

Review

Recent Progress in Low-Cost Catalysts for Pyrolysis of Plastic Waste to Fuels

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Abstract: The catalytic and thermal decomposition of plastic waste to fuels over low-cost catalysts like zeolite, clay, and bimetallic material is highlighted. In this paper, several relevant studies are examined, specifically the effects of each type of catalyst used on the characteristics and product distribution of the produced products. The type of catalyst plays an important role in the decomposition of plastic waste and the characteristics of the oil yields and quality. In addition, the quality and yield of the oil products depend on several factors such as (i) the operating temperature, (ii) the ratio of plastic waste and catalyst, and (iii) the type of reactor. The development of low-cost catalysts is revisited for designing better and effective materials for plastic solid waste (PSW) conversion to oil/bio-oil products.

Keywords: plastic; waste-to-fuels; low-cost catalysts; solid acid catalysts



Citation: Fadillah, G.; Fatimah, I.; Sahroni, I.; Musawwa, M.M.; Mahlia, T.M.I.; Muraza, O. Recent Progress in Low-Cost Catalysts for Pyrolysis of Plastic Waste to Fuels. *Catalysts* **2021**, *11*, 837. <https://doi.org/10.3390/catal11070837>

Academic Editor: Gartzzen Lopez

Received: 9 June 2021

Accepted: 7 July 2021

Published: 10 July 2021

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1. Introduction

Pollution of plastics in the environment has become a serious issue in recent years, producing more than 300 million tons per year [1]. One of the problems is the microplastics issue which is related to the non-degradable properties of the plastic polymer. Many efforts have been reported to reduce and overcome the presence of plastics and microplastic wastes, and one of the promising alternatives is the conversion of plastic waste into renewable energy [2,3]. More than just overcoming the environmental problems, with a designed plastic waste management system, the conversion of plastic waste into renewable energy will also contribute to the vital issue of energy conservation [4,5]. As hydrocarbon is the backbone of plastics, catalytic processes of plastic structure within the pyrolysis technique can produce hydrogen and liquid fuel. The conversion mechanisms include cracking, hydrocracking, and hydrogenation can restore the energy contained in plastic, as a sustainable process for sustainable energy [6–8]. For those mechanisms, catalysts play important roles in determining the effectiveness and efficient conversion process. Although in the perspective of kinetics and thermodynamic, the catalyst's role is to accelerate the reaction, it in fact determines the dominant product of the reaction which is further called selectivity, the optimum condition for the reaction, and also the energy required for the process [9]. The use of the solid catalyst for the catalytic pyrolysis is established and favorable, as it is easily handled, efficient in mass transfer conditions to obtain a high yield. Pyrolysis can be performed by thermal or catalytic processes. However, compared to the thermal decomposition method, the catalytic method has some advantages that could be carried out at a lower temperature and reduce the solid residues such as carbonized char and volatile fraction, short time process, high product selectivity, high octane number, etc. [10].

Moreover, in pyrolysis by cracking catalytic process, the used catalyst can be easy to reuse and reproduce, which can be classified into sustainable approaches [11]. The main factor for the mechanism lays in the domination of radical propagation steps in thermal pyrolysis instead of cationic propagation occurs in the catalytic process, leading to an uncontrolled decomposition. These advantages are feasible from the economic point of view.

Moreover, the combination of plastic or plastic waste with biomass as feed for pyrolysis, also called co-pyrolysis, has also gained much attention. The combination in the catalytic pyrolysis mechanism has been reported to provide synergistic effects such as minimizing coke formation and increasing yield and selectivity towards gasoline and aromatic fraction [12,13]. Wang et al. (2021) reported that the addition of low-density polyethylene (LDPE) to biomass waste could improve the selectivity and aromatics product, including xylene, benzene, and toluene [14]. However, the selectivity conversion also depends on the different types of catalysts used. Dai et al. (2021) studied the pyrolysis process using different types and tandem catalysts [15]. Their study revealed that tandem catalysts could improve the selectivity of naphtha. Many solid catalysts are reported with specific results, and some of them are the catalysts based on zeolite, bimetallic and clay with the comparable popularity expressed in Figure 1. Among these kinds of catalysts, zeolite-based catalysts are the most popular for both pyrolysis and co-pyrolysis for the combined plastic waste/biomass. An intensive catalytic mechanism is provided by reactant migration and surface reaction over the microporous structure of zeolite. Even though a similar mechanism also occurs on clay, clay-based catalyst receives less attention for the processes [16]. By considerations of many possible modifications towards clay, clay-based catalysts are good candidates as low-cost catalysts for plastic waste pyrolysis. With many modifications for zeolite and clay framework with metals or metal oxides zeolite, the catalytic activity enhancements were attempted by increasing the effectiveness of the reaction pathways such as hydrogenation, hydro-deoxygenation, cracking, etc. Catalysts' thermal and chemical stability refers to the use of high-temperature conditions and very complex reactions involved within the mechanisms as important characters, besides the solid acidity and capability to provide efficient mass transport in the catalytic steps. Referring to their abundant sources in nature, both clay and zeolite materials are found as cheap minerals [17–19].

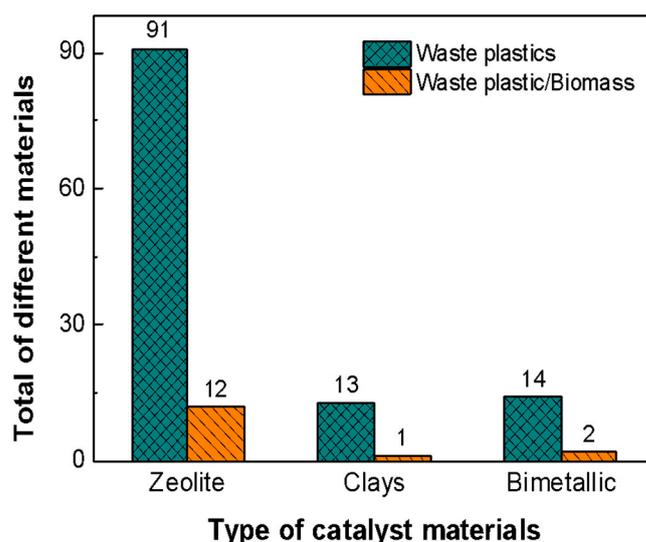


Figure 1. Popularity of different types of catalytic materials for pyrolysis of plastic waste from 2015 to 2020. (Source: Web of Knowledge, <https://www.webofknowledge.com>, accessed on 1 April 2020).

However, there is no clear conclusion or generalization obtained regarding reference [16]'s effect of catalyst performance. Other factors such as temperature, pressure and plastic/biomass ratio in co-pyrolysis allow for the discernment of the impact on the

result within these perspectives, and bimetal catalysts are also developed, especially for improvement on gaseous products and hydrogen. In this review, we discuss some essential properties of low-cost catalysts for plastic waste pyrolysis.

2. Clay-Based Catalysts for Plastic Pyrolysis

Catalytic reactions of plastic pyrolysis depend on solid acid mechanisms on the surface which include cracking, isomerization, oligomerization, cyclisation and aromatization reactions. These various mechanisms are governed by acidity, density, porous size, and porous structure of the catalyst surface. Both Lewis and Brønsted acid sites of a clay catalyst play roles in the cracking mechanism which is initiated by the abstraction of the hydride ion from the polymer structure by Lewis acid sites of the catalyst, or the addition of a proton to the C–C bonds by Brønsted acid sites of the catalyst [20]. The higher amount of Brønsted acid sites on the surface of the catalyst provides more hydrogen ions for double bond cleavage and further propagation steps. Meanwhile, with a different role, the Lewis acid sites influence the surface interaction of catalysts with polyolefin, which is an important part of the whole surface reaction in heterogeneous catalysis.

The surface acidity and high specific surface area of the catalyst play an important role in producing liquid products instead of gas products. The availability of micropores in the clay structure has the potency to act as a heat sink and allows a greater residence time for feed molecules to absorb the heat and have interactions that result in hydrogen transfer [21]. The main role of solid catalyst in the liquid product is enhancing the ability to crack the polymer structure to form an intermediate in the mechanism. This influences by increasing the liquid product along with decreasing the wax content. Less wax from the use of bentonite clay refers to the presence of surface acidity but the surface acidity of clay is lower than zeolite as the impact of Si/Al ratio [22]. Less surface acidity led to the lower Brønsted acidity compared with zeolite which minimizes the potential of secondary reaction such as an over-cracking mechanism, so more liquid product distribution is achieved [23]. Increased conversion and selectivity in producing liquid were exhibited by modifying clay structure via pillarization using aluminum. The increasing conversion not only came from increasing the specific surface area and Lewis's surface acidity distribution, but also came from the thermal stability of the integrity of the clay structure for the sustained pores and surface area for the cracking mechanism [24,25].

Moreover, the stability of pillared clay led to the renewability properties whereas regenerated and reused catalysts showed practically identical conversion and yield values compared with the fresh catalyst. According to the identification of the composition of oil yield from pyrolysis reaction, the presence of metal oxide as a pillar minimizes the side-reaction mechanism. Two main mechanisms: (i) cyclization/aromatization of pyrolytic intermediate and (ii) cracking dominantly occur and play roles in producing diesel fraction in the liquid product together with the high yield of hydrogen gas. Another important aspect from the study on varied metal oxide impregnated onto acid-washed bentonite clay for polypropylene (PP) and high-density polyethylene (HDPE) pyrolysis is the importance of Lewis acid sites from metal ions for facilitating reactions via the formation of the hydration of a proton or the hydride ion due to its surface acidity of catalyst materials [26]. The β -scission of chain-end carbonium ion is the following reaction from acid interaction with polymer chain for the further production of gas and liquid fractions. The β -scission mechanism is presented in Figure 2.

The more effective acid–polymer interaction in the mechanism also prevents residue such as coke formation on the surface as shown by the comparison on acid-washed bentonite clay (AWBC) and metal oxide impregnated AWBC [20]. Table 1 presents the pyrolysis reaction of plastic waster over the different types of clay catalysts.

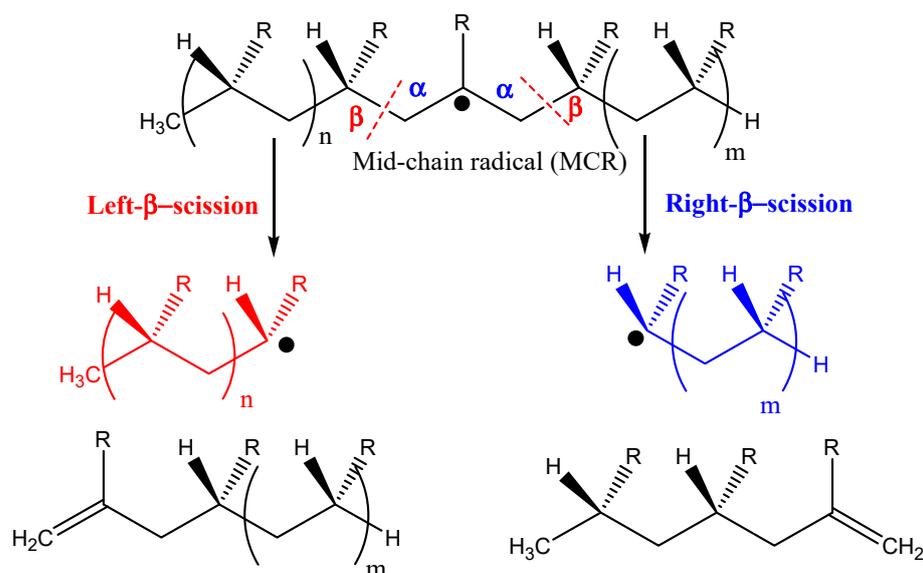


Figure 2. The mid-chain radical mechanism for obtaining low molecular product.

Table 1. Recent works on pyrolysis of plastic waste over clay catalysts.

No	Catalyst	Plastic Type	Result	Ref
1	Calcium Bentonite	Polypropylene (PP), low-density polyethylene (LDPE), and high-density polyethylene (HDPE)	The yield was influenced by temperature and ratio of effect to catalyst. The major product as condensable fraction was in the temperature range 400–550 °C and the optimum condition was at 500 °C at the catalyst to plastics ratio of 1:3	[27]
2	Kaolin	PP	Ahoko kaolin exhibited as effective as a low-cost catalyst for producing gasoline/diesel grade fuel with the PP as waste sources. The yield was influenced by catalyst to plastic ratio	[28]
3	Restructured and pillared clay	polyolefin	Restructured and pillared clay showed good selectivity towards aliphatic, produced more liquid	[29]
5	Fe, Ti, Zr- pillared clay	HDPE, polystyrene [PS], PP	Fe-pillared clay showed excellent yield of diesel fraction in liquid product and H ₂	[30]
6	Fe-pillared clay	Heavy gas oil(HGO)/HDPE	The presence of HGO improved the oil yield from both thermal and catalytic pyrolysis of HDPE	[31]
7	Tungstophosphoric acid (TPA)/kaolin	Low-density polyethylene (LDPE)	TPA loaded kaolin (5-TPA-K) produced higher percentages of gasoline-like hydrocarbons (C ₁₁ –C ₁₄)	[32]
8	Co, Fe, Mn, Zn impregnated acid-washed bentonite clay (AWBC)	PP and HDPE	Metal oxide impregnation on acid-washed bentonite clay not only improves conversion but also yield reduce coke formation	[20]

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Referring to the product distribution of pyrolysis reaction, it can be summarized that catalyst surface acidity and pore characteristics are mainly responsible for catalytic performance. The mesoporous structure with a high surface area is closely related to the Si/Al ratio of the catalyst. The surface acidity facilitated the mechanism of the reaction by the formation of the hydride ion or the addition of a proton due to the inherent acidity, which is simultaneously incorporated with the impregnated metals. This mechanism increased the liquid yield as a substantial improvement over thermal cracking which has a tendency to produce gas as the result of the radical mechanism, also called the random scission mechanism [28,29]. The study on HDPE pyrolysis over HZSM-12 revealed that the solid acidity linearly decreased the activation energy (E_a), as proof of the important role of the acid mechanism in accelerating the reaction [33]. However, the extremely high acidity leads to increased yield by the over-cracking that leads to the formation of much smaller molecules. For this reason, aluminum-pillared clay, which has mild acidity while producing a higher liquid yield (~70%) [34], is similar to the use of ultra-stable zeolite (USY (71%) [35], which is higher compared to the yield by ZSM-5 (61%) [36]. The plot in

Figure 3 represents the relationship between the solid acidity and the liquid yield from several papers.

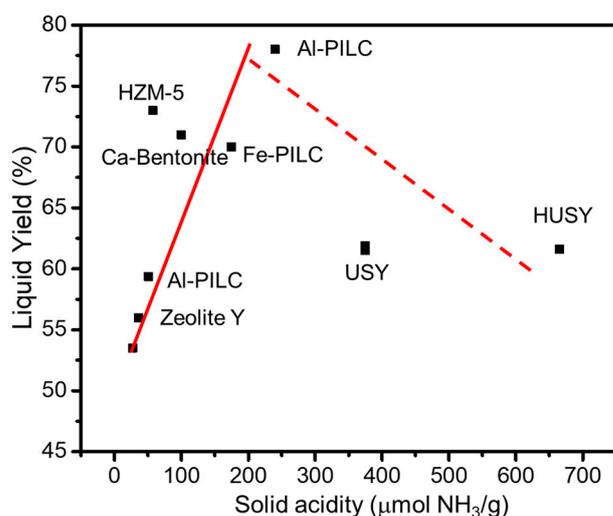


Figure 3. Relationship between solid acidity and liquid yield [27,33–37].

3. Plastic Waste-to-Fuel over Zeolite Catalysts

Zeolite (ZSM-5) has been widely reported as an effective and selective material catalyst for producing biofuel through the thermocatalytic reaction [38]. Besides its catalyst base, ZSM-5 is a low-cost catalyst for the conversion of plastic waste to biofuel. The ZSM-5 catalyst also presents excellent thermal stability, good selectivity, activity, and deactivation by coke [39,40]. In thermocatalytic reactions, the ZSM-5 effectively enhances the deoxygenation and cracking reaction to produce stable oil [41,42]. Onwudili et al. (2019) have studied the influence of temperature and type of zeolite as a catalyst for pyrolysis reaction to convert the plastic waste to biofuel liquid products [43]. Using different catalysts at temperatures of 500 and 600 °C showed no significant results of fuel-range liquid products. However, the increasing temperature resulted in the increasing gas composition of the products. Besides that, the high acidic catalyst can lead to a faster production of gases. More acidity promotes the formation of the hydrogenation steps, leading to the synthesis of other free radicals which resulted in β -scission for the gas production [16,44,45]. The related study by Kassargy et al. (2019) also reported that the yields of the liquids fractions are linearly dependent on the proportion and the type of plastic waste in the mixture [44].

Miscolczi et al. (2019) studied the effect of the loading metal to zeolite structure for catalysis plastic to fuel [45]. The authors modified the zeolite catalyst with several metal ions like $\text{Fe}^{2+/3+}$, Cu^{2+} , Ce^{2+} , H^+ , Mg^{2+} , Ni^{2+} , Sn^{2+} , and Zn^{2+} . Their studies revealed that the presence of metal loading (8–10%) to zeolite structure could affect the pore diameter and the macropore surface area of the materials. The surface area is an essential factor in the pyrolysis reaction process besides the acidity of the catalyst [46,47]. Therefore, modification with several metal ions to zeolite structure can easily control the surface area of the catalyst materials which affects the decreasing temperature decomposition of the plastics during the pyrolysis process. Gorbannezhad et al. (2020) revealed that the co-pyrolysis also depended on the composition of the zeolite catalyst [48]. The authors studied the co-pyrolysis process by combining zeolite (HZSM-5) and sodium carbonate/gamma-alumina for improving the hydrocarbon products of the reaction process. Their study showed that the combination of catalysts could improve the hydrocarbon product to 8.7% at the temperature process of 700 °C. The presence of sodium salt in the composition of the catalyst can improve the deoxygenation reaction so that the breakdown process of macromolecules becomes faster and more effective to produce low molecular compounds such as hydrocarbons. Besides that, the other studies also reported that the catalytic pyrolysis process is affected by the type of zeolite catalyst [49,50]. Several types of catalyst-based zeolite have a difference in

the pore size and acidity which affected the produced product [51]. For example, the larger pore size facilitates the conversion of the plastics as source materials to polyalkylaromatics while the smaller pore size only converts to aromatic compounds with small dynamic diameters. Based on their study, the use of suitable zeolite as a catalyst in the pyrolysis reaction is a crucial step to determine the produced product during the reaction process.

Susastriawan et al. (2020) studied the effect of zeolite size on pyrolysis of LDPE plastic waste at low temperatures [52]. The authors revealed that reducing zeolite size could enhance the reaction rate, pyrolysis temperature, heat transfer rate, and the oil products because the smaller size has a high surface-active area to contact with the plastics during a pyrolysis process. The zeolite size of 1 mm showed the highest value of oil yields; however, the particle size of 1–3 mm did not indicate the results of oil produced significantly. In the other studies also reported by Kim et al. (2018), the authors showed that the presence of the phenolic functional group on lignin could enhance 39% of the aromatic hydrocarbon in the totally resulted product [53]. The presence of a hydroxyl group on the chemical structure of lignin gives good selectivity on the decomposition of reactant to form an aromatic hydrocarbon as a major product [54,55]. In addition, the presence of a hydroxyl group on the surface of a zeolite-type catalyst can contribute to the condensation process during pyrolysis. Besides that, hydroxyl can accelerate the formation of aromatic hydrocarbon products through dihydroxylation, aromatization, isomerization, and oligomerization mechanism. Table 2 shows the comparison of zeolite types for pyrolysis reaction of plastic waste. All researchers confirmed that the zeolite catalyst can improve the acid-activation and thermal activation in the pyrolysis reaction of plastic waste (PE, PP, PVC, PET, and PS) [56,57].

Table 2. Pyrolysis of plastic waste over zeolite-based catalysts.

Type of Plastic	Catalyst	Reaction Condition	Conversion	Selectivity to	Remark (Catalyst/Plastic Ratio)	Ref
Polystyrene and polyolefins (PS/PO)	Y-zeolite	600 °C for 30 min under N ₂ gas	High yield valuable aromatics such as benzene and toluene	90% of the aromatic content	2 g of catalyst and 2 g of plastic	[43]
Polyethylene and polypropylene (PE/PP)	USY-zeolite	500 °C	Liquid fractions are dominated by hydrocarbon (C ₅ –C ₇), C ₃ and C ₄ for gaseous products.	80% of liquid production	Catalyst/plastics ratio of 1:10	[44]
Polystyrene (PS)	Natural/Synthetic zeolite	450 °C for 75 min	60.8% conversion to ethylbenzene and 38.3% conversion to alpha-methylstyrene for natural and synthetic zeolite respectively	54% and 50% of liquids products for natural and synthetic zeolite, respectively	Catalys/PS ratio of 0.1 kg:1 kg	[1]
High density Polyethylene (HDPE)	Co-Y-zeolite	600 °C for 30 min	40% of gas yield	68% of hydrogen production	Catalys/HDPE ratio of 2:1	[58]
Plastic mixtures (HDPE/PP/PS/PET/PVC)	Regenerated ZSM-5	440 °C for 30 min	Almost 60% of plastic waste conversion to liquids phase	97.4% of aromatics with 23% of styrene as major composition	Catalyst/plastic waste ratio of 1:10	[59]
Plastic mixtures (PE/PP/PS/PET/PVC)	ZSM-5	500 °C for 30 min	58.4% conversion to gases phase	50.7% of C ₃ –C ₄ types and 27.9% of styrene	Catalyst/plastic waste ratio of 1:10	[60]

4. Effect of Co-Feeding with Biomass Feedstock

The biomass feedstock consists of extractive (0–14%), lignin (16%), hemicellulose (20%), and cellulose (>40%) [61–63]. Generally, the yields of the produced biofuels are dependent on several factors such as the composition of the nature of the feedstock, the moisture content of biomass feedstocks, reactor design, and operating temperature conditions [64–67]. In the pyrolysis process, the biomass feedstock can be mixed with other materials to improve the quantity and the quality of the product as shown in Table 3.

There are some pathways for the pyrolysis of biomass like the chemical, biological, and thermochemical conversion as shown in Figure 4. However, the thermochemical reaction is commonly used for the pyrolysis reaction of biomass feedstock because the process has high energy to split and stretch the rigid structure that has biomass [68]. The synergistic effect is remarkable, coming from the presence of produced free radicals from biomass decomposition that contribute to enhancing the scission of chain hydrocarbons from plastics. Decreasing activation energy and the pyrolysis index, representing the easiness of the pyrolytic reaction for producing volatile products (methane, aliphatic hydrocarbon (paraffin), carbon dioxide, aromatic hydrocarbon), are the quantitative parameters revealed to be advantageous of co-pyrolysis [69]. The characteristics of biomass, especially the ratio of hydrogen to carbon effective (H/C_{eff}), heavily influences the product distribution. Higher H/C_{eff} significantly improves olefin and aromatic yield and reduces coke formation [70–72]. In addition, Bhoi et al. (2019) reported operating conditions such as heating rate, type and particle size of biomass, temperature, carrier gas, type of catalyst, and vapor residence time [73]. The authors and the other related studies reported that the type of catalyst and temperature have major impacts on quality and biofuel yields [74–76]. However, the choice of temperature during the pyrolysis reaction depends on the main composition of the biomass sources, for example, hemicellulose and cellulose degrade at approximately 200–350 °C and 330–370 °C, respectively, while lignin occurs at 400 °C [77,78].

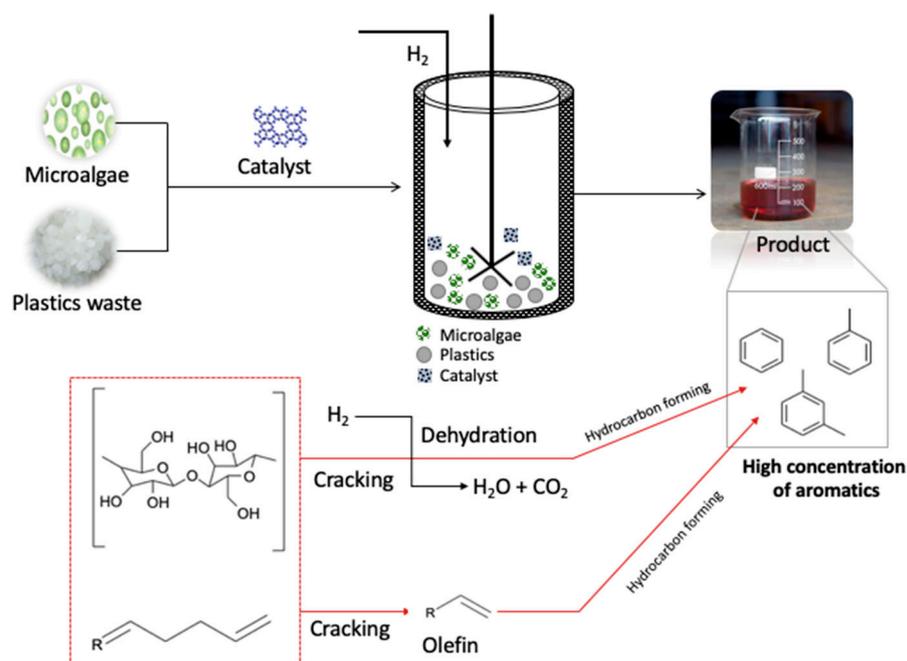


Figure 4. The illustration of pyrolysis process with the natural biomass and plastic waste as a feedstock.

Xu et al. (2020) studied the pyrolysis reaction with the mixing of microalgae (*Enteromorpha prolifera*) and HDPE plastics using the HZSM-5 catalyst [79]. The authors reported that the presence of microalgae in the plastic waste could increase the concentration of aliphatic hydrocarbons and decrease the nitrogen/oxygen-containing compounds and the acidity of the products. Algae as natural resources have received attention because they can produce a high amount of bio-oil than the other resources of biomass [80]. The related study also reported that using microalgae as a pyrolysis feedstock has many advantages like faster rate of growth and high lipid content, lower energy consumption during a process with the percent of energy recovery of 76%, increase in the carbon content to 89%, and decrease in the oxygen content to 0.3% [81–83]. Furthermore, Qari et al. (2017) reported that the characteristics of microalgae significantly affected the types and the yields of biofuel products [84]. In the produced bio-oil product, the mixing between biomass and plastic

waste can reduce the moisture content because the hydroxyl group in the biomass can directly bind with the plastics which contain the high hydrogen atom to form the hydrogen bonding [85]. Figure 4 shows the process of pyrolysis reaction with the mixing feedstock between natural biomass of microalgae and plastic waste.

Table 3. Effect of co-feeding with other feeds.

Type of Biomass/Polymer	Catalyst	Reaction Condition	Conversion	Selectivity to	Remark (Catalyst/Plastic Ratio)	Ref
Laminaria japonica/polypropylene	Pt/mesoporous MFI, Mesoporous MFI, HZSM-5 Al-SBA-16	500 °C, 1 atm	60.50 59.11 58.15 52.44	20–40% of monoaromatic hydrocarbon, 5–20% of polyaromatic hydrocarbon	Biomass/plastic/catalyst ratio = 10:10:1	[86]
Corn stalk/HDPE	ZSM-5	700 °C, 1 atm	90% of hydrocarbon	20–30% of aromatic hydrocarbon	Biomass/plastic/catalyst = 1:4:1	[87]
pine sawdust/LDPE	Ni-CaO-C	-	90% of gas product	86.74% to H ₂ gas	Biomass/plastic/catalyst: 1:1:2	[88]
Corn stalk/Polystyrene	ZSM-5	600 °C	90% of liquid product	78.89% of monoaromatic hydrocarbon	4:1:0.1	[89]
<i>L. japonica</i> /polypropylene	Al-SBA 15	500	30% of liquid product	35% of liquid product is oxygenate	Seaweed/polypropylene/catalyst = 1: 1:1	[90]
Rice husk/PE	Ni/γ-Al ₂ O ₃	Pyrolysis at 600 °C followed by catalytic reforming at 800 °C	80% of H ₂ and CO	45% of gaseous product is H ₂	50–75% PE proportion	[91]

Muneer et al. (2019) studied the effect of catalyst ratio to feedstock for the pyrolysis of corn stalk (CS) and polypropylene in a bed reactor at 500 °C [89]. The increase in the catalyst could enhance the liquid oil yield to 66.5% at ZSM-5 catalyst to feedstock ratio of 1:4. ZSM-5 catalyst was found as an effective material for polymer cracking and dehydration of biomass because of its high surface area and high selectivity to produce the hydrocarbon [92]. The production of bio-oil from biomass feedstocks depends on the acidic site and the pore structure of the catalyst because the acidic site increases the rate of polymer cracking. Similar results were also reported by Balasundram et al. (2018); their study revealed that the increasing catalyst amount four times could improve the coke decomposition by 17.1% [93]. It can be summarized that the addition of biomass in the co-pyrolysis enhances the efficiency to produce liquid products and reduce activation energy. By using ZSM-5 catalyst and corn stalk in the co-pyrolysis of HPDE, it was found that increased hydrocarbon yield and H/C eff were obtained on increasing biomass/HDPE ratio, along with decreasing coke [87]. Hydrogen atoms for the co-pyrolysis process were provided by HDPE, leading to an improvement in the rate of hydrocarbon production, meanwhile, oxygenated compounds in the biomass play a role to promote the cracking of HPDE and the chain scission. However, at a certain level, the increasing catalyst dosage may affect the increased charring, which leads to reduce liquid product. For example, the co-pyrolysis of cellulose/polyethylene over montmorillonite K10. A similar trend is also identified on cellulose pyrolysis using montmorillonite on cellulose. The availability of more surface acidity in Al-SBA enhances the co-pyrolysis to produce more C1–C4 hydrocarbon compounds, CO, CO₂, and deoxygenation reactions [86].

5. Recent Reports Bimetallic Catalysts for Pyrolysis of Plastics

Bimetallic catalysts have been widely used for the pyrolysis reaction of plastic waste to biofuel. Previously, the monometallic type has been widely studied and reported for the catalytic cracking process. For example, Wen et al. (2014) prepared Ni-loaded to CNTs for polyolefin; although the material showed good performance as the catalyst, the concentration of carbon was relatively very high [94]. Therefore, bimetallic with integrating the different types of material catalyst provides some advantages in the pyrolysis reaction such as large surface area due to its smaller size, good stability, and synergy effect between combined two metals [95]. Yao et al. (2017) studied the Ni-Fe bimetallic catalyst at a ratio of 1:3 for the pyrolysis of waste plastics [96]. The authors reported that the presence of a bimetallic catalyst could enhance H₂ production to five times higher compared to the process without a catalyst. Chen et al. (2020) also reported that the Fe-Ni bimetallic

modified MCM-41 could improve the produced oil to 49.9% with a percentage of single styrene hydrocarbon of 65.93% at 10%Fe-10%Ni/MCM-41 [97]. Besides that, the presence of bimetallic/MCM-41 can reduce the bromine content from 10% to 2.3% (wt.). The developed catalyst provides a large surface area; thus, the plastics can directly enter the pore structure for the cracking process. The iron metals act as the base site which converts the raw materials to styrene, while the combination with nickel–metal oxides increases the acidity of the catalyst, thus the multi-ring compounds can also be converted to a single hydrocarbon structure. The character of the external surface and pore size determines the chemisorption, and these are designable by the synthesis method. In this case, the higher pore diameter of Fe-Ni catalyst tends to give higher H₂ desorption [98], which is in line with the trend of long-chain products by the high pore size of Co/SBA-15 [51].

Li et al. (2016) reported the bi-functional Mo-Ni/SiO₂-Al₂O₃ catalyst for the thermal pyrolysis of crude oil [99]. The presence of the bimetallic of Mo-Ni on the composite catalyst could improve the catalytic reactivity and the amount of yield of fuel oil produced to 57.9%. The metallic of Mo and Ni has several advantages for catalyst in pyrolysis like low-cost adsorbent, excellent stability performance, high surface area, and also ease of regeneration [100]. However, their study reported that the reactivity of the bimetallic catalyst is dependent on the sulfurization process. The increased sulfurization process can regularly improve the percentage of conversion of crude oil to fuel oil until it reaches 86.9%. In addition, some related studies have reported that the bimetallic catalyst type has good selectivity conversion [101,102]. A more specific capability of bimetallic catalyst is shown by Fe-Ni/MCM-41 for not only the decomposition of polymer structure but also to conduct debromination mechanism for plastic waste containing brominated flame-retardant (BFR) pyrolysis. The results indicated that iron showed a satisfactory capability for debromination, in combination with Ni's ability to produce gaseous products via the hydrogenation mechanism. One of the proposed pathways of the reaction mechanism that occurs is the interaction between organobromine and some metal oxides to produce non-brominated organic compounds, elimination of β-H by Lewis acid sites and dissociative adsorption two-stage reaction [97].

Cai et al. (2020) reported the carbon-based Fe-Ni bimetallic catalyst for fast pyrolysis of plastic waste [103]. The pyrolysis reaction was carried out in a fixed-bed reactor with the ratio of catalyst to plastic waste at 1:2 (wt. ratio) at a temperature of 500 °C. The fixed-bed reactor has some advantages for pyrolysis reaction such as a simple design with the catalyst loaded into the bed column, irregularity in plastic shape, and low thermal experiments [104,105]. The authors explained that Fe-Ni as a bimetallic catalyst played a crucial role in the oxygen reduction reaction (ORR). Moreover, the developed catalyst has good methanol tolerance and stability, avoiding the aggregation and corrosion process on the surface of the catalyst due to its oxygen-containing functional groups on the surface [106]. Zhou et al. (2020) also reported that the bimetallic Ni-Fe/ZrO₂ catalyst showed excellent decomposition of polystyrene at a low-temperature process (500 °C) [107]. Their studies revealed that the presence of bimetallic catalysts could improve the catalytic activity in the decomposition of waste. The combined properties between Ni-Fe could decrease the water–gas shift reaction and the activation energy of the reforming reaction [108–110]. Table 4 presents the different types of bimetallic catalysts for the pyrolysis process.

Table 4. Recent reports bimetallic catalysts for pyrolysis of plastics.

Type of Plastic	1st Metal	2nd Metal	Condition, Pressure (atm), Temperature (°C)	Conversion	Selectivity to	Remark (Catalyst/Plastic Ratio)	Ref
Low density polyethylene (LDPE)	Mo-MgO	Fe	Atmospheric pressure, 750 and 400 °C	LDPE waste plastic to carbon nanotubes	High quality carbon nanostructures materials	0.5 g:15 g plastics	[111]
Polypropylene (PP)	La ₂ O ₃	Ni-Cu	500 °C, 700 °C for 2.5 h	PP to Carbon nanotubes and carbon nanofibers	Carbon yields of 1458% produced	0.5 g:15 g plastics	[112]
Polypropylene (PP)	MgO	Ni/Mo	800 °C, 10 min	PP to CNT	394% of carbon product	0.15 g:5 g polymer	[113]
Polypropylene (PP)	Ni-	Al	800 °C	PP to MWCNTs	85%	Dependence on the ratio Ni/Al and the amount of Ni-Al catalyst	[114]
Polypropylene (PP)	Ni-Al	Zn, Mg, Ca, Ce, Mn	500 °C	PP to CNTs	The highest carbon deposition 62% and hydrogen 86.4% to Ni-Mn-Al	1 g:2 g waste polypropylene	[115]
Polyethylene (PE)	Ni	Ce (Ni-Ce core by silica)	800 °C	PE to hydrogen	Hydrogen concentration 60%	Weight ratio Catalyst:plastic 1.0	[116]
LDPE	Ni	Fe	800 °C	Carbon nanotubes (CNTs)	Maximum hydrogen concentration and hydrogen yield 73.93% and 84.72 mg.g ⁻¹	0.5 g:1 g waste plastic	[96]
Low-density polyethylene (LDPE) waste	MgO	Co/Mo	400 °C	High quality multi-walled Carbon Nanotubes and hydrogen	Optimum CNTs 1040% wtCoMo(6.5) MgO	0.75 g:15 g plastics	[117]
Polypropylene (PP)	Ni	Fe	500 °C	CNTs	93% filamentous carbon nanotubes	0.5 catalyst:1 g PP	[118]
HDPE	Ni	Mn-Al	800 °C	Hydrogen and carbon nanotubes	48% total carbon (with no steam), hydrogen yield 94,4% (with steam)	0.5 g catalyst:1 g waste plastic (HDPE)	[119]

6. Factor Affecting in Pyrolysis Process

In the pyrolysis process, many reaction parameters strongly affect the quantity and quality of the resulting products, such as temperature, heating rate, composition blending ratio, and the type of reactor design. However, the reactor designs play a crucial factor in obtaining a high yield quantity and the quality of the product. Previous studies have already reported several types of reactor design for the pyrolysis process, such as fixed-bed, transported bed, rotating cone, plasma pyrolysis, vortex centrifuge, circulating fluidized, entrained flow, etc. [120]. The fixed-bed reactor is commonly used for the pyrolysis process due to the simple process, a large sample quantity and a high product yield. However, the reactor experiences several drawbacks, such as the catalyst being difficult to replace during a pyrolysis process, side reaction and product, and the required high temperature and pressures. Therefore, recently, many types of reactor-based fast pyrolysis reactors have been developed. The principle of the reactors is to optimize the percentage of products in low temperatures and pressure during the pyrolysis process.

Xue et al. (2015) reported the fast pyrolysis of HDPE waste using a fluidized bed reactor [121]. Their study found that HDPE waste could increase the formation of acid and furans in the products and decrease the formation of phenol and vanillin compounds at a relatively lower temperature process. Orozco et al. (2021) studied the pyrolysis of plastic waste using a spouted bed reactor in continuous mode [122]. Their study revealed that the synergy effect between the plastic-type and the total amount of catalyst could decrease the temperature. The reaction design of fast pyrolysis reaction is based on optimizing the product yields by decreasing the size of plastic waste to less than 1 mm and flowing the carrier gas as shown in Figure 5. However, despite the lack of the reactor, there is still a high amount of oxygen content in products. A related study has been reported for removing the oxygen content in pyrolysis products by hydrotreating formate-assisted pyrolysis [123]. Reducing oxygen in the resulting product can improve the percentage of the product by up to 92%.

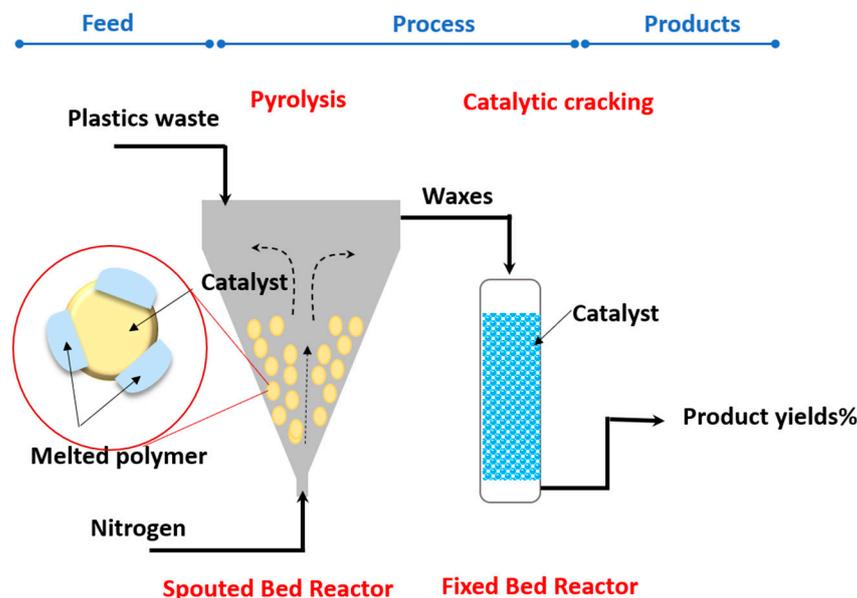


Figure 5. The illustration of combined pyrolysis reactor designs for improving the yields products.

7. Conclusions and Future Prospect

In summary, we reported and focused on the catalytic decomposition of plastic waste to produce liquid fuel using a low-cost catalyst. Several types of low-cost catalysts were summarized, such as zeolite, clay, and bimetallic. Generally, some studies reported that the low-cost catalyst could be used for catalytic cracking of plastic waste to liquid fuel. However, several factors are still required for improving the quantity and quality of the

products, such as decreasing the particle size of waste in feedstocks, temperature, pressure, ratio composition between catalyst to feedstocks, type of catalyst, and type of reactor design. Unbeatably, pyrolysis and co-pyrolysis of plastic waste to produce fuel is a promising sustainable technology. Several conditions of the operation process influence the yield of the products such as (i) heating rate, (ii) the ratio of blending materials, and (iii) the pyrolysis temperature [104]. Additionally, the heterogeneous catalyst plays an important role in the conversion, and from the techno-economic point of view, exploration of the low-cost catalyst with high efficiency and lifetime is still required. Designing an appropriate catalyst is a major challenge in developing the technique, and referring to this study, the selectivity of a catalyst toward a specific product becomes important in the design of the reaction set up, as well as the lifetime of the catalyst. Catalyst solid acidity along with the specific surface area governs the optimum condition of the conversion, and these are related to the structure of solid support and their combination with active metal/bimetals on the surface. Compared to commercial solid acid catalysts, natural zeolite and clays are better options since they are cost-effective and more selective towards liquid products [1]. Referring to decoking capability, tunable performance of bimetallic catalysts and the potencies of zeolite and clay utilization, bimetallic-modified zeolite and clay catalysts are interesting for exploration. The designed Fe-Ni with zeolite or clay supports, for example, is a good candidate for a low-cost pyrolysis catalyst for bromide-containing plastic wastes which are abundantly produced from flame-retarded plastic production. In addition, some strategies to create integrative plastic waste management including co-pyrolysis of biomass/plastic wastes with these catalyst candidates need to be investigated for furthermore well-implemented.

Funding: Funding was provided by World Class Professor Program, Ministry of Research and Higher Education, Republic of Indonesia, 2020.

Data Availability Statement: The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest: The authors declare no conflict of interest.

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