Review

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A Review on Catalyst Chemical Recycling Technologies for Production of Light Gaseous Compounds from Polyolefin Waste

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Abstract

Chemical recycling of polyolefins is essential to mitigate plastic waste accumulation and promote circular economy strategies. Among the various chemical recycling pathways, catalytic pyrolysis, tandem catalyst systems, ethenolysis, hydrocracking, and hydrogenolysis have emerged as promising approaches for converting polyolefin waste into valuable hydrocarbons, including gaseous, liquid, and solid products. This review provides a survey of recent research on these methodologies, with a particular focus on the production of light gaseous hydrocarbons (C1–C4), bypassing the intermediate pyrolysis oil stage, which is often associated with contaminants and increased processing costs. The novelty of the present work lies in its emphasis on gaseous fractions, in contrast to most existing studies that primarily target oil recovery. Aspects such as catalyst selection, reaction conditions, and product distribution are analyzed. Additionally, the current Technology Readiness Level (TRL) of the studied processes, their relative advantages, limitations, and perspectives for industrial applications are discussed. The analysis highlights catalytic pyrolysis with zeolites as the most mature and scalable technological alternative for manufacture of light compounds directly from polyolefin waste, while tandem catalyst systems and ethenolysis constitute promising but still emerging alternatives for targeted gas production.

Keywords: polypropylene; polyethylene; chemical recycling; catalytic recycling; gas production; circular economy

1. Introduction

The global production and consumption of plastic materials have increased over the past decades, leading to an urgent need for effective waste management strategies. Among various types of plastics, polyolefins — such as polyethylene (PE) and polypropylene (PP) — represent a significant portion of post-consumption plastic waste due to their extensive use in packaging, consumer products, and industrial applications [1–3]. Despite their versatility and durability, these materials pose environmental challenges, as they are not readily biodegradable and tend to accumulate in landfills and marine environments [1–5].

Mechanical recycling, the most widely used method for processing plastic waste, involves melting and reshaping plastic pieces and materials into new products. However, this approach has several limitations, including polymer degradation and contamination issues, for example [1,3,4,6]. As a result, chemical recycling constitutes an important alternative solution, as it allows the

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breakdown of plastic polymers into smaller molecules, which can be reused as raw materials for new chemical processes [1,3–6].

Several chemical recycling techniques have been explored to improve the efficiency of plastic waste valorization. As detailed in our previous review on promising processes to generate monomers from polyolefin waste, direct and consistent conversion remains a challenge for most current techniques; however, catalytic pyrolysis stands out as the most promising strategy for olefin recovery and the promotion of a circular economy [7]. Among these, catalytic pyrolysis, can yield gases, liquid fuels, and solid residues, depending on factors such as temperature, catalyst type, and reaction time. Catalysts play a crucial role in improving reaction selectivity, lowering energy requirements, and reducing unwanted byproducts [3,5,6].

A more recent and promising approach adopts the concept of 'tandem catalysts', where multiple catalytic steps are integrated to optimize the conversion of polyolefins into target products. This method enhances reaction efficiency by tailoring catalyst properties and reaction conditions to achieve higher selectivity and lower operational costs [5,8,9]. Dearomatization has additionally been explored as a method to reduce the formation of aromatic compounds. Since aromatic hydrocarbons can be undesirable for certain applications, strategies for controlling product composition through careful catalyst selection and reaction optimization are crucial for improving process efficiency [10,11].

Ethenolysis has also emerged as a viable alternative for chemical recycling, utilizing ethylene to crack polyolefin chains via olefin metathesis [12,13]. This process enables the selective degradation of plastics into valuable short-chain hydrocarbons, such as propylene, with potential applications in chemical synthesis and fuel production [12,13].

Hydrogenolysis and hydrocracking are additional techniques that involve the cleavage of polymer chains using hydrogen in the presence of metal catalysts [1,2]. These processes produce saturated hydrocarbons that can be used as chemical feedstocks or fuel. While hydrogenolysis offers the advantage of producing high-purity hydrocarbons, the need for hydrogen and catalyst deactivation remains a challenge for industrial applications [1,2].

Based on the previous paragraphs, the present review provides a survey and a comprehensive bibliometric analysis of these chemical recycling technologies, with a particular focus on the production of light gaseous hydrocarbons (C2-C4). The interest on light gaseous products is related to simplification of the process flowsheet, when one is interested in the manufacture of circular monomers. In this case, by avoiding the production of the intermediate pyrolysis oil, it can be possible to minimize process effects associated with contaminants and to reduce the processing costs. In order to do that, this review evaluates the use of different technologies, catalysts, operating conditions and obtained product distributions. By analyzing recent advances and research trends, the present work aims to contribute to the development of efficient and sustainable plastic recycling solutions, discussing the relative advantages and disadvantages of competing technologies and presenting some perspectives for future developments.

2. Methods

This review adopts a bibliometric and qualitative analysis approach to map recent developments regarding the chemical recycling technologies of polyolefins with a focus on production of light gaseous compounds (particularly light hydrocarbons, C1–C4). Literature searches were conducted using the *"Web of Science"* platform, considering publications available until December 2025. To cover different facets of the topic, searches were performed using specific keyword sets for each subtheme. The inclusion criteria focused on studies involving polyolefin feedstocks and relevant outcomes regarding production of gaseous products, especially through pyrolysis, hydrogenolysis, hydrocracking, and ethenolysis. Studies centered on unrelated products (such as fuels and aromatics) or based on mathematical modeling without presentation of experimental validation were excluded from the present analyses.

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2.1. Catalytic Pyrolysis

In this case, the search included the keywords *"Pyrolysis Plastic Catalyst Review"* in the article titles, covering publications up to December 2025. After downloading the manuscripts, their reference lists were examined to complement the analysis. In this context, the 12 papers identified were used as a basis to determine the main catalysts employed for the production of gaseous products. Subsequently, the selected reviews, shown in Figure 1, were analyzed, as they discuss a range of catalysts used in catalytic polyolefin pyrolysis, with emphasis on their physicochemical properties, reaction conditions, and gas-phase product distribution. The key information extracted included catalyst types, reaction pathways, and polymer feedstocks.

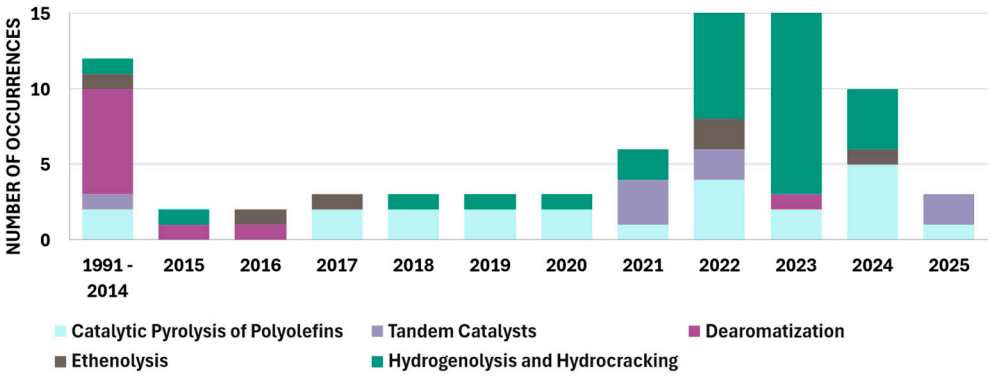

Figure 1. Temporal distribution of selected publications within the defined scope of this review, categorized according to technological route for the production of light gaseous hydrocarbons from polyolefin waste.

Following the analysis of the reviews, a second search was conducted using the keywords *"Pyrolysis Plastic Zeolite"* in the article titles. This search was concentrated on use of zeolites because these are the catalysts used most often to perform catalytic pyrolysis investigations. The searched period covered publications until December 2025. After downloading the manuscripts, the lists of references were used to complete the analyses. As said previously, the considered publications were those focused on polyolefin feedstocks and reporting mainly the production of gaseous products. 72 publications identified, but only 23 studies were retrieved, shown in Figure 1, discussing the role of zeolite-based catalysts in catalytic pyrolysis processes, especially regarding the influence on gas yields, the characterization of physicochemical and morphological features (such as the pore structure and acidity) and the selectivity towards light hydrocarbons.

2.2. Catalytic Pyrolysis with Tandem Catalysts

In this case, the search included the words *"Pyrolysis Plastic Tandem Catalyst"* in the title and the abstract. This search was concentrated on the use of tandem catalysts because the use of such catalysts constitutes an emerging promising alternative for development of innovative pyrolysis technologies. The searched period covered publications until December 2025. After downloading the manuscripts, the lists of references were used to complete the analyses. As said before, the considered publications were those focused on polyolefin feedstocks and reporting mainly the production of gaseous products. 39 publications identified, of which 8 studies met the inclusion criteria, as shown in Figure 1, discussing the combination of multiple catalysts (containing acid and metal functions) to improve the yields of gases, enhance the selectivity and facilitate cascade reactions during polyolefin pyrolysis.

2.3. Dearomatization and Aromatic Cracking

In this case, the search included the words *"Dearomatization Catalyst"*, *"Aromatic Cracking"*, *"Benzene Cracking"*, *"Dearomatization Pyrolysis"* and *"Toluene Cracking"* in the title. This search was

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concentrated on application of dearomatization techniques because the manufacture of aromatics constitutes a problem for the circular production of olefin monomers, as aromatics are concentrated in the liquid phase and demand additional cracking stages for production of light gaseous compounds. The searched period covered publications until December 2025. After downloading the manuscripts, the lists of references were used to complete the analyses. Once more, the considered publications were those focused on polyolefin feedstocks and reporting mainly the production of gaseous products. 268 studies were retrieved and only 10 studies were selected, as shown in Figure 1, addressing the cracking or removal of aromatic compounds from the pyrolysis oil in order to shift product distribution towards gaseous aliphatic hydrocarbons.

2.4. Ethenolysis

In this case, the search included the words *"Ethenolysis"*, *"Ethenolysis Plastic"* and *"Ethenolysis Polyolefin"* in the title and the abstract. This search was concentrated on the investigation of ethenolysis reactions because the use of this technology constitutes an emerging promising alternative for manufacture of gaseous compounds from polyolefin waste. The searched period covered publications until December 2025. After downloading the manuscripts, the lists of references were used to complete the analyses. Once more, the considered publications were those focused on polyolefin feedstocks and reporting mainly the production of gaseous products. 84 studies were retrieved and only 6 studies were selected, as shown in Figure 1, discussing the ethenolysis of polyolefins (PE and PP) as a route to produce short-chain olefins like propylene.

2.5. Hydrocracking and Hydrogenolysis

In this case, the search included the words *"Hydrocracking Plastic"*, *"Hydrocracking Polyolefin"*, *"Hydrogenolysis Plastic"* and *"Hydrogenolysis Polyolefin"* in the title and the abstract. This search was concentrated on the investigation of hydrocracking and hydrogenolysis technologies because these processes are very mature in the petrochemical field and have been investigated as alternatives for manufacture of gaseous compounds from polyolefin waste. The searched period covered publications until December 2025. After downloading the manuscripts, the lists of references were used to complete the analyses. Again, the considered publications were those focused on polyolefin feedstocks and reporting mainly the production of gaseous products. 71 studies were retrieved and only 29 studies were selected, as shown in Figure 1, discussing the use of metal-supported catalysts (such as Ru, Pt and Ni) under hydrogen-rich reaction conditions to break C–C bonds in polyolefins and produce C1–C4 gaseous compounds.

Considering the defined inclusion criteria and the focus on light gaseous hydrocarbons (C1–C4), the graphical results obtained from each subtheme were consolidated into a single representative figure. Instead of presenting individual plots for each technological route, only the studies strictly aligned with the scope of this review (namely those reporting experimental production of gaseous fractions from polyolefin feedstocks) were selected. Figure 1 summarizes the temporal distribution of the selected publications according to the investigated technology, providing a comparative overview of research trends in catalytic pyrolysis, tandem catalysis, dearomatization, ethenolysis, and hydrogenolysis/hydrocracking. This consolidated representation highlights the evolution of scientific interest in processes directed toward light gas production while excluding studies centered primarily on liquid fuels, aromatics, or purely theoretical approaches.

3. Catalytic Pyrolysis of Polyolefins

3.1. Fundamentals

The pyrolysis of polyolefins is a well-established and extensively studied technology for plastic recycling, with various parameters clearly defined and understood. The process yields gaseous, liquid, and solid fractions. Key variables governing the process include temperature, reactor type,

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residence time, and pressure. The yield of each fraction primarily depends on the nature of the pyrolyzed material, as bond cleavage occurs based on the functional groups present in each material. The thermal degradation of polyolefins predominantly follows a free radical mechanism. This degradation process can produce a wide distribution of products across a broad range of carbon numbers (C5–C80) [14,15].

Catalytic pyrolysis of polyolefins aims to optimize the process and enhance product selectivity by employing catalysts, thereby accelerating the reaction mechanisms under investigation [16]. The use of catalysts in the pyrolysis of polyolefins has garnered commercial interest due to its potential to produce automotive fuels (diesel and gasoline) and light hydrocarbons (HC), which are in high demand within the petrochemical industry. In addition to lowering the pyrolysis process temperatures, catalysts guide product formation and can be reused at the end of the process when applied in heterogeneous systems and ex-situ processes [17].

There are various examples of heterogeneous catalysts used to perform the pyrolysis of polyolefins in the literature, including zeolites, nanocrystalline zeolites (HUSY, n-HZSM-5, Hβ, HMOR), silica-alumina, alumina, FCC (Fluid Catalytic Cracking), MCM-41, cement powder, clay/sand, kaolin, SBA-16, metal oxides, and molecular sieves, among others used in polyolefin pyrolysis reactions (Figure 2). The catalyst properties that influence the process include acidity, pore size, adsorption capacity, and specific area of the catalyst. The previously mentioned catalysts differ in these characteristics, influencing reaction rates, product distribution, and other reaction parameters [18,19].

The study of catalytic pyrolysis of polyolefins using zeolites is based on the premise that a significant portion of research has demonstrated effective cracking activities and appropriate product selectivities with these types of catalysts. In this context, it is noteworthy that their intrinsic acidic properties and their ability to exhibit reactant selectivity can play a crucial role in the pyrolysis process of plastics. The possibility of controlling the products by restricting diffusion through the pores, leading to smaller hydrocarbon fractions, has garnered considerable interest, as these hydrocarbon fractions are widely utilized as fuels and are in high demand within the chemical industry.

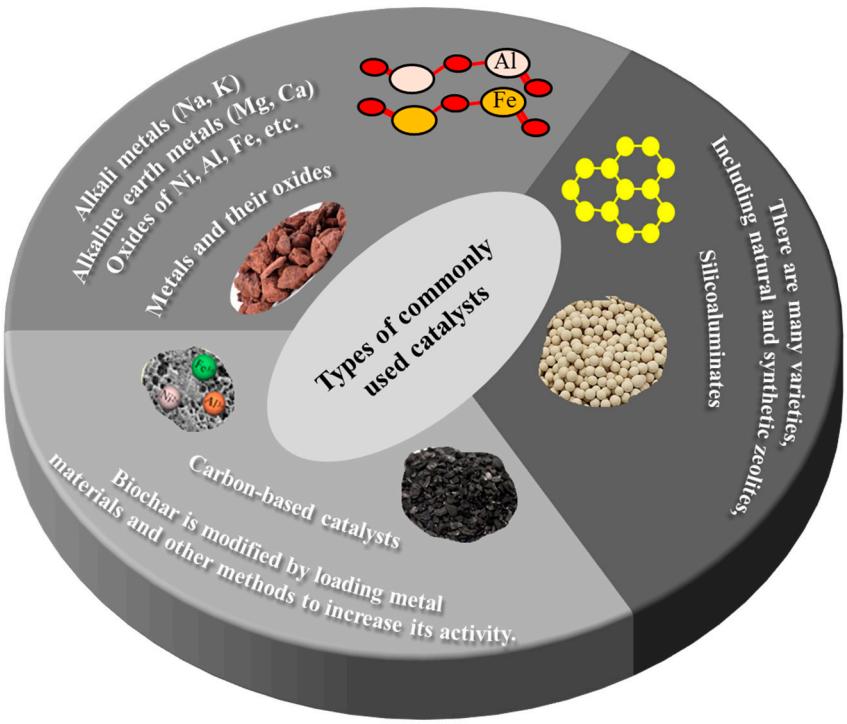

Figure 2. Typical catalysts used in catalytic polyolefin pyrolysis reactions (Adapted from XIE, 2024).

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3.2. Previous Works

Through an investigation of reviews that cite *"Pyrolysis Plastic Catalyst Review"*, it was possible to obtain indications of the main ways by which light fractions are produced in pyrolysis.

The review by Jadhav et al. (2024) analyzes the role of various heterogeneous catalysts in plastic pyrolysis, noting that acidity, surface area, and material structure dictate conversion rates and product selectivity . The most widely used zeolites include ZSM-5, USY, HY, and REY [20]. While they promote efficient cracking for liquid hydrocarbon production, highly acidic zeolites accelerate free radical synthesis and β-scission reactions, which increases the generation of hydrocarbon gases. Bimetallic catalysts, such as Ni-Fe and Mo-Ni, exhibit synergistic effects that lower activation energy and strongly direct the reaction toward the co-production of carbon nanotubes and hydrogen-rich gas. Among carbon-based alternatives, biochar inhibits solid wax formation and achieves notable gas yields; however, this gas fraction can contain up to 90% hydrogen by volume, rather than hydrocarbon gases. Activated carbon acts effectively in deoxygenation and the selective removal of contaminants, and its use also contributes to the generation of light gaseous hydrocarbons, such as light alkanes [20].

In their comprehensive review, Peng et al. (2022) emphasize that catalyst choice and process conditions dictate product distribution, noting that bimetallic catalysts exhibit distinct reaction behaviors compared to zeolites. Zeolite- and clay-based catalysts generally operate under milder temperature and pressure conditions than bimetallic or oxide catalysts. While mild-acidity clays restrict over-cracking to favor heavier liquid hydrocarbons and base catalysts primarily maximize the recovery of 1-olefin-rich oils, microporous zeolites (such as HZSM-5, HY, HMOR, and HUSY) promote severe cracking, significantly favoring the formation of aromatics and light gases. To optimize these reactions and mitigate deactivation, zeolites are often modified to adjust acid strength or create bimodal porosity, which enhances mass transfer to the active sites. Operating typically between 375 and 550 °C, zeolites can yield up to 95 wt% gas—comprising 60–67 wt% C1–C4 fractions—depending on the polymer used (PP or HDPE). Maximizing this gas formation is highly dependent on operational parameters [5].

An example of high gas recovery cited in the review by Peng et al. (2022) is the work of Lin and Yen (2005). For instance, a gas yield of 94.77 wt% was achieved during polypropylene pyrolysis at 360 °C over HZSM-5 in a fluidized bed reactor operating with a polymer-to-catalyst ratio of 40 wt%. This high gas selectivity is driven by the fluidization dynamics: the reactor inherently increases the polymer's residence time, which favors the generation of thermally stable non-condensable gases and light hydrocarbons [21].

Pawelczyk et al. (2022) explored pyrolysis-catalytic dry reforming (PCDR), a promising approach that integrates plastic pyrolysis with dry reforming to convert hydrocarbons and CO_2 into synthesis gas (syngas). The efficiency of the dry reforming stage is heavily dictated by the feedstock's chemical structure; specifically, aliphatic alkanes and alkenes derived from polyolefins like LDPE, HDPE, and PP are easily and highly reformed into syngas. Because PCDR is highly endothermic, achieving high conversion rates requires highly active and stable catalysts. To facilitate the reforming reactions, a variety of catalysts are employed. Nickel-based catalysts are the most common due to their high activity and comparatively low cost, often modified with promoters like cobalt, magnesium, and ruthenium, but other materials such as molybdenum and tungsten carbides have also been investigated to improve stability and prevent coke deposition. To mitigate catalyst deactivation from sintering and coke deposition, these primary catalysts are often enhanced with specific supports (such as Al_2O_3 or ZSM-5) and metal promoters. Ultimately, depending on the chosen catalyst and the operating temperature, the resulting syngas can be tuned for synthesizing formaldehyde and polycarbonates (H_2/CO ratio ~1), methanol and Fischer-Tropsch fuels (ratio ~2) or NH_3 and H_2 (ratio >3). Despite this great potential, PCDR remains largely at a laboratory scale, facing industrial challenges such as high energy demands and the frequent production of syngas with an H_2/CO ratio below 1, which requires subsequent adjustments for commercial viability. [22]

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Specific metal oxide catalysts effectively shift the pyrolysis product distribution toward the gas phase by promoting the breakdown of long hydrocarbon chains. For example, Muthee et al. (2025) reported that while the non-catalytic pyrolysis of low-density polyethylene (LDPE) yielded only 18.51 wt% of gas, the introduction of Al_2O_3 and Fe_2O_3 catalysts increased the gas yield to 47.18 wt% and 61.74 wt%, respectively. This increase in gas production occurred concurrently with a reduction in the liquid oil fraction, demonstrating that transition metal oxides, particularly iron-based catalysts, accelerate cracking reactions to favor the generation of lighter gaseous products [23].

Furthermore, based on the convergence of results reported in the literature, Yuan et al. (2022) elucidated the role of transition metals in modulating zeolite acidity and porosity, whereas hierarchical zeolites promote enhanced aromatic formation. In the catalytic pyrolysis of HDPE, transition metals such as Ni, Fe, Mo, Ga, Ru, and Co supported on Y-zeolite promoted aromatic production and increased hydrogen yield. The hierarchical pore structure of zeolites facilitates molecular diffusion within the crystals, allowing macromolecules to access active sites more efficiently, ultimately enhancing aromatic compound formation. In the catalytic pyrolysis of LDPE and mixed polyolefins (MPO), hierarchical HZSM-5 exhibited better resistance to coking deactivation when compared to conventional HZSM-5, demonstrating its potential for improved catalytic stability and performance. Understanding the specific interactions between different polyolefins and zeolites is essential for optimizing catalytic performance, enhancing product selectivity, and maximizing the yield of value-added chemicals [24].

Daligaux et al. (2021) investigated the deactivation and regeneration of zeolite-based catalysts conventionally used in plastic waste pyrolysis. While catalytic pyrolysis using zeolites is highly promising, its large-scale industrial application is hindered by the complex necessity of continuously regenerating deactivated catalysts. The principal regeneration techniques currently employed are standard oxidation, gasification, and hydrogenation; however, Advanced Oxidation Processes (AOPs) emerge as the most promising alternative to efficiently achieve coke removal while overcoming severe thermal degradation limitations. The authors analyze several studies on pyrolysis using zeolites, contrasting them with thermal pyrolysis results [17]. A prominent comparison relies on the work of Seo et al. (2003), which evaluates the performance of high-density polyethylene (HDPE) under catalytic and thermal processes. In the catalytic process, the gas yield significantly increased from 13 wt% to 63.5 wt%, whereas the liquid yield dropped from 84 wt% to 35 wt%. Furthermore, variations in catalyst selection directly affect product distribution. Zeolites and silica-alumina catalysts with varying Si/Al molar ratios lead to different gas fraction yields. This behavior is attributed to catalyst acidity: lower Si/Al ratios correspond to higher acidity, which promotes cracking reactions and enhances the formation of light gaseous products. Conversely, catalysts with lower acidity—such as those with higher Si/Al ratios—tend to favor the production of liquid hydrocarbons [25].

In general, considering the pyrolysis characteristics of various plastics, zeolites (HZSM-5, HY, Hβ, MCM-41, SBA-15, among others) and clay-based catalysts are frequently selected for the catalytic cracking of polyolefins. In contrast, alkaline catalysts are commonly employed for the depolymerization of polyesters, such as PET. CaO or $MgCO_3$ are commonly used to promote the homolytic cleavage of C–C bonds between aromatic rings and carbonyl groups, forming phenyl radicals and favoring the production of liquid-phase aromatic hydrocarbons over gaseous products [5].

In line with these findings, a search using the keywords *"Pyrolysis Plastic Zeolite"* corroborates the capacity of zeolites to achieve high gas yields. Valizadeh et al. (2024) studied the influence of the SiO_2/Al_2O_3 ratio on the catalytic pyrolysis of plastic waste, particularly for production of light olefins. They verified that the adjustment of the SiO_2/Al_2O_3 ratio enhanced the yield of C3/C4 olefins, as demonstrated by the superior performance of HZSM-5 (SiO_2/Al_2O_3 = 200) when compared to Hβ (SiO_2/Al_2O_3 = 300). This was attributed to the optimized acidity and shape selectivity of the high-silica zeolite, which facilitates the formation of light olefins while minimizing secondary reactions and coke formation. This suggests that manipulation of the SiO_2/Al_2O_3 ratio and modification of catalyst

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properties, such as the incorporation of Co into HZSM-5 (SiO_2/Al_2O_3 = 200), can constitute effective strategies for enhancing the production of valuable light olefin [26].

Although the primary focus of the study by Ratnasari et al. (2017) was the production of light oils, specifically maximizing gasoline-range hydrocarbons through a sequential layered configuration of MCM-41 and ZSM-5 in the two-stage catalytic pyrolysis of plastic waste, their findings also strongly highlight the system's severe cracking potential. As the proportion of MCM-41 increased, the yield of C2 gases decreased, while the production of C3–C4 gases increased. ZSM-5, with a high Si/Al ratio of 20 and a predominantly microporous structure, provided strong acidity and enhanced activity for C–C bond scission, favoring the formation of light gases such as ethylene. In contrast, MCM-41 presents a lower Si/Al ratio of 4 and a mesoporous framework with approximately three times more mesopores, which results in moderate acidity and greater accessibility for the diffusion of long-chain polymer fragments. These characteristics can enhance the cracking of polyethylene into heavier hydrocarbons, particularly within the gasoline range [27].

Lee et al. (2021) investigated the pyrolysis of low-density polyethylene (LDPE) and reported a substantial increase in pyrolytic gas yield upon the introduction of an H-ZSM-11 catalyst. The non-catalytic pyrolysis of LDPE yielded only 28.6 wt% of gas, whereas the catalytic process using H-ZSM-11 increased this yield to 80.8 wt%. This enhancement is attributed to the catalyst's ability to expedite the thermal cracking of high-molecular-weight pyrolytic vapors into lighter non-condensable gases. Furthermore, the use of H-ZSM-11 altered the gas composition, increasing the propylene content by promoting the dehydrogenation of propane through monomolecular and protolytic pathways [28].

The production and selectivity of light olefins can also be observed during the pyrolysis of other organic feedstocks, such as oleic acid and naphtha, using conventional zeolite catalysts. At the laboratory scale, Liu et al. (2025) evaluated the performance of a modified ZSM-5 zeolite structure, converted into hierarchical ZSM-5 nanosheets (HZN), for the catalytic cracking of an oleic acid feed (0.03 $mL \cdot min^{-1}$). Under a N_2 atmosphere, the catalytic cracking experiments showed that HZN yielded 52% light olefins at 500 °C, compared with 38.9% obtained using 0.5 g of conventional ZSM-5 zeolite. For both catalysts, the formation of approximately 10–20% C_1–C_4 alkanes and 5–15% BTX was observed, depending on the operating temperature (450, 500, or 550 °C) and the physicochemical properties of the catalyst [29]. Similarly, Wan et al. (2008) used 15 g of ZSM-5 zeolite in a fluidized-bed reactor to promote the cracking of a naphtha feed (15 $g \cdot h^{-1}$), composed of 63.8% paraffins, 29.8% naphthenes, 1.9% olefins, and 4.5% aromatics, at temperatures between 630 and 680 °C. At 680 °C, the authors obtained approximately 55% light olefins, 20% light paraffins, and 15% BTX, resulting in a total conversion close to 90% [30].

Serra et al. (2023) analyzed plastic recycling processes, discussing the advantages and disadvantages of various methods. The research focused on the formation of Polyaromatic Hydrocarbons (PAHs) during catalytic pyrolysis and examined the properties of zeolites and natural and modified clays. The differences in acidity and porosity of these catalysts were shown to affect the distribution of solid, liquid, and gaseous products. Notably, a higher yield of aliphatic hydrocarbons in the gasoline and diesel range could be associated with the lower acidity of clay-based catalysts when compared to zeolite-based catalysts [31].

Zeolites obtained from volcanic ash via hydrothermal treatment have been evaluated in the catalytic pyrolysis of polypropylene at 450 °C using 10 wt% catalyst loading by Almirón et al. (2025). The results indicated a significant increase in gaseous product yields compared to thermal pyrolysis, reaching up to 80 wt% in certain synthesis conditions. Among the materials exhibiting well-defined zeolitic phases, gas yields of approximately 58 wt% were reported. The gaseous fraction was mainly associated with the formation of light hydrocarbons in the C2–C4 range, including ethylene and propylene, which are key building blocks in the petrochemical industry. These findings suggest that synthesis parameters such as temperature and alkalinity influence phase composition, acidity, and structural properties, thereby affecting selectivity toward light olefins. Such studies reinforce the growing interest in developing low-cost zeolitic materials capable of promoting the production of valuable gaseous fractions during plastic waste valorization [32].

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3.3. Perspectives

Catalytic pyrolysis processes are very flexible and can offer various opportunities for use of catalysts for enhanced plastic recycling. The identification of catalyst classes is crucial for obtaining the desired products, as their properties can significantly influence reaction mechanisms, making them a key factor for definition of product selectivity and yield. In this context, zeolites constitute the most relevant class of catalysts among the evaluated studies for the catalytic cracking of plastic waste [17]. Figure 3 the distribution of the most utilized catalyst types in the catalytic pyrolysis of polyolefins for production of gaseous compounds is illustrated. Owing to their acidic characteristics and mesoporous structure, these catalysts are predominantly employed in the process.

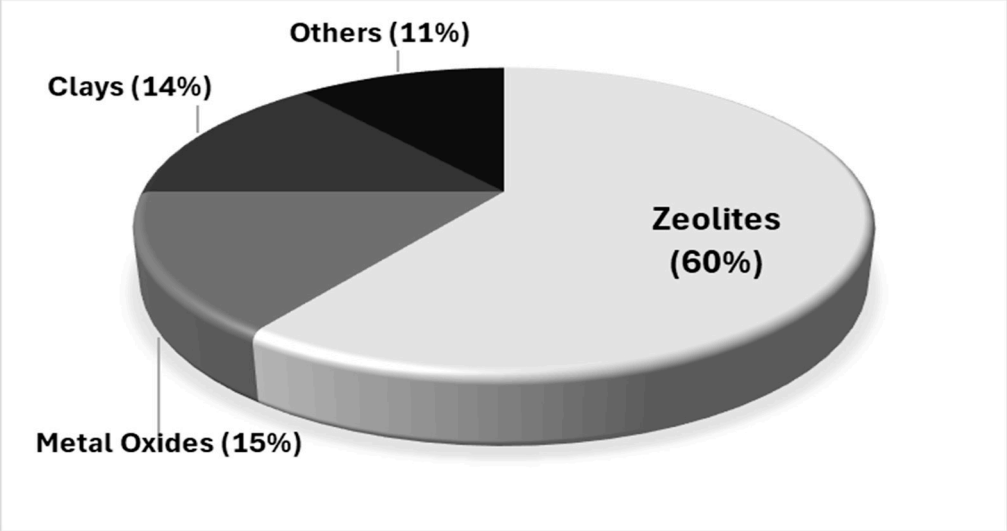

Figure 3. Types of catalyst used most often to perform the pyrolysis of polyolefins for production of light gaseous compounds.

The large-scale implementation of catalytic pyrolysis systems faces several challenges, including the presence of contaminants and non-polymeric species in waste streams, highlighting the need for pre-sorting. Additionally, the high variability in plastic composition, especially in plastic blends, complicates process optimization. Moreover, the impact of certain additives on catalyst deactivation and potential equipment corrosion remains unclear. Unfortunately, these aspects of catalytic pyrolysis technologies have not been sufficiently investigated in the literature. For this reason, although the Technology Readiness Level (TRL) of the conventional pyrolysis process has advanced significantly and is well established at the commercial scale (TRL 9), catalytic pyrolysis of polyolefins for producing light hydrocarbons remains at a lower TRL values, primarily due to challenges to achieve the desired product distribution, assure the sufficiently long catalyst activity and allow the optimization of reaction conditions [33].

The most used catalysts in pyrolysis are acidic catalysts, which are highly efficient in cracking plastic waste. Zeolites are promising alternatives for plastic pyrolysis, as they facilitate the cracking of long polymer chains, although they generate high fractions of aromatics in the product. Studies on catalysts for polyolefins pyrolysis processes have demonstrated that zeolites exhibit substantial potential for application in plastic conversion, with a predominant focus on optimizing liquid fuel yields. Recent research indicates that employing mixed (tandem) catalysts could enhance pyrolysis efficiency, particularly in the production of light hydrocarbons such as C2-C4 fractions [5].

4. Tandem Catalysts

4.1. Fundamentals

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The term *"tandem catalysts"* refers to catalytic systems that integrate different catalytic functions to act synergistically in a single process step. The concept behind this process is to employ a system capable of converting intermediate products directly into a final product without altering the reaction conditions. A fundamental pillar of tandem systems is the interdependence between catalysts—meaning the function of the second catalyst is complementary and synergistic to that of the first [34].

It is important to emphasize this concept because many authors use the term "tandem" to describe studies that simply combine two catalysts to enhance the product [35]. From a practical perspective aimed at obtaining the final product, this distinction may not be significant. However, it becomes crucial when designing a system that seeks to explore and optimize the synergy between catalysts and their respective functions.

4.2. Previous Works

In the context of tandem catalytic processes, various catalysts have attracted considerable interest. Al_2O_3 catalysts are distinguished from traditional zeolites by their larger pore sizes, which help to mitigate steric and diffusional barriers [35]. In contrast, zeolites are characterized by their acidic sites and typically smaller pore sizes, offering a distinct set of properties for catalytic applications. For these reasons, some studies have attempted to develop tandem catalysts based on a combination of Al_2O_3 and zeolites.

Dai et al. (2021) investigated the selectivity of various zeolites (ZSM-5, Y5.1, F20, MCM-41, Al2O3, and Al2O3+ZSM-5) to enhance the quality of liquid products within the gasoline range. The authors combined Al2O3 and ZSM-5 catalysts, proposing the existence of synergistic effect between them. However, a particularly noteworthy result demonstrated the high selectivity (~90 wt%) for C5-C12 hydrocarbons and low aromatic yields when virgin PE was pyrolyzed in a CDS 1500 microreactor using F20 and Y5.1 catalysts (zeolites) at temperatures of 500, 550, 600, and 650°C [35].

Ellis et al. (2021) proposed a mechanism that generates an olefin intermediate during the PE cracking process. The process involves the initial dehydrogenation (Pt/γ-Al_2O_3, SnPt/γ- Al_2O_3) step, followed by an olefin metathesis (Re2O7/γ- Al_2O_3) step at 200°C. The reaction was conducted on a laboratory scale using 130 mg of virgin PE in n-pentane. The author reported a reduction of 73 wt% in the average molar mass of the product, along with enhanced conversion and increased C2–C15 yields upon the incorporation of Sn into the Pt/γ- Al_2O_3 catalyst. The total yield exceeded 100 wt% because the catalyst also promoted the partial transformation of the solvent [36].

Other researchers, such as Eschenbacher et al. (2022), aimed to enhance product yields for hydrocarbons in the C2-C4 range and high-value chemicals while minimizing coke, methane (CH_4), and hydrogen (H_2) formation in plastic recycling. The authors combined steam-treated FCC and HZSM-5 catalysts at different temperatures in a micro-pyrolyzer. At 700 °C, the HZSM-5 catalyst achieved a light olefin yield of 69 wt%, with propylene comprising 31 wt%, while producing minimal amounts of methane. The steam-treated catalysts showed lower coking and deactivation, indicating their potential for converting plastic waste into valuable chemicals like light olefins and aromatics [37].

Wang et al. (2022) introduced a novel tandem process, which represents an improvement over a previously reported method for cracking of unsaturated PE chains. Typically, the ethenolysis process involves cleaving a double bond in PE chains, followed by isomerization. In this updated approach, the author incorporated a dehydrogenation step to create additional unsaturations in the chains. The reaction was conducted in a stainless steel stirred-tank reactor at 70 °C (using Ru-based ethenolysis catalyst, Ultracat, in toluene solution) or at 100°C (with MTO/Cl-Al_2O_3). The pyrolysis of 250 mg of PE yielded over 70 wt% propylene (C_3H_6) and butylene (C_4H_8) [9].

4.3. Perspectives

In the context of plastic recycling, the use of tandem catalysts exhibit a low TRL and can be regarded as an emerging technology. Current efforts are focused on testing hypotheses with significant uncertainties regarding scalability. For instance, the use of solvents poses a major

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scalability challenge, as processing large volumes of plastic would require proportional amounts of solvents [9,36]. Moreover, the catalysts employed may exhibit instability under the reaction temperatures typically used to perform pyrolysis and hydrogenolysis reactions [9].

Nonetheless, some studies explore the use of conventional catalysts with modified pore properties, such as Al_2O_3, which demonstrate cracking functionalities distinct from traditional zeolites. [35,37] In this regard, the current applicability of the technology lies in the combination of traditional catalysts, which can promote a synergistic effect, enabling the production of higher yields of light fractions (C2–C4) while minimizing the formation of aromatics, coke, CH_4, and H_2. It is expected that future publications are likely to explore these opportunities in the near future.

5. Dearomatization

5.1. Fundamentals

Although some authors demonstrate that certain properties of zeolites can reduce aromatic contents to levels below 5 wt% [35], numerous studies on the pyrolysis of plastic waste (HDPE, LDPE, PP, PS, and others) report the production of high aromatic levels during catalytic degradation, particularly when zeolites are used as catalysts [38–42]. From the perspective of producing light fractions (C2–C4), the formation of aromatics indicates the partial cracking of the feedstock and manufacture of a hydrogen-deficient product. In this context, the investigation of aromatic cracking focuses on understanding the specific mechanisms involved in cracking aromatic rings for enhancement of the quality of pyrolysis products. In particular, this knowledge aims to inform processes where the cleavage of long polymer chains can be optimized to yield lighter hydrocarbon fractions.

5.2. Previous Works

Although the topic of dearomatization has been widely discussed in literature, the results that align with the objective of the present work were primarily found in older studies. Many of these studies focused on the cracking of specific aromatic molecules tailored to the authors' purposes, which are significantly different from those encountered in plastic cracking.

Ledoux et al. (1991) worked on improving fuel quality by breaking down aromatic compounds. The authors reported over 90 wt% cracking of toluene, cis-decalin, and thiophene over NiW, Pd/U, and Ru/U catalysts on sulfided support at 300-425 °C for 2 hours. Despite indicating catalysts that promote the cracking of cyclic compounds, a more detailed evaluation of the product from the perspective of light olefins production was not described. Additionally, the use of sulfur-containing compounds resulted in the production of H_2S [43].

Al-Khattaf et al. (2002) found that benzene yields are intrinsically connected to the characteristics of Y zeolites. The authors investigated the cracking of cumene, 1,3-di-isopropylbenzene, and 1,3,5-tri-isopropylbenzene, analyzing benzene selectivity across different temperature setups and crystal sizes. The results suggested that it is also possible to control propylene yields by managing these reaction parameters, although this was not the primary focus of the study [44].

Light hydrocarbon fractions were identified in other studies. Shimada et al. (2015) used FCC catalyst (USY zeolite with low and high percentage of rare earth metal oxide) in a pyrolysis process for cracking 2- and 3-ring aromatics. The method resulted in a 75 wt% conversion of 1-methylnaphthalene (1-MN)/n-hexadecane (n-HD) and a 99 wt% conversion of 9-methylanthracene (9-MA)/n-hexadecane (n-HD). The yield of liquefied petroleum gas varied between approximately 10-40 wt% [45].

Jalil et al. (2001) investigated benzene adsorption in HPW/MCM-41 catalysts and also reported high C3 (~51 wt%) and C4 (~27 wt%) yields in n-hexane cracking over these catalysts [46]. Bamwenda et al. (1993) described an efficient process for the cracking of benzene to acetylene with over 90 wt% selectivity. The reactions were induced by a pulsed microwave technology over alumina and silica supported Nickel catalysts [47].

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Ishihara et al. (2021) investigated the dehydrocyclization-cracking of methyl oleate using NiMo/ZnZSM-5-alumina composite catalysts in a continuous fixed-bed flow reactor under 0.5 MPa of H_2. At 450°C, the catalyst with a high metal loading (16NM/ZnZSM-5-Al2O3) exhibited intense hydrocracking activity, resulting in 45% C1-C4 gases, 42% gasoline, 0.49% kerosene, 3% diesel, and 5.8% CO/CO_2. The main conclusion was that an optimal balance between the NiMo and ZnZSM-5 components allows for the full conversion of the ester via decarboxylation and decarbonylation, followed by the cyclization of light olefins to achieve up to a 20 wt% yield in aromatic compounds [48].

5.3. Perspectives

The improvement of products derived from the pyrolysis of plastics, particularly concerning the degradation of aromatic rings, is grounded on established and well-documented literature. Notably, the zeolites employed for cracking aromatics are similar to those used in plastic pyrolysis. This pyrolysis process results in the formation of the same aromatic compounds, which are the focus of the cracking process investigated in the present study.

In general, authors report conversion rates exceeding 90 wt% in the cracking process. However, these studies are not optimized to produce C2-C4 fractions, especially olefins. This is because the authors do not completely eliminate aromatics but rather aim to reduce polyaromatics to monoaromatics or adjust process conditions to target specific products, such as acetylene and higher-quality fuels. Therefore, it can be said that dearomatization of pyrolysis products constitutes an important line of investigation that has been largely overlooked in literature. The combination of dearomatization and cracking functions in a single process step can indeed constitute a major breakthrough for those interested in the circular manufacture of monomers and production of light gaseous compounds.

6. Ethenolysis

6.1. Fundamentals

Ethenolysis is a chemical process that uses ethylene to break down complex molecules through olefin metathesis in which a carbon-carbon double bond (C=C) is broken and reorganized in the presence of a catalyst, usually based on transition metals such as ruthenium (for example, Grubbs catalysts), as illustrated in Figure 4 [9,13,49]. The catalyst and the material can form metal-carbene complexes that facilitate the cleavage reaction [13]. Through cycloaddition and cycloreversion steps, the catalyst enables the systematic breakdown of long polymer chains into shorter and more useful molecules while operating under relatively mild conditions when compared to traditional thermal cracking methods [13,50].

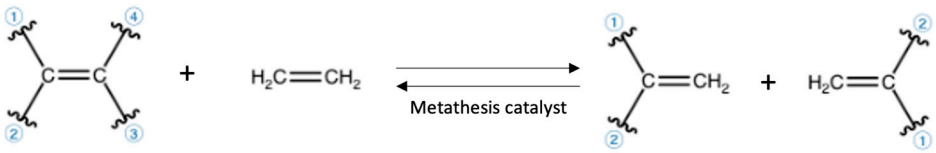

Figure 4. Schematic representation of ethenolysis of linear olefins.

Ethenolysis has emerged as a promising technology for the chemical recycling of plastics, especially polyolefin-based ones such as PE and PP, converting them into valuable chemical intermediates or feedstocks, which have greater added value and can be reused as raw materials to produce new polymers [9,49,50]. Ethenolysis can also reduce the formation of undesirable byproducts during plastic conversion, leading to cleaner product streams and reduced waste generation during the recycling process [49]. The reaction promotes the valorization of low-quality

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or mechanically non-recyclable plastic waste, contributing to a more efficient circular economy approach [49,50].

Grubbs or Hoveyda-Grubbs catalysts have been widely used to perform ethenolysis reactions due to their high selectivity and efficiency under mild conditions [13,51]. This group of catalysts allows the process to occur at relatively low temperatures and pressures, reducing energy consumption and CO_2 emissions when compared to more conventional recycling methods [9,52]. However, the mentioned catalysts remain expensive, with low stability and reduced lifetime, which may limit large-scale applications [13,53].

6.2. Previous Works

Buluchevskii et al. (2017) studied the conversion of 1-hexene into light olefins, with high selectivity for propylene, using $Re_2O_7/SO_4^{2-}/ZrO_2–Al_2O_3$ and $Re_2O_7/B_2O_3–Al_2O_3$ catalysts at 60 °C and 0.1 MPa. However, the controlled conditions of the feedstock (1-hexene) revealed the specificity and limitations of applying this process to plastic degradation [54].

Bidange et al. (2016) published a review about the ethenolysis process and reported that it could be used for small ring opening, small ring rearrangement, and medium-sized rings. It could also cleave aliphatic linear olefins, double bonds in functionalized alkenes, and polyolefin chains [13].

Wang et al. (2022) developed a tandem catalysis strategy for recycling PE into propylene using ethylene, combining olefin metathesis and isomerization to selectively produce propylene with high efficiency. Experiments were performed in a 40 mL stainless-steel stirred-tank reactor for 5 hours. Two different catalysts were tested. For the Ultracat in toluene solution the reaction was conducted at 70 ºC, while for $MTO/Cl–Al_2O_3$ the temperature was 100 ºC. The study demonstrated high selectivity for propylene (94 mol%) and successful conversion of monounsaturated PE with $MTO/Cl–Al_2O_3$ as the catalyst. The experiment showed that the highest conversion and propylene formation rate occurred early in the reaction, with the process achieving 50 wt% conversion of monounsaturated PE in 5 hours. Additionally, the tandem approach allowed for the efficient conversion of saturated PE, although further improvements in catalyst lifetime and dehydrogenation efficiency are needed. The preliminary life cycle assessment (LCA) suggested that this method could reduce greenhouse gas emissions (GHG) by approximately 13% when compared to conventional propylene production, highlighting its potential for sustainable plastic recycling [9].

Conk et al. (2022) explored the production of propylene through the partial dehydrogenation of polyethylene followed by tandem isomerizing ethenolysis of the desaturated polymer. Dehydrogenation of HDPE was achieved by using either an iridium-pincer complex or platinum/zinc supported on silica, resulting in dehydrogenated material containing up to 3.2 mol% of internal olefins. Subsequently, the combination of a second-generation Hoveyda-Grubbs metathesis catalyst and $[PdP(t\,Bu)_3(m\text{-}Br)]_2$, employed as an isomerization catalyst, selectively degraded the unsaturated polymer to propylene, achieving yields exceeding 80 wt%. In this case, the experiments were conducted at 200 ºC for the dehydrogenation process (12 hours), followed by 130 ºC for the ethenolysis process (16 hours). Propylene could be produced from polyolefin waste using a dehydrogenation and isomerizing ethenolysis (DIE) process involving olefin metathesis and isomerization, with potential for scalable applications through heterogeneous catalysts [49].

Conk et al. (2024) also studied the production of propylene through the conversion of PE and PP on a Parr reactor, for 90 minutes. A new catalyst system using tungsten oxide on silica and sodium on gamma-alumina achieved over 90 wt% yield of propylene or a mix of propylene and isobutylene at 320 °C without dehydrogenation [55].

6.3. Perspectives

In the context of plastic recycling, ethenolysis exhibits a low TRL value. The results of the studied process are highly promising, achieving propylene production yields exceeding 70 wt%. However, the approach faces several limitations, including the stringent reaction conditions required, such as high pressures, the use of specific solvents, and the high costs associated with catalysts. Additionally,

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the process demands the presence of double bonds in the polymer structure, demanding the prior dehydrogenation of polyethylene. The cracking mechanism relies on cleavage initiated at the double bond, which is preserved in the smaller resulting fragments. These findings highlight the potential for a tandem catalytic sequence combining dehydrogenation and ethenolysis, which could optimize the process and broaden its applicability.

In addition to the high cost of the previously mentioned catalysts, the purity of the plastic feedstock and the process scalability remain as important challenges to be overcome. Recycled plastics are often constituted of a mixture of different polymers and contaminants, which can reduce the efficiency of ethenolysis [55] and, as the technology is still under development, it is not close for industrial-scale applications [6,56].

Nevertheless, ethenolysis represents an innovative approach to addressing plastic recycling challenges, offering a chemical pathway to valorize plastic waste that cannot be recycled mechanically. With advances in research on more efficient and cost-effective catalysts, improvement in catalyst recovery methods, integration with existing recycling infrastructure, and optimization for mixed plastic waste streams, this technology has the potential to become a cornerstone of the circular plastic economy, significantly reducing the environmental impact of plastics [49].

7. Hydrogenolysis and Hydrocracking

7.1. Fundamentals

Hydrogenolysis and hydrocracking are potential technologies for chemical recycling, making use of hydrogen molecules to break chemical bonds in plastic waste, frequently employing heterogeneous catalysts [2]. In the case of polymers, for example, they can be converted into lower molar mass products and be reapplied as chemical intermediates or fuel materials [2,57]. While the hydrocracking process involves breaking carbon-carbon (C-C) chemical bonds through reaction with hydrogen (H_2), the hydrogenolysis process also involves breaking carbon-heteroatom bonds (C-O or C-N, for example) [1,2,57]. These technologies have gained attention due to their potential to constitute a pathway towards the development of more sustainable and circular recycling solutions [1,6,58].

The hydrogenolysis and hydrocracking reaction conditions must be controlled to achieve ideal conversions and selectivity [2,6]. Thus, factors such as temperature, pressure, and catalyst must be considered and tested simultaneously [6]. Metal catalysts (such as those based on nickel, platinum, palladium, rhenium, and ruthenium) are used in the reactions to activate the hydrogen molecule and promote bond breaking [1,2,4,57,58].

In the context of plastic recycling, these techniques have been widely employed in PET recycling, generating high-value products such as benzoic acid derivatives and ethylene glycol [59]. When applied to polyolefins, such as polyethylene and polypropylene, the process can generate alkanes of different chain lengths (such as hexane, octane, and other alkanes), suitable for fuel applications or as raw materials for new chemical products [4,6].

7.2. Previous Works

Iqbal et al. (2022) published an article about the catalytic cracking and hydrocracking of PS and PE. The catalyst selected in this case was USY/SBA-16 aiming to make the process cost-effective and efficient. The experiments were conducted in a high-pressure autoclave with pressure between 1 and 290 psi, temperatures ranging between 350 and 425 ºC, residence time of 45 minutes, polymeric load of 5 g, and catalyst varying 0, 1, 4, 9, and 16 wt%. At the end of the process, the most predominant fractions were the oil and solid streams. The largest gas fraction obtained was 2.12 g in a reaction conducted without a catalyst but under a pressure of 290 psi, However, since this fraction was not analyzed, it was not possible to determine whether monomers had been recovered. It was concluded that catalytic cracking with the USY/SBA-16 composite catalyst was identified as the most economical

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and efficient method for converting polystyrene waste into liquid fuel. Hydrocracking, while effective, was less cost-efficient due to hydrogen usage [60].

Munir et al. (2020) evaluated the use of B-zeolite in the hydrogenolysis of a mixture of virgin and waste plastics, specifically HDPE (40 wt%), LDPE (10 wt%), PP (30 wt%), and PS (20 wt%), at temperatures of 360, 375, and 400 ºC for 60 minutes in a 500 mL stirred autoclave. A polymer-to-catalyst ratio of 1:20 was used, resulting in a liquid fraction yield of 60 wt%, while no information was provided regarding the composition of the gas products [61].

Tedstone et al. (2022) studied the synthesis and use of zeolite beta, zeolite 13X, MCM-41 and an amorphous silica-alumina catalyst support impregnated with the single-source precursor (SSP) nickel (II) ethylxanthate on the hydrocracking of mixed polyolefin waste (virgin LDPE, HDPE, PP and PS). Operation parameters, such as 10 g of polymer feedstock, polymer:catalyst ratio of 10:1, pressure of 20 bar, reaction temperature of 330 ºC and reaction time of 60 min were kept constant throughout all the experiments on a 300 mL stainless steel Parr reactor. For the polymer mixture, the liquid conversion ranged from 20.3 to 28.9 wt%, and the gas conversion ranged from 17.2 to 64.5 wt%, depending on the catalyst used. In the experiments conducted with pure LDPE, the liquid conversion ranged from 0 to 74.3 wt%, while the gas conversion ranged from 18.6 to 57.2 wt%, depending on the catalyst used. The gas fraction showed a higher concentration of C3 and C4 [62].

Darwanta et al. (2023) investigated the synthesis and use of Ni/SiO_2 pillared clay catalyst on HDPE hydrocracking into liquid fuels. In the experiments, a semi-batch reactor was used at 450 ºC, for 2 hours, and with a polymer:catalyst weight ratio of 5:1. As a result, the liquid, solid and gas fractions ranged from 32.33 to 45.50 wt%, 0.03 to 3.20 wt%, and 51.56 to 67.65 wt%, respectively. Tests were also conducted at 475 and 500 ºC for one specific catalyst studied and at 500 ºC experiment the gas fraction reached 70.42 wt%. The obtained liquid fraction contained gasoline and diesel, and the gaseous fraction was not analyzed [63]

Zhao et al. (2022) also used nickel-based catalyst to perform the hydrogenolysis of virgin LDPE on a 50 mL stainless autoclave reactor, for 60 minutes at 280 ºC and a pressure of 3 MPa. In this case, the employed catalysts were Ni/ZrO_2, Ni/Al_2O_3, Ni/CeO_2, Ni/AC, Ni/SiO_2 and Ni/MgO. The authors observed that the reaction using Ni/SiO_2 obtained around 10 wt% of gas on the product yield, and this was the highest amount of gas produced, which was mainly composed of methane. It was also reported that increasing the reaction time for 12 hours, the gas fraction could also increase to around 40 wt%. It was observed that the reuse of the catalyst was possible, although it decreased the amount of gas produced and increased the amount of residue and wax [64].

Zichittella et al. (2022) studied the hydrogenolysis of PE and PP using cobalt supported on ZSM-5 zeolite catalysts to produce propane. The experimental conditions selected were 523 K, 40 bar and residence time of 20 hours. The cobalt/ZSM-5 ratio on the catalyst was varied to maximize the yield of propane on the gas phase. According to the obtained results, the highest gaseous fraction was around 90 wt%, consisting mainly of propane (around 80 wt%), followed by ethane and butane (around 10 wt% each) [65].

Mason et al. (2022) studied the hydrogenolysis of linear polyethylene (PE) homopolymer, isotactic polypropylene (i-PP), polyethylene-co−1-octene (PECO), and a post-consumer HDPE polymer waste mediated by AlS/$ZrNp_2$ catalyst. Experiments were performed on a 350 mL dry heavy-walled glass reactor at 200 ºC, for 2 hours, at 2 atm using 1.5 or 1.0 g of polymer. The amounts of volatiles fraction of product mass were 61 wt% for PE, 77 wt% for i-PP and 88 wt% for PECO, although the detailed compositions of the obtained gas fractions were not reported [66].

Mason et al. (2021) also published an article about an organozirconium catalyst on a Brønsted acidic support that enabled the efficient hydrogenolysis of polyolefins and saturated hydrocarbons into low molar mass products under mild conditions via a β-alkyl transfer mechanism. The catalyst selected was AlS/$ZrNp_2$ to catalyze PE, i-PP and PECO in a solventless hydrogenolysis process. The experiments were conducted at 150/190 ºC and 2 atm in a 350 mL vessel for 120 minutes. Although the reaction lasted 120 minutes, product analysis at different time points showed that, for the PE sample, solids were the predominant fraction at 10 minutes, while volatiles became more prominent

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as the reaction progressed. In the 120-minute reactions, the volatile fractions obtained were 61% for PE, 77% for PP, and 88% for PECO, consisting mainly of C1 and C2 in the gas phase and predominantly C12 in the liquid phase [67].

Nguyen-Phu et al. (2023) investigated the influence of an Ru/SBA-15 catalyst on the hydrogenolysis of LDPE. Experiments were conducted in a stainless-steel autoclave at a pressure of 3 MPa and a temperature of 250 ºC, with reaction times ranging from 30 minutes to 4 hours. The maximum gas fraction, accounting for 22.5 wt% of the total products, was obtained after a 2-hour reaction. Analysis of the gas revealed a composition of 64.1 wt% methane, 14.2 wt% ethane, 11.4 wt% propane, and 10.3 wt% butane. Across all experiments, regardless of variations in catalyst composition, system pressure, or reaction time, the gas fractions predominantly consisted of methane. The authors also evaluated the reusability of the Ru/SBA-15 (10) catalyst — prepared with a nominal triethylamine-to-ruthenium (TEA/Ru) molar ratio of 10 — which demonstrated excellent stability and reusability in LDPE hydrogenolysis, consistently maintaining high conversion rates and yields with minimal structural changes after multiple uses [68].

Wang et al. (2023) investigated the hydrocracking of LDPE, PP, and PS using a PtSn/SiAl catalyst to produce fuel-range products, achieving a maximum yield of 20 wt% for C1–C4 fractions [69]. Similarly, Ding et al. (2015) reported a gas yield of up to 30 wt% from the hydrocracking of polyolefin waxes using a ZSM-5-based catalyst for efficient wax cracking [70].

Further studies on HDPE hydrocracking were conducted by Ding et al. (1997) and Azam et al. (2024), employing a Zeolite/Silica-Alumina-supported Ni/Ni−Mo sulfide catalyst and a dealuminated Y zeolite catalyst, respectively [71,72]. Azam et al. (2024) achieved a maximum gaseous fraction of 26 wt% [72].

Depolymerization of PE under hydrogen has also been explored using various catalysts, including $(SiO)_3ZrH$ [73], HZSM-5 [74], ZSM-5 [75], electrophilic organo-tantalum [76], and 1Pt/A with hierarchical FAU zeolites [77]. These studies reported product yields in the C2 and C3 range of 11.9 wt%, 50 wt%, 10 wt%, 56 wt%, and 10 wt%, respectively [73–77].

Rorrer et al. (2021), Chu et al. (2023), and Kim et al. (2023) focused on ruthenium-based catalysts for the hydrogenolysis of PP, LDPE, and HDPE, respectively, predominantly yielding methane in the gaseous fraction [78–80].

In contrast to these low gas yields studies, Utami et al. (2018) and Edenfield et al. (2023) obtained volatile fractions of 82 wt% and 92 wt%, respectively. However, the composition of these gaseous fractions was not analyzed, precluding further conclusions [81,82].

7.3. Perspectives

The reviewed studies primarily focus on the production of light liquid fractions rather than gas formation, with hydrogen being utilized in combination with catalysts, predominantly zeolites, to achieve these results. Methane is consistently reported as the major component of the gas fraction, while the production of significant amounts of ethane and propane is relatively rare. These studies typically involve experiments conducted under high pressures and long reaction times, with maximum temperatures lower than those employed in conventional pyrolysis processes, highlighting a distinct approach to achieving controlled conversion of plastic feedstocks.

The above-mentioned processes present several advantages when compared to conventional recycling processes, such as specific bond breaking, operating temperatures lower than those used in pyrolysis, reduced char production, and also the production of stable saturated compounds [1,57]. Furthermore, the selective characteristics of hydrogenolysis/hydrocracking tend to result in cleaner products, with the removal of heteroatoms such as chlorine, bromine, and fluorine commonly present in waste plastics, resulting in products more suitable for future applications [57].

Currently, the main challenges faced in implementing industrial scale hydrogenolysis/hydrocracking are the cost and availability of hydrogen, the need for high pressures in the process, which increases operational costs, and difficulties with the catalyst, such as costs, availability, deactivation, and reuse of it [1,4,6].

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Hydrogenolysis/hydrocracking offers a promising approach for chemical recycling of plastics, particularly for oxygen-containing polymers like PET [59]. Furthermore, integrating hydrogenolysis/hydrocracking with other technologies, such as pyrolysis and gasification, can create even more efficient and sustainable hybrid systems for plastic recycling [1,4].

8. Conclusions

In summary, this review offers a comprehensive bibliometric analysis of polyolefin chemical recycling technologies, particularly focusing on the production of light gaseous products for enhancement of circular plastic manufacture. By evaluating different catalysts, operating conditions, and product distributions, this review provides a broad perspective on the current advancements and research trends in this field.

The analysis of recycling technologies directed at olefin production reveals different approaches with varying levels of technological readiness. Ethenolysis, for instance, can provide high propylene yields, exceeding 70 wt%, although its industrial application remains limited due to high catalyst costs, solvent use, pressure requirements, and the need for higher-quality plastic feedstock. Conversely, pyrolysis using zeolite catalysts is a well-established process with scalable applications, showing diverse product distributions, including light olefins. Its efficiency in cracking plastic waste reinforces its potential for industrial implementation, although the catalyst stability and activity regeneration at actual operation conditions remain unclear.

Furthermore, advancements in dearomatization and tandem catalyst technologies indicate opportunities for improving product quality in traditional processes. Dearomatization primarily employs well-known catalysts, such as zeolites, to convert polyaromatics into monoaromatics or enhance fuel properties. Meanwhile, tandem catalyst systems leverage the distinct characteristics of silica and alumina, creating a synergistic effect that enhances light olefin yields. The integration of these methods into conventional recycling processes could significantly improve efficiency and product selectivity.

Additionally, hydrogenolysis and hydrocracking offer a different perspective by enabling the production of cleaner products through impurity removal and high hydrocarbon cracking efficiency. However, challenges persist, particularly regarding the high-pressure requirements and substantial hydrogen demand compared to pyrolysis. Future advancements in process optimization, such as reducing methane yields to enhance ethane and propane production under ambient conditions, could mark a turning point in the technology's readiness level. Ultimately, the continued development of these recycling strategies will be crucial for achieving sustainable and efficient plastic waste management.

Finally, and based on the previous review, it can be expected that the number of investigations exploring combinations of different catalyst functions in a single process step will increase over the next years. This can be expected because some catalyst technologies are mature in the petrochemical field and can provide elementary support for solving problems with the existing polyolefin technologies when one is interested in obtaining light gaseous compounds, such as the undesired production of aromatics. For this reason, the fields of catalytic pyrolysis and use of tandem catalysts in pyrolysis reactions are expected to evolve faster in the upcoming years.

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Abbreviations

The following abbreviations are used in this manuscript:

PE	Polyethylene
PP	Polypropylene
TLR	Technology Readiness Level
HC	Hydrocarbons
FCC	Fluid Catalytic Cracking
PCDR	Pyrolysis-catalytic dry reforming
LDPE	Low-density polyethylene
HDPE	High-density polyethylene
MPO	Mixed polyolefins
AOP	Advanced Oxidation Processes
PAHs	Polyaromatic Hydrocarbons
LCA	Life cycle assessment
GHG	Greenhouse gas emissions
DIE	Dehydrogenation and isomerizing ethenolysis
SSP	Single-source precursor
i-PP	Isotactic polypropylene
PECO	Polyethylene-co−1-octene

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