



# Critical Review of Heterogeneous Catalysts: Manufacturing of Fuel from Waste Plastic Pyrolysis

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## Abstract

The escalating demand for plastic presents an immense peril to both the environment and humanity. Not only have there been notable advancements in the creation of advanced biodegradable polymers, but there has also been a lack of attention towards tackling the current issue of plastic waste. Processing fuels via plastic waste valorization provides a feasible approach to recycle plastics and mitigating pollution for the improvement of society. This review addresses a comprehensive analysis of various heterogeneous catalysts in the context of plastic pyrolysis to produce fuel, intending to identify an eco-friendly method for recycling garbage. The choice of catalyst has a substantial effect on the disintegration process of waste plastic, dictating the properties of the resulting fuel, encompassing both the amount and the quality. Pyrolysis, an alternative method for addressing the increasing waste disposal issue, is a non-toxic process that does not release hazardous pollutants, in contrast to incineration. The waste plastic serves as a feedstock for pyrolysis process, employing innovative, environmentally friendly catalysts derived from natural and other sources, to generate fuel oil that possesses similar physical characteristics to the diminishing petroleum-based fuels. This critical review analyzes the impact of different heterogeneous catalysts on the process of transforming waste plastic to produce fuel through pyrolysis. Heterogeneous catalysts are crucial to the process of turning discarded plastics into oil, offering significant potential for improving not only economic and environmental conditions but also benefiting both industry and society.

**Keywords** Waste plastic · Pyrolysis · Heterogeneous catalyst · Fuel

## Abbreviations

LDPE	Low density polyethylene	PET	Polyethylene terephthalate
HDPE	High density polyethylene	ZSM-5	Zeolite socony mobil-5
PP	Polypropylene	HZSM-5	H <sup>+</sup> zeolite socony mobil-5
PS	Polystyrene	REY	Rare earth metal-exchanged Y-type
PE	Polyethylene	USY	Ultra stable zeolite
PO	Polyolefins	HUSY	Hierarchical H-style ultra-stable Y zeolite
SA	Silica alumina	FCC	Fluid catalytic cracking
PCDR	Pyrolysis combined with dry reforming	RON	Research octane number
		GCV	Gross calorific values
		PONA	Paraffins, olefins, naphthenes and aromatics
		HGO	Heavy gas oil
		Ea	Activation energy
		AWBC	Acid washed bentonite clay
		PILC	Pillared interlayer clay
		WEEE	Waste plastic derived from electronic equipment
		MCM-41	Mobil composition of matter no. 41
		ORR	Oxygen reduction reaction
		MCM	Mobil composition of matter
		CNT	Carbon nanotube
		AC	Activated carbon

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BAC	Biomass derived activated carbon
WPC	Waste plastic derived charcoal
H/Ceff	Hydrogen to carbon effective ratio

## Introduction

Plastics are indispensable components in the daily lives of humans, serving as critical materials for a multitude of routine activities. The justification for this dependence can be supported by the merits that these materials exhibit relative to alternative options, predominantly their low weight and economical price. These materials have a crucial role in various areas like packaging, automotive, construction, agriculture, and electronics, among others [1]. Currently, 0.35 billion tons of plastic are produced annually worldwide. However, new rigorous studies indicate that each year about 1–2 million tons of waste plastic are introduced into oceans and 0.5% of plastic garbage is deposited in the ocean. A government report now states that India produces over 26,000 tons of plastic waste daily, with 10,000 tons of this plastic remaining unresolved and rejected [2].

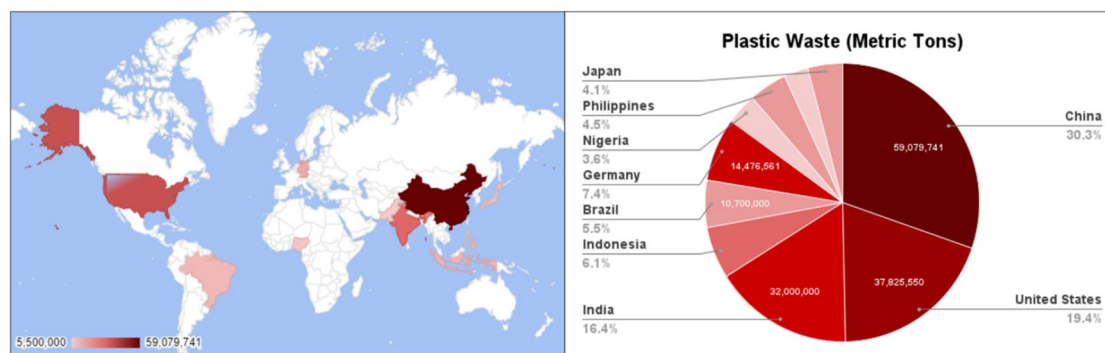
The term ‘plastics’ commonly denotes synthetic materials that are manufactured using chemical methods. Plastic can incorporate additional chemicals, aside from polymers, to save expenses and enhance performance. The desired form of these polymers can be achieved through either molding or extrusion [3]. Several initiatives have been documented to reduce and address the issue of plastic waste, solely most potential solutions are alteration of plastic trash to green energy [3, 4]. It will make a significant contribution to crucial matters concerning the environment and the conservation of energy [5, 6]. The utilization of environmentally friendly catalysts to convert disposable plastics into fuel has significant potential in terms of both environmental and economic aspects. Analysis of global plastic waste generation in 2023 (Fig. 1) reveals that China, the United States, and India are the top three contributors, collectively accounting for

66.06% of the total. Their combined plastic waste generation amounts to a staggering 128,905,291 metric tons, highlighting their significant role in the global plastic pollution challenge [7]. The amount of plastic waste produced in 2023 in metric tons by 20 nations is shown in Table 1.

Currently, there exist multiple techniques for transforming waste plastic into fuel or oil. The predominant techniques are incineration, pyrolysis, catalytic cracking, gasification, and de-polymerization. Each of these strategies possesses its own merits and drawbacks. By contrast, alternative techniques for transforming waste plastic into fuel, such as

**Table 1** The top 20 nations in terms of metric tons of plastic waste produced in 2023

Countries	Plastic waste generation in 2023 (Metric tons)
China	5,90,79,741
United States	3,78,25,550
India	3,20,00,000
Germany	1,44,76,561
Brazil	1,07,00,000
Indonesia	1,18,52,055
Philippines	87,20,852
Japan	79,93,489
Nigeria	77,00,000
Pakistan	61,03,122
Russia	59,50,093
Bangladesh	55,00,000
Egypt	52,07,105
Vietnam	48,91,600
Iran	45,27,581
Turkey	42,09,000
Thailand	40,08,136
South Africa	38,80,117
United Kingdom	35,48,723
France	33,62,337



**Fig. 1** Worldwide plastic waste generation in 2023 in metric tons

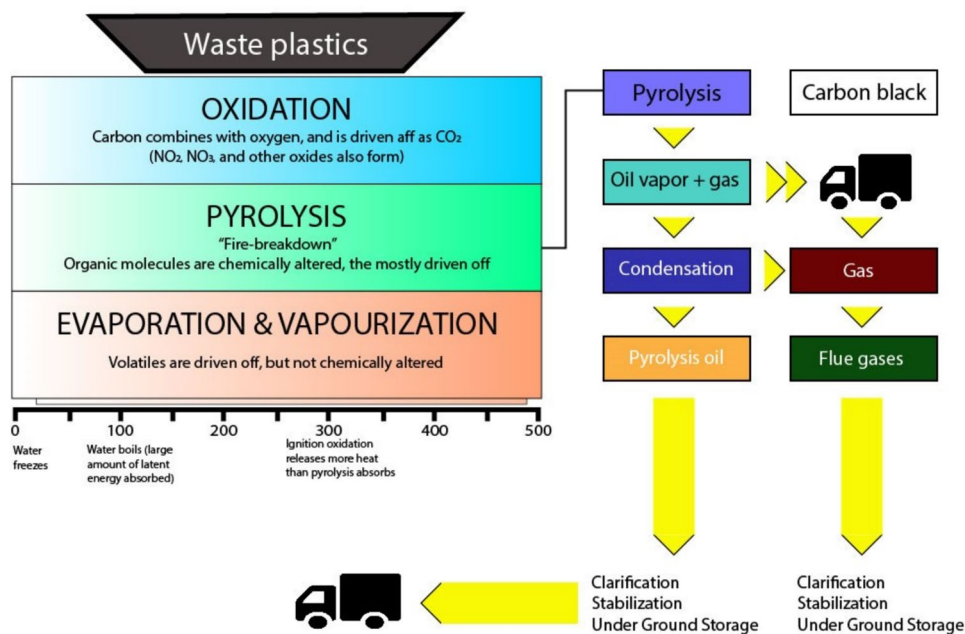
catalytic cracking and gasification, are characterized by more intricacy and costliness, while yielding a more limited array of products. Depolymerization is now in the developmental stage and is not yet economically feasible, despite being the most efficient technique. Pyrolysis, particularly catalytic pyrolysis, is widely recognized and utilized globally as the most efficient and economical technique for transforming waste plastic into fuel. This is mostly due to the lower reaction temperature, shorter reaction time, greater selectivity, better octane number of fuel, and reduced solid residue produced. Solid catalysts are essential in catalytic pyrolysis as they significantly improve the conversion process and help to achieve the necessary product selectivity. Due to their simplicity of handling and efficient mass transfer qualities, they are a preferred choice for this application [8].

Pyrolysis is a process where polymeric materials undergo thermal decomposition under an inert atmosphere at temperatures amidst 250 °C and 450 °C, causing the breakdown of their macromolecular structure. Pyrolysis yields carbonized char (solid residues) alongside a blend of compressible hydrocarbon oil and high-calorific non-compressible vapors. Waste plastic pyrolysis is considered a highly viable and efficient technology for large-scale energy regeneration [9]. Pyrolysis treatment is regarded as the most accurate route, despite mechanical and chemical procedure having elevated efficiency as well as profitable production. Additionally, pyrolysis oil exhibits superior calorific value and economic performance [10–14]. Hence, numerous authors have conducted study on pyrolysis operation to enhance value of plastic trash. The goal of these investigations was to determine the optimal parameters, catalysts for achieving the highest possible oil production through plastic pyrolysis. These

conditions mainly include the catalyst, catalyst weight, reactor type, temperature, and conversion time [15, 16]. Furthermore, the diverse range of plastic waste necessitates individualized pyrolysis conditions owing to their inherent composition [17]. Hence, the process of pyrolysis for plastic waste can be categorized into two primary groups: pure plastic waste and metalized plastic waste [18]. Figure 2 depicts the pyrolysis process, its principles and further procedures after pyrolysis.

The process of pyrolyzing plastics involves choosing a catalyst, which has a significant impact on the final product composition and yield. The studies have demonstrated that some catalyst combinations can synergistically improve the process, resulting in decreased coke formation, higher output, and enhanced preference for gasoline and aromatic fractions [19, 20]. Pawelczyk et al. (2024) investigated nickel catalysts modified with various metal carbides for plastic waste pyrolysis combined with dry reforming (PCDR). The carbide dopants influenced the catalysts' properties and activity in the PCDR process. Among the tested catalysts, Ni-TiC/MgAl<sub>2</sub>O<sub>4</sub> exhibited the highest efficiency for syngas production at 800 °C and minimized carbon deposition. It also delivered a superior syngas yield compared to the conventional catalyst under various conditions. This study suggests that Ni-TiC/MgAl<sub>2</sub>O<sub>4</sub> is a promising catalyst for PCDR of waste plastics due to its enhanced activity and stability [21]. Balazs et al. (2024) investigated converting waste polypropylene (PP), polystyrene (PS), low-density polyethylene (LDPE), and high-density polyethylene (HDPE) into fuels through pyrolysis and distillation. The yield of usable fuel (WPG) varied depending on the plastic type, with PS showing the highest yield (77.63%) and LDPE the lowest

Fig. 2 An illustration of the essential principles and process flow for plastic pyrolysis



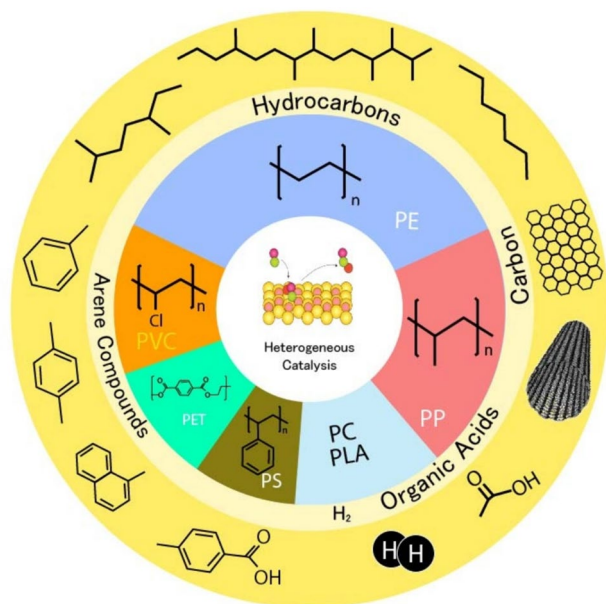
(35.81%). The results suggest that pyrolysis with distillation offers a promising approach for converting plastic waste into fuels, promoting waste reduction and creating valuable products [22]. Ashish et al. (2023) underscores the critical role of catalysts in optimizing PET plastic's chemical recycling via pyrolysis. Their investigation emphasizes heterogeneous catalysts due to their advantageous reusability and stability in industrial settings. The study reveals a strong influence of catalyst type on the product distribution during PET pyrolysis. Notably, basic catalysts promote the formation of liquid hydrocarbons such as benzene, biphenyl, toluene, styrene, acetophenone, benzaldehyde, whereas acidic catalysts selectively generate benzoic acids, acetophenone, vinyl benzoate, benzophenone, and fluorenone. However, achieving large-scale implementation necessitates addressing catalyst deactivation caused by char formation and the economic limitations associated with certain high-cost catalysts. [23]. Sekyere et al. (2023) investigated co-pyrolysis of pine and LDPE using various catalysts to improve light olefin and aromatic production. They explored basic, acidic, and tandem acid–base catalysts. Their findings showed a synergistic effect between pine and LDPE, with catalysts significantly reducing activation energy. Calcium aluminate (CaAl) and ZSM-5 (Si/Al ratio of 40) were identified as the optimal base and acid catalysts, respectively. A 1:1 CaAl-Z40 tandem catalyst at 600 °C yielded the highest content of light olefins and BTX (69.45%). This study highlights the effectiveness of tandem base-acid catalysts in enhancing desired products during co-pyrolysis of biomass and plastics [24].

Wang et al. (2021) propose that the incorporation of biomass waste into LDPE can provide a promising strategy for improving the efficiency and selectivity of aromatic chemical production, including xylene, benzene, and toluene [25]. Nevertheless, the degree to which a reaction is focused on a particular product can be altered by the selection of a catalyst. Gaurav et al. (2014) proposed a method that utilized pyrolysis and catalysis in a two-step process to transform high-density polyethylene into hydrocarbon oil with a range of C<sub>8</sub>–C<sub>12</sub>, which is suitable for use as gasoline. Initially, the plastic underwent pyrolysis, resulting in the generation of hydrocarbon gases. Subsequently, these gases underwent catalysis in the second phase with catalysts made of solid acid, leading to the creation of hydrocarbons within its gasoline scale. To improve this transformation of waste plastic into hydrocarbons suitable for use as gasoline, a two-stage catalytic process was utilized. This approach involved the use of a meso-porous catalyst followed by a micro-porous catalyst [26]. Through a series of experiments, Dai et al. (2021) explored the effects of various catalysts, individually and in tandem, on the pyrolysis process [27]. According to their research, co-pyrolysis of plastic waste and biomass using tandem catalysts demonstrates a significant improvement in the selectivity of naphthagenesis. Wide spectrums

of solid catalysts are zeolite-based, bimetallic, clay catalysts, biochar's and activated carbon have been documented to have comparable efficacy, showing encouraging outcomes. Zeolite-based catalysts have emerged as frontrunners within the domain of thermochemical conversion of waste plastic and biomass, particularly in pyrolysis and co-pyrolysis processes. Zeolites demand is due to their distinctive microporous structure, which enables efficient movement of reactants and surface interactions, resulting in improved catalytic activity. Despite the presence of a similar mechanism in clay, catalysts generated from clay are frequently disregarded in these procedures.

Acid sites contribute to the catalytic activity of polyolefin pyrolysis. As a result, catalysts based on zeolite, due to their high acidity, have superior conversion rates in comparison to catalysts that do not contain zeolite. Songip et al. [29] conducted the study and investigated the effectiveness of REY, HZSM-5, silica-alumina (SA) and HY zeolite catalysts in the conversion of polyethylene to transportation fuel. Their findings indicated that REY zeolite displayed superior performance, yielding plastic fuel that includes a high-octane number and gasoline fraction. Among those the three zeolites that were examined, REY demonstrated the most favorable characteristics for the manufacturing of high-octane gasoline. The increased pore size and appropriate acidity of the material enabled a highly effective conversion of the feedstock into gasoline with a high-octane number. Although the octane numbers of the gasoline produced by both Y and ZSM-5 zeolites were similar, their yields were considerably lower compared to that of REY, suggesting that REY exhibits greater catalytic performance. Building upon previous work, Manos et al. [30] explored the breakdown by catalysis of polyethylene by means of a highly stable Y zeolite. Clay-based catalysts show great potential for cost-effective pyrolysis of plastic waste, thanks to their ability to undergo numerous changes. Metals or metal oxides were used to modify zeolite and clay frameworks to enhance their catalytic activity. Utilizing silica-alumina has demonstrated a substantial increase in the production of liquid product. Clay and zeolite, which are plentiful and affordable minerals, are highly efficient catalysts for pyrolysis because of their extensive availability in nature [31–33]. The following Fig. 3 illustrates importance of utilizing heterogeneous catalysis in converting waste plastic via pyrolysis.

In addition to conventional fuels such as gasoline and kerosene, plastic can be pyrolyzed to create diesel-range hydrocarbons with superior qualities that are comparable with diesel fuel that is sold commercially. For the extraction of sustainable fuel, this offers an alternative option. High cetane number, low sulfur content, good cold flow qualities, and reduced particulate matter emissions are only a few of the important characteristics of the diesel-range hydrocarbons produced by plastic pyrolysis. Jahirul et al. investigated



**Fig. 3** Circular diagram highlighting the potential of using heterogeneous catalysis to convert plastic waste into various valuable products

the conversion of plastic waste, primarily HDPE, PS, and PP, into liquid fuels through pyrolysis and vacuum distillation. Batch pyrolysis at 540 °C yielded crude oil, which was fractionated into gasoline, diesel, and heavier components. HDPE produced lower oil yields due to wax formation. The resulting diesel fractions from HDPE and PP exhibited cetane numbers of 60 and 55 respectively, surpassing the minimum automotive diesel standard of 46. The higher heating values of all fuel fractions were comparable to fossil fuels, indicating their potential as energy sources. While PS predominantly produced gasoline, HDPE and PP yielded significant amounts of diesel. The overall findings suggest that plastic waste can be effectively transformed into high-quality diesel fuel, providing a sustainable alternative to conventional petroleum-based products [34]. Similarly, Alberto et al. carried out experiments and investigated the potential of altering industrial and post-consumer plastic waste into diesel like fuels through pyrolysis. The resulting pyrolysis oils were characterized and compared to commercial diesel. Pyrolysis oils exhibited a significant hydrocarbon fraction within the diesel boiling point range (180–380 °C). Cetane number, a crucial ignition quality parameter, was comparable to commercial diesel, primarily due to a higher paraffin content in the oils derived from post-waste plastic waste. Moreover, the higher heating value of all pyrolysis oils was similar to diesel fuel. Importantly, chlorine levels were negligible in all samples and sulfur content was below the diesel standard in oils from post-waste plastic waste. Other fuel properties like polycyclic aromatic hydrocarbon content, water content, lubricity, and total acid number met diesel

specifications. However, density, distillation curve, kinematic viscosity, flash point, and cold filter plugging point of the raw pyrolysis oils did not comply with diesel standards. To address this, distillation was employed to isolate the diesel fraction. The resulting distillate met diesel standards except for density and cold filter plugging point. To further enhance fuel quality, a blend of the distilled pyrolysis oil with commercial diesel was formulated in a 50:50 weight ratio. This blend successfully met all diesel fuel specifications, demonstrating its suitability as a transportation fuel. The findings underscore the potential of pyrolysis as a viable pathway for plastic waste valorization and contribute to the circular economy [35].

This critical analysis intends to examine the essential characteristics of cost-effective catalysts for the pyrolysis of plastic waste to fuel. Prior investigations into plastic pyrolysis have predominantly targeted the characterization of the vapor, fluid, and solid products yielded throughout the procedure. However, despite significant research on plastic pyrolysis using catalysts, a gap exists in the literature regarding the application of low-cost alternatives. Therefore, our research aims to provide valuable insights for aspiring scientists regarding the process of converting plastics into fuel using cost-effective, novel catalysts. This approach has the potential to transform the challenge of waste management into a lucrative opportunity for generating income.

## Clay-Based Catalysts

The gasoline industry relied on the robust acidic catalytic properties of clays for refining processes, before the advent of zeolites. Because of their economic practicality, clays are being endlessly modified through selective Si–Al leaching, pillaring, and acid treatment. Unlike their parent materials, the pillared clays pyrolysis produces 2-D patterns through uniform arrangement [36]. Solid acid catalysts engage a fundamental role by mediating catalytic reactions of plastic pyrolysis. The surface characteristics of these catalysts, including pore size, density, pore structure and acidity, exert a significant influence on the reaction mechanisms and product distribution. Cracking, isomerization, oligomerization, cyclization, and aromatization are among the key mechanisms that govern alteration of waste plastic into important yields [37]. Exposing aluminum sites in clay introduces Lewis's acidity, while protonated oxygen at silicon-oxygen sites contributes to Brønsted acidity. The abundance of Brønsted acid sites on catalyst surface facilitates double bond cleavage and subsequent propagation steps by providing a ready supply of protons. Simultaneously, Lewis's acid sites, acting in a distinct capacity, modulate the surface interactions between the catalyst and polyolefin, a crucial aspect of heterogeneous catalysis. The catalyst's significant

area of surface and acidic areas serves an essential function in embracing the synthesis of liquid products over gaseous ones. The microporous nature of clay matrix facilitates thermal management and extends the adsorption time of reactant molecules. This extended residence time allows for increased heat absorption and promotes favorable interactions, ultimately enhancing hydrogen transfer efficiency [38]. Calcination after chemical processing of clay increases its firmness during high-temperature pyrolysis. The efficacy of montmorillonite, saponite, and pillared clay catalysts in PE pyrolysis was examined by Manos et al. [39]. Their findings revealed that these catalysts promote efficient PE conversion to liquid products at moderate temperatures, while minimizing coke formation.

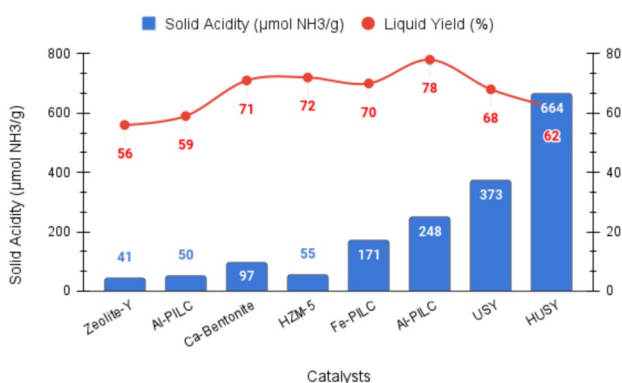
The incorporation of solid catalysts into liquid reaction media can significantly enhance the cracking of polymeric structures to generate intermediate species in the reaction mechanism. This translates to a surge in liquid product yield while a concomitant decline in wax formation. This observed reduction in wax content upon employing bentonite clay is attributed to its surface acidity. While bentonite clays exhibit surface acidity, it is intrinsically less pronounced compared to zeolites. This disparity is primarily attributed to the difference in the Si/Al ratio between the two materials [40]. The enhanced conversion is attributed to not only the increased specific surface area and favorable distribution of Lewis acid sites but also thermal stability of clay configuration, which preserves surface area and pores essential for the cracking process [41, 42]. The exceptional solidity of pillared clay catalysts facilitated their reusability, as revitalized and recycled catalysts exhibited nearly matching alteration and yield numbers in contrast to their pristine counterparts. The presence of metal oxide pillars within the clay structure effectively minimized undesirable side reactions, as evidenced by configuration of the pyrolysis-derived fuel. The formation of diesel fuel from pyrolytic intermediates is primarily driven by two mechanisms: cyclization/aromatization and cracking. These processes lead to the production of diesel-range hydrocarbons and a significant amount of hydrogen gas. This study demonstrates the critical role of Lewis acid sites, generated by various metal oxides supported on acid-treated bentonite clay, in promoting the PP and HDPE pyrolysis reactions. These acid sites facilitate the formation of hydrated protons or hydride ions, which in turn significantly impact the activity of the catalyst materials [43]. Compared to acid-washed bentonite clay (AWBC) alone, the incorporation of metal oxides into the AWBC matrix demonstrably enhances acid-polymer interactions, leading to a significant reduction in the formation of surface residues such as coke [37]. Supattra et al. (2024) explored the catalytic effects of pelletized bentonite clay on the pyrolysis of plastic waste. The study found that the use of pelletized bentonite as a catalyst in the pyrolysis of plastic wastes (PS,

PP, LDPE, and HDPE) resulted in a substantial increase in the calorific value of the produced liquid oils compared to traditional thermal pyrolysis methods. GC-MS and FTIR analyses reveal that the oils from PS primarily consist of aromatic hydrocarbons in the gasoline range ( $C_5-C_9$ ), while those from PP, LDPE, and HDPE contain longer aliphatic hydrocarbons suitable for diesel engine applications. Notably, the use of catalyst pellets eliminates pressure drop and reduces pyrolysis processing time to a mere 10 min for 1 kg of plastic waste. The high acidity (low  $SiO_2:Al_2O_3$  ratio) of bentonite, in contrast to less acidic heterogeneous catalysts, effectively prevents wax formation during the pyrolysis process. This catalytic activity contributes to the production of pyrolysis oils with superior emissions and performance characteristics when used in diesel and gasoline engines. Specifically, catalytic oils derived from PS exhibit lower CO and  $CO_2$  emissions in gasoline engines, while all catalytic oils demonstrate comparable engine power to commercial fuels. Moreover, the engine temperature remains relatively unaffected by the use of catalytic pyrolysis oils. These findings suggest that pelletized bentonite could serve as an effective catalyst for the pyrolysis of plastic waste, paving the way for the production of liquid fuels from waste materials [28]. Table 2 presents an investigation into the efficacy of various clay catalysts for the conversion, via pyrolysis, of waste plastic into usable fuel products. This table provides a comparative analysis of the different clay types and their influence on the pyrolysis process.

The catalyst surface's acidic properties enhanced the reaction mechanism by promoting the generation of hydride ions or protonation. This inherent acidity, synergistically enhanced by occurrence of impregnated metals, presides to a considerable improvement in liquid product compared to thermal cracking. Thermal cracking, characterized by a radical mechanism, often results in gas production due to random scission of molecular bonds [44, 45]. The investigation of HDPE pyrolysis over HZSM-12 demonstrated a proportional correlation involving activation energy ( $E_a$ ) and solid acidity, substantiating the crucial part of the acid mechanism in expediting the reaction. The acid mechanism is essentially a catalytic process that uses the catalyst's acidic properties to break down HDPE into smaller hydrocarbon molecules. The catalysts acidic sites strength has a direct impact on how quickly the reaction proceeds due to formation of carbonium ions at active sites (It actually triggers rate of reaction). An increase in acidity typically results in a decrease in activation energy, allowing the reaction to proceed more readily and fast at lower temperatures [46]. Nevertheless, excessive acidity can result in enhanced product yield due to excessive cracking, which yields smaller molecules. Aluminum-pillared clay demonstrates potential as a catalyst for converting biomass to liquid fuels. Despite exhibiting mild acidity, it achieves a higher liquid yield (~70%) compared to ZSM-5

**Table 2** Leveraging distinct clay catalysts to speed up the reaction which leads to the pyrolysis of plastic trash

Catalyst	Plastic type	Result	Ref
Calcium bentonite	HDPE, LDPE and PP	Condensable product yield exhibited a temperature dependence, peak productivity occurring between 400 and 550 °C. Further analysis revealed an optimal catalyst-to-plastics ratio of 1:3 under these temperature conditions	[40]
Kaolin	PP	The study identified Ahoko kaolin as a promising low-cost catalyst for converting waste PP into gasoline/diesel-grade fuels. The efficiency of this conversion was found to be highly dependent on the ratio of catalyst to plastic used in the process	[41]
Restructured and pillared clay	Polyolefin	Chemically modified clays exhibited enhanced selectivity for aliphatic hydrocarbons, resulting in increased liquid product yield	[42]
Fe, Ti, Zr- pillared clay	HDPE, PP, PS	The use of Fe-pillared clay as a catalyst yielded significant quantities of diesel fraction and H <sub>2</sub> during the conversion process	[43]
Fe-pillared clay	Heavy gas oil (HGO)/HDPE	HGO co-processing with HDPE significantly enhanced the production of liquid hydrocarbons through pyrolysis, regardless of the catalytic approach	[44]
Tungstophosphoric acid (TPA)/kaolin	LDPE	Incorporation of TPA onto kaolin (5-TPA-K) resulted in an enhanced yield of gasoline-range hydrocarbons (C <sub>11</sub> –C <sub>14</sub> )	[45]
CO, Fe, Mn, Zn impregnated AWBC	HDPE and PP	The incorporation of metal oxides into AWBC can simultaneously enhance conversion efficiency while minimizing coke formation	[31]

**Fig. 4** Relationship between solid acidity and liquid yield [44, 46–50]

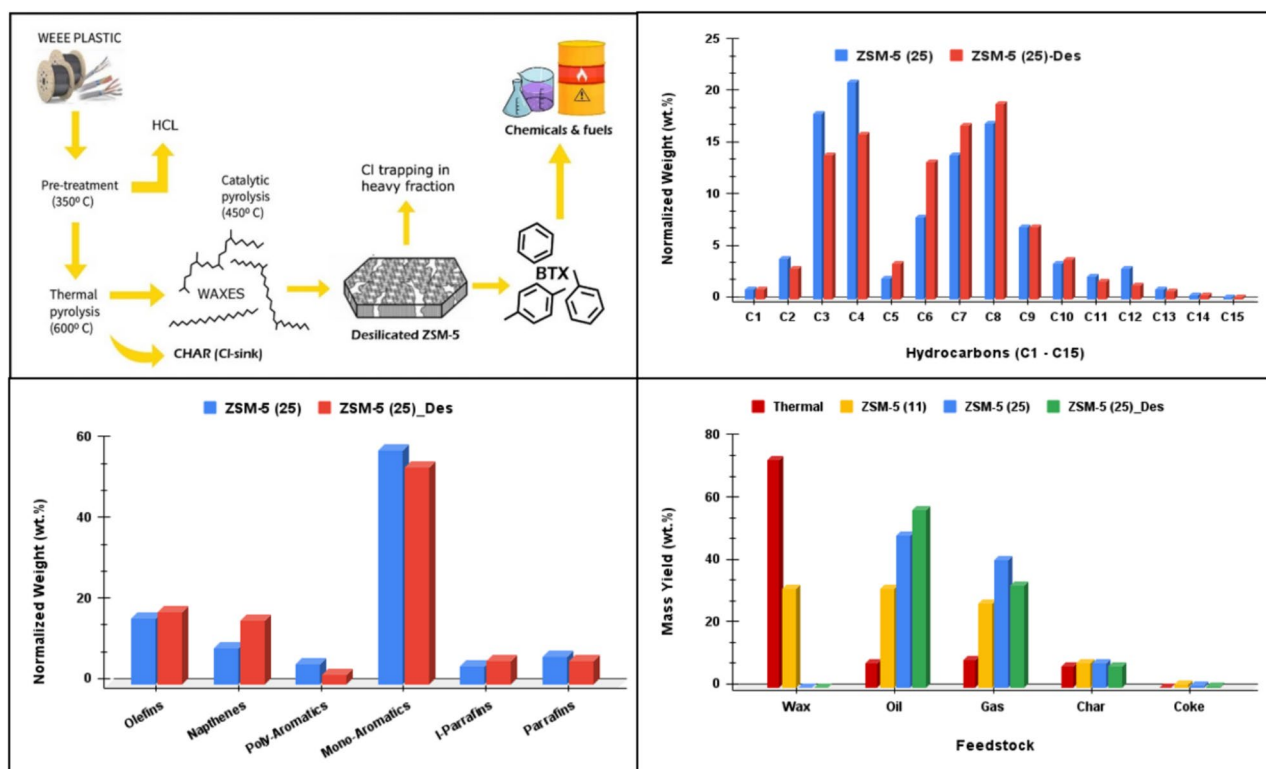
(61%) [47]. This performance is comparable to ultra-stable zeolite (USY), which generates a 71% yield [48]. Notably, USY surpasses ZSM-5 in terms of liquid fuel production [49]. The link between the solid acidity and the yield of liquid is depicted in Fig. 4, which is based on multiple studies.

## Zeolite as Catalysts

Zeolites are the prevalent class of catalysts employed in refining sector for pyrolysis in presence of catalyst, as depicted in Fig. 5. ZSM-5 zeolite emerges as potential heterogeneous catalyst for the production of biofuels via thermocatalytic processes, owing to its exceptional selectivity and catalytic prowess [51]. ZSM-5 zeolite exhibits exceptional properties for the catalytic conversion of plastic waste

into biofuel, including low cost, high thermal stability, selectivity, and activity. Notably, ZSM-5 demonstrates remarkable resistance to coke deactivation [52, 53]. The Si/Al ratio of a zeolite catalyst significantly influences its catalytic activity, acidity, and product distribution. Aluminum incorporation enhances the zeolites acidity, enabling the cracking of lighter gases and the polymerization of naphthenes and olefins into extended hydrocarbon chains. In contrast, zeolites with higher Si content promote the formation of long-chain hydrocarbons resembling diesel fuels, base oils, and waxes. The catalytic effect of HUSY on PP pyrolysis following heating pretreatment at different temperatures was investigated using PI-TOFMS [54]. Pre-treating HUSY at 200 and 800 °C diminished its catalytic activity and gave rise to elevated concentrations of alkenes, dienes, and aromatics.

Zheng et al. (2024) explored co-feeding peanut shells with LDPE and a modified zeolite catalyst during microwave pyrolysis. This approach aimed to optimize bio-oil yield and hydrocarbon content for biofuel production. The study achieved a significant increase (12–30%) in bio-oil yield compared to controls, with the highest yield (34.25%) at 450 °C and a specific catalyst dosage. Analysis revealed a dominant presence of aromatic hydrocarbons (51–68.4%) in the bio-oil, with higher catalyst loading favoring increased hydrocarbon content (up to 68.36%) and decreased phenols. Response surface analysis confirmed the crucial role of temperature and catalyst dosage in optimizing bio-oil composition [55]. Syie et al. (2023) explored a groundbreaking application of induction heating for plastic pyrolysis, investigating the impact of HZSM-5 and FCC catalysts. This method achieved remarkably rapid plastic conversion



**Fig. 5** Assessing the feasibility of ZSM-5 zeolite-assisted pyrolysis as a potential technology for the valorization of genuine WEEE plastics containing PVC

(within 10 min) due to the swift temperature rise from induction heating. Compared to thermal pyrolysis, which primarily yielded wax (72–74 wt%), the presence of catalysts significantly enhanced both gas (70.6–73.9 wt% for HZSM-5 and 62.4–75.2 wt% for FCC) and liquid product yields (24.0–27.2 wt% for HZSM-5 and 0–35.9 wt% for FCC). Interestingly, the type of catalyst played a crucial role in product distribution. HZSM-5 steered the reaction pathway towards aromatics, particularly C<sub>7</sub>–C<sub>10</sub> (toluene, ethylbenzene, xylene, naphthalene, and alkyl benzene isomers). In contrast, FCC yielded a wider range of liquid products rich in alkanes and alkenes spanning C<sub>9</sub>–C<sub>40</sub>. These contrasting outcomes can be attributed to the unique textural properties and acidity profiles of each catalyst, highlighting their ability to modify product distribution even under short residence times [56]. The composition of the zeolite catalyst has a profound influence on the proficiency with which co-pyrolysis works. Gorbanezhad and colleagues (2020) studied the co-pyrolysis process using a blend of HZSM-5 zeolite and Na<sub>2</sub>CO<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub> to enhance the yield of hydrocarbon-based outputs [57]. Their findings revealed that this catalyst combination effectively increased hydrocarbon production at a relatively intense heat of 700 °C, to 8.7%. Sodium salt's incorporation into the catalyst framework promotes de-oxygenation reaction, accelerating and

streamlining the disintegration of macromolecules into lower-molecular-weight elements such as hydrocarbons. Additionally, existing literature supports the notion that the type of zeolite catalyst significantly impacts the catalytic pyrolysis process [58, 59]. In catalytic pyrolysis, ZSM-5 demonstrates enhanced deoxygenating and cracking activity, promoting the production of stable liquid hydrocarbons [60, 61]. An investigation by Onwudili et al. (2019) explored the impact of temperature and zeolite type as catalysts on the pyrolysis reaction to transform plastic waste into biofuel liquid products [62]. The employment of various catalysts around 500–600 °C in temperature yielded no substantial production yields of oil-based fuel. Nevertheless, an elevation in temperature gave rise to a concomitant surge in gas mixture of resultant products. Furthermore, the utilization of a highly acidic catalyst facilitated an expedited production of gases. This enhanced acidity promoted hydrogenation steps development, consequently synthesizing additional free radicals that triggered β-scission, ultimately leading to gas generation [28, 63, 64]. A concurrent study by Kassargy et al. (2018) likewise demonstrated a linear relationship between the division and kind of waste plastic in combination and the yields of the liquid's fractions [63]. Miscolczi and colleagues (2019) investigated the influence of metal stacking on the zeolite's anatomy catalytic activity in plastic-to-fuel



conversion [64]. The incorporation of various metal cations, including  $\text{Fe}^{2+}/3+$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{H}^+$ ,  $\text{Ce}^{2+}$ ,  $\text{Sn}^{2+}$ , and  $\text{Cu}^{2+}$ , into the zeolite structure was investigated. The results demonstrated that metal loading levels of 8–10% significantly influenced the macropore surface area and pore diameter of the resulting substances. The catalyst's acidic characteristics and surface area are both critical factors influencing the course of the pyrolysis reaction. [65, 66]. Consequently, tailoring the surface area of zeolite catalysts by incorporating metal ions effectively modulates the level of heat at which polymers break down during pyrolysis.

Nattadon et al. investigated the production of diesel fuel through the catalytic pyrolysis of PE, PP, and HDPE plastic waste. The catalytic process was conducted at 500 °C using ZSM-5, dolomite, and kaolin as catalysts. Results indicate that natural catalysts, such as kaolin, yielded a higher fuel volume compared to synthetic catalysts like ZSM-5. For instance, kaolin produced up to 60.4 wt% fuel from PE. While ZSM-5 enhanced the calorific value of PE-derived fuel to 42.2 MJ/kg, fuels produced using natural catalysts exhibited lower calorific values due to increased benzene content. This compositional difference resulted in reduced engine braking horsepower and increased fuel consumption for fuels derived from naturally catalyzed pyrolysis. However, these fuels demonstrated superior air pollution mitigation compared to those produced with synthetic catalysts. Specifically, kaolin-catalyzed fuel reduced CO and NO<sub>x</sub> emissions. While natural catalysts offer a higher fuel yield, the resulting fuel quality, as indicated by lower calorific value and engine performance, requires optimization. Reducing benzene and acid content in the fuel could potentially bridge the performance gap between fuels produced with natural and synthetic catalysts [67]. Kassargy et al. conducted batch reactor experiments to study the thermal degradation of PE and PP in the presence and absence of USY zeolite. Without a catalyst, PE primarily produced wax around 80 wt%, while PP yielded a liquid fraction of 85.5 wt%. When USY zeolite was added, both PE and PP showed significant increases in liquid yield (71 and 82 wt%, respectively) with minimal coke formation. The liquid products from catalytic pyrolysis contained a wide range of hydrocarbon components, from C<sub>5</sub> to C<sub>39</sub> for PE and C<sub>5</sub> to C<sub>30</sub> for PP. This suggested the possibility of phase separation into gasoline and diesel like fractions. To optimize separation, three temperatures were tested at 130, 150, and 170 °C. The 170 °C separation temperature resulted in the most effective separation, producing light and heavy fractions with properties similar to gasoline and diesel fuel. The gasoline-like fractions, comprising 60.6% of PP oil and 57% of PE oil, had high octane numbers (RON = 96 and RON = 97, respectively). The diesel like fractions, accounting for 36.5% of PP oil and 35.3% of PE oil, exhibited promising cetane numbers of 52 and 53 [48]. Ghaffar et al. explored potential solutions

to the growing problem of plastic pollution. Their research focused on techniques to remediate plastic waste, identifying thermal decomposition as a promising method. They specifically examined the use of a ZSM-5 catalyst to facilitate the decomposition of HDPE. This study delved into the influence of heating rate and reaction duration on the yield and quality of pyrolytic oil products derived from a two-stage reactor configuration. The pyrolysis reactor was operated at varying heating rates at 2–18 °C/min and reaction times 75–105 min. The resulting oil products were characterized by their gross calorific values (GCV) and hydrocarbon composition (PONA distribution). The optimal oil yield of 61.05 wt.% was attained at a heating rate of 2 °C/min and a reaction time of 75 min. The GCV of the oil products fell within the range of conventional diesel (44–45 MJ/kg). The hydrocarbon composition primarily comprised C<sub>10</sub>–C<sub>24</sub> compounds, aligning with the diesel range. While paraffin content was generally elevated, naphthene and aromatic levels were relatively low compared to conventional diesel. Increasing heating rate and reaction time resulted in a decrease in oil and solid yields and an increase in gas yield. The GCV of all oil products remained within the specified range for conventional diesel. The carbon number distribution revealed that over 68% of the oil products were C<sub>10</sub>–C<sub>24</sub> hydrocarbons, suitable for diesel or kerosene applications. However, the PONA distribution varied, with some products meeting the conventional diesel specifications [49].

The impact of selecting different zeolite catalysts on HDPE pyrolysis was explored by Olazar et al. [68]. HZSM-5's specific morphology and acid strength suppressed side reactions such as hydrogen transfer and radical coupling, resulting in higher yields of light olefins and mono-aromatics with reduced coke formation. Coke regeneration was achieved by air combustion at temperatures below 550 °C. To elucidate the processes occurring after volatile substances have evaporated, LDPE was decomposed by both thermal and catalytic means in a two-stage reactor at temperature levels around 300 and 600 °C with residence times of 17.7–53.0 s [69]. The production of lighter hydrocarbons through thermal pyrolysis necessitates higher volatilization temperatures and prolonged residence times. The introduction of a commercial HY zeolite catalyst resulted in an enhanced production of low-temperature liquid products. An investigation by Marino et al. (2022) explored the pyrolysis in presence of catalyst by using chlorinated waste plastic derived from electronic equipment (WEEE) using ZSM-5 zeolites. The WEEE feedstock contained approximately 3.4% PVC and was subjected to thermal pretreatment at 350 °C to reduce chlorine content by 87%. Pyrolysis studies had been carried out in a stainless-steel downdraft fixed-bed reactor. The thermal zone was kept at 600 °C, an elevated temperature, while the catalytic zone operated at a lower temperature of 450 °C. The ZSM-5 sample treated

with desalination exhibited a significantly higher oil yield (60 wt %) and monoaromatic content, primarily consisting of BTX, exceeding 50 wt%, as shown in Fig. 5. Chlorine distribution analysis revealed that approximately 90% of the chlorine accumulated in the char fraction, likely due to capture by inorganic constituents in the unrefined WEEE trash. Among the analyzed fractions, coke displayed the subsequent-highest concentration of chlorine, surpassed only primarily by the oil and wax fractions. Notably, chlorine was almost entirely absent in the gas fraction. In their study, the desilicated zeolite exhibited a superior capacity for chlorine removal from oil, achieving a final concentration below 90 ppm [70].

The pore size and acidity of catalyst-based zeolites considerably influence the yields generated during pyrolysis [71]. For instance, zeolites with larger pores favor the conversion of plastics into polyalkylaromatics, whereas those with smaller pores exclusively produce aromatic compounds with restricted dynamic diameters. These findings underscore the importance of zeolite selection as a catalyst in pyrolysis reactions, as it dictates the characteristics of the yield formed. Susastriawan et al. (2020) observed a direct relationship between decreasing zeolite particle size and enhanced temperature during pyrolysis, reaction rate, thermal transfer rate, and oil production throughout low-temperature pyrolysis of LDPE plastic waste [72]. This suggests a positive influence of smaller sizes of particles during the whole pyrolysis procedure. This enhancement is attributed to the increased surface-active area of smaller zeolite particles, facilitating greater contact with the plastic waste during pyrolysis. While zeolite particles with a range of 1 mm yielded the peak fuel production, particles size between 1 and 3 mm did not exhibit significant differences in oil production. Kim et al. (2018) demonstrated that, incorporation of phenol functional groups into lignin optimized a substantial yield of aromatic hydrocarbons in the final output by 39% [73]. The occurrence of hydroxyl groups within the lignin structure favorably enhances the selectivity during the decomposition reaction, resulting in aromatic hydrocarbons as the predominant product [74, 75]. Zeolites, a class of microporous aluminosilicate materials, serve as effective catalysts for the pyrolysis of plastic waste. Their hydroxylated surfaces promote condensation reactions and accelerate the formation of aromatic hydrocarbons through a series of mechanisms, including dihydroxylation, aromatization, isomerization, and oligomerization. As demonstrated by multiple studies, zeolite catalysts enhance the acid and thermal mobilization processes of polyethylene, polypropylene, polyvinyl chloride, polyethylene terephthalate, and polystyrene are among the plastics capable of being pyrolyzed [76, 77]. Following Table 3 illustrates different zeolite-based catalysts with reaction conditions for pyrolysis of waste plastic.

## Bimetallic Catalysts for Pyrolysis of Plastics

In the area of producing biofuel using plastic waste by catalytic pyrolysis, bimetallic catalysts have emerged as a prominent choice. Prior to the widespread adoption of bimetallic catalysts, monometallic catalysts were the subject of extensive research and documentation in the context of catalytic cracking processes. Building upon previous research, Zhou et al. (2020) reported a significant advancement in polystyrene decomposition with the development of a bimetallic Ni–Fe/ZrO<sub>2</sub> catalyst. Notably, this catalyst exhibited superior performance at 500 °C, which is a comparatively low temperature, highlighting its potential for efficient and sustainable waste management strategies [82]. Their findings highlight the enhanced catalytic activity achieved through the incorporation of bimetallic catalysts in waste decomposition processes. The synergistic effects between Ni and Fe contribute to the suppression of the shift reaction between water and gas and a reduction in the Ea required for the reforming reaction [83–85].

In a 2020 study, Cai and colleagues demonstrated the effectiveness of a carbon-based iron and nickel bimetallic catalyst in the rapid pyrolysis of waste plastic [86]. Using a catalyst, the catalytic pyrolysis was carried out in a fixed-bed reactor with a loading of 1 wt.% relative to the plastic waste, at a reaction temperature of 500 °C. Packed-bed reactors offer several benefits for pyrolysis reactions, including a straightforward drawing, accommodation of irregular plastic shapes, and reduced thermal requirements [87, 88]. The authors attributed the superior catalytic performance to the cooperation ambiguously among Ni and Fe that facilitated oxygen reduction reaction (ORR) through an enhanced electronic structure and charge transfer pathway. Additionally, the synthesized catalyst displayed exceptional resistance to methanol poisoning and degradation. This superior performance is explained by the existence of functional groups that are oxygenated on its surface, thereby effectively inhibits catalyst aggregation and corrosion [89]. Building upon previous research, in 2020, Chen et al. looked into the application of a bimetallic catalyst supported on MCM-41 to enhance the cracking efficiency of waste plastics. The catalyst was found to increase the yield of cracking products to 49.9%, with a selectivity of 65.93% for styrene at 10% iron-nickel/MCM-41 [90].

The inclusion of the bimetallic catalyst produced a significant reduction in the bromine amount of the cracking products, decreasing from 10 to 2.3%. Considering the catalyst's large surface area, it provided unhindered access for plastic molecules to penetrate the internal pore structure, thereby facilitating their efficient cracking. Iron-based catalysts are capable of converting primary

**Table 3** Employing zeolite-based catalysts for the pyrolysis of plastic trash

Type of plastic	Catalyst	Reaction condition	Conversion	Selectivity	(Catalyst/ Plastic ratio)	Refs
PS and PO	Y-zeolite	600 °C for 30 min under N <sub>2</sub> gas	Efficient production of economically significant aromatic compounds, including benzene and toluene	90% of the aromatic content	1:1	[62]
PE and PP	USY-zeolite	500 °C	Hydrocarbons (C <sub>5</sub> -C <sub>7</sub> ) are the primary components in liquid products, while C <sub>3</sub> and C <sub>4</sub> dominate the gaseous fraction	80% of liquid production	1:10	[63]
PS	Natural/Synthetic zeolite	450 °C for 75 min	Natural zeolite exhibits 60.8% conversion to ethylbenzene, while synthetic zeolite converts 38.3% to alpha-methyl styrene	54% and 50% of liquids products for natural and synthetic zeolite	0.1:1	[81]
HDPE	Co-Y-zeolite	600 °C for 30 min	0.4 times the gas output	68% of H <sub>2</sub> production	2:1	[78]
Plastic mixtures (HDPE/PP/PS/PET/PVC)	Regene-rated ZSM-5	440 °C for 30 min	Approximately 60% of plastic waste can be converted to a liquid state	97.4% of aromatics with 2.3% of styrene as major composition	1:10	[79]
Plastic mixtures (PE/PP/PS/PET/PVC)	ZSM-5	500 °C for 30 min	58.4% gasification	50.7% of C <sub>3</sub> -C <sub>4</sub> types and 27.9% of styrene	1:10	[80]

components to styrene. The addition of Ni-metal oxides enhances the catalyst's acidity, enabling conversion of polycyclic mixtures into uni-ring hydrocarbons. The catalyst's peripheral shell characteristics and pore range influence chemisorption, which can be tailored through a synthesis method. The higher pore diameter of Fe–Ni catalysts is associated with increased H<sub>2</sub> desorption [91], similar to the observation of long-chain products obtained from Co/SBA-15 catalysts with large pore sizes [71]. While Ni-loaded CNTs developed by Wen and colleagues (2014) displayed promising catalytic activity for polyolefin pyrolysis, their high carbon content posed a significant drawback [92]. Bimetallic catalysts, on the other hand, offer several advantages in this reaction due to their smaller size-induced large surface area, enhanced stability, and synergistic effects arising from the combination of two metals [93]. Another study in 2017 by Yao and colleagues investigated the effectiveness of iron-nickel catalyst in waste plastic pyrolysis, employing a 1:3 molar ratio of Ni to Fe [94]. Their findings demonstrated that the incorporation of this bimetallic catalyst significantly enhanced H<sub>2</sub> production, achieving a five-fold increase compared to the catalyst-free process. In a 2016 study, Li et al. investigated the potential of a Mo–Ni/SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> catalyst for the thermal decomposition of fuel oil [95]. The Mo–Ni bimetallic composite catalyst demonstrated enhanced catalytic reactivity, increasing the fuel oil yield to 57.9%. The combination of nickel and molybdenum offers numerous benefits for pyrolysis catalysts, including price efficient, exquisite strength and elevated exterior region [96]. On the other hand, the investigation noted that the reactivity of the bimetallic catalyst is affected by the sulfurization method. Increasing the sulfurization extent can progressively enhance the crude oil to fuel oil conversion percentage, reaching up to 86.9%. Moreover, other studies have reported the favorable selectivity of bimetallic catalysts [97, 98]. Wang et al. conducted a study to improve the quality of plastic pyrolysis oil through catalytic upgrading. Using a 2-kg separation system, they evaluated the effectiveness of zeolite 4A, copper-based (MDC-7), and nickel-based catalysts in producing various oil fractions. Without catalysts, they determined an optimal temperature range (107–305 °C) for separating the diesel-like middle fraction C<sub>11</sub>–C<sub>22</sub>. Catalytic upgrading significantly reduced the heavy carbon content in the oil, particularly with the nickel-based catalyst, which demonstrated superior deoxygenation capabilities due to its strong acidic properties. This catalyst outperformed the others in terms of deoxygenation efficiency. The catalytic reactions and coke formation were concentrated on these strong acid sites. MDC-7 catalyst favored the production of aromatic and naphthenic compounds, while the nickel-based catalyst promoted dehydration and decarboxylation

reactions. The upgraded pyrolysis oils exhibited physical properties comparable to petroleum-based fuels. Overall, the nickel-based catalyst proved to be an effective choice for producing diesel like fractions with minimal oxygen content from plastic pyrolysis oil [99].

The bimetallic catalyst Fe–Ni/MCM-41 exhibits a unique ability to not only decompose polymer structures but also to facilitate debromination of brominated flame retardant (BFR) during plastic waste pyrolysis. This synergistic effect stems from iron's debromination prowess and nickel's ability to generate gaseous products through hydrogenation. A plausible reaction mechanism involves the interaction of organobromines with metal oxides, leading to the formation of non-brominated organic compounds. Additionally, the eradication of β-H via Lewis acid sites and a two-stage dissolution adsorption operation plays crucial roles in this debromination process [90]. Following Table 4 presents numerous bimetallic catalysts for plastic pyrolysis.

## Bio-char Based Catalysts

Biochar, a carbonaceous material generated through the controlled pyrolysis of biomass under oxygen-limited conditions, exhibits a very permeable framework and diverse functional groups on its edges. These characteristics render it an attractive candidate for catalytic applications. Through strategic modification with specific elements or treatments, biochar's act of catalyzing can significantly augment, leading its effective promotion of targeted reactions during waste plastic pyrolysis. A cheap, porous carbon substance, biochar is mostly made through biomass. Its utility extends beyond traditional fuels, finding applications as catalysts, catalyst supports, and adsorbents due to its high surface area and specific functionalities [109–112]. Interestingly, feedstocks for biochar production are not limited to conventional biomass; sewage sludge, microalgae, coal, and even manures can be employed [113]. Thermo-chemical conversion processes like pyrolysis, gasification, and hydrothermal liquefaction provide various routes for biochar generation [111].

Despite the fact that conventional pyrolysis presents a promising avenue for plastic waste valorization through fuel and chemical production, its tendency to generate undesirable heavy oils and waxes necessitates innovative approaches. Biochar catalysts emerge as a pivotal tool in this regard, offering the potential to dramatically alter the distribution of the products and enhance the efficiency of plastic waste conversion. Guillermo et al. (2024) evaluated the environmental impact of using different char management strategies in contaminated mixed plastic waste pyrolysis. Their findings show that all scenarios (char combustion, char activation with CO<sub>2</sub>, and char activation with KOH) outperform landfilling due to the environmental benefit of

**Table 4** Plastic pyrolysis using the numerous types of bimetallic catalysts

Type of plastic	1st metal	2nd metal	Condition	Conversion	Selectivity	(Catalyst/Plastic ratio)	Refs
LDPE	Mo-MgO	Fe	400 °C	LDPE waste plastic to carbon nano-tubes	High quality carbon nanostructures materials	0.5:15	[100]
PP	La <sub>2</sub> O <sub>3</sub>	Ni-Cu	500 °C , 700 °C for 2.5 h	PP to CNTs and carbon nanofibers	Carbon yields of 1458% produced	0.5:15	[101]
PP	MgO	Ni/Mo	800 °C , 10 min	PP to CNT	394% of carbon product	0.5:15	[102]
PP	Ni	Al	800 °C	PP to MWCNTs	85%	Depends on Ni/Al Ratio	[103]
PP	Ni-Al	Zn, Mg, Ca, Ce, Mn	500 °C	PP to CNTs	The highest carbon deposition 62% and H <sub>2</sub> 86.4% to Ni-Mn-Al	1:2	[104]
PE	Ni	Ce (Ni-Ce core by silica)	800 °C	PE to H <sub>2</sub>	H <sub>2</sub> concentration 60%	1	[105]
LDPE	Ni	Fe	800 °C	CNTs	Maximum H <sub>2</sub> concentration and H <sub>2</sub> yield 73.93% and 84.72 mg. g <sup>-1</sup>	0.5:1	[94]
LDPE	MgO	Co/Mo	400 °C	High quality multi-walled CNTs and H <sub>2</sub>	Optimum CNTs 1040% wt. Co-Mo (6.5) MgO	0.75:15	[106]
PP	Ni	Fe	500 °C	CNTs	93% filamentous CNTs	0.5:1	[107]
HDPE	Ni	Mn-Al	800 °C	H <sub>2</sub> and CNTs	48% total carbon (with no steam), hydrogen yield 94,4% (with steam)	0.5:1	[108]

replacing diesel with pyrolysis oil. However, char activation with CO<sub>2</sub> resulted in the greatest environmental impact compared to char combustion, highlighting the importance of char management strategy selection for environmentally sustainable pyrolysis [114]. In a study by Chenxi et al. (2020), two biochar catalysts made from Douglas fir and corn stover were used to analyze the catalytic pyrolysis of model LDPE and actual waste polymers. The corn stover biochar demonstrated exceptional performance, generating approximately 40% liquid product devoid of wax formation. Mono-aromatic hydrocarbons (20%), C<sub>8</sub>-C<sub>16</sub> aliphatic hydrocarbons (60%) and C<sub>17</sub>-C<sub>23</sub> aliphatic hydrocarbons made up the majority of this liquid product's composition. Notably, the output of gas reached around 60%, with a remarkable hydrogen content of 60–80 volume %. Interestingly, the corn stover biochar catalyst displayed significantly increased stability and activity in LDPE degradation in contrast to the Douglas fir catalyst. This disparity can likely be attributed to the distinct mineral compositions of the biochar. While the Douglas fir catalyst exhibited a rapid decline in activity and increased wax production after just 10 recycling cycles, the corn stover biochar retained its effectiveness even after 20 cycles. This

suggests that the mineral composition of the corn stover biochar might be quite important in enhancing its catalytic activity and longevity for LDPE degradation [115]. Recent endeavors by Chenxi et al. (2021) explored the promising use of a novel nanocellulose-derived biochar catalyst for the thermo-chemical upcycling of waste plastics at lower temperatures. This catalyst demonstrated significant effectiveness in transforming plastic waste, particularly with model LDPE. Its introduction notably suppressed the undesirable solid wax formation, reducing its yield from 77 wt. % in the uncatalyzed process at 500 °C to just 16 wt. % at 450 °C. Furthermore, the gaseous product exhibited a substantial increase in hydrogen concentration, reaching 89.76 volume % compared to the non-catalytic value of 20.43 volume%. Moreover, at 500 °C, the biochar facilitated complete degradation by converting the LDPE paradigm into profitable liquid and gas fractions, accompanied by an impressive hydrogen content of 92 volume % in the gaseous product [116].

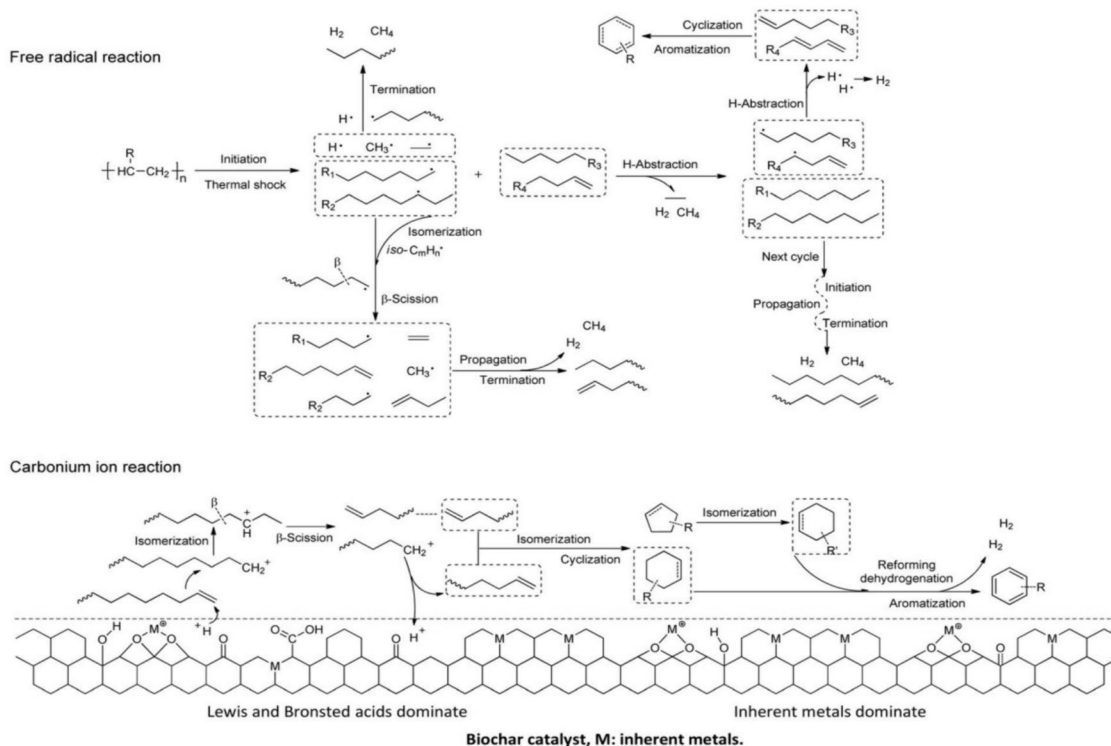
The work of Wang et al. (2018) contributes to the growing evidence of biochar's catalytic efficacy in pyrolysis. Their study revealed that ZnCl<sub>2</sub>-activated biochar significantly increased the aromatic yield in pyrolysis oils obtained

from mixed waste plastics. This highlights the promising potential for tailoring biochar catalysts to selectively target specific product streams, opening new avenues for valorizing waste plastics [117]. Biochar-catalyzed cracking holds promise for the efficient transformation of biomass into transportation fuels (gasoline, diesel) and syngas, a versatile feedstock for further chemical transformations, while also unlocking the potential for clean hydrogen production. The majority of evidence suggests that the main mechanism by which heat cracking occurs is free radical, while catalytic cracking predominantly involves carbonium ion intermediates [109, 118–120].

In this work, LDPE's complex structure serves as a platform to investigate its thermal decomposition, dominated by a free-radical chain reaction mechanism. As Fig. 6 illustrates, this mechanism unfolds in three consecutive steps: initiator-driven cleavage (initiation), monomer addition to growing chains (propagation), and ultimately, radical recombination or disproportionation (termination). The long-chain alkane nature of LDPE contributes significantly to the intricacies of this process. The initial thermal shock in pyrolysis fragments hydrocarbons into smaller free radicals. These radicals then undergo a propagation stage involving H-abstraction (yielding  $H_2$ ,  $CH_4$ , etc.),  $\beta$ -scission (generating olefins), and isomerization (favoring more stable carbonium ions). Notably,  $\beta$ -scission of  $C_mH_n^*$  radicals afford

conjugated olefins via self-H-abstraction. Cyclization and aromatization of these olefins result in the synthesis of aromatic substances. Finally, in the termination stage, radical coupling produces short-chain alkanes and alkenes,  $H_2$ , and  $CH_4$ . The locations of Lewis and Brønsted acids in biochar initiate the carbonium ion reaction pathway in hydrocarbon reforming.  $C=C$  double bonds are protonated, generating carbonium ions. These ions can further react with alkanes to produce more, potentially via isomerization favoring secondary ions. Long-chain carbonium ions undergo  $\beta$ -scission, yielding olefins and new ions. These new ions can either participate in another cycle or return a proton to the catalyst, regenerating acid sites and forming olefins. Isomerization and cyclization of these olefins lead to naphthenic hydrocarbons, which are then converted to aromatics and hydrogen under the catalytic influence of intrinsic metal content of biochar. This metals' process is significantly influenced by the parameters of dehydrogenation, mirroring their function in traditional petroleum reforming [115].

Importantly, the biochar catalysts effectively converted real-world plastic trash, such as used shopping bags, cardboard cartons, and filtered beverage containers, into valuable products. This study presents a promising, sustainable approach for upcycling waste plastic into high-value fuels and hydrogen using readily available and eco-friendly biochar catalysts. While activated carbon often boasts high



**Fig. 6** Potential mechanism of reaction for pyrolysis of LDPE using biochar catalysts [115]

efficiency in waste plastic conversion, its relatively high cost and potential environmental concerns during production have spurred interest in exploring alternative materials. Biochar, a cost-effective and potentially more sustainable carbon material, has yet to be thoroughly investigated for its efficacy in plastic waste conversion. This knowledge gap presents an exciting research opportunity to explore the potential of employing raw biochar as a solution to the global plastic pollution crisis [115].

## Activated Carbon

In an array of applications, activated carbon (AC)—also termed as active carbon, coal, and activated charcoal, is an incredibly powerful adsorbent. Research in catalytic processes for different methods has developed due to its unique advantages [121, 122]. Furthermore, AC demonstrates remarkable resilience to both acidic and basic environments, as well as exceptional stability under hydrothermal conditions. These exceptional properties contribute to its enhanced resistance to the pronounced rigidity and pressurizing effects experienced by metal oxides in hydrothermal settings [123]. Building on the work of Huo et al. (2020), this study investigated employing biomass-derived activated carbons (BACs) produced from biomass to catalyze the pyrolysis of waste plastics and MgO as catalysts, aiming to produce H<sub>2</sub>-loaded vapor substances and jet fuel. The findings revealed that LDPE catalytic pyrolysis, particularly with optimized catalyst placement, offers promising potential for generating high-purity jet fuel. The combination of BACs and MgO promoted H<sub>2</sub> as the primary gaseous product, highlighting the remarkable potential of this approach for sustainable production of both jet fuel and H<sub>2</sub>. Interestingly, the type of BAC and pyrolysis conditions were able to enhance the manufacturing of specific vaporous HCs, such as H<sub>2</sub> and light alkanes, opening up exciting possibilities for fuel production and chemical feedstock applications [124].

AC's closed-loop nature, enabled by its recyclability and reusability, coupled with its impressive catalytic activity in pyrolysis, aligns perfectly with the principles of sustainable resource utilization. This combination makes it a promising candidate for sustainable pyrolysis applications. The collaborative impact of –P–O and –P–O functionalities on the AC surface, as reported by Zhang et al. (2018), facilitated decarboxylation, dehydration, aromatization, and Diels–Alder pathways in glucose pyrolysis, resulting in a shift towards desired product formation [125]. In a recent study by Fernandez et al. [126], catalytic pyrolysis of glycerol over activated carbon within a fixed-bed reactor demonstrated an enhanced synthesis gas yield, reaching up to 81% volume. Pyrolysis of biomass and plastic over AC has as shown its potential as a route for the selective manufacturing

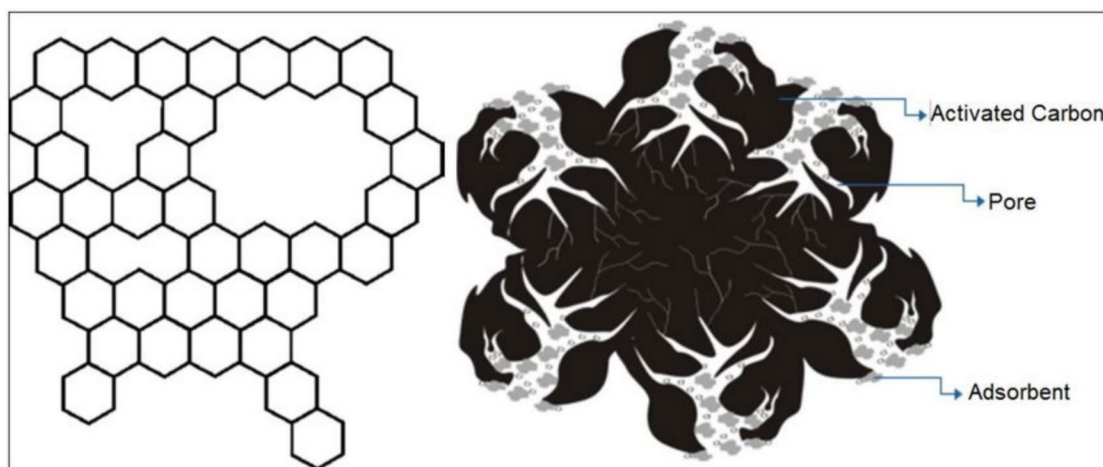
of important chemicals. Research indicates that AC effectively catalyzes the formation of phenols [125, 127, 128] and levoglucosenone [129], while also offering potential for generating aromatics [117] and contributing to jet fuel production [130, 131]. The presence of 9,10-dihydroanthracene (H/Ceff) considerably influences the quality of bio-oil, primarily due to its impact on both the hydrogen-to-carbon (H/C) ratio and soap stock formation. While AC-catalyzed pyrolysis has explored hydrogen-enriched feedstocks like soap stock and others, the majority of research has focused on individual pyrolysis of plastic or biomass. Notably, plastic's co-pyrolysis and feedstocks, particularly WPC waste, has received limited attention.

In research conducted by Miskolczi et al. (2017), the utilization of AC as a catalyst during pyrolysis demonstrably enhanced both gaseous and pyrolysis oil yields. Notably, the sulfur content within the pyrolysis oil was significantly reduced, suggesting a purification effect. Furthermore, the presence of a naphtha-like fraction within the pyrolysis oil was identified, indicating potential for further refinement. The authors attributed these changes to the ability of activated carbon to selectively remove heteroatoms such as sulfur and nitrogen from the oil, thereby generating a cleaner and more valuable product. Remarkably, reductions in sulfur content of up to 80% were reported, highlighting the substantial purification potential of activated carbon in pyrolysis processes [132]. The textural properties of activated carbon materials set them apart from zeolites. Notably, activated carbons exhibit more developed porosity with broader pore size distributions, leading to a greater abundance of internal surface area. Figure 7 further illustrates this disparity in pore structure [133, 134].

## Impact of Using Biomass Feedstock in Co-feeding

The lignocellulosic biomass comprises various components, primarily cellulose, lignin and hemicellulose, amid minor proportions of extractives. Cellulose, the most abundant constituent, accounts for over 40% of the biomass, followed by hemicellulose at approximately 20% and lignin at around 16%. Extractives, the least abundant component, make up the remaining 0–14% [135–137]. The conversion efficiency of biomass to biofuels is influenced by various factors, including the feedstock's chemical composition, moisture content, reactor configuration, and operational temperature parameters [138–141]. The blending of biomass feedstock with complementary materials during pyrolysis may boost the output and worth of the subsequent outputs, as demonstrated in Table 5.

Various methods exist for the biomass pyrolysis, including thermo-chemical, biological, and chemical alteration.



**Fig. 7** Typical activated carbon lattice [133]

Among these, thermo-chemical conversion is the most prevalent method due to its ability to effectively break down the rigid structure of biomass using high-energy processes [142]. The method of co-pyrolysis exhibits an impressive cumulative impact assign to the existence of loose radicals created while biomass disintegration. These free radicals promote the cleavage of chain hydrocarbons in plastics, leading to enhanced production of volatile compounds such as methane, aliphatic hydrocarbons (paraffins), carbon dioxide, and aromatic hydrocarbons. The observed synergy manifests as a decrease in both  $E_a$  and the pyrolysis index, implying enhanced thermal reactivity and facile generation of volatiles throughout the pyrolysis procedure [143]. The  $H/C_{eff}$  of biomass engages an essential function in determining the yield circulation of biomass thermo-chemical conversion processes. A higher  $H/C_{eff}$  promotes the production of valuable olefins and aromatics while suppressing coke generation [144–146]. A study conducted by Bhoi et al. (2019) identified several working parameters that influence pyrolysis, including heating rate, temperature, biomass characteristics, carrier gas, catalyst category, and vapor residence time [147]. The different catalysts and reaction temperatures are particularly crucial for determining bio-fuel quality and yield [148–150]. The optimal temperatures for pyrolysis rely on the primary constituents of biomass feedstock. In the 200–350 °C temperature range, hemicellulose and cellulose undergo thermal breakdown, with cellulose exhibiting a slightly higher degradation onset at 330–370 °C compared to hemicellulose. Lignin, on the other hand, demonstrates significantly greater thermal stability, degrading primarily around at 400 °C [151, 152].

Chiun et al. (2023) explored pyrolysis as a viable method for biofuel production from biomass. Co-pyrolysis, the simultaneous processing of biomass and plastic, offers advantages over traditional biomass pyrolysis. Synergistic

interactions between the feedstocks can enhance the yield and quality of biochar, bio-oil, and syngas. This technique allows control over the product distribution by manipulating key process parameters. These parameters include the type of biomass and plastic used, the blending ratio, pyrolysis temperature, and heating rate. Generally, a higher plastic content in the feedstock leads to increased bio-oil and syngas production, while decreasing biochar yield. Additionally, higher temperatures and heating rates favor the formation of bio-oil and syngas. Fast pyrolysis (> 500 °C and heating rate of 10–200 °C/s) and flash pyrolysis (900–1200 °C and heating rate of > 1000 °C/s) are commonly employed to maximize the yield of liquid and gaseous products [153]. Pyrolysis conversion of *Enteromorpha prolifera* and HDPE blend was investigated by Xu et al. (2020) using HZSM-5 as the catalyst [154]. Their findings revealed that Integration of microalgae with plastic waste during thermo-chemical conversion promoted the selective formation of aliphatic hydrocarbons, accompanied by a reduction in N/O-functionalized moieties and diminished product pH. Microalgae, as organic means, have garnered interest due to their potential to obtain an elevated bio-oil output in contrast to different biomass sources [155]. Additionally, employing microalgae as a pyrolysis raw material offers several benefits, including a rapid growth pace, higher lipid amount, reduced power expenditure throughout the progression, a portion of power revival of 76%, an enhance in carbon matter to 89%, and a shrink in oxygen matter to 0.3% [156, 157]. The composition of microalgae has a substantial impact on the types and quantities of biofuel products that can be derived from them, as demonstrated by Qari et al. (2017) [158]. The moisture content of the resulting bio-oil can be decreased by co-pyrolyzing biomass and plastic trash through the establishment of intermolecular hydrogen bonding between the hydroxyl moieties in the biomass and the hydrogen atoms within the



**Table 5** Co-feeding with other feeds and their influence

Type of biomass/ polymer	Catalyst	Reaction condition	Conversion	Selectivity	(Biomass: plastic: catalyst ratio)	Refs
Laminaria japonica/PP	Pt/mesoporous MFI, Mesoporous MFI, HZSM-5 Al-SBA-16	500 °C, 1 atm	60.50 59.11 58.15 52.44	The composition exhibits 20–40% monoaromatics and 5–20% polyaromat- ics	10:10:1	[160]
Corn stalk/HDPE	ZSM-5	700 °C, 1 atm	90% of hydrocarbon	20–30% of aromatic hydrocarbon	1:4:1	[161]
Pine sawdust/LDPE	Ni-CaO-C	–	90% of gas mixture	86.74% to H <sub>2</sub> gas	1:1:2	[162]
Corn stalk/PS	ZSM-5	600 °C	90% (v/v) liquid	78.89% of monoar- omatic hydrocarbon	4:1:0.1	[163]
L. japonica/PP	Al-SBA 15	500 °C	30% (v/v) liquid	35% of liquid product is oxygenate	1: 1:1	[164]
Rice husk/PE	Ni/γ-Al <sub>2</sub> O <sub>3</sub>	Pyrolysis at 600 °C followed by cata- lytic reforming at 800 °C	80% of H <sub>2</sub> and CO	45% of gaseous prod- uct is H <sub>2</sub>	50–75% PE propor- tion	[165]

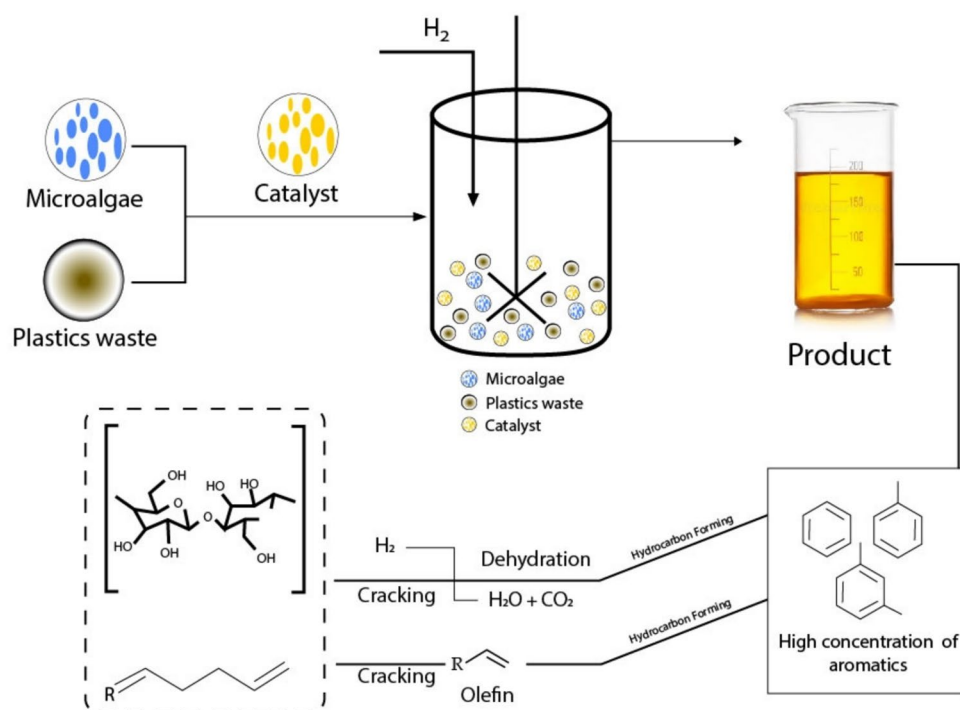
plastic polymers. This interaction can facilitate dehydration reactions, leading to bio-oil with reduced water content [159]. Figure 8 illustrates how natural biomass from microalgae and plastic trash are mixed to create a pyrolysis reaction feedstock.

In a 2019 study, Muneer et al. examined the role of catalyst-to-feed ratios in influencing the pyrolysis behavior of corn stalk (CS) and PP. This research employed a fixed-bed reactor system operated at 500 °C [163]. Increasing the catalyst proportion resulted in a higher fluid fuel output, reaching 66.5% at a ZSM-5 catalyst-to-feedstock ratio of 1:4. ZSM-5 catalyst emerged as a valuable substance for cracking of polymer and biomass dehydration due to its extensive shell region and elevated selectivity towards HC yield [166]. Bio-oil production from biomass raw materials is contingent upon the catalyst's acidic sites and pore structure, as acidic sites expedite polymer cracking. Consistent findings were similarly documented in an analysis carried out by Balasundram et al. in 2018. Their investigation demonstrated the augmenting the catalyst quantity by a factor of four resulted in a notable enhancement of 17.1% in coke decomposition [167]. The incorporation of biomass into the co-pyrolysis process has been demonstrated to improve liquid product yield and lower *E<sub>a</sub>*. ZSM-5 catalyzed co-pyrolysis of HPDE with corn stalk demonstrated a positive correlation between biomass loading and hydrocarbon production reflected by elevated H/C ratios and reduced coke yields [161]. The addition of hydrogen atoms from HDPE during co-pyrolysis accelerates hydrocarbon production. Oxygenated compounds in biomass promote HDPE cracking and chain scission. However, excessive catalyst loading can increase charring and reduce liquid product yield. This trend is observed in cellulose/polyethylene co-pyrolysis over montmorillonite K10 and cellulose pyrolysis using montmorillonite. Al-SBA's enhanced surface acidity promotes co-pyrolysis, producing more C<sub>1</sub>–C<sub>4</sub> hydrocarbons, CO, CO<sub>2</sub>, and de-oxygenation products [160].

## Factors Affecting Pyrolysis Process

The reactor configuration is essential for determining the quantity and caliber of compounds produced during pyrolysis. Although variables like temperature, rate of heating, kind of feedstock, and ratios of mixing affect the procedure, the structure of reactor remains the dominant determinant of the pyrolysate characteristics. Researchers have explored various reactor designs, including packed-bed, moving-bed, rotating cone, plasma-assisted, vortex centrifuge, fluidized bed with regenerator, and entrained flow. Further research may uncover additional promising designs [168]. Fixed-bed reactors are the most prevalent technology for pyrolysis due to their simplicity, scalability, and ability to produce

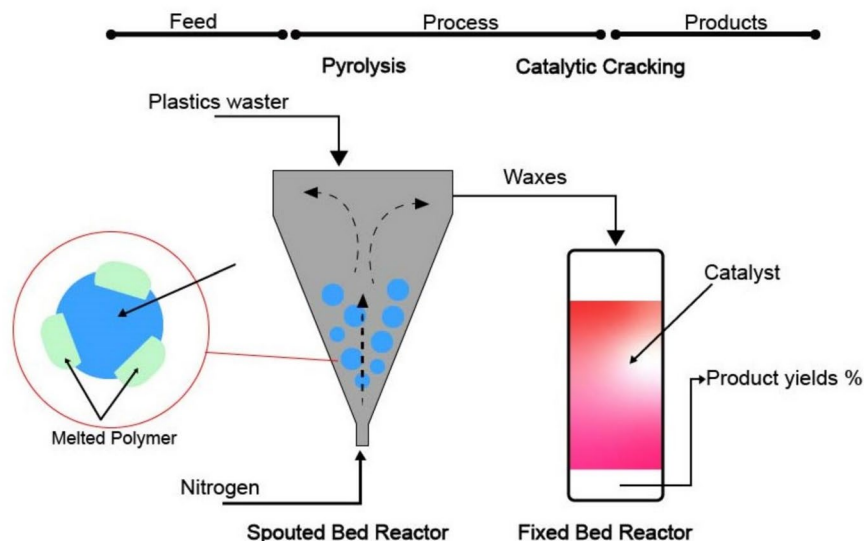
**Fig. 8** The pyrolysis procedure is depicted using plastic trash and natural biomass as fuel



high yields. Nevertheless, their inherent drawbacks, such as difficulties in catalyst regeneration, side product formation, and stringent temperature/pressure demands, have driven the exploration of alternative fast pyrolysis reactor designs. These innovative reactors focus on maximizing product yields under milder operating conditions, specifically at lower temperatures and pressures. In their study of the fast HDPE waste in a packed bed reactor, Xue et al. (2015) discovered a distinct product distribution at lower temperatures [169]. The use of HDPE feedstock in pyrolysis processes resulted in an increased formation of acidic and

furanic compounds, while the yields of phenol and vanillin were reduced compared to conventional pyrolysis processes. This finding shows that the characteristics of the products of pyrolysis can be restrained by selecting the appropriate feedstock and optimizing the reaction temperature. Additionally, Orozco et al. (2021) demonstrated the effectiveness of a continuously operated spouted bed reactor in trash plastic pyrolysis by investigating the synergistic relationship between the type of plastic and the catalyst loading, which resulted in reduced operating temperatures [14]. A fast pyrolysis reaction strategy was devised to maximize

**Fig. 9** A diagram revealing how to develop controlled co-pyrolysis reactors to increase product yields



output yields by synergistically combining the minimization of waste plastic size below 1 mm with the application of a specific carrier gas flow as displayed in Fig. 9. Interestingly, despite the absence of a specialized reactor, a significant amount of oxygen remained in the products. A recent study investigated the effectiveness of hydrotreating formate-assisted pyrolysis in alleviating this oxygen burden [170]. The elimination of oxygen resulted in a substantial increase in product percentage, reaching up to 92%

## Conclusion

In our comprehensive review, we delve into the realm of catalytic pyrolysis to turn out trash plastic into liquid fuel, highlighting its role for cost-effective catalysts. A diverse range of low-cost catalysts, including clay, zeolite, bimetallic, biochar and activated carbon catalysts, have been investigated. Extensive research has highlighted the importance of cost-effective catalysts in the catalytic cracking of trash plastic for liquid fuel–oil production. On the other hand, beyond catalysis, various parameters influence the product's quantity and quality, including feedstock particle size, temperature, pressure, catalyst-to-feedstock ratio, catalyst characteristics, and reactor type. The findings of this review reveal the thermal and catalytically degradation of waste plastic via pyrolysis and co-pyrolysis has the potential to be a sustainable and economically viable technology for fuel production. Product yield is also influenced by heating rate, blending material ratio, and temperature [87]. Enhancing the efficiency, reusability, and lifespan of techno-economic catalysts remains a pressing challenge. Catalyst design poses a significant hurdle in this endeavor, particularly in ensuring product selectivity during reactions. Our review demonstrates that catalyst conversion is primarily dictated by solid acidity, pore size and surface area. These catalyst properties, in turn, are influenced by structure, support material, and doping with active metals or bimetals on the catalyst surface. Notably, natural zeolites and clays outperform commercial solid acid catalysts due to their abundance availability, lower cost and enhanced selectivity towards liquid products [81]. Metallic modified zeolite like ZSM-5 and clay catalysts have garnered significant research interest due to their enhanced decoking capabilities and resilience of bimetallic, zeolite, and clay components. Specifically engineered Fe–Ni catalysts supported on zeolite and clay exhibit superior performance and cost-effectiveness for the pyrolysis of plastic wastes containing bromide. Biochar's porous structure and functional groups crack heavy hydrocarbons for abundant liquid fuels and gases, while AC excels at deoxygenation and contaminant removal for cleaner products. Both biochar and AC potentially requires lower temperatures, making them a versatile toolbox for optimizing sustainable waste

plastic conversion based on desired products and feedstock. Additionally, biomass and waste plastic co-pyrolyzing in charisma of these catalysts provides promising approach for plastic waste management. Further investigations into these strategies are warranted for their future implementation. The findings of this study pave the way for interconnected research initiatives towards waste plastic valorization, prioritizing environmental and societal benefits. Furthermore, it underscores the transformative potential of catalysis in the development of commercially viable technologies and products, showcasing its critical role in the circular economy for plastics.

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## Declarations

**Conflict of interest** No competing interests were declared by the authors.

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