion and tailored reactivity, while alkaline earth metals like MgO and CaO contribute strong basicity and notable thermal resilience. Metal-organic frameworks (MOFs), including MIL-53 and UiO-66, represent a highly tunable class of materials, with large surface areas and pore structures adaptable to different depolymerization targets, though their long-term stability can vary. Collectively, these systems underscore the importance of integrating catalytic function, structural support, and process compatibility to achieve efficient and scalable plastic waste valorization. Building on these foundational design principles, the selection and tuning of catalysts for specific depolymerization pathways—such as catalytic cracking or PET recycling—requires a nuanced understanding of how catalyst composition, acidity, and structure influence product distribution and process viability. For catalytic cracking, strongly acidic catalysts can generate alkylbenzenes and gaseous hydrocarbons while lower acidity catalysts tend to generate liquid fractions. Higher value base oils (for lubricants) for example, require carefully controlled acidity and benefits from using zeolites due to their controlled pore sizes. PET is a popular choice for catalytic chemical recycling and several depolymerisation methods have been reported. Numerous catalysts including several salts as well as some acids and bases have been used. Glycolysis and alcoholysis are by far the most common and most promising routes to PET depolymerisation due to the suitability of the products for re-polymerisation, as demonstrated by several companies including Green Lizard, Poseidon Plastics and Carbios. Zinc acetate and enzymes are among the catalysts of choice although more exotic catalysts have been reported, for example nickel-modified cobalt phosphate. The increasing quantity of PET in textiles is driving greater commercial interest in the chemical recycling of PET-rich materials, using techniques such as enzyme catalysis and microwave activation. While the reuse of fibres from items like old clothing is generally preferred, worn garments can be so damaged that fibre recovery is impractical. Chemical recycling offers a way to return lower-quality textile waste back up the value chain by producing valuable low molecular weight products, including monomers for new polymer production. The value of the products obtained through this method has been estimated at \$350 per ton of PET waste. Other polymers used in high-volume textiles may be more difficult to valorize from waste streams. Polyamides in Nylon 6 (polycaprolactam) and Nylon 6,6 (polyhexamethylene adipamide) are challenging to break down, but reasonable monomer yields can be achieved when catalysts are used in chemical recycling—although these yields may still be insufficient for commercialisation [19]. Using such durable materials as general chemical feedstocks or depolymerizing them to produce monomers that are useful for creating other types of materials, might present a better waste valorization opportunity. The chemical valorization of waste cotton from used textiles can be improved—or at least diversified in terms of products—through the use of simple Lewis or Brønsted acid catalysts, for example, to produce porous carbons [20]. Of course, if the cellulose is first converted into mono- or oligosaccharides, there are many chemo- and biocatalytic pathways to several valuable chemicals, including HMF, CMF, and levulinic acid [21]. Recycling rates of plastic waste are likely to increase with increased regional circular economy and 3 R efforts. However, there are still various environmental and technological challenges. These challenges need to be addressed so that design, use, disposal, recycling and recovering of plastic resources become environmentally sound with an aim to finally substituting a large share of virgin materials. This can be through reuse as plastics materials or through recovery of the chemical value for use in making new polymers of any chemical products. Current technologies for achieving chemical value from polymer and plastic waste is heavily skewed towards polyesters and PET in particular. It is vital that we develop new, efficient and clean catalytic technologies for the chemical valorisation of polyolefins in particular. IDTechEx predicts that by 2034, all forms of chemical recycling will process more than 17 million tonnes of plastic waste per year [22]—helpful but only a “drop in the ocean” of waste polymers. We need to significantly increase this number if we are to make a significant contribution to the replacement of traditional feedstocks and reduce the demand for petroleum. By making waste plastic recycling valuable to the chemical and allied industries, and preferably as more than just a co-feed, we add real value to the process and can view recycling as more than just an environmental remediation exercise, vital though that might be.

2.2. Catalytic Pyrolysis

Catalytic pyrolysis is a thermochemical process in which organic materials, such as biomass or plastics, are decomposed into smaller molecular compounds in the presence of a catalyst, under an inert and oxygen-free environment, using heat. By transforming waste plastics and biomass into high-value products, this technology presents a dual solution for waste reduction and resource recovery. The pyrolysis of plastics, a thermal degradation process carried out in the absence of oxygen, relies on a wide spectrum of catalysts to influence product distribution, lower reaction temperatures, and improve selectivity. Zeolites such as ZSM-5, HY zeolite, and Beta zeolite are widely used for their strong acidity and microporous structures, which promote the cracking of long-chain hydrocarbons into valuable light fractions. Metal oxides including alumina (Al_2O_3), silica–alumina ($\text{SiO}_2\text{--Al}_2\text{O}_3$), magnesium oxide (MgO), titanium dioxide (TiO_2), and zirconia (ZrO_2) contribute thermal stability and catalytic functionality. Transition metal-supported catalysts like $\text{Pt/Al}_2\text{O}_3$, Ni/ZrO_2 , $\text{Co--Mo/Al}_2\text{O}_3$, and $\text{Fe--Zn/Al}_2\text{O}_3$ offer excellent activity and selectivity, facilitating hydrogen transfer and enhancing hydrocarbon conversion. Bimetallic systems such as Ni--Fe , Fe--Co , and Ni--Cu introduce synergistic effects that improve both catalytic efficiency and resistance to deactivation. Clays, including montmorillonite, layered double hydroxides (LDHs), and mesoporous MCM-41, as well as natural minerals such as kaolin, hematite, and white sand, serve as effective and abundant low-cost catalytic materials. Carbon-based catalysts—such as activated carbon, carbon nanotubes (CNTs), and graphene oxide—play dual roles as both active materials and catalyst supports, enhancing adsorption and reaction kinetics. Acidic catalysts, including sulfate-modified zirconia ($\text{SO}_4^{2-}/\text{ZrO}_2$) and phosphoric acid on silica ($\text{H}_3\text{PO}_4/\text{SiO}_2$), further promote bond cleavage and isomerization reactions. Bifunctional catalysts such as Pt/ZSM-5 , $\text{Ni--Mo/Al}_2\text{O}_3$, Pd/HY , Cu/HY , and hybrid systems combining metal-organic frameworks (MOFs) with zeolites merge acidic and metallic functions, enabling multi-step catalytic pathways. Ionic liquids—particularly those based on imidazolium and phosphonium ions—have emerged as versatile solvents and catalysts, enhancing solubilization and reaction rates. Nanocomposite materials, including core–shell nanocatalysts such as Ni@SiO_2 and Fe@C , as well as trimetallic systems like Ni--La--Pd supported on TiCa, offer high dispersion and tailored activity. Transition metal sulfides, notably MoS_2 and WS_2 , are effective in promoting thermal decomposition and hydrogenation. Alkaline earth metal-based catalysts like K_2CO_3 , CaO , and MgO contribute basicity and thermal resistance. Advanced mesoporous materials, including desilicated Beta zeolites and Al-MSU-F , offer enhanced accessibility to active sites. Meanwhile, metal-organic frameworks such as UiO-66 (a zirconium-based MOF), Fe-MOF, DUT-5, and MIL-53 (based on aluminum) provide high surface areas and structural versatility, expanding the frontier of pyrolysis catalysis. Single-atom catalysts like 1 wt % Fe/CeO_2 , Co/CeO_2 , Ni/CeO_2 , and other M_1/CeO_2 systems (where $\text{M} = \text{Fe, Co, Ni}$) exhibit remarkable catalytic efficiency due to their maximized atom utilization, well-defined active sites, and strong metal–support interactions—offering precise control over product selectivity and enhanced performance in plastic pyrolysis applications.

Recent advances in catalyst design have significantly enhanced the efficiency and selectivity of plastic and biomass conversion processes (Table 2):

As seen in Table 2, Nickel- or platinum-based Fe_3O_4 catalysts supported on zeolites and ceria have demonstrated impressive results when applied to high-density (HDPE) and low-density polyethylene (LDPE) in induction heating reactors. Pristine LDPE conversion reached up to 94%, with minimal formation of aromatics, coke, or methane. However, post-consumer LDPE (i.e., plastic bags) showed a reduced conversion yield of approximately 48%, reflecting feedstock quality influences [23]. Magnesium oxide-supported iron and cobalt catalysts have proven effective for polypropylene (PP) derived from face masks and nitrile gloves. Operating at 800 °C in fixed-bed tubular reactors, these systems yielded 33% nitrogen-doped carbon nanotubes (N-CNTs), with minor production of syngas and residual carbon. Synergistic effects between Fe and Co played a key role in boosting activity and stability [24]. Montmorillonite clay, used as a catalyst for mixed plastic streams (PE, PP, PS), enabled 70–80 wt% conversion to pyrolysis oil in fluidized-bed reactors at 500 °C, notably producing no wax. Its moderate acidity and high surface area contributed to efficient thermal cracking [25]. In composite waste treatment, carbon fibers employed under microwave irradiation at 450 °C achieved complete conversion (100%), offering a straightforward route to valorizing thermoset materials [26]. Nickel/aluminum metal-organic frameworks (Ni/Al-MOF) have emerged as potent catalysts for the pyrolysis of post-consumer PP. Batch fixed-bed reactors operated at 450 °C yielded up to 72.8% oil from plastic waste and 58.9% from surgical masks [27]. The catalytic system promoted simultaneous cracking and hydrogenation, reducing coke formation while enhancing aromatic yields. Trimetallic Ni--La--Pd supported on TiCa nanocatalysts were utilized for cellulose conversion in Parr benchtop reactors at 800 °C, achieving 98.7% phenol conversion and 99.6% hydrogen yield. The high surface area, strong basicity, and homogeneous Pd distribution contributed to their remarkable activity

[28]. Magnesium oxide (MgO) has also been applied to the depolymerization of PET bottles in autoclaves across a 500–900 °C range. The resulting product was a 3D meso/macroporous carbon material with an exceptionally high surface area (1863.55 m²/g) and pore structure (1478.46 m²/g), underscoring its potential in energy storage applications [29]. A series of modified HZSM-5 zeolite catalysts (CBV23, CBV55, and CBV80) were evaluated for PP pyrolysis using a two-stage micro-pyrolyzer system. At 400–600 °C, CBV80-ZM enabled a 41 wt% yield of propylene, while methyl acrylate and light olefins reached up to 92 wt%. Enhanced acidity and tailored pore structures were critical to their performance [30]. Nano MOF-derived MIL-53 Cu/Y zeolites were employed for mixed plastic streams (HDPE, LDPE, PP, PS, PET, PVC) in fixed-bed reactors between 450–550 °C. Total fuel yields reached 73.1%, while catalytic crystallinity strongly influenced product distribution—favoring gasoline and diesel fractions under different operational modes [31]. Multilayer stainless-steel 316 (SS 316) catalysts, used in a two-stage fixed bed system at 500 °C, facilitated the conversion of PE and PP into multi-walled carbon nanotubes (MWCNTs) and hydrogen, with yields up to 86% (C) and 70% (H₂), respectively [32]. Spinel-type catalysts such as NiZnFe₂O₄, NiMgFe₂O₄, and MgZnFe₂O₄ were tested under microwave conditions at 450 °C for HDPE degradation. The NiMgFe₂O₄ catalyst exhibited outstanding hydrogen generation (87.5% H₂), while NiZnFe₂O₄ favored cleaner CNT production. Notably, 90% H₂ conversion was achieved within just two minutes, indicating the remarkable reactivity of these systems [33]. Plasma-enabled catalytic pyrolysis using 1 wt% M₁/CeO₂ single-atom catalysts can convert pure or mixed household plastics (HDPE, LDPE, PP, PS, PET) into hydrogen at up to 46.7 mmol H₂·g^{−1} with nearly quantitative H-atom recovery. In catalyst-free plasma on HDPE, 43.3 mmol H₂·g^{−1} (≈48.7% of theoretical) is obtained with ~60.6% H₂ selectivity. When a brief thermal step over Co₁/CeO₂ is added, H₂ yield rises to 46.7 mmol·g^{−1} (≈64.4% theoretical) and achieves ~100% H-atom recovery by the seventh cycle, while Fe₁/CeO₂ still delivers ≈42.9 mmol H₂·g^{−1} (≈64% theoretical) even after ten consecutive runs [34].

Table 2. Recent developments in catalytic pyrolysis technologies for waste polymer valorization.

Type of Catalysts	Example	Polymer Feedstock	Performance/Notes
Transition metals supported catalysts	Ni- or Pt-based Fe ₃ O ₄ on zeolites and ceria	HDPE, LDPE	Up to 94% conversion from pristine LDPE or ~48% from bags.
Bimetallic catalysts	MgO-supported Fe and Co catalysts	PP (face masks), nitriles (gloves)	33% N-CNTs (nitrogen-doped carbon nanotubes), minor syngas and residual carbonaceous materials.
Clays	Montmorillonite Clay	Plastic Mixture (PE, PP, PS)	70–80 wt% conversion into pyrolysis oil, no wax.
Carbon-based	Carbon fibers	Composites	100% conversion
Bifunctional catalysts	Ni/Al-MOF	Post-consumer PP	72.8% oil from PP waste or 58.9% from surgical masks; light gases and minimal coke.
Nanocomposites	Trimetallic Ni-La-Pd/TiCa	Cellulose	98.7% phenol conversion and 99.6% H ₂ yield.
Alkaline earth metals	MgO	PET bottles	3D Meso/Macroporous Carbon material with high surface area of 1863.55 m ² /g, and a meso/macropore surface area of 1478.46 m ² /g were obtained.
Modified zeolites	CBV23, CBV55, and CBV80 (modified HZSM-5 catalysts with SiO ₂ /Al ₂ O ₃)	PP	41 wt% propylene by CBV80-ZM, light olefins and methyl acrylate of 92 wt%.
MOFs	Nano MOF-Derived Loaded Y Zeolite (MIL-53 Cu/Y)	Mixed HDPE, LDPE, PP, PS, PET, PVC	73.1% total fuel at 525 °C and 36.7% diesel. 41.4% gasoline yield at 381 °C
Structured metallic catalysts	Multilayer stainless-steel 316 (SS 316)	Mixed plastics (PE and PP)	Up to 86% of C and 70% of H ₂ conversion into MWCNTs (multi-walled carbon nanotubes) and H ₂ .
Composite ferrite catalysts	NiZnFe ₂ O ₄ , NiMgFe ₂ O ₄ , and MgZnFe ₂ O ₄	HDPE	Almost 90% of H ₂ conversion in 2 min.
Single-atom catalysts	1 wt% Fe ₁ /CeO ₂ , Co ₁ /CeO ₂ , Ni ₁ /CeO ₂	Household plastic waste: milk containers, packaging bags, fruit packing boxes, yogurt cups, drink bottles	≈64.4% H ₂ , with nearly 100% hydrogen-atom recovery by the 7th cycle. Carbon residues are also obtained.

A growing number of companies worldwide are revolutionizing catalytic pyrolysis technologies to convert plastic waste into pristine monomers and commercially valuable products used in everyday life. ExxonMobil (Houston, TX, USA) uses its proprietary Exxtend™ technology and collaborates with NREL to advance catalytic pyrolysis of plastic waste, particularly using zeolite-based catalysts at 450–650 °C [35]. Its Baytown facility (40,000 t/year) began operations in 2022, with major expansions planned across the U.S., Europe, and Asia. ExxonMobil also co-founded Cyclyx International to improve plastic waste collection and supports global circular economy efforts through the AEPW [36]. Bridgestone (Warwick, UK) plans a pilot catalytic pyrolysis plant in Japan (2027) for closed-loop tire recycling with partners including AIST and ENEOS [37]. GreenMantra Technologies (Brantford, ON, Canada) uses a thermo-catalytic Ceranovus™ process (350–500 °C) [38] to convert plastics into waxes and polymers, expanding globally with partners like Harke Group (Mülheim an der Ruhr, Germany) and Westec. Neste (Espoo, Finland), mainly using thermal pyrolysis, explores catalytic methods and partners with Mura Technology. LyondellBasell (Houston, TX, USA) employs its MoReTec catalytic pyrolysis [39] for circular feedstocks, with new plants in Germany (2025) and Texas. Pyrowave (Montreal, QC, Canada) uses catalytic microwave tech to depolymerize polystyrene into monomers, enabling energy-efficient recycling [40]. Klean Industries (Vancouver, BC, Canada) applies catalytic liquefaction to convert plastic waste into diesel fuel [41]. SABIC (Riyadh, Saudi Arabia) transforms mixed plastic waste into pyrolysis oil using Ni, Mo, Co, and zeolite-based catalysts under its TruCircle™ initiative [42]. It supports certified circular polymers used in food-safe packaging, reducing CO₂ footprints by up to 61%. Covestro (Leverkusen, AG, Germany) [43] leads the EU's CIRCULAR FOAM project with 21 partners to recycle rigid PU foams. Dow (Midland, MI, USA) collaborates with Freepoint Eco-Systems to source 65,000 t/year of circular pyrolysis oil for new plastics [44]. BASF purifies pyrolysis oils via its PuriCycle® tech, while Clariant's HDMax® and Clarit™ catalysts enhance yields and purity, supporting efficient steam cracking [45]. Finally, natural polymer recycling includes cellulose valorization. Circa Group's (Parkville VIC, Australia) Furacell™ process uses phosphoric acid in sulfolane (150–220 °C) to convert cellulose waste into levoglucosenone (LGO) [46], which is further converted to the high-efficiency solvent Cyrene™.

While numerous companies are advancing catalytic pyrolysis technologies, techno-economic factors such as product value, catalyst lifetime, and scalability remain critical to their commercial success. ExxonMobil's Exxtend™ technology, operating at 450–650 °C with zeolite-based catalysts, has shown potential for large-scale deployment, but catalyst deactivation via coking requires periodic regeneration, which affects operational efficiency and cost. Pyrowave's microwave-assisted process for depolymerizing polystyrene into monomers offers high product purity and reduced energy input, improving yield value and decreasing lifecycle emissions, though the technology is best suited for relatively clean PS streams. GreenMantra's Ceranovus™ process prioritizes wax and polymer output, commanding higher product margins, yet must manage catalyst lifespan in mid-range thermal environments (350–500 °C). SABIC's TruCircle™ initiative emphasizes both product quality (e.g., food-grade circular polymers) and environmental performance, reporting up to 61% CO₂ reduction; however, maintaining high-value pyrolysis oil quality depends on catalyst robustness (Ni, Mo, Co, zeolites) and impurity tolerance. Clariant's HDMax® and Clarit™ catalysts enhance product selectivity and steam cracker compatibility, offering longer cycle lives and reduced coke formation—key advantages in minimizing operational costs. Klean Industries and Bridgestone focus on fuel-grade outputs or tire-derived oils, which are lower in value but benefit from simpler purification steps and greater feedstock flexibility. Ultimately, integrating high-throughput catalyst screening, robust regeneration strategies, and value-chain optimization is essential for improving economic viability across diverse pyrolysis pathways.

2.3. Catalytic Gasification

Catalytic gasification is an advanced thermochemical process that converts carbonaceous feedstocks, including biomass, plastic waste, and other organic residues, into syngas, in the presence of a catalyst and a gasifying agent (e.g., steam, oxygen, air). Syngas is primarily a mixture of H₂ and CO, with some CO₂, and it can be used to synthesize methanol and ammonia, generate electricity, produce gas-to-liquid fuels, or serve as a source of hydrogen. The catalytic gasification of waste polymers has gained increasing attention as a promising route for sustainable fuel and hydrogen production. Gasification of plastics involves the conversion of solid polymeric waste into synthesis gas (a mixture of CO and H₂) through thermal and catalytic processes, with a range of catalysts employed to enhance efficiency and selectivity. Zeolites such as ZSM-5, HY, and Beta zeolite are utilized for their acidity and structural properties, which aid in cracking large molecules and facilitating secondary reactions. Metal oxides—including alumina (Al₂O₃), silica-alumina (SiO₂–Al₂O₃), cerium oxide (CeO₂), titanium dioxide (TiO₂), iron oxide supported on ceria (Fe₂O₃/CeO₂), and magnetite (Fe₃O₄)—provide

redox-active surfaces and thermal stability, crucial for high-temperature gasification reactions. Carbon-based materials such as activated carbon, carbon nanotubes, and graphene oxide are often employed as supports or active catalysts, enhancing surface interactions and aiding in tar cracking and gas-phase reactions. Transition metals like nickel, cobalt, iron, and molybdenum are key components in many catalytic systems, offering strong activity in reforming and partial oxidation reactions. Alkali and alkaline earth metal compounds—including potassium carbonate (K_2CO_3), calcium oxide (CaO), magnesium oxide (MgO), sodium carbonate (Na_2CO_3), calcium carbonate (CaCO_3), and magnesium carbonate (MgCO_3)—serve as both catalysts and gasification promoters, enhancing carbon conversion and reducing tar formation. Noble metals such as ruthenium, platinum, and palladium further improve activity and resistance to coking, particularly in configurations like RuO_2 , Ru supported on alumina or silica, Pt on ceria or alumina, and Pd on alumina or zirconia. Bifunctional catalysts such as $\text{Ni}/\text{Al}_2\text{O}_3$, $\text{Co-Mo}/\text{Al}_2\text{O}_3$, and $\text{Pt}/\text{ZSM-5}$ combine metallic and acidic functions, facilitating both reforming and cracking reactions. Additionally, naturally occurring carbonate minerals like dolomite ($\text{CaMg}(\text{CO}_3)_2$) are frequently used for their catalytic and sorptive properties, promoting tar reduction and improving gas quality. These catalytic systems collectively enable more efficient, cleaner, and higher-yield gasification processes for converting plastic waste into valuable energy carriers. A range of catalysts have been explored to improve gas yield, reduce tar formation, and operate under milder conditions (Table 3):

Table 3. Recent developments in catalytic gasification technologies for waste polymer valorization.

Type of Catalysts	Example	Feedstock	Yield
Bifunctional catalyst	$\text{Ni}/\text{X-Al}_2\text{O}_3$ (X = Ti, Sr, or La)	Plastic waste-derived wax	74.78 wt% syngas and 25 wt% tar.
Metal oxide	Magnetite (Fe_3O_4)	Plastics and corn stover	H_2 yield >98% and 9% tar
Carbon-based	Activated carbon (AC), calcinated dolomite and NiO	Lignocellulosic biomass	Up to 62.54 vol% H_2
Carbonaceous char catalyst	Tire char	Waste HDPE, PP, PS, PET, PVC	39.08 wt% gas
Alkaline earth metals and alkali metal carbonates	K_2CO_3 , CaO , MgO , Na_2CO_3 , CaCO_3 , MgCO_3	Lignin	69.96% gas and 110.34 mmol/g syngas
Composite catalysts	$\text{Ni-CaO-Ca}_2\text{SiO}_4$	Plastic waste bottles	84.4 vol.% (53.1 vol.% of H_2 and 31.3 vol.% of CO)
Carbonate mineral	Dolomite $\text{CaMg}(\text{CO}_3)_2$	Beech wood and PE	80 wt% syngas and 5 wt% heavy tars
Co-reactant	Formic acid	PP	80% of carbon conversion

As seen in Table 3, Nickel-based catalysts supported on modified alumina ($\text{Ni}/\text{X-Al}_2\text{O}_3$, where X = Ti, Sr, or La) have shown strong potential in the gasification of plastic waste-derived wax. Operated in fixed-bed stainless-steel reactors between 700–800 °C, the 10Ni/5Ti-Al variant produced 74.78 wt% syngas and 25 wt% tar. Increasing the temperature favored gas formation while reducing tar, with peak hydrogen yields observed at 700–750 °C. This process employed air gasification as the oxidant medium [47]. Magnetite (Fe_3O_4) has also been employed in microwave-assisted gasification systems for mixed plastic and biomass (corn stover) feedstocks. At 700 °C, hydrogen yields reached 30.5 mmol H_2 /g feed, with tar levels as low as 9%. Across a broader temperature window (700–950 °C), H_2 yields surpassed 98%, demonstrating the high efficiency of this approach [48]. Another noteworthy system utilized activated carbon (AC), calcinated dolomite, and nickel oxide (NiO) for lignocellulosic biomass gasification. Conducted in a two-stage fixed-bed reactor at 700–900 °C, NiO/PAC-SD-1 produced 51.14 vol% H_2 , which increased to 62.54 vol% upon co-application with calcinated dolomite. The mechanism involves initial biomass pyrolysis followed by catalytic gasification of volatiles and char. Interestingly, the AC also self-gasified, contributing to overall hydrogen production [49]. Tire char was explored as both a catalyst and a reactive medium in the gasification of mixed plastics (HDPE, PP, PS, PET, PVC). In a two-stage fixed-bed reactor operated at 900–1000 °C, a maximum of 39.08 wt% gas was achieved at 900 °C. The pyrolysis–gasification sequence proved synergistic, and the char played a dual role by also contributing to H_2 formation [50]. Alkaline and alkaline earth metal salts—such as K_2CO_3 , CaO , MgO , Na_2CO_3 , CaCO_3 , and MgCO_3 —have shown catalytic activity in lignin gasification. At 850 °C, Na_2CO_3 achieved the highest yield, producing 69.96% gas and 110.34 mmol/g syngas, surpassing other salts in catalytic efficiency [51]. A composite catalyst of $\text{Ni-CaO-Ca}_2\text{SiO}_4$ was applied to gasify plastic bottle waste in a two-stage fixed-bed reactor at 800 °C. The process yielded 84.4 vol% syngas, comprising 53.1 vol% H_2 and 31.3 vol% CO. This two-step method (pyrolysis followed by gasification) allows greater control over gas composition and tar

minimization [52]. Dolomite ($\text{CaMg}(\text{CO}_3)_2$) has also been tested for mixed biomass and polymer gasification (e.g., beech wood and PE). Conducted in a fluidized-bed reactor at 850 °C, the system yielded 80 wt% syngas and only 5 wt% heavy tars. A fluidizing medium (sand) and a controlled oxidizing atmosphere further enhanced conversion efficiency [53]. Formic acid has emerged as a novel co-reactant for the supercritical water gasification of polypropylene (PP). Operated in quartz tube reactors at 750 °C, this method achieved 80% carbon conversion, highlighting a low-emission pathway for plastic valorization under aqueous conditions [54].

Resonac (Tokyo, Japan) uses eco-friendly partial oxidation to convert plastic waste into CO_2 , ammonia, and hydrogen without fossil fuels, processing over 100 tons since 2003. Its KPR plant recycles 70,000 tons annually, with hydrogen powering the first ammonia-fueled vessel. Resonac also recycles semiconductor plastic waste and partners with ITOCHU to convert plastics and textiles into acrylonitrile for textile manufacturing [55]. Klean Industries (Vancouver, BC, Canada) employs pyrolysis and gasification to recover resources from plastic waste, using catalytic liquefaction to produce high-grade diesel fuel.

2.4. Catalytic Chemical Oxidation

Catalytic chemical oxidation refers to the controlled breakdown of plastic polymers into smaller, valuable molecules using oxidizing agents and catalysts. This process selectively cleaves carbon–carbon or carbon–heteroatom bonds, converting complex plastics into simpler, functionalized compounds. Catalytic chemical oxidation in polymer depolymerization is a targeted approach to breaking down plastic waste into valuable chemicals using oxygen and catalysts. The catalytic chemical oxidation of plastic waste employs a diverse range of catalysts tailored to promote selective oxidative degradation of resilient polymer structures. Zeolites such as ZSM-5, HY, and Beta zeolite are frequently used for their well-defined pore architectures and strong acidity, which facilitate the oxidation process. Metal oxides including titanium dioxide (TiO_2), cerium oxide (CeO_2), and zinc oxide (ZnO) provide redox-active surfaces capable of initiating and sustaining oxidation reactions. Noble metal-based catalysts, exemplified by gold supported on nickel oxide (Au/NiO_x), offer high efficiency and selectivity in oxidative pathways. Carbon-based materials like activated carbon, carbon nanotubes, and graphene oxide serve both as active catalysts and supports, enhancing surface interactions and dispersing active species. Transition metal catalysts such as iron, copper, and manganese play essential roles in redox cycling and radical formation, driving the oxidative depolymerization of plastic substrates. Bifunctional catalysts—combinations of metal and support systems—add synergistic effects, as seen in $\text{Pt}/\text{Al}_2\text{O}_3$, $\text{Ru}/\text{ZSM-5}$, $\text{Fe-Cu}/\text{Al}_2\text{O}_3$, and Au/NiO , where the metal component promotes redox activity while the support offers structural and acidic properties. Metal-organic frameworks (MOFs), including MIL-47 (a vanadium-based framework), MIL-100(V), MIL-101(Cr), and ZIF-8, introduce high surface area and tunable pore environments conducive to oxidation reactions under mild conditions. Enzymatic oxidation is also gaining traction, with enzymes like laccase and various peroxidases—including horseradish peroxidase (HRP), manganese peroxidase (MnP), lignin peroxidase (LiP), and versatile peroxidase (VP)—as well as a range of fungal enzymes, contributing to environmentally benign and selective oxidative cleavage of polymer chains. Together, these catalytic systems represent a powerful and evolving toolbox for transforming plastic waste into valuable or benign products through controlled chemical oxidation. Recent innovations have introduced hybrid chemical and biological approaches, visible-light activation, and robust heterogeneous systems—all contributing to greener, more selective upcycling processes. Below, we detail recent developments in this growing field (Table 4):

Table 4. Recent developments in catalytic oxidation technologies for waste polymer valorization.

Type of Catalysts	Example	Feedstock	Performance/Notes
Metal oxides	CeO_2	PE waste	PHB yields of up to 0.28 g/g PE
Carbon-based catalysts	Graphitic carbon nitride ($\text{g-C}_3\text{N}_4$)	PS	90% conversion into benzoic acid, acetophenone, benzaldehyde.
Bifunctional catalyst	$\text{Au}/\text{NiO-x}$	PET	>99% terephthalic acid (TPA) and >87% glycolic acid
Bifunctional catalyst	Ru/TiO_2	PE	Up to 97% dicarboxylic acids and 95% conversion
Organometallic catalyst	Mn stearate	PE, PP	80% conversion into fatty acids
Inorganic metal salt catalyst and microbial catalyst	$(\text{CH}_3\text{CO}_2)_2\text{Co}$ and <i>Pseudomonas putida</i>	Mixed PET, PS, HDPE	~63 mol% of benzoic acid from PS, ~34 mol% $\text{C}_4\text{-C}_{22}$ from HDPE and ~68 mol% terephthalic acid from PET.

As seen in Table 4, Cerium oxide (CeO_2) has been successfully employed for the oxidative transformation of polyethylene (PE) waste. Conducted in a stainless-steel batch reactor between 200–450 °C, this system enabled the conversion of PE into polyhydroxybutyrate (PHB), with yields reaching 0.28 g/g PE. The process utilizes water as the solvent and molecular oxygen as the oxidant, making it an environmentally benign method that aligns with green chemistry principles. Notably, this hybrid system combines chemical and biological steps to achieve polymer valorization [56]. Graphitic carbon nitride ($\text{g-C}_3\text{N}_4$), a visible-light responsive photocatalyst, was employed to activate polystyrene (PS) under illumination from a Xenon lamp at 150 °C. This mild process achieved 90% conversion to valuable aromatic compounds such as benzoic acid, acetophenone, and benzaldehyde. The approach exemplifies the potential of photo-oxidative methods for depolymerizing plastics with high selectivity under sustainable conditions [57]. Gold-doped nickel oxide (Au/NiO_x) has demonstrated remarkable efficiency in the oxidation of polyethylene terephthalate (PET). In a batch reactor at 180 °C, this system yielded over 99% terephthalic acid (TPA) and more than 87% glycolic acid, two valuable monomers. The catalyst exhibited high selectivity and stability, highlighting its promise for closed-loop recycling strategies [58]. Ruthenium supported on titania (Ru/TiO_2) was utilized for the upcycling of PE under mild oxidative conditions—160 °C, 1.5 MPa air, and water as the reaction medium. The process achieved up to 97% yield of dicarboxylic acids and 95% conversion, representing a highly effective one-pot oxidative depolymerization route. The use of a robust heterogeneous catalyst ensured catalyst recyclability and minimized process waste [59]. Manganese stearate enabled the oxidative breakdown of PE and polypropylene (PP) in a custom-designed quartz reactor operating between 150–360 °C. This pyrolysis-oxidation system, utilizing a temperature-gradient thermolysis method, achieved 80% conversion to long-chain fatty acids with molar masses of up to ~700 Da. This method offers a tunable platform for producing bio-based surfactants or lubricants from plastic waste [60]. A particularly innovative dual-system approach combined cobalt(II) acetate ($(\text{CH}_3\text{CO}_2)_2\text{Co}$) with the engineered bacterium *Pseudomonas putida* for the oxidation and biological funneling of mixed plastics. The oxidation stage, run at 160–210 °C and 8–72 bar, converted PS to benzoic acid (~63 mol%), HDPE into C_4 – C_{22} aliphatic acids (~34 mol%), and PET to TPA (~68 mol%). In the subsequent biological step, these oxygenates were funneled by *P. putida* into β -ketoadipate, achieving up to 73% yield. This hybrid method demonstrates a powerful model for integrating synthetic and biological catalysis for mixed plastic streams [61].

Catalytic oxidation has potential for polymer recycling but faces challenges like low selectivity, overoxidation, and catalyst instability, limiting commercial use. EcoCatalytic (Sunnyvale, CA, USA) [62] offers a solution with its chemical looping system, using proprietary metal oxides to convert plastic waste into high-value chemicals while reducing CO_2 emissions by over 80% and eliminating NO_x . In 2019, the company received a U.S. DOE SBIR grant for this technology.

While catalytic oxidation offers a selective and often low-temperature route for polymer depolymerization, its commercial viability depends heavily on the value and downstream use of the oxidation products. Compounds such as terephthalic acid (TPA) and dicarboxylic acids are high-demand chemical building blocks in the production of polyesters, nylon intermediates, surfactants, and speciality monomers. For example, TPA produced from PET oxidation can be directly reincorporated into virgin PET manufacturing, offering both economic and circularity benefits. Long-chain aliphatic acids obtained from polyethylene and polypropylene oxidation are used in lubricants, plasticizers, and bio-based surfactants, where their market value can exceed \$2,000–3,000 per tonne depending on purity and chain length [63]. However, photocatalytic oxidation technologies, while promising for low-temperature processing, face significant scale-up challenges. The efficiency of light-driven systems is limited by low quantum yields, restricted light penetration in slurry reactors, and the high cost or instability of photocatalysts (i.e., graphitic carbon nitride). Continuous operation over extended periods can lead to catalyst fouling, photo-corrosion, or activity loss, particularly under industrial light intensities. Overcoming these barriers will require reactor engineering solutions (e.g., structured photoreactors or immobilized photocatalysts) and the development of more durable visible-light-responsive materials.

2.5. Enzymatic Catalysis

Enzymatic catalysis offers a biologically elegant and environmentally benign route for the degradation and valorization of synthetic polymers. In catalytic enzymatic depolymerization, enzymes selectively break down polymer chains into smaller molecules under controlled conditions. Enzymes typically act as the catalyst; but in some cases, another catalyst is used in combination with the enzyme to enhance reaction efficiency, improve selectivity, or facilitate depolymerization under milder conditions. With increasing interest in green chemistry and circular plastic economies, enzymes have shown immense promise in selectively cleaving polymer chains under mild conditions, often with high specificity and low energy input. Enzymatic depolymerization harnesses

the remarkable specificity and efficiency of biological catalysts to break down polymeric materials under mild conditions. Among the primary enzymes involved are hydrolases such as PETase, cutinase, and esterase, which facilitate the hydrolysis of ester bonds in polyesters like PET. Oxidoreductases, including laccase and peroxidase, contribute through oxidative cleavage mechanisms, enhancing the breakdown of more resistant polymers. Lipases also play a critical role, with notable examples such as *Candida antarctica* lipase B and *Thermomyces lanuginosus* lipase, which are effective in catalyzing ester bond hydrolysis. Cutinases from species like *Fusarium solani* and *Humicola insolens* exhibit strong depolymerization potential, particularly against polyesters. Engineered enzymes, fine-tuned with metal cofactors like Ca^{2+} , Cu^{2+} , and Mn^{2+} , such as engineered PETase and engineered cutinase, offer enhanced activity, stability, and substrate specificity. Metal ion-based enzymes, including manganese peroxidase, lytic polysaccharide monooxygenases, and cutinase-like enzymes, expand the catalytic repertoire by combining metal coordination chemistry with enzymatic selectivity. Finally, biomimetic catalysts—including cyclodextrins, crown ethers, metalloporphyrins, endocellulase, exocellulase, and β -glucosidase—mimic natural enzymatic processes to facilitate efficient polymer degradation, bridging the gap between biological and synthetic catalytic systems. The following highlights recent breakthroughs in enzymatic systems targeting diverse polymeric waste streams (Table 5):

Table 5. Recent developments in enzymatic catalysis technologies for waste polymer valorization.

Type of Catalysts	Example	Feedstock	Performance/Notes
Hydrolases	PETase from <i>Ideonella sakaiensis</i>	PET bottles	17.2% MHET
Oxidoreductases	BaLac (<i>Botrytis aclada</i>), BsLac (<i>Bacillus subtilis</i>)	LDPE	40% reduction in molecular weight.
Lipases	Lipase B from <i>Candida antarctica</i> (CALB)	Post-consumer PLA	100% conversion to lactic acid.
Cutinases	<i>Thermobifida fusca</i> cutinase	PE	47.4% reduction of molecular weight of LDPE.
Engineered enzymes	PETase and DepoPETase	PET waste	100% depolymerization
Metal ions-based enzymes	Laccase and manganese peroxidase from <i>Penicillium simplicissimum</i>	PE	38% UV-treated, 16% autoclaved and 7.7% surface-sterilized degradation.
Biomimetic catalysts	Mimicking Endocellulase, Exocellulase, β -Glucosidase, $\text{NP}_6\text{-CO}_2\text{H}$	Cellulose	Up to 45% conversion and 76% activity after ten cycles.
Dual enzyme system	Hydrolase PES-H1 FY, (poly)urethanase UMG-SP-2	Mixed PET, PU, PBAT	40%

As seen in Table 5, one of the landmark discoveries in this field is PETase, derived from *Ideonella sakaiensis*, which catalyzes the depolymerization of polyethylene terephthalate (PET). In a simple flask setup at 30 °C, using 10 M NaOH as solvent, the enzyme produced 17.2% mono-(2-hydroxyethyl) terephthalate (MHET) within the first 24 h. PETase effectively cleaves ester bonds in polyesters, showcasing moderate to high turnover under ambient conditions [64]. The oxidative degradation of polyethylene (PE) has been explored using laccases from *Botrytis aclada* (BaLac) and *Bacillus subtilis* (BsLac). When applied to UV-treated LDPE films at 30 °C, a 40% reduction in molecular weight was achieved. This process involved the use of synthetic mediators—ABTS, HBT, and TEMPO—which facilitated electron transfer during the oxidation cascade [65]. For poly(lactic acid) (PLA), lipase B from *Candida antarctica* (CALB) proved exceptionally effective. At temperatures between 40–90 °C and pH 6–8, 100% conversion to lactic acid was achieved within 40 h at 90 °C. CALB was stabilized in ionic liquids, enhancing both its solubility and catalytic lifetime [66]. An interesting hybrid system combined CALB with cutinase from *Thermobifida fusca* for the depolymerization of LDPE. At 40 °C, this biocatalytic pairing led to a 47.4% reduction in molecular weight. The process involved a Baeyer–Villiger oxidation, followed by enzymatic hydrolysis, representing a sophisticated approach to activating chemically inert polymers [67]. Further enhancement in PET biodegradation has been demonstrated through engineered enzymes, such as DepoPETase. This evolved variant operated in a litter-scale reactor at 50 °C, achieving 100% depolymerization of PET waste. These results mark a significant step forward in scalable enzymatic recycling technologies [68]. The laccase and manganese peroxidase from fungus *Penicillium simplicissimum* also contributed to polyethylene degradation. On agar plates at room temperature, it demonstrated differential activity based on pretreatment, degrading 38% of UV-treated PE, 16% of autoclaved, and 7.7% of surface-sterilized samples. This indicates the importance of pre-oxidation in improving enzymatic accessibility [69]. Synthetic biomimetic catalysts inspired

by endocellulase, exocellulase, and β -glucosidase have shown promise in cellulose degradation. The compound NP6-CO₂H, tested at 90 °C and pH 6.5, retained 17% activity, while combinations like NP6-CO₂H: NP7-(CO₂H)₂: NP11-(CO₂H)₂ reached 44–45% activity. Remarkably, these synthetic constructs maintained 76% activity after ten cycles and outperformed commercial cellulases from *Aspergillus niger* and Novozyme blends [70]. A one-pot enzymatic system comprising hydrolase PES-H1 FY and polyurethanase UMG-SP-265 targeted mixed waste streams containing PET, PU, and PBAT. Operating between 30–60 °C, this system achieved a 40% depolymerization yield, offering a versatile platform for tackling diverse, multi-component plastic blends [71].

AI accelerates enzyme development for plastic recycling. Companies like Protein Evolution, in partnership with Agile BioFoundry, and tools like AlphaFold, help design enzymes for polymer breakdown. The ENZYCLE project uses enzymes like LCC and PHL7 to degrade 90% of PET in 16 h and cut microplastic weight by 30%. Carbios (Clermont-Ferrand, France) leads in enzymatic PET recycling, with a 50 kt/year plant and partnerships with brands like L'Oréal, Nestlé, and PUMA. A larger facility in Longlaville is set for 2027. Samsara Eco (Sydney, Australia) developed enzymes for Nylon 6 recycling, collaborating with ANU and Lululemon to turn waste into apparel. Covestro and Novozymes are advancing enzymatic solutions for plastics and wastewater, with Covestro also investing in BTX recovery *via* BioBTX tech in the Netherlands.

2.6. Catalytic Hydrocracking

Hydrocracking catalysis has emerged as a powerful thermochemical approach for converting plastic waste into valuable hydrocarbon fuels and chemicals. By combining metal sites for hydrogenation with acidic supports for cracking, recent systems have achieved remarkable selectivity and conversion under relatively moderate conditions. Hydrocracking of plastics employs a diverse and evolving array of catalytic systems designed to promote selective bond cleavage, hydrogenation, and molecular rearrangement. Traditional systems often rely on zeolites such as ZSM-5, HY, and Beta for their high surface area and strong acidity, which are critical for cracking long-chain hydrocarbons. These are frequently combined with metal-supported catalysts that drive hydrogenolysis, including Pt/HY, Ni/HZSM-5, NiMo/Al₂O₃, Pt/USY, and Al-MCM-41. Bifunctional catalysts, which pair metallic hydrogenation sites with acidic cracking domains (e.g., Pt/SAPO-11, NiW/ZrO₂, CoMo/Al₂O₃, Pt/ β zeolite), remain central to process efficiency. Bimetallic systems such as Pt–Sn, Ru–Co, Ni–Ru, Ni–Cr, and Co–Mo introduce synergistic effects that enhance activity, selectivity, and resistance to deactivation. While noble metals like Pt and Ru exhibit superior hydrogenation performance, recent research has increasingly focused on non-precious metal alternatives to improve cost-effectiveness and sustainability. Catalysts based on nickel (Ni), cobalt (Co), and iron (Fe)—including NiMo/Al₂O₃, CoMo/Al₂O₃, Ni–Cr alloys, and Fe-based mixed oxides—have demonstrated promising hydrocracking activity, particularly when paired with acidic supports or optimized reaction conditions. Sulfide-based catalysts (e.g., NiMoS/Al₂O₃, CoMoS/Al₂O₃, MoS_x/H-beta) also offer excellent hydrogenolytic performance, especially in sulfur-tolerant environments. Acidic metal oxides (e.g., ZrO₂, WO₃/ZrO₂) and hybrid systems such as Pt/WO₃/ZrO₂ or Ni–W on ZrO₂ provide additional flexibility in tailoring catalytic function. Furthermore, carbon-based supports like activated carbon, carbon nanotubes, and graphene oxide improve metal dispersion and thermal stability. Alkaline earth metal additives (K₂CO₃, CaO, MgO) introduce basicity that can influence cracking behavior and suppress coke formation. Emerging materials such as metal-organic frameworks (MOFs)—including DUT-5-RuH₂ and MIL-53-RuH₂—demonstrate the potential for highly dispersed active sites within tunable pore environments. These advances underscore a growing shift toward cost-efficient, earth-abundant catalyst systems, balancing performance with long-term scalability in plastic hydrocracking technologies.

Recent advancements in catalytic hydrocracking have significantly improved efficiency, selectivity, and process stability, enabling the conversion of waste plastics into high-value liquid fuels and gases under milder conditions (Table 6):

As seen in Table 6, nickel supported on hierarchical β -zeolites has shown notable efficiency in hydrocracking high-density polyethylene (HDPE). In a Parr reactor at 325 °C and 30 bar, the system achieved conversion rates of 66.8%, 79.4%, and 87.7% for the parent H β , DAH β , and DSH β catalysts, respectively. The Ni–H β system yielded 26.1% gaseous and 73.9% liquid hydrocarbons, with its high surface area and porosity playing a pivotal role in the observed performance [72]. Platinum loaded on ultra-stable Y zeolite (Pt/USY) enabled the efficient conversion of polyethylene (PE) and polypropylene (PP) in a stainless-steel autoclave at 280 °C and 30 bar, resulting in over 90% selectivity toward gasoline-range hydrocarbons (C₅–C₁₂) [73]. The dual functionality of the catalyst—metallic hydrogenation and acidic cracking—proved essential in achieving such high product specificity. A multi-functional system composed of Pt/WO₃/ZrO₂ and HY zeolite demonstrated robust activity toward mixed polyolefins, including PE, PP, and polystyrene (PS). Conducted in a Parr reactor at

225–250 °C, this setup achieved 85% yield of liquid hydrocarbons. Platinum facilitated C–C bond cleavage, while the WO₃/ZrO₂ matrix offered strong Brønsted acidity, enabling efficient isomerization and hydrocracking across varied hydrocarbon chains [74]. For post-consumer polypropylene waste, Pt/Al₂O₃ and NiMo/Al₂O₃ catalysts were explored in a batch autoclave at 450 °C and 20 bar. The NiMo/Al₂O₃ system produced 86 wt% liquid hydrocarbons, whereas Pt/Al₂O₃ delivered the highest gasoline fraction, reaching 49.85 wt%. These results demonstrate the adaptability of conventional hydroprocessing catalysts to plastic feedstocks [75]. A novel sulfided molybdenum catalyst on H-beta zeolite (MoS_x-Hβ) has shown exceptional versatility across LDPE, LLDPE, HDPE, and PP. Operating at 180–250 °C under 20–30 bar, the system yielded up to 96% small alkanes at 180 °C, and 85–97% conversion at 200 °C. Importantly, the catalyst minimized coke formation while promoting hydrogenolysis and cracking, highlighting its stability under repeated thermal cycling [76]. Ruthenium dispersed on a zeolite support (RuZ) achieved near-complete conversion of PE, PP, and PS in an autoclave at 300–350 °C, yielding over 97% methane. This extreme selectivity underscores the potential for targeted monomolecular production through careful catalyst and reaction condition tuning [77]. In a broader application, Ru-MO catalysts processed a range of polyolefins in an autoclave above 100 °C, achieving 100% conversion. Product distributions included 83.7% liquid fuels (C₅–C₂₁), lubricating oils (C₁₅–C₄₅), light gases (C₁–C₄), and wax fractions (C₂₂–C₄₅). This flexible product slate points to the potential of tailored catalytic systems for generating specific petrochemical streams from waste polymers [78].

Table 6. Recent developments in catalytic hydrocracking technologies for waste polymer valorization.

Type of Catalysts	Example	Feedstock	Performance/Notes
Bifunctional catalysts	Ni onto hierarchical β-zeolites	HDPE	Up to 87.7% conversion, 26.1% selectivity of gases and 73.9% of liquids.
Metal supported catalysts	Pt/USY	PE, PP	>90% selectivity to gasoline (C ₅ –12)
Multifunctional system	Pt/WO ₃ /ZrO ₂ and HY zeolite	PE, PP, PS	85% yield of liquid hydrocarbons
Bi-functional catalysts	Pt/Al ₂ O ₃ and NiMo/Al ₂ O ₃	Waste PP	Up to 86 wt% liquids
Sulfide-based catalysts	MoS _x -Hbeta	LDPE, LLDPE, HDPE, PP	96% yield of small alkanes at 180 °C or 85–97% at 200 °C.
Metal–zeolite catalyst	RuZ	PE, PP, PS	>97% methane
Transition metal catalysts	Ru-MO	Polyolefins	100% conversion and 83.7% liquid fuel (C ₅ –C ₂₁), lubricating oil (C ₁₅ –C ₄₅), gas (C ₁ –C ₄) and wax (C ₂₂ –C ₄₅).

Importantly, the environmental impact of hydrocracking is strongly influenced by the source of hydrogen used in the process. Most reported systems use gray hydrogen—typically derived from natural gas via steam methane reforming—which carries a significant carbon footprint. To reduce the climate impact of catalytic hydrocracking, there is increasing interest in integrating green hydrogen produced from renewable energy sources (i.e., electrolysis powered by wind or solar). Substituting gray with green hydrogen can significantly lower overall greenhouse gas emissions, aligning the process with circular economy and decarbonization goals. However, the cost and availability of green hydrogen remain major constraints for industrial implementation, highlighting the need for system-level integration of clean energy and waste valorization.

Dow (Midland, MI, USA) invested in Plastogaz (Saint-Sulpice, Switzerland) in 2022 to support catalytic hydrocracking of mixed plastic waste into high-quality hydrocarbons using hydrogen and proprietary catalysts [79]. The University of Manchester has developed NovaCrack[®], a low-temperature (200–350 °C), fast (5 min) hydrocracking process converting plastics like PE, PP, PS, and PET into up to 90% liquid products using Pt/USY catalysts. Using Pt/USY, it achieved 70–90% liquid and 10–30% gas at 225–310 °C for pure polymers [80] and 80% liquid, 20% gas at 310–400 °C for polymer blends [81]. The University of Delaware’s CPI (USA) has created a hydrocracking method using Pt/WO₃/ZrO₂ and HY zeolite at 225–250 °C, to convert plastics into jet fuel, diesel, and lubricants at 85% yield with 50% lower energy use and zero CO₂ emissions [82].

2.7. Catalytic Hydrogenolysis

Catalytic hydrogenolysis is a hydrogen-assisted cleavage process that breaks C–C and C–X bonds (X=O, N, Cl) in organics, in the presence of catalysts and molecular hydrogen. This selective C–C bond cleavage process, facilitated by tailored metal-based catalysts, enables controlled depolymerization with high conversion and

minimal gas formation. In the hydrogenolysis of plastics, a diverse set of catalytic systems is employed to break down complex polymer structures—such as polyolefins and polyesters—into valuable fuels, monomers, and chemical intermediates. Zeolites like HY, Beta, mordenite, ZSM-5, and ferrierite provide essential acidity and microporous architecture that enhance cracking and hydrogenolysis performance. Traditionally, noble metal-based catalysts—including platinum, palladium, and ruthenium—have been widely used for their high hydrogenation activity and stability. These metals are often supported on oxides such as Nb₂O₅, TiO₂, SrTiO₃, and ZrO₂, or on carbon materials, as demonstrated in systems like Ru/Nb₂O₅, Ru/TiO₂, Pt/SrTiO₃, Pd/C, and Ru-XZr. However, growing emphasis on cost-effective and sustainable catalyst development has led to increased research into non-precious metal alternatives, particularly those based on nickel (Ni), cobalt (Co), and iron (Fe). These transition metals offer robust hydrogenolysis performance and are typically supported on acidic or neutral oxides such as ZrO₂, Al₂O₃, SiO₂, or incorporated into zeolitic frameworks (e.g., Ni/ZrO₂, NiMo/Al₂O₃, Co/ZrO₂, Ni/SiO₂, Co/ZSM-5). They not only reduce dependence on scarce noble metals but also show good stability under reductive conditions. Transition metal sulfides such as MoS₂ and WS₂ are also effective hydrogenolysis catalysts under sulfiding conditions, often used for their tolerance to impurities and ability to operate at high temperatures. Bimetallic catalysts further enhance performance by combining functionalities of different metals. Systems such as RuFe₃, RuCo₃, Ni–Ru/SiO₂, Pt–Sn/CeO₂, and Ru–Pd/ZrO₂ have demonstrated synergistic effects in terms of selectivity, reaction rate, and resistance to deactivation. Meanwhile, acidic metal oxides (e.g., ZrO₂, Nb₂O₅) and alkaline earth materials (e.g., K₂CO₃, CaO, MgO) play auxiliary roles, contributing to bond scission or altering the reaction environment to suppress undesired side reactions. Carbon-based supports—including activated carbon, carbon nanotubes, and graphene oxide—are commonly used to disperse active metal species and provide tunable surface chemistry. Metal–zeolite hybrids, such as Pt or Pt–Sn embedded in MFI, CHA, LTL, and TON frameworks, offer combined acidic and metallic functionality for one-pot conversions. In parallel, metal-organic frameworks (MOFs) are emerging as advanced supports or active catalysts in hydrogenolysis, offering high surface area, porosity, and tunability. Ru-based MOFs and Mg-IRMOF-74 variants provide efficient metal dispersion and access to confined reaction environments. Single-atom catalysts (e.g., Ru₁/CeO₂, Fe₁/CeO₂, Ru₁Co alloys, Pd₁/PU, Fe₁-TiO₂) and organo-Zr single-site catalysts represent the frontier of precision catalysis. These systems maximize atom economy, enable selective C–C and C–H bond cleavage, and significantly reduce the quantity of precious metals required—thus aligning high catalytic performance with economic and environmental sustainability. Recent studies have yielded impressive results across diverse catalytic systems and reactor setups (Table 7):

Table 7. Recent developments in catalytic hydrogenolysis technologies for waste polymer valorization.

Type of catalysts	Example	Feedstock	Performance/Notes
Noble metal- based catalysts	Mesoporous mSiO ₂ /Pt-X/SiO ₂	PE, PP	60–75% conversion
Transition metal catalysts	Ni/SiO ₂	LDPE, PP, PS, PE	65 wt% n-alkanes (C ₆ to C ₃₅)
Transition metal catalysts	RuCo ₃ /CeO ₂ and RuNi ₃ /CeO ₂	LDPE	Up to 70% C ₂ –C ₁₅ selectivity by RuCo ₃ /CeO ₂ , RuNi ₃ /CeO ₂ and 90% selectivity for methane by Ru/CeO ₂
Bimetallic catalysts	Ru–Pt/TiO ₂	PE	85.1% conversion
Bimetallic catalysts	Ru ₅ Pt ₁ /CeO ₂	LDPE	99%
Bifunctional catalyst	Pt/SrTiO ₃	i-PP	95wt% liquid products
MOFs	DUT-5-RuH ₂ and MIL-53-RuH ₂	LDPE	98% conversion into liquid alkanes and 80% selectivity of liquid hydrocarbons ranging from C ₈ to C ₂₄
Silica	Mesoporous silica shell	HDPE, PP	Up to 98% conversion into liquids and solid residue
Single-atom catalysts	Ru ₁ /CeO ₂	Mixed plastic waste	90% conversion, >99% CH ₄

As seen in Table 7, a multistage hydrogenolysis approach was developed using mesoporous mSiO₂/Pt-X/SiO₂ catalysts for the treatment of PE and PP. In a mechanically stirred autoclave at 300 °C and 30 bar, the process followed a three-step conversion: an initial 25% PE conversion producing 65% waxy hydrocarbons, followed by further breakdown yielding 60–75% conversion, and finally over-hydrogenolysis into volatile species. Notably, minimal gas formation was observed, while light hydrocarbons were recovered in high yield under these mild, tunable conditions [83]. Cost-effective and accessible, Ni/SiO₂ catalysts have shown

efficacy across a broad feedstock range—LDPE, PP, PS, and PE. Operated in a Parr batch reactor at 300 °C and 30 bar, this system delivered up to 65 wt% n-alkanes (C₆–C₃₅). Their efficiency in C–C bond scission is strongly influenced by metal-support interactions and nickel dispersion, offering a flexible and economical platform for industrial adoption [84]. Bimetallic systems such as RuCo₃/CeO₂ and RuNi₃/CeO₂ demonstrated fine-tuned selectivity for the hydrogenolysis of LDPE. At 250 °C and 18 bar, RuCo₃/CeO₂ achieved up to 70% selectivity for C₂–C₁₅ hydrocarbons, whereas monometallic Ru/CeO₂ led primarily to methane production (~90% selectivity). This contrast highlights the advantage of cooperative metal interactions in modulating product distribution [85]. A hybrid system of Ru–Pt supported on TiO₂ achieved high-performance depolymerization of pristine PE and PE waste in a high-pressure reactor at 325 °C, 10 bar. This method integrated hydrogenolysis with aqueous-phase reforming using methanol, resulting in 85.1% conversion for virgin PE and 88.9% for PE waste, alongside a remarkable 81% selectivity toward desirable products [86]. At significantly milder conditions, Ru₅Pt₁/CeO₂ enabled near-complete conversion of LDPE in a stainless-steel autoclave at 200 °C and 5 bar, achieving 99% total conversion. Comparatively, monometallic Ru and Pt analogs achieved only 55% and <1%, respectively, underscoring the synergy between Ru and Pt in promoting effective hydrogenolysis [87]. Highly selective outcomes were also reported with Pt supported on SrTiO₃ for isotactic polypropylene (i-PP) processing. At 300 °C and 12 bar, this catalyst delivered a remarkable 95 wt% yield of liquid products, further reinforcing the role of structured oxide supports in tuning catalytic behavior [88]. Metal–organic frameworks (MOFs), such as DUT-5-RuH₂ and MIL-53-RuH₂, were employed for LDPE depolymerization. In a Parr reactor at 200 °C, DUT-5-RuH₂ achieved 98% conversion, with 80% selectivity toward C₈–C₂₄ liquid alkanes. These catalysts benefit from high porosity and tunable coordination environments, allowing for precise control over product distribution [89]. Mesoporous silica shell catalysts embedded with metal nanoparticles showed strong performance across HDPE and PP substrates. Operated in a Parr autoclave between 250–300 °C and 8–52 bar, these systems achieved up to 98% conversion, producing a mix of liquid hydrocarbons and carbon-rich residues. The tailored architecture of the mesoporous shell enhanced reactant access and stabilized metal active sites, leading to high durability and consistent performance [90]. Single-atom Ru on CeO₂ (Ru₁/CeO₂) was tested on an unsorted “real mixed plastic” feed—containing PE, PP, PS, PET, PVC, and other common polymers—and showed exceptional hydrogenolysis performance. In a stirred autoclave at around 300 °C under ~50 bar H₂, the catalyst achieved over 90% conversion of the mixed plastics, with >99% of the carbon recovered as methane. Because Ru atoms are atomically dispersed on the CeO₂ surface, each polymer fragment—regardless of origin—encounters a uniform active site; strong metal–support interactions with ceria’s oxygen vacancies promote efficient H₂ activation and inhibit coking. As a result, the Ru₁/CeO₂ system maintained high activity and selectivity over multiple cycles, converting diverse plastic waste streams into nearly pure CH₄ under mild hydrogenolysis conditions [91].

Crucially, the environmental footprint of hydrogenolysis is heavily influenced by the source of hydrogen used in the process. Most catalytic systems rely on gray hydrogen, typically generated from fossil fuels like natural gas via steam methane reforming (SMR), which results in substantial CO₂ emissions. In contrast, green hydrogen, produced through electrolysis powered by renewable energy, offers a carbon-neutral alternative that can dramatically reduce the life-cycle emissions of plastic upcycling processes. However, the widespread adoption of green hydrogen is currently limited by high production costs and infrastructure challenges. As hydrogenolysis becomes more industrially relevant, integrating green hydrogen pathways will be essential to meet circular economy and decarbonization goals. The choice of hydrogen source must therefore be considered in both catalyst design and process development, especially for assessing the overall sustainability of polymer-to-chemical conversion platforms.

In the UK, Green Lizard [92] uses a proprietary catalyst to efficiently depolymerise PET waste into TPA and EG, which can be reused to make new PET or high-value chemicals. A recent merger with North Tees Group supports one of the UK’s first green “power-to-liquids” hubs for e-fuels. Aeternal Upcycling (Lemont, IL, USA) applies catalytic hydrogenolysis using platinum-coated nanocubes to convert polyolefins into waxes, lubricants, and cosmetics. Operating at lower temperatures than pyrolysis, their method boosts efficiency and cuts emissions by ~75%, according to Argonne data. Aeternal Upcycling is transitioning from gram- to kilogram-scale production and intent to open a full-scale facility. Sels Group’s BIOCON (Bangalore, India) advances Reductive Catalytic Fractionation (RCF), using metal catalysts (Ru, Ni, Pd) and hydrogen under mild conditions to convert lignin into stable phenolic monomers while preserving cellulose. BIOCON is now at pilot scale, with multi-kg processing and a facility at KU Leuven, supporting lignocellulosic biomass upcycling [93].

2.8. Catalytic Solvolysis

Catalytic solvolysis presents a versatile and increasingly refined approach for breaking down synthetic polymers into their monomeric or oligomeric constituents using a solvent in the presence of a catalyst. The solvolysis of polymer waste employs a diverse array of catalysts. Zeolite and solid acid catalysts such as H-ZSM-5, HY, SAPO-34 (Silicoaluminophosphate), and γ -Al₂O₃ are commonly used. Acid catalysts include H₂SO₄, BF₃, AlCl₃, HCl, p-Toluenesulfonic Acid (PTSA), ZnCl₂, and TiCl₄. Basic conditions are often facilitated by NaOH, Ca(OH)₂, KOH, triethylamine, and piperidine. Transition metals like nickel, cobalt, iron, and molybdenum serve as effective catalysts, as do alkaline metal oxides such as MgO/NaY and CaO (as well as SrO and BaO) supported on MCF. Noble metals including platinum, palladium, and ruthenium are also employed for their high catalytic activity. Organometallic catalysts, particularly those based on tin and titanium, offer another route. Additionally, ionic liquids such as [BMIM]Cl, [EMIM]Br, and [P14,6,6,6]Cl, along with deep eutectic solvents like choline chloride combined with zinc chloride (ChCl/ZnCl₂), present modern and versatile alternatives in catalytic solvolysis processes. Through innovations in catalysts and reaction environments, recent work has achieved impressive yields, enhanced selectivity, and greater alignment with green chemistry principles (Table 8):

Table 8. Recent developments in catalytic solvolysis technologies for waste polymer valorization.

Types of Catalysts	Example	Feedstock	Performance/Notes
Lewis acid catalysts	ZnCl ₂	PET	Up to 98.31% terephthalic acid (TPA) with 97.14% purity.
Lewis acid catalysts	ZnCl ₂	PU	23.58%, 26.40% and 44.57% of 2,4-diaminotoluene, MOCA and PTMEG respectively
Base catalysts	NaOH	PET bottles	Over 90% conversion to TPA (purity 99.6%)
Bifunctional catalyst with both acidic and basic properties	MgO/NaY	PET	99% conversion and 91% of dimethyl terephthalate yield.
Ionic liquids	[Ch][X], X = Gly, Ala, Phe, Pro, Trp	PET waste	Up to 85% conversion of PET with a 62% yield of bis (2-hydroxyethyl) terephthalate (BHET).
Deep Eutectic Solvents	Deep Eutectic Solvents based on choline chloride-urea and choline chloride-thiourea	PET waste	~99% conversion of PET to TPA, monohydroxyethyl terephthalate (MHET), and BHET with yield yield of 62.79–80.66%, 17.22–34.79% and 0.54–0.59% respectively.
Nanocomposites	2D holey MnO ₂ /graphene oxide nanosheets	PET	100% BHET
Heterogeneous bifunctional catalyst	ZnO/ γ -Al ₂ O ₃	PET	92.2% diethyl terephthalate
Composite multifunctional catalyst	CoFe ₂ O ₄ /C10-OAC	PET	100% conversion of PET, BHET yield 95.8%
Salts and enzymes	Zn(CH ₃ CO ₂) ₂ and <i>Humicola insolens</i> cutinase	PET from textile waste	Up to 97% TA and small oligomers
Homogeneous Lewis-acid catalyst	Tetranuclear titanium	Post-consumer PET	Over 95% yield of methyl terephthalate and ethylene glycol

As seen in Table 8, zinc chloride (ZnCl₂) has proven highly effective in promoting solvolytic reactions. Applied to PET, it enabled up to 98.31% yield of terephthalic acid (TPA) with 97.14% purity in simple aqueous conditions at 180 °C [94]. Similarly, when used with polyurethane (PU) at 140 °C, ZnCl₂ facilitated the recovery of valuable intermediates including 2,4-diaminotoluene, MOCA, and PTMEG, with yields ranging between 23–45%. Despite the high activity, these reactions often require post-treatment neutralization, especially when conducted in acidic aqueous media [95]. Strong base-mediated solvolysis using NaOH has demonstrated exceptional performance for both commercial and post-consumer PET bottles. A two-stage process in a water–ethanol mixture followed by acid precipitation yielded over 90% TPA, with a remarkable purity of 99.6%, showcasing the practicality and scalability of alkaline hydrolysis in real waste streams [96]. Hybrid catalysts

such as MgO/NaY have shown promise for methanolysis of PET in high-pressure systems. At 180–220 °C, conversion reached 99%, with 91% dimethyl terephthalate (DMT) yield. Impressively, the 21% MgO/NaY catalyst remained active across six cycles, underlining its durability and efficiency in transesterification-based depolymerization [97]. Ionic liquids, particularly choline-based salts like [Ch][Gly], [Ch][Ala], and [Ch][Phe], offer a tunable, low-volatility environment for PET solvolysis. At 190 °C, these systems achieved PET conversions of 70–85%, with bis(2-hydroxyethyl) terephthalate (BHET) yields ranging from 50–62%, depending on the ionic liquid. Their recyclability and selective action under mild conditions make them attractive for green processing [98]. Similarly, deep eutectic solvents (DESs) based on choline chloride-urea and choline chloride-thiourea enabled near-complete microwave-assisted solvolysis of PET in ethylene glycol. Within minutes at 180–250 °C, PET was converted with \approx 99% efficiency, producing TPA, MHET, and BHET in varying yields. Post-consumer PET showed 96.8–98.2% conversion, demonstrating the adaptability of this ultrafast, two-step glycolysis–hydrolysis approach [99]. A standout system using 2D holey MnO₂/graphene oxide nanosheets offered 100% BHET yield from PET in just 10 min at 200 °C. The high activity was attributed to the catalyst's large surface area and abundant active sites from the MnO₂–GO interface. Remarkably, full catalytic performance was retained after five cycles, confirming its robustness [100]. For supercritical solvolysis, ZnO/ γ -Al₂O₃ exhibited strong performance in ethanol at 270 °C, yielding 92.2% diethyl terephthalate. This reusable catalyst, stable across five cycles, underscores the potential of high-pressure systems for fast and efficient PET breakdown [101]. Another reusable platform involved CoFe₂O₄/C10-OAC, a magnetic catalyst used in ethylene glycol at 195 °C, reaching 100% PET conversion and 95.8% BHET yield, with recyclability maintained for up to 10 cycles. This magnetic recovery route enhances process simplicity and sustainability [102]. A chemoenzymatic approach combined Zn(CH₃COO)₂ with cutinase from *Humicola insolens* to valorize textile-derived PET. In a two-step process, the chemical phase at 180–250 °C yielded 85% TPA and oligomers, while the enzymatic phase at 50 °C converted remaining oligomers to 97% pure TPA, highlighting the synergy between catalytic and biocatalytic pathways for high-purity product recovery [103]. Using a multinuclear titanium catalyst in a stirred batch reactor at 120–140 °C, post-consumer PET is efficiently methanolized into methyl terephthalate and ethylene glycol with over 95% yield, and the catalyst retains more than 90% of its activity after five reuse cycles [104].

LyondellBasell acquired APK AG's solvent-based tech to recycle LDPE from flexible plastics, producing high-purity materials under its Circulen brand. Reju (Nanterre CEDEX, France), with Technip and IBM, uses VolCat—an organic catalyst process—for polyester recycling, cutting CO₂ by 50% and producing high-quality yarn. Its German plant processes 1000 tonnes/year, with two more facilities planned by 2027 [105]. Reju partners with Goodwill and WM® to source textile waste for circular polyester regeneration. Teijin Frontier (Kita-ku, Osaka, Japan) uses ethylene glycol and proprietary catalysts to depolymerise colored PET into BHET, simplifying recycling and enabling reuse of mixed or contaminated fibers [106]. Loop Industries (Terrebonne, QC, Canada) breaks down PET into monomers like BHET and DMT using methanol and a catalyst to make virgin-quality PET [107]. Poseidon Plastics (Liverpool, UK) [108] also uses ethylene glycol and a catalyst to convert PET into BHET. Ioniqa Technologies (Eindhoven, The Netherlands) [109] uses a solvent system and solid catalyst to depolymerise PET into monomers for high-grade recycled PET.

2.9. Innovations and the Role of AI in Advancing Catalysts and Reactor Design

The escalating accumulation of plastic waste poses significant environmental challenges, necessitating the development of efficient recycling methods. Catalytic depolymerization offers a promising avenue by breaking down polymers into valuable monomers and chemicals. Recent advances in artificial intelligence (AI) and computational tools have further streamlined this workflow—extending AI applications from routine tasks like plastic-waste sorting to sophisticated challenges such as discovering novel catalysts and optimizing depolymerization process (Figure 3):

Machine learning algorithms analyze vast datasets to predict the performance of potential catalysts, expediting the discovery of materials with desired properties. This data-driven approach reduces reliance on trial-and-error experimentation, leading to more efficient catalyst development. Recent advances have demonstrated that machine learning can profoundly accelerate the discovery and optimization of catalysts for plastic-waste depolymerization. Lu et al. demonstrate how a structure-based machine-learning algorithm can rapidly engineer a hydrolase—specifically, PETase—for vastly improved PET depolymerization [110]. Starting from a training set of over 5000 known cutinase/PETase homologs and thousands of variants, they extracted 18 structural and sequence features (e.g., active-site loop flexibility, electrostatic potential, solvent accessibility) and fed these into a gradient-boosted decision-tree model. That model then predicted which combinations of point

mutations would most increase catalytic efficiency (k_{cat}/K_M) at moderate temperatures. Guided by these ML-derived rankings, the authors synthesized a “FAST-PETase” variant (initially bearing five mutations: S238F, S238Y, etc.), which was further refined to include stabilizing substitutions such as T59I and Q119K. In application, FAST-PETase depolymerizes untreated post-consumer PET (ranging from thermoformed packaging to amorphous bottle fragments) at 50 °C, pH 7.5, releasing >90% of its mass as terephthalic acid (TPA) and ethylene glycol (EG) within 24 h for amorphous samples and within one week for crystalline bottle pieces. For example, a whole water-bottle body (~23 g) was fully converted to monomers in 48 h merely by shaking with 1 μ M FAST-PETase. Yields routinely exceed 95 mol% TPA (relative to PET repeat units), with EG recovered in stoichiometric amounts. Thus, this work illustrates machine-learning-guided “reverse design”—using ML to predict which mutations will most improve both activity and stability—and validates that approach by producing a PETase variant whose performance on real packaging waste outstrips all previous hydrolases under mild, scalable conditions. A structure-based deep-learning model (MutCompute) was trained on the crystal structure of TfCut2 to evaluate the local environments of each amino acid and rank mutations by their likelihood to enhance hydrolytic activity and stability [111]. From the top ten predicted substitutions, iterative screening and recombination yielded the variant L32E/S113E/T237Q, which depolymerizes PET films and powders far more efficiently than wild-type TfCut2. Under QCM-D-monitored conditions, L32E/S113E/T237Q achieves a 2.9-fold increase in hydrolysis of amorphous PET film and a 5.3-fold boost on crystalline PET powder (crystallinity > 40%), releasing TPA, MHET, and BHET as products. This triple mutant also exhibits a 5.7 °C higher T_{50}^{60} thermal inactivation temperature, confirming that the ML-guided substitutions both accelerate PET depolymerization and improve enzyme robustness. Zheng and co-workers use a reverse-design, machine-learning framework to optimize polyoxometalate (POM) catalysts for lignin oxidation [112]. After compiling a dataset of POM compositions and monomer yields, they train gradient-boosted regression trees to predict which formulations maximize C–O bond cleavage under mild oxidation. The ML model highlights descriptors—such as addenda metal oxidation state and heteroatom charge density—that correlate with performance. Guided by these insights, they synthesize a vanadium-substituted Dawson-type POM, $H_8P_2Mo_{16}V_2O_{62}$ (“V-POM”), which at 150 °C in MeOH/H₂O (8:2) under 1 MPa O₂ yields 24% aromatic monomers from larch lignin in 4 h—surpassing previous POMs. Its superior activity stems from an optimal balance of Mo/V redox potential and P-centered acidity, both identified by ML. This work shows how ML-assisted reverse design can discover novel POM catalysts for enhanced oxidative depolymerization. A Transformer-based deep-learning model was first trained on thousands of sequence–function pairs from known PET hydrolases to predict which residue substitutions would most improve catalytic turnover and stability. From these predictions, the authors engineered a variant called TurboPETase, which features mutations that reshape and flexibly expand its PET-binding groove [113]. In enzymatic hydrolysis experiments at 50–65 °C and pH 8.0, TurboPETase depolymerized post-consumer PET bottles (200 g kg^{−1} solids loading) to nearly 100% conversion within 8 h, achieving a maximum production rate of 61.3 g hydrolyzed PET L^{−1} h^{−1}. The only products detected were terephthalic acid and ethylene glycol, with no detectable oligomeric intermediates. Notably, TurboPETase outperformed all benchmark hydrolases under these industrially relevant, high-solids conditions.

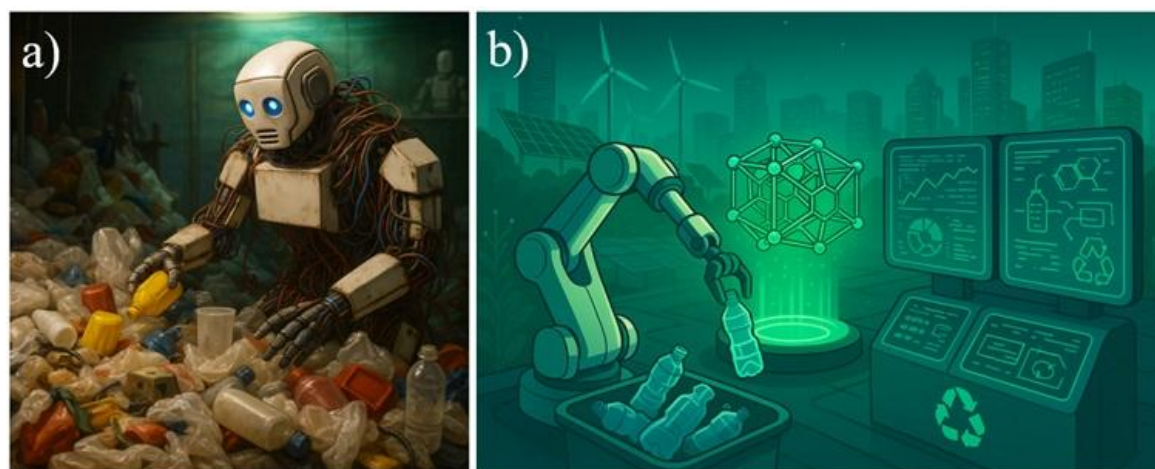


Figure 3. The use of AI in plastic waste sorting (a) and in the optimization of the depolymerization process (b). Images generated by the author using the AI tool ChatGPT (DALL·E).

Several industrial initiatives have successfully integrated AI and novel catalysts into their depolymerization processes. Carbios has developed an industrial application of enzymes that render plastic waste compostable. Their technology focuses on the depolymerization of plastics using engineered enzymes, facilitating efficient recycling processes. Samsara Eco (Sydney, NSW, Australia) has developed enzymes that break down plastics like Nylon 6, enabling indefinite recycling. They employ machine learning algorithms to design enzymes targeting various plastics, contributing to waste reduction in the fashion industry. Epoch Biodesign (London, UK) is developing a library of plastic-degrading enzymes. By utilizing generative AI models, they accelerate the discovery and engineering of enzymes that can efficiently depolymerize plastics, aiming to address plastic pollution through biorecycling. Protein Evolution (New Haven, CT, USA) employs AI to design enzymes capable of breaking down polyester textiles into their original monomers. This approach facilitates the recycling of old polyester into materials that perform like new.

Currently, specific companies dedicated to using artificial intelligence (AI) for optimizing reactors in the catalytic depolymerization of plastic waste are not prominently documented. However, research in this area is active, with studies exploring the integration of AI techniques to enhance process prediction and optimization. For instance, recent research has employed artificial intelligence methods to predict and optimize the co-pyrolysis process of biomass and plastic waste, demonstrating the potential of AI in improving such systems [114]. Given the rapid advancements in AI and its applications in chemical processing, it is plausible that companies may begin to incorporate AI-driven reactor optimization techniques into their catalytic depolymerization processes in the near future. A robotics startup from University of Massachusetts has developed an AI-powered robotic system to improve waste sorting and recycling [115]. Using computer vision and AI, the system quickly and accurately identifies and separates materials like plastic, paper, and cardboard, reducing contamination and increasing efficiency in materials recovery facilities. rStream piloted its mobile sorting unit—capable of processing up to a ton of waste per hour—at UMass Amherst's dining commons and Waste Recovery Facility in March 2025. These tests helped refine its AI algorithms and demonstrated the system's real-world effectiveness. By automating sorting, rStream's technology enhances recycling output, lowers labour costs, and supports more sustainable waste management. Using AI-powered image recognition and remote sensing is used to identify and track plastic waste in marine environments [116]. It highlights AI's role in detecting and monitoring waste, optimizing sorting and recycling operations, and forecasting pollution trends.

Catalytic processes like hydrocracking, gasification, and pyrolysis are key to renewable energy and net-zero goals, but their complex behavior requires advanced modelling for optimization. A hybrid machine learning model combines a physics-based kinetic model with an artificial neural network [117]. Applied to hydrocracking, the model achieved high accuracy ($MSE < 0.01$) and was integrated with a genetic algorithm (NSGA-II) for multi-objective optimization. The approach effectively identified trade-offs between yield and selectivity, showing strong potential for accelerating smart design and optimization of catalytic processes. Machine Learning Integration was used in optimizing the pyrolysis reactor performance [118]. ML algorithms, including neural networks and support vector regression, are employed for predictive modeling and interpretation, enabling accurate forecasting of product yields and quality, reduce environmental impact, and advance sustainable plastic waste management efforts, thereby promoting a circular economy model. Due to the variability of post-consumer plastics, machine learning (ML) is a powerful tool for optimizing plastic pyrolysis. By analyzing historical data and sensor inputs, ML algorithms can adjust process parameters in real-time to improve yield, efficiency, and product quality while reducing costs. Techniques like neural networks (NN), support vector regression (SVR), decision trees (DT), and Gaussian processes (GP) have all shown success in modeling and forecasting pyrolysis outputs. When combined with GC/MS, ML can also predict and analyze liquid products. This approach supports waste-to-energy strategies, promotes circular economy goals, and reduces reliance on fossil fuels and greenhouse gas emissions. An innovative approach to enhancing the hydrocracking process of waste plastic pyrolysis oil (WPOH) named "WPOH-Pro" integrates process simulation with advanced deep learning models to achieve multi-objective optimization [119]. The WPOH-Pro process demonstrates a 50.44% increase in net profit compared to the original WPOH process. This enhancement is primarily due to higher yields of gasoline and naphtha, with an associated production cost of \$4.58 million per annum. Life cycle analysis reveals a 22.9% reduction in non-renewable energy consumption and a significant decrease in greenhouse gas emissions, quantified at 390.24 tCO₂ equivalent per million GDP. Additionally, compared to the WPOH process, WPOH-Pro achieves a reduction in CO₂ emissions of 99.38 tCO₂ equivalent per million GDP. This study is pioneering in its combination of process simulation with deep learning-driven optimization for waste plastic hydrocracking. The framework not only accelerates process parameter optimization but also addresses key environmental concerns, providing a robust foundation for engineering applications in waste plastic recycling and promoting the circular economy.

ML-guided prediction and interpretation accelerates zeolite screening and optimizes catalytic pyrolysis of waste plastics, leading to near-quantitative liquid fuel yields under the identified conditions [120]. Zeolite-catalyzed pyrolysis of mixed waste plastics—mainly polyethylene, polypropylene, and their blends—is analyzed by constructing a machine-learning model that predicts and optimizes liquid-fuel (oil) and C₅–C₁₂ hydrocarbon yields. A database of experimental runs includes variations in plastic composition (i.e., PE fraction), zeolite properties (surface area, Si/Al ratio), and reaction temperature. Using Extreme Gradient Boosting (XGBoost), oil and gasoline-range hydrocarbon yields are predicted with R² values of approximately 0.85–0.87. By interpreting feature importance, ML reveals that the PE ratio in the feed, reaction temperature, zeolite surface area, and Si/Al ratio most strongly influence product yields. Using inverse design on this ML model, they identify an optimal zeolite (high surface area, moderate Si/Al) and conditions (≈550 °C, PE-rich feed), predicting a maximum oil yield of 80.85%. Experimentally, pyrolyzing a mixed-plastic stream over that zeolite in a lab-scale fixed-bed reactor delivers 87.82% oil yield with C₅–C₁₂ selectivity, within 7.93% prediction error.

Structural imperfections in plastics influence its catalytic dehydrogenation, a key process in chemical upcycling of plastic waste. Utilizing density functional theory (DFT) calculations, the researchers examined the interaction between a (tBu₄POCOP)-Ir pincer complex catalyst and PE chains containing common in-chain impurities such as carbonyl, hydroxyl, epoxide groups, and chlorine atoms [121]. The findings reveal that these impurities form stable complexes with the catalyst, significantly increasing the energy barriers for the initial C–H bond activation step and thereby inhibiting the overall catalytic performance. Additionally, the study indicates that while dehydrogenation is hindered in crystalline PE due to steric constraints, highly distorted PE chains and side alkane chains exhibit greater susceptibility to the catalyst, suggesting that polymer chain morphology plays a crucial role in catalytic efficiency. These insights underscore the importance of considering polymer imperfections and structural variations in developing effective catalytic upcycling strategies for plastic waste.

An advanced AI-based decision-making framework was used to evaluate plastic recycling methods [122]. This research offers a sophisticated AI-driven tool for policymakers and industry stakeholders to make informed decisions in selecting optimal plastic recycling strategies, thereby contributing to environmental conservation and sustainable waste management practices. By combining the ELECTRE method with bipolar dual hesitant fuzzy sets, the approach enables more nuanced assessments of recycling strategies. Using entropy-based weighting, the study ranked environmental, economic, social, technical, and safety factors, with economic feasibility rated most important. Among the three recycling methods analysed—mechanical, chemical, and thermal—mechanical recycling emerged as the most effective. The framework's reliability was confirmed through sensitivity analysis, offering a valuable tool for guiding sustainable plastic waste management decisions. Ultimately, AI predictions can help researchers and industry professionals refine depolymerization processes to achieve desired product yields and compositions, while also tailoring process parameters to specific requirements.

3. Conclusions

Catalytic upcycling represents a transformative approach to addressing the escalating global polymer waste crisis. Unlike traditional mechanical recycling, which often leads to downcycling and compromised material quality, catalytic processes enable the selective depolymerization of synthetic and natural polymers into high-value products, thereby recovering the intrinsic chemical value of waste materials. This review has explored a broad array of catalytic pathways—including pyrolysis, gasification, oxidation, hydrocracking, hydrogenolysis, solvolysis, and enzymatic depolymerization—that collectively form a powerful toolkit for polymer waste valorization. Among these, catalytic depolymerization of polyesters, particularly PET, is currently the most commercially advanced, with industrial players like Carbios, Loop Industries, and Poseidon Plastics pioneering scalable solutions. However, significant innovations are now extending this capability to more chemically resistant and abundant polymers such as polyolefins, nylons, polyurethanes, and multi-component waste streams including textiles and composites. The development of robust, reusable catalysts—ranging from zeolites and metal-organic frameworks to earth-abundant metals and biocatalysts—has significantly improved efficiency, product selectivity, and environmental compatibility across different polymer classes. Hybrid technologies combining catalytic and biological steps, as well as chemoenzymatic routes, offer new levels of selectivity under mild conditions, further enhancing the sustainability of polymer upcycling. Additionally, the integration of artificial intelligence and machine learning is revolutionizing catalyst design, reactor optimization, and process control, accelerating the discovery and industrial deployment of next-generation recycling technologies. These digital tools have shown promise in improving process yields,

energy efficiency, and predictive maintenance, supporting the transition to smart, adaptive circular economy systems. Nevertheless, several critical challenges remain. The economic and environmental feasibility of catalytic upcycling must be improved through cost-effective catalyst synthesis, extended catalyst lifetimes, and greater energy efficiency. Managing complex, mixed, and contaminated waste streams requires advanced sorting, preprocessing, and purification methods. Furthermore, commercial scalability depends not only on technical readiness but also on supportive policy frameworks, robust supply chains for post-consumer waste, and market incentives for recycled and upcycled products. To achieve meaningful impact, catalytic upcycling must be embedded within holistic waste management strategies that integrate infrastructure development, cross-sector collaboration, and lifecycle thinking. Scaling these technologies will reduce reliance on fossil-derived virgin feedstocks, mitigate plastic pollution, and enable the production of sustainable chemicals and materials. In doing so, catalytic recycling can shift perceptions of plastic waste—from an environmental burden to a valuable chemical resource—and play a central role in building a resilient, resource-efficient circular economy.

4. Perspective

The global shift toward circular economies presents an urgent need for more effective and sustainable strategies to manage polymer waste. Catalytic upcycling has emerged not merely as a scientific advancement but as a pivotal enabler for this transformation. The innovations reviewed in this work underscore the vast potential of catalysis to convert plastic waste into high-value monomers, fuels, commodity and high value chemicals under increasingly efficient and environmentally benign conditions. The next frontier in polymer valorization lies at the intersection of advanced catalysis, digital innovation, and systems integration. Artificial intelligence and machine learning are rapidly evolving from conceptual tools to practical accelerators in catalyst design, process control, and reactor optimization. In parallel, multi-functional hybrid catalysts and integrated chemo-enzymatic pathways are redefining what is possible in terms of selectivity and mild operating conditions. Such approaches offer a glimpse into future processes that are not only more effective but also more adaptive and resilient. Despite these breakthroughs, considerable gaps remain between laboratory-scale discoveries and full industrial implementation. Addressing the challenges of feedstock variability, catalyst stability, energy intensity, and economic feasibility requires a concerted effort across disciplines. Collaborative frameworks involving academia, industry, and policy stakeholders will be essential to align scientific progress with practical deployment. Looking forward, catalytic upcycling can redefine polymer waste not as a burden, but as a resource—capable of contributing to decarbonization, reducing reliance on virgin petrochemicals, and enabling the production of next-generation materials. To unlock this potential, further research should focus on developing low-cost, scalable catalysts for recycling challenging polymers such as polyolefins and multi-layer composites, expanding the scope of biocatalysis, and embedding circularity principles into product and process design from the outset. In this critical decade for climate and resource sustainability, catalytic solutions for polymer waste must move from innovation to implementation. Doing so will not only help close the loop on plastics but also demonstrate the central role of green chemistry in building a truly circular and regenerative economy.

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