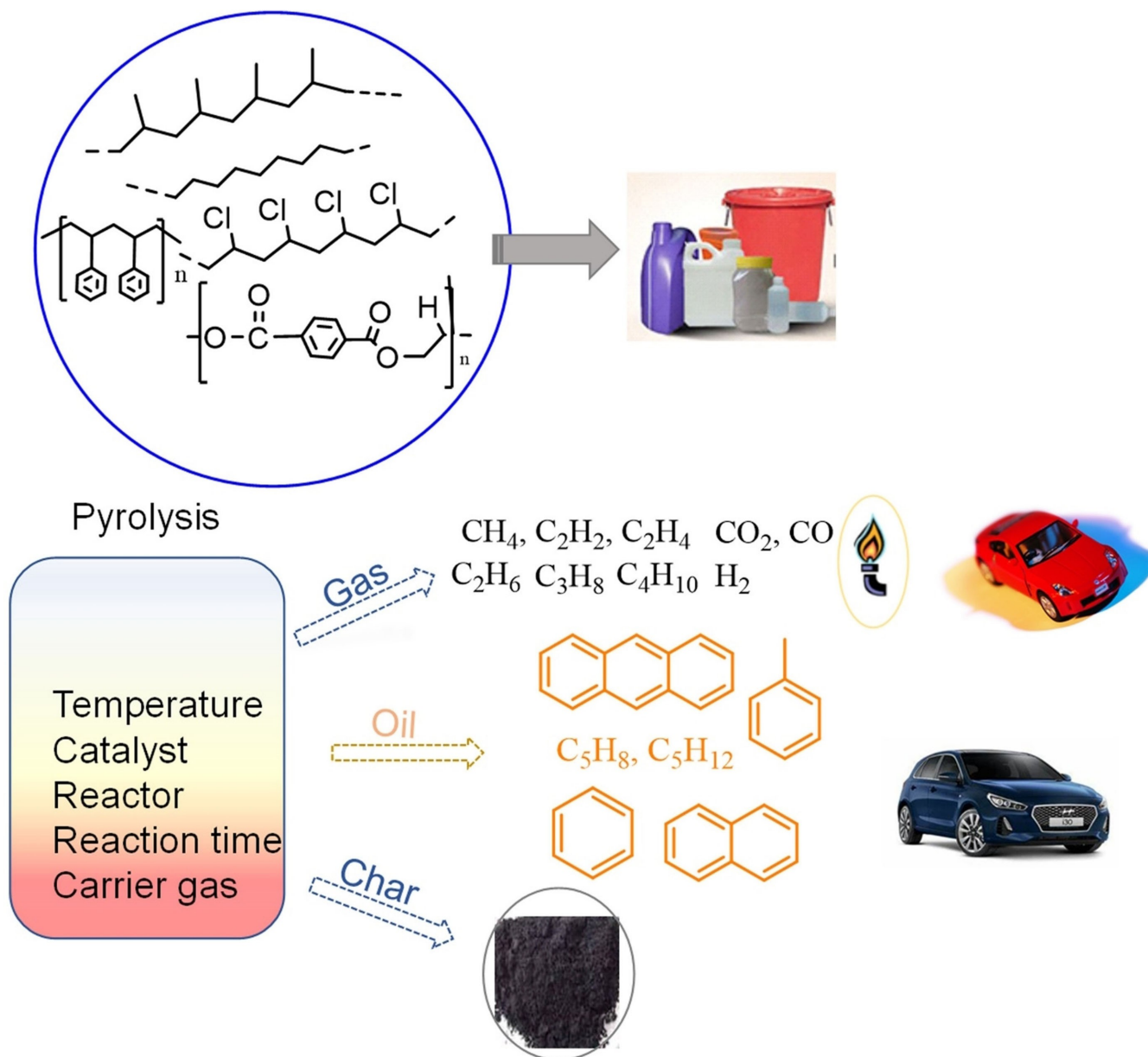


Recent Trends in the Pyrolysis of Non-Degradable Waste Plastics

Shushay Hagos Gebre,^{*,[a]} Marshet Getaye Sendeku,^{*,[b, c]} and Mohamed Bahri^[c]



Waste plastics are non-degradable constituents that can stay in the environment for centuries. Their large land space consumption is unsafe to humans and animals. Concomitantly, the continuous engineering of plastics, which causes depletion of petroleum, poses another problem since they are petroleum-based materials. Therefore, energy recovering through pyrolysis is an innovative and sustainable solution since it can be practiced without liberating toxic gases into the atmosphere. The most commonly used plastics, such as HDPE, LDPE (high- and low-density polyethylene), PP (polypropylene), PS (polystyrene), and, to some extent, PC (polycarbonate), PVC (polyvinyl

chloride), and PET (polyethylene terephthalate), are used for fuel oil recovery through this process. The oils which are generated from the wastes showed caloric values almost comparable with conventional fuels. The main aim of the present review is to highlight and summarize the trends of thermal and catalytic pyrolysis of waste plastic into valuable fuel products through manipulating the operational parameters that influence the quality or quantity of the recovered results. The properties and product distribution of the pyrolytic fuels and the depolymerization reaction mechanisms of each plastic and their byproduct composition are also discussed.

1. Introduction

Plastics are among those materials innovated by human beings for their need. They are highly inevitable materials employed in a wide range of applications making our day-to-day activities easy in home, shop packing, marketing, constructions, and healthcare, due to their lightweight, chemical stability (do not rust or rot), availability, and can be used repetitively. Their replacement for natural resources such as metal pipes and woody materials gains much acceptance.^[1] Single-use plastics such as masks, gloves, containers, medical packaging, and utensils of the ongoing COVID-19 pandemic are certainly affecting waste plastic management.^[2] Plastics do not have natural equivalents because they can replace many natural nonrenewable resources such as metals, woods, glasses in different sectors.^[3] The ceaseless growth of the consumption of plastics is vast and has been rising steadily because of the advantage derived from their flexibility, low cost, and durability throughout the world. As shown in Figure 1 below, the USA leads the world plastic per capita consumption with 142 Kg/year.^[4] Nearly 6.3 billion metric tons of plastics have been manufactured in 2015, of which 79% of the total product was sent to landfill, 12% incinerated, and 9% recycled.^[5] Half of the total plastics manufactured in the European Union end up as waste every year and become the third-largest contributor to municipal solid waste (MSW) after food and paper wastes.^[1,6,7] The annually generated plastic waste is expected to grow at a rate of 3.9% per year.^[8] Globally, the population growth, industrial expansion, consumer demand, and depletion of

resources have contributed to the wide usage of plastics and become more serious to the environment than ever. These days, plastics are among the most environmentally devastating and challenging wastes due to their huge quantities and disposal difficulties.^[10] The huge volume of waste plastics that resulted from the dramatic growth in their production and consumption give rise to serious concerns, as they do not degrade and remains in municipal refuse for decades. Plastic wastes are more voluminous than the other organic wastes and thus take up a lot of landfill space that is becoming scarce and expensive. Incineration of the accommodated waste plastics cannot be a popular solution since a huge amount of gases (HCl, dioxins, SO_x, NO_x, and CO₂ among others), are emitted, and if these toxic gases are inhaled for a long period of time, it can lead to respiratory problems in addition to their contribution to the global warming and acid rain.^[11,12] Recycling requires an effort to perform the transformation sequence, which may lead to environmental, labor-intensive, and cost impacts. Moreover, recycling faces a lot of challenges such as logistics, manpower, and financial concerns, as well as a lack of consumer awareness and education. The cost could be an issue if recycled plastic has to compete with virgin plastics that are manufactured at a comparatively low cost. Besides, not all plastic wastes are equally good for recycling.^[13]

Disposal of waste plastics does not stop in one location as they can enter into oceans, lakes, rivers, and water bodies which causes the formation of garbage patches that can poison the health of the entire aquatic life. Furthermore, they can also affect the economy and food supply of the societies that have depended on fishing.^[14] Waste plastics not only cause damage to the ocean but also damage groundwater sources.^[15,16]

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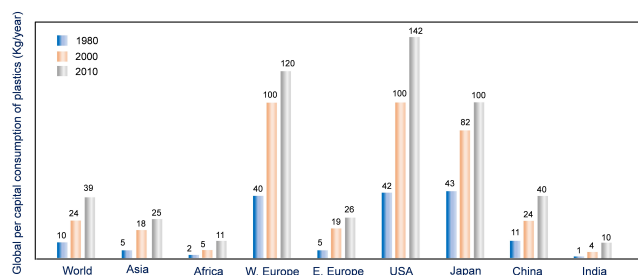


Figure 1. Global per capita consumption of plastics (Kg year⁻¹). Reproduced with permission from Ref. [9]. Copyright 2010, Elsevier.

Plastics such as high-density polyethylene (HDPE), low-density polyethylene (LDPE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC), polyethylene terephthalate (PET), and polycarbonate (PC) are now indispensable, relatively cheap, durable, and versatile synthetic materials and their application in industrial fields are continually increasing. Petroleum-based plastics are mainly composed of hydrocarbons, but they contain different additives like antioxidants, colorants, stabilizers, and plasticizers. When the plastics are discarded, the additives are also undesirable from the environmental point of view since they might be water-soluble. Plastics are non-biodegradable materials that are extremely troublesome components for landfilling since their lifespan is too high (Table 1).^[4,10,11,17]

According to their origin, wastes plastics are classified as industrial and municipal waste that have different compositions and properties when subjected to different management strategies.^[19] These days, waste plastic managements are challenging in urban settings, since their huge quantities accommodate as a byproduct or faulty product from the commerce and agriculture sectors. Of the total waste plastics, over 78 wt% correspond to thermoplastics, and the remaining are thermosets. Thermoplastics such as HDPE, LDPE, PP, PS, and PVC are composed of polyolefins that have the possibility to be recycled easily. However, recycling of thermosets waste plastics is challenging due to epoxy resins and polyurethane origins.^[9]

HDPE, LDPE, PP, PS, PVC, and PET are reported as the most common municipal solid wastes in Europe.^[20] However, PE plastics (HDPE and LDPE) are the most popular and make up over 40% of the total content of municipal solid wastes.^[21] The chemical processes such as thermal and catalytic methods of converting the waste into energy and value-added fuels/chemicals are promising techniques to eliminate the plastic refuse, which otherwise is a major cause of environmental contamination. Extracting fuel oils from waste plastics can also decrease the dependence on fossil fuel since the plastic

Table 1. Density, crystallinity and lifespan of thermoplastic polymers.^[18]

Plastic	Density [23/4 °C]	Crystallinity [%]	Lifespan [year]
PE	0.91–0.925	50	10–600
PP	0.94–0.97	50	10–600
PS	0.902–0.909	0	–
PET	1.03–1.09	0–50	450
PVC	1.35–1.45	0	50–100+

manufacturing industry uses nearly 6% of petroleum produced worldwide. Therefore, it is like ‘killing two birds with one stone’ in terms of saving the supply of energy and alleviating environmental concerns.^[22–24] Nowadays, tertiary recycling technologies of converting waste plastics to chemicals and value-added fuels such as pyrolysis, gasification, and depolymerization are of recent interests for waste management. Pyrolysis (also called thermolysis), thermal cracking, catalytic cracking, and liquefaction convert waste plastics to gases, liquids, and waxes under high temperatures, either in the absence of a catalyst (thermal) or in the presence of a catalyst (catalytic pyrolysis).^[25]

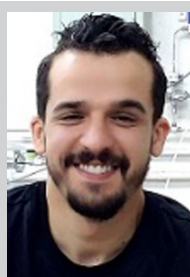
Waste plastics are resources that open many opportunities like job-creating, growth, innovation, and sustainability and have multiple effects on society and the economy. Some countries banned landfill and incineration; therefore, energy recovery from the waste resources through pyrolysis is the best choice for waste management. Having all the environmental risks of the non-degradable waste plastics, it is timely and urgent to review their conversions to energy fuels through thermal or catalytic pyrolysis. Prior to our review, some excellent review papers had already been communicated by Miandad et al.,^[26,27] Kasar et al.,^[28] Williams,^[29] Dwivedi et al.,^[30] Lopez et al.,^[31] Wong et al.,^[32] Chen et al.,^[33] which basically deal with the effect of the operational parameters on the pyrolysis,



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and the latest review by Hou et al.^[25] summarizes the catalytic degradation of the plastics that cover the reaction mechanisms of the polymers in detail. However, the present review is presented in a comprehensive way of discussing the pyrolysis of the most frequently used polymers, including the factors that affect the pyrolysis process, physicochemical properties of the recovered fuels, proposed reaction (depolymerization) mechanism of each plastic which has not been covered in detail in the previous review articles. Therefore, this review could be used as a guide for the researchers to rationally design their experiments and to improve new approaches.

2. Pyrolysis of Waste Plastics

Pyrolysis is a technique of converting high molecular weight waste plastics into gasoline, kerosene, and diesel by emerging technological solutions to the vast amount of plastic that cannot be economically recovered by conventional mechanical recycling. Pyrolysis is a tertiary recycling technique in which higher molecular weight organic polymers are converted into liquid oil, char, and gases at high temperatures through thermal or catalytic decomposition without burning the polymer waste.^[34,35] The main advantage of the pyrolysis technology is that it can convert both thermoplastic and thermoset waste plastics to high-quality oils and chemicals. Furthermore, it can be employed to treat any mixed, unwashed and unsorted waste without releasing toxic substances into the atmosphere. It is environmentally friendly and solves the complex problem of municipal waste management.^[36] The pyrolysis of miscellaneous waste plastics yields an average of 45–50% of oil, 35–40% of gases and 10–20% of char, depending on the pyrolysis technology. Previous research reports indicated that more than 80 wt% of oil could be recovered from the pyrolysis of individual plastic, which is higher than the pyrolysis of wood-based biomasses.^[37]

Waste minimization through pyrolysis is an auspicious method that involves the thermochemical decomposition of the plastics at an elevated temperature (usually at 300–900 °C). It is carried in the absence of oxygen to ensure that no oxidation reaction is taking place to extract the fuels. Basically, four different mechanisms may occur during the plastic waste pyrolysis, namely, random-chain scission, end-chain scission or depolymerization, cross-linking, and chain stripping.^[38,39] It is important to conduct proximate analyses of the waste plastic compositions based on their moisture content, fixed carbon, volatile matter, and ash content. Thus, the volatile matter and ash contents are the major factors influencing pyrolysis yields. The amount of volatile matter favored oil production while high ash content decreased the amount of liquid oil, and, consequently, increased the gas yield and char formation.^[40]

In thermal or catalytic pyrolysis, the feedstocks are allowed to melt at a high temperature, and the polymer macromolecules are broken down into fragments and small molecules, mainly aliphatic and aromatic hydrocarbons. Finally, the pyrolytic products are separated into oil, gases, and chars.^[10,41] The composition of the obtained products depends on the type

of the waste plastic; more CO and CO₂ are obtained if the feedstock is PET; benzene-rich (aromatic) yields are obtained if PS and PET are pyrolyzed, and aliphatic hydrocarbon-based waxes are obtained if the waste materials are HDPE, LDPE, and PP.^[42] Among the polymer recycling methods, thermal and/or catalytic degradation of waste plastics to fuels show the highest potential for successful future commercialization because plastic wastes are available everywhere.^[43]

Thermal pyrolysis takes place by employing high temperatures to decompose the waste materials under inert atmospheric pressure. Polyolefins-based waste plastics are broken down through a random-chain scission mechanism to produce heterogeneous products; a wide range of products such as linear paraffin and olefin are formed that may need further improvement and upgrading of their quality.^[9,44–46] On the other hand, more core/waxes are formed from thermal degradation of the polymers that may jam the apparatus due to the high viscosity and low heat transfer rate.^[47] However, catalyst-assisted pyrolysis breaks down the polymers at lower temperatures and shorter times by lowering the activation energy and boiling temperature. Thus, catalytic pyrolysis has more benefits than its thermal counterpart due to the decreasing consumption energy, forming a narrow range distribution of hydrocarbon products depending on the carbon number atoms directed to high-quality products such as aromatic, branched or cyclic hydrocarbons.^[9,44–46,48]

A comparative study of thermal and catalytic pyrolysis of LDPE has been carried out using a two-stage reactor (pyrolizer and reformer). Iron-modified ZSM-5 catalysts were used in this catalytic pyrolysis process. In both cases, an increase in the pyrolysis temperature from 400–500 °C results in decreasing the amount of condensable gases. However, increasing the pyrolysis temperature showed less effect on the aromatization content of liquids in the thermal pyrolysis, but the liquid product's aromatic content was higher (70% in the liquid fraction) applying the catalyst.^[49] The produced liquids or waxes are highly viscous and composed of alkanes and alkenes with high boiling points. Wax is an intermediate product which was dominantly obtained under fast pyrolysis conditions, and further fluid catalytic cracking (FCC) is applied to convert it into liquid oils. Fast pyrolysis, which is performed in a continuous setup, produces more waxes than the slow pyrolysis, which is performed in a batch setup due to the short vapor residence time and reduced cracking reaction that minimizes secondary reactions.^[50]

A comparative analysis of the thermal and catalytic pyrolysis of waste plastics under certain operational conditions is demonstrated in Table 2. High pyrolytic oil (wax) is obtained in the non-catalytic process; however, the oil yield decreases in the catalytic pyrolysis as the gas yield increases, which might impact the quality of the resulting fuel oil from the catalytic process. The pyrolytic oil yield of PE and PP under hydrogen and nitrogen carrier gases/fluidizing gases leads to a high conversion but lower yields of gas and no solid residue products.^[51] For example, the pyrolysis of HDPE in a packed-bed reactor using the thermal process gave 100% wax of a dark yellow color and high viscosity. Similarly, using a silica sand

Table 2. Product yields from the thermal and catalytic pyrolysis of waste plastics.

Plastic	Thermal Temp. [°C]	Time [min]	Oil (wax) [%]	Gas [%]	Char [%]	Catalyst	Temp. [°C]	Catalytic Oil [%]	Gas [%]	Char [%]	Ref.
PS	450	75	80.8	13	6.2	Natural zeolite	450	54	12.8	32.8	[62]
						Synthetic zeolite	450	50	22.6	27.4	[62]
PS	330	–	80	–	–	Silica aluminum	290	50	–	–	[63]
LDPE	437–486	–	94	–	–	Zeolite	–	51	–	–	[53]
PP	378–456	–	86	–	–	Zeolite	–	58	–	–	[53]
PP	350	–	82.6	–	–	Silica aluminum	320	59.57	–	–	[63]
PP	450	30	67.48	8.85	23.67	Kaolin	450	69.75	14.01	16.24	[64]
HDPE	–	–	84	13	3	ZSM-5	–	35	63.5	1.5	[65]
HDPE	–	–	–	–	–	Mordenite	450	78.5	18.5	3	[66]
HDPE	–	–	–	–	–	Alumina	450	82	15.9	2.1	[66]
HDPE	430	–	75.5	20	4.5	FCC	–	79.7	19.4	0.9	[66]
HDPE	450	–	82	18	–	Silica/NaOH	450	81	19	0	[52]
HDPE	450	–	80	–	–	Silica aluminum	350	48.3	–	–	[63]
PP	540	–	61	31	7	Fe-SBA-15	540	73–77	24–21	2–0.8	[67]
PP	–	–	–	–	–	Calcium bentonite	500	88.5	–	–	[68]
LDPE	–	–	–	–	–	Calcium bentonite	500	82	–	–	[68]
HDPE	–	–	–	–	–	Calcium bentonite	500	82.5	–	–	[68]
LDPE	550	–	93.1	14.6	–	HZSM-5	550	18.3	70.7	0.5	[69]
HDPE	550	–	84.7	16.3	–	HUSY	550	41.0	39.5	1.9	[69]
LDPE	375	–	68	–	22	KAB/kaolin	295	84	–	< 1	[70]
HDPE	430	2.5 h	72.66	–	–	10% dolomite	430	80.73	–	–	[71]
LDPE	450	2.5 h	73.91	–	–	10% dolomite	450	83.04	–	–	[71]
PP	400	1.5 h	83.81	–	–	10% dolomite	400	85.2	–	–	[71]

“–”: Data not available.

bed, 54, 40, and 9% yields of gas, liquid, and wax were produced, respectively. Using a cement powder bed, 82% liquid, 18% gas yields, and no wax was obtained. However, under catalytic pyrolysis conditions, the silica sand bed with NaOH yields 81% liquid, 19% gas, and no wax, the cement and white clay beds under catalyst hierarchical H-style ultra-stable Y (HUSY) gave the highest yield of gas (54 and 45%) over that of the liquid (40 and 40%), respectively.^[52] Mostly, the liquid yield is when thermal pyrolysis is considered as a single step. However, those liquid products can followingly be further cracked by the action of a catalyst to lower the amount of hydrocarbon products (gas and liquid) which reduces the liquid yield in the catalytic pyrolysis.^[53]

Additionally, different valuable products such as fine chemicals, hydrogen, petrochemicals, carbon black (as a source for carbon nanotubes (CNTs)) and others can be generated from the waste plastics as shown in Figure 2.

Saturated hydrocarbon gases are formed using metal-containing catalysts when carried out at higher temperatures.^[54] A wide range of hydrocarbon gases (methane, acetylene, natural gas) and liquids (benzene) which are obtained during the pyrolysis can be used as a feedstock to produce CNTs, by interaction with a suitable catalyst like nickel plates along with the recovery of value-added fuels.^[55] Nickel-based/hybrid catalysts are promising for the production of CNTs through catalytic pyrolysis of plastics due to their excellent ability to cleave C–C and C–H bonds.^[56] Waste plastic pyrolysis using a two-stage bed reactor was carried out for the production of hydrogen and CNTs using a bimetallic NiFe (1:3) catalyst. CNTs with good thermal quality and a high yield of H₂ (8.47 g g^{−1} plastic and 73.93 vol%) was obtained with the NiFe catalyst.^[57] Similarly, a

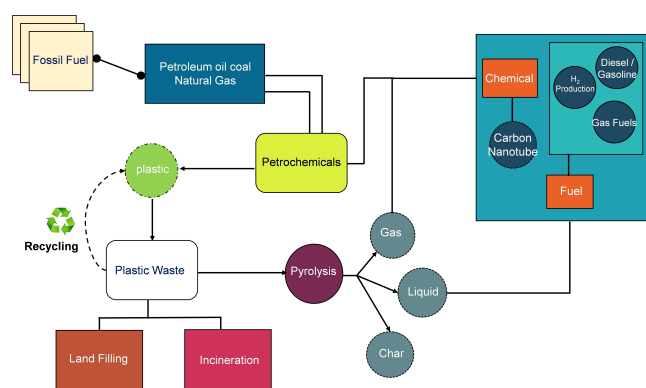


Figure 2. Schematic depicting the ways of utilizing plastic wastes through pyrolysis.

Ni/Mo/MgO catalytic system (4/0.2/1) has been reported for the fabrication of CNTs using polypropylene waste as a precursor. A maximum yield of 150 mg CNTs out of 5 g PE waste was obtained at a combustion temperature of 800 °C.^[58]

In another study, Wu et al. reported the production of both high-value CNTs and hydrogen using a trimetallic Ni–Mn–Al catalyst system and applying the pyrolysis-reforming technology in a two-stage reaction system, in the presence of steam and waste HDPE/PVC and waste plastics consisting of plastics from a motor oil container (MOC).^[59] The presence of PVC played a significant role in reducing the quality of the CNTs; however, the presence of sulfur showed less influence. Nearly 94.4 mmol g^{−1} plastic of H₂ were obtained in the presence of steam at a reforming temperature of 800 °C using this catalyst. Further increasing the amount of steam results in increased hydrogen production while the CNT yield and quality are

reduced. Generally, the pyrolysis-reforming and steam-gasification of waste plastic are among the latest research interests of forming hydrogen/syngas and high-value CNTs. A two-state pyrolysis process is applied to produce a good yield of CNTs and hydrogen gas simultaneously.^[60] For example, the in-line catalytic steam reforming pyrolysis using a conical spouted bed reactor-fluidized bed reactor (CSBR-FBR) configuration generates 34.8–37.3, 29.1, and 18.2 wt% of H₂ from polyolefins, PS, and PET waste plastics, respectively.^[61]

2.1. Factors Affecting the Pyrolysis Process

The pyrolysis of waste polymers can be impacted by several parameters, including temperature,^[72] retention time, feedstock composition, moisture content, particle size, catalyst choice,^[73] reactor type, pressure, and carrier gases,^[27] among others. These factors play a significant role in the quality, quantity, reaction time, and distribution of the products. In this section, we highlight the impacts of the aforementioned parameters on the pyrolysis process during plastic waste conversions.

2.1.1. Temperature

Temperature is considered as the most determinant factor that affects both the quality and quantity of the pyrolytic results because it affects the cracking reactions to various oil fuel, gases with little influence on char production. The effect of temperature is strongly seen in the fast or flash pyrolysis process due to the rapid heating rate and short residence time (<3 s), which vaporizes feedstocks to gases at high temperature to form liquid after condensing, thereby reducing the amount of chars.^[74] The effect of temperature mainly depends on the heating rate. Under fast pyrolysis, the heating rate is high (1000 °C min⁻¹), which enhances the production of liquid fuels from the condensed gases in various reactors such as fluidized-bed reactors. However, under slow pyrolysis conditions, solid/residue products are predominantly formed, and no significant changes of product distributions are observed due to the low heating rates (1–10 °C min⁻¹) and prolonged residence times. Char yields are decreased if a continual increase of temperature takes place while condensable gas yield increases.^[75] Slow pyrolysis is performed at temperatures between 350 and 550 °C, whereas fast pyrolysis is performed at 500–700 °C. Flash pyrolysis takes place above 700 °C.

Long-chain hydrocarbon oil fuels are produced at low temperatures whereas short carbon chain compounds are produced at higher temperatures due to the rapid cracking of C–C bonds. Similarly, aromatic compounds are formed at higher temperatures as a result of the triggering secondary process reactions.^[76,77] Sogancioglu and coworkers investigated the pyrolysis of unwashed HDPE and LDPE carried out at 300, 400, 500, 600, and 700 °C to yield 88.39, 87.87, 87.62, 87.55, 83.86 and 78.39, 76.58, 69.19, 73.20, 72.85 % of oils corresponding to HDPE and LDPE, respectively.^[78] A study by Ahmad et al. on the pyrolysis of PP showed an overall conversion of 86.32% (250 °C

and 98.66% (300 °C), which corresponds to 57.27 to 69.82% liquid oil.^[79] This is related to the easily degradable PP polyolefin resulting from its branched structure. Further raising the temperature from 300 to 350 °C and then from 350 to 400 °C results in decreasing the liquid oil yield to 67.74 and 63.23%, respectively. Thus, the yield of the liquid product reaches a maximum at the optimum temperature and then begins to decrease with a further increase in temperature. In another study, Miandad et al. investigated the effect of time and temperature on PS waste transformation to fuel oils at temperatures of 400, 450, and 500 °C, and 60, 75, and 70 min reaction times.^[26] At 400 °C, the char yield was maximal (16%), whereas the gas yield was only 8%, while the liquid oil yield amounted to 76%. At 500 °C, the gas yield was doubled to 16.8%, and the char yield was lowered to 4.5%. A maximum liquid oil yield (80.8%) was obtained at 450 °C and this was therefore considered the optimum temperature as confirmed by TGA. Therefore, the pyrolytic liquid content has been increased upon raising the reaction temperature and time but further increasing the temperature and reaction time does not show any further enhancement until it starts to slow down the yield of the fuel oil. Liu et al. reported that the pyrolysis of PS using a fluidized-bed reactor and nitrogen fluidizing gas yields 97.6% of crude oil at 450 °C, but it decreases to 90.2% as the temperature is raised to 700 °C.^[80] On the other hand, the amount of gas increases from non-detectable to 3.54%. A recent study by Panda et al. on the pyrolysis of PP, HDPE, LDPE, and mixed plastics by employing a sulphated zirconium catalyst at a temperature range of 400–500 °C showed a production of low yield of condensates that have low viscosity products at a minimum temperature of 400 °C.^[81] But when the temperature was increased to 450 and 475 °C the yield and viscosity of the products increased gradually, too. 500 °C was considered as an optimum temperature since a high yield of the condensed product oils of 82.5, 76.6, 78.9, and 77.2 wt% had been obtained corresponding to PP, LDPE, HDPE, and mixed plastics, respectively.

The temperature not only affects the yield products; it also affects the compositions of the fuel oils. Jung et al. studied the pyrolysis of PP and PE under different temperatures, and PP pyrolysis provides 53 wt% oil, mainly benzene toluene and xylene (BTX), at 746 °C while PE pyrolysis at 728 °C gives 32 wt% of BTX fractions.^[82] The formation of aromatics in the pyrolysis of polyolefins takes place through Diels-Alder reactions followed by dehydrogenation. PP undergoes a random chain scission mechanism to generate, in a first step, primary and secondary radicals, followed by intramolecular radical transfer reactions that produce tertiary radicals. The β -cleavage of the tertiary radicals finally leads to the formation of propene. Benzene, among the BTX aromatics, has been formed in significant yield in both the PP and PE fractions.

2.1.2. Retention Time and Feedstock Composition

Retention time and feedstock compositions also affect the pyrolysis process and products. However, their impact is lower

compared to temperature. As reviewed by Miandad et al., at shorter retention times, aromatic hydrocarbons are produced, especially when the feedstock consists of PS plastic.^[27] 60% of aromatic hydrocarbons are formed from the pyrolysis of mixed plastics of PS, PP, and PE at 350 °C.^[83] However, as nearly similar carbon chain-containing fractions were obtained at each temperature even though the retention time was varied, an insignificant effect of the retention time on carbon chain fractions was deduced. On the other hand, fractions which have $>C_{13}$ were observed with increasing temperature. This is due to the long retention time in the reactors, as plastic and its derivatives decomposed to generate high carbon chain compounds in comparison to light carbon chain compounds that are formed at low retention time.^[27] The type of feedstock composition also affects the pyrolysis process. For instance, PE- and PP-based plastic required higher temperatures for their complete degradation as compared to PS plastic due to their complex structures.^[77] The capacity of PS to produce a monomer is superior compared to PE and PP. For the case of PS, liquid evolution started at much lower temperatures.^[84] Jan et al. reported the pyrolysis of HDPE at different time intervals using a batch reactor.^[85] 5 g of waste HDPE was allowed to degrade at 450 °C using a catalyst at an optimum catalyst/polymer ratio of 0.1. The degradation reaction was conducted for 0.5 h, 1.0 h, 1.5 h, 2.0 h, 2.5 h, and 3 h, keeping the other reaction conditions constant. The total conversion was found to have increased when the reaction time was raised from 0.5 h to 2 h with a subsequent increase in oil yield and wax. About 96% total conversion was achieved, resulting in a 41.33% oil yield at 2 h. Beyond 2 h reaction time, no significant change in the quantity of any of the reaction products was observed which means the reaction has been completed, and therefore, a reaction time of 2 h reaction time was considered optimal. Miandad and coworkers studied the pyrolysis of PS at an optimum temperature of 450 °C at 60, 75, and 120 min reaction times.^[77] Varying the reaction time between 75 and 120 min does not show a significant difference in the yield of the fuel oil. 80.8% and 80.7% oil yield has been obtained in 75 and 120 min reaction times respectively. A comparable amount of char was produced at 75 min reaction time as compared to 120 min (6.1% versus 5.3%). Thus, the formation of a similar yield of oil at 75 min and the extra time indicated that 75 min is the optimum reaction time. However, more chars are produced at 60 min reaction which indicated that 60 min reaction time is not enough for the PS to yield the maximum amount of oil. Similarly, a research team led by Motawie reported the pyrolysis of HDPE at 450 °C in 0.5–3 h time intervals.^[86] Only 52.2 wt% oil and 41.2 wt% of gas yields were obtained at 3 h reaction time. Conducting the pyrolysis reaction for about 0.5 h, the oil yield was found at a higher 72 wt%, while the gas yield amounted to only 12 wt%. When the reactor is operated for a longer time (residence time), a secondary reaction may take place in which longer carbon chain oils may crack and be consumed towards the gas formation. At 30 and 60 min, the oil contained 23 wt% paraffin within the range C_5 – C_9 as the main compounds. However, $>C_9$ alkanes are formed in less than 23 wt%. C_5 – C_9 alkenes gave a total

concentration of 30 wt%. The composition of the oil produced at 0.5 h residence time was similar to the oil produced at 1 h residence time and was dominated by light alkanes. The oil products at higher residence times (2 and 3 h) gave higher alkene and smaller alkane yields. At a residence time of 2 and 3 h, 19 and 13 wt% paraffinic compounds (C_5 – C_9) were formed, respectively. The effect of residence time was much more pronounced on the alkenes than alkanes. Adnan et al. studied the effect of added PET on the catalytic pyrolysis of PS oil products.^[87] They designed the experiment as PS and 10 wt% PET+PS (500 °C, 60 min, sample to catalyst ratio of 1:0.2), 20 wt% PET+PS (450 °C, 60 min, sample to catalyst ratio of 1:0.2) and for 30 wt% PET+PS (450 °C, 90 min, sample to catalyst ratio of 1:0.2) using an Al–Al₂O₃ catalyst. The pyrolysis of only PS yielded 92.69% liquid, 7.31% gas, and no residue; the 10 wt% PET+PS add mixture yielded 76.40% liquid, 21.30% gas, and 2.30% residue, 20 wt% PET+PS yielded 44.60% liquid, 50.51% gas and 3.89% residues and 30 wt% PET+PS gave 22.50% liquid, 71.80% gas, and 5.70% solid. Accordingly, excess addition of PET results in the liquid yield decline and gas yield increase.

2.1.3. Use of Catalysts

Catalytic pyrolysis has an advantage over conventional, purely thermal pyrolytic processes in fuel recovery from waste plastics. Various heterogeneous catalysts have been used; the most common conventionally used ones are natural and synthetic zeolites like the catalysts employed in the cracking of heavy petroleum fractions.^[73] Catalysts play a vital role in improving the quality of pyrolysis oil as well as reducing, mostly, temperature and retention time of the process.^[88] Catalysts such as Fe₂O₃,^[89] Ca(OH)₂,^[89] FCC,^[90] Al₂O₃,^[91] natural^[17,55] and synthetic zeolite,^[92] and sawdust^[93] are commonly used in the pyrolysis technology. The use of catalysts increases the rate of the cracking reactions, leading to an increase in the gas yield of but reducing the yield of liquids. However, the quality of the liquid oil is improved, as some of the larger carbon chain compounds are either adsorbed in the catalyst or further broken down into smaller carbon chain compounds.^[77]

Reactor design, residence time, and contact of the fused plastics with catalyst as well as the contact time of the volatiles with the catalyst can strongly affect the efficiency of the catalytic process and the respective catalyst. The cracking of waste polymers such as HDPE is carried out as follow i) the polymers melt inside the reactor; ii) coating of the catalyst on the surface of the fused plastics; iii) pyrolysis of the fused plastics; iv) catalytic cracking of the fused plastics and vaporizations.^[94] The acidity, pore size, surface area to volume ratio, and thermal stability of the catalyst are important in the catalytic pyrolysis mechanism and product distributions. The reactions such as cracking, isomerization, oligomerization, cyclization, and aromatization take place on the surface of the catalyst. Zeolite catalysts were selected since their surface feature Lewis- and Brønsted-acidic sites: the abstraction of a hydrogen ion from the waste polymer is initiated by the Lewis

acid site, while the addition of a proton to the C–C bond is carried out by the Brønsted acid sites. Therefore, if the catalytic surface contains more Brønsted acid sites, more hydrogen is provided for the double bond.^[95,96]

The catalysts employed for the pyrolysis of waste plastics can be applied either directly in the reaction system (in situ) or through a second reactor for the actual catalytic process (ex situ).^[97] A recent study by Fan et al. used continuous-stirred microwave pyrolysis (CSMP) and a batch microwave system for the pyrolysis of linear LDPE (LLDPE) in the presence and absence of HZSM-5.^[98] Using CSMP, long hydrocarbons (C₁₄–C₂₀) are obtained selectively. In contrast, using the batch system, more gaseous products (CH₄) are produced. An ex situ catalytic bed with HZSM-5 was applied to increase the amount of gasoline-range hydrocarbons. Both the catalytic continuous-stirred and batch process showed almost similar yields but differed in chemical selectivity. Mono-aromatics with 72.3% are obtained in the CSMP.

A two-stage fixed-bed reactor catalytic pyrolysis has been reported by Akubo et al., using transition-metal-impregnated Zeolite catalysts for HDPE pyrolysis.^[99] The first stainless steel reactor holds the waste plastics and heats to 600 °C at a heating rate of 10 °C min⁻¹. The second reactor holds the catalyst, which receives the volatiles from the first reactor. Non-catalytic pyrolysis of HDPE using the two-stage fixed bed reactor leads to a high oil yield (≈70 wt%) of 100% aliphatic hydrocarbons. Introducing a Y-zeolite catalyst results in a decrease of the oil yield, but >80% of the oil consisted of mono- or bicyclic aromatic compounds). The connection of two reactors in line

with the catalytic pyrolysis and reforming steps can also be applied to improve the yield of hydrogen production. Continuous plastic pyrolysis and catalytic reforming can be conducted in in-line fluidized-bed-fixed-bed, fixed-bed-fixed-bed, spouted-bed-fixed-bed, spouted-bed-fluidized-beds, and screw-kiln-fixed-bed two-stage reactor combinations as shown in Figures 3a–f.^[100]

Pinto and coworkers used unsorted municipal plastics composed of PE, PP, and PS to study the effect of the catalyst on pyrolysis.^[102] More than 90% of the total conversion to oil occurred without any catalyst, producing very little gaseous products. However, in the presence of ZnCl₂ and NH₄-Y-zeolite (NH₄Y), a decrease in the liquid yield to lower than 90% was noted, whilst gas yields increased. Homogeneous catalysts which have a Lewis-acidic nature, such as AlCl₃, are also used for polyolefin plastic pyrolysis.^[91] The use of heterogeneous catalysts is, however, preferred due to the ease of separating and recycling them from the reacting mixtures. Nanocrystalline zeolites, aluminum pillared clays, conventional acidic solids, mesostructured catalysts, superacidic solids, gallosilicates, metals supported on carbon, and basic oxides are among the heterogeneous catalysts used.^[45] The pyrolysis of PE in the absence of any catalyst results in 95 wt% oil yields, no char, and low gas yield, but with various zeolite Y beds and temperatures of 500 °C, the oil yield was reduced to 85 wt%. However, when the zeolite bed temperature was raised, the oil yield was decreased with a consequent increase in the gas yield.^[103] In another study by Zeaiter from 2014,^[104] non-catalytic pyrolysis of HDPE generates 78.7%, 17.8%, and 3.5% of liquid

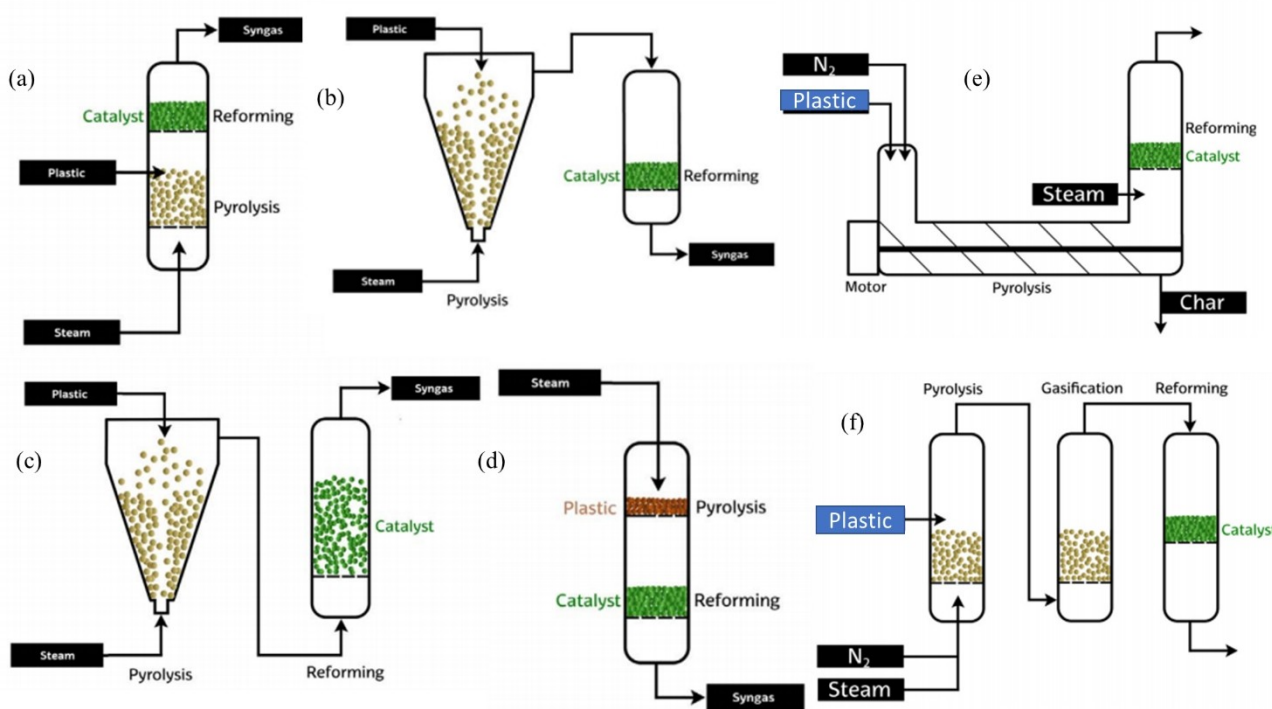


Figure 3. Different reactor configurations used in the pyrolysis and in-line reforming process: (a) in-line fluidized bed and fixed bed, (b) spouted bed and fixed bed, (c) spouted bed and fluidized bed, (d) fixed bed and fixed bed, (e) screw kiln-fixed bed reactor (f) fluidized bed, entrained flow and fixed bed reactor. Reproduced with permission from Refs. [100] and [101]. Copyright 2018, Elsevier.

wax yield, gas, and residue, respectively, using a tubular reactor. However, when zeolite catalysts were added to the pyrolysis process, the waste HDPE generated high gas yields; H-Beta zeolite produces the highest gas yield of 95.7%, 2.4% liquid, and 1.9% residue, followed by HUSY (93.2% of gas, 4.9% liquid and 1.9% residue) at 450–470 °C.

Kumar et al. studied PS, PP, PE, and PET waste pyrolysis in a batch reactor individually and by mixing them without and in the presence of charcoal, activated carbon, and CaO catalysts.^[105] They obtained 80%, 60.7%, 75%, and 66.86% of liquid yields from PS, PP, PP, and mixed PS + PP + PE, respectively, without the use of catalysts. On the other hand, using activated carbon, 82.43% liquid yield from PS + PP + PE, using charcoal, 95.54% from PS + PP + PE, and applying a mixture of activated carbon and CaO as a catalyst provides 75.50% of liquid yield from PE + PP + PS PET.

The type of the catalysts also affects the product oil composition. Ratnasari et al. reported an oil obtained from the zeolite catalytic pyrolysis of HDPE using a two-stage reactor (pyrolysis and catalytic reactor).^[11] Mesoporous MCM-41 and zeolite socony mobil-5 (ZSM-5) catalysts were used, and aliphatic hydrocarbon-based oils were obtained by the first catalyst, whereas by using the microporous zeolite ZSM-5 catalyst, a mostly aromatic-based oil was produced.

During PP degradation employing NiO catalyst in the form of solution yields more oil fuel when compared to its counter catalyst in solid form, and the composition of the oil is reported to be rich in 1-olefins and poor in aromatics and branched isomers.^[106] Pyrolysis of PS was carried out with zeolite and Ni/Si catalysts at 460 °C; 130 g of PS foam was pyrolyzed in the presence of zeolite and nickel/silica catalysts to give yields of 86.69% oil or 112.70 mL and 91.65% liquid or 119.15 mL, respectively.^[107] Similarly, fluidized bed reactor-assisted pyrolysis of PS results in the production of 90 wt% liquid fractions through thermal pyrolysis at 580 °C, while by employing a BaO catalyst, a 93.4 wt% yield was obtained at only 350 °C. A 91% yield of oil was observed when zeolite ZSM-5 was applied at 500 °C.^[108] Singh et al. studied the conversion of HDPE to energy fuels using 0, 2, 5, and 8 wt% loading of a CuCO₃ catalyst.^[109] A maximum of HDPE-derived liquid (94%) was obtained at a 5 wt% loading of the catalyst. Similarly, 85%, 90%, and 92% liquid yields were obtained applying 0, 2 and 8 wt% loading. 14.67%, 9.66%, 5.64%, 7.45% light gases and 0.33%, 0.34%, 0.36%, 0.55% residues have additionally been reported from this experiment using 0, 2, 5 and 8 wt% loading of the catalyst, respectively.

Catalytic pyrolysis of PET was investigated by Park et al., using a carbon-supported Pd nanocatalyst in a tube furnace.^[110] More solids and gases than pyrolytic liquid oil have been produced at 400 °C, but as the temperature was raised to 800 °C, pyrolytic oils gave way to pyrolytic gases (CO, CH₄, and H₂) due to the operation of the free radical mechanism and thermal cracking with the help of the Pd catalyst that, on its surface, accelerates ring-opening reactions. The mass balance indicates that 16% char, 42% liquid, and 42% gas products had been obtained without any catalyst; using Pd:PET (0.01 w/w), a product composition of 18% char, 39% liquid, and 43% gas

was obtained. Further increasing the catalyst-to-PET ratio to 0.05 w/w yielded 19% char, 33% liquid, and 49% gas at 800 °C.

Kassargy et al. reported a comparative study on the thermal and catalytic pyrolysis of PE and PP applying a batch reactor.^[111] 80 wt% of wax and 85.5 wt% of liquid yields were obtained from the thermal pyrolysis at 450 °C. In contrast, applying USY zeolite in the catalytic pyrolysis showed 71 and 82 wt% yields of liquid with a mixture of C₅–C₃₉ and C₅–C₃₀ corresponding to PE and PP, respectively. Further separation of the products by distillation results in the production of 60.6% and 57% of gasoline with a high octane number of 96 and 97 corresponding to PP and PE. 36.5% and 35.3% yields of diesel with cetane numbers of 52 and 53 have been reported from PP and PE, respectively.

2.1.4. Reactor Types

The reactor is considered as the heart of pyrolysis which is used to control the quality of heat transfer, mixing, gas and liquid phase, residence times, and the escape of main products. The design and setup of the reactors is grouped under one of the following categories as shown in Figure 4: Batch, semi-batch, continuous-flow reactors such as fluidized-bed, fixed-bed, and conical spouted bed reactors (CSBR).^[9,27]

2.1.4.1. Batch and Semi-Batch Reactor

The batch reactor operates as a closed system with no inflow or outflow of inputs or outputs when the reaction is being carried out. High conversions of the reactor can be achieved by keeping the reactant in the reactor for a prolonged time which is one of its advantages. However, batch reactors provide inconsistent products from batch to batch, high labor costs per batch, and are difficult to adapt for large-scale production.^[112]

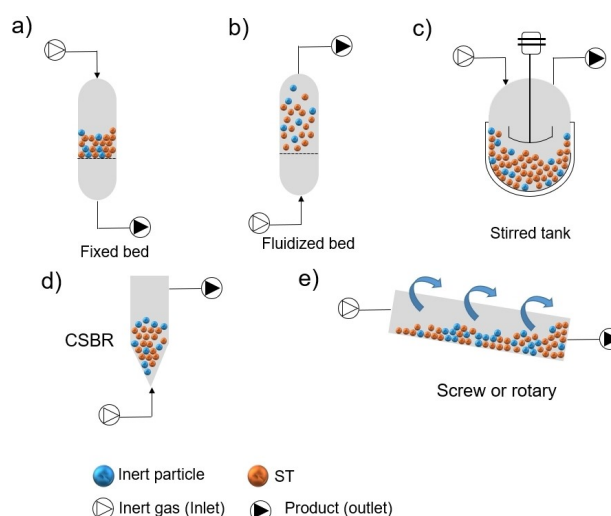


Figure 4. Different types of reactors (CSBR – Conical spouted bed reactor)

The flexibility of adding reactants over time is an advantage of the semi-batch reactor in terms of reaction selectivity. However, the semi-batch reactor is similar to the batch reactor in terms of labor cost and difficulty of large-scale production.^[113,114] Pyrolysis in a batch reactor or semi-batch reactor is normally performed at a temperature range of 300–900 °C and reaction time of 30–90 min for both thermal and catalytic pyrolysis.^[32] Catalysts are added with the plastics to improve hydrocarbon yield and to upgrade products inside the reactor. Such reactors are, however, not preferable for catalytic pyrolysis due to the formation of coke on the surface of the catalyst, which reduces the catalyst efficiency over time. It is furthermore a challenge to separate the catalyst from the residue at the end of the reaction. Both these reactors are suitable for thermal pyrolysis to obtain high oil yield due to their easily controlled parameters, but, as previously mentioned, are difficult to scale up.^[115]

Thermal and catalytic pyrolysis of HDPE was carried out in a pyrex batch reactor at a temperature of 400–450 °C. Increasing the temperature increases the yield of the liquid products in both the catalytic and the noncatalytic system. Using the thermal process, 74.5, 5.8, and 19.5 wt% yields of liquid, gas, and residue were achieved at 450 °C.

However, using FCC and HZSM-5 results in the production of 78.5 and 81.0 wt% yields of liquids, 6.5 and 15.1 wt% gas, and 11.2 and 3.9 wt% residue, respectively.^[116] A semi-batch reactor was also designed for the pyrolysis of HDPE at a higher temperature range of 400–550 °C. 7.86 wt% liquid, 71.22 wt% of viscous wax, 18.42 wt% gas, and 2.5 wt% residues were observed at 550 °C and 54 min residence time. More wax was formed at a higher temperature.^[117] Thermo-catalytic pyrolysis of PS have been conducted using batch and semi-batch reactors. The oil yield was higher in the semi-batch reactor. Applying MgO as a catalyst, the amount of styrene monomer was increased in both reactors. However, the quantities of dimers and trimers were higher in the semi-batch than in the batch reactor. On the other hand, the gas yield was higher in both the catalytic and noncatalytic pyrolysis using the batch reactor.^[118]

2.1.4.2. Fixed and Fluidized Bed Reactors

The technology of the fixed bed reactor is simple, reliable, and proven for fuels that are relatively uniform in size and have a low content of fines.^[119] The reactor contains a gas cooling and cleaning system.

In a fixed-bed reactor, the catalyst is usually present in palletized form and packed in a fixed bed. The design is relatively easy. The feedstock is placed in the reactor (often made from stainless steel), which is heated externally. There are some constraints, such as the irregular particle size and shape of feedstocks, that need to be considered or would otherwise cause a problem during the feeding process. Besides, the accessibility of the surface area of the catalyst during the reaction is limited. In certain conditions, fixed-bed reactors are merely used as a secondary pyrolysis reactor because the

product from primary pyrolysis can be easily fed into the fixed-bed reactor, which generally consists of a liquid and a gaseous phase.^[112] The fixed-bed reactor is characterized by a low heating rate, and as a result of its low heat transfer coefficient, the temperature is not uniform inside the sample, and the feedstock is decomposed at different temperatures simultaneously.^[33]

On the other hand, the fluidized bed reactor solves some of the problems that occur in a fixed-bed reactor. In contrast to a fixed-bed reactor, the catalyst in a fluidized bed reactor sits on a distributor plate where the fluidizing gas passes through it, and the particles are carried in a fluid state. Therefore, there is better access to the catalyst to be well-mixed with the fluid, thus providing a very high surface area for the reaction to occur in uniform temperature distribution. This reduces the variability of the process conditions with a high heat transfer coefficient. Besides, it is also more flexible than the batch reactor, and frequent feedstock charging can be avoided, avoiding the need to pause the process too often. A fluidized bed reactor is considered to be the best reactor to perform catalytic plastic pyrolysis since the catalyst can be regenerated many times without the need of discharging, especially worth considering if the catalyst is a very expensive substance. It is also the most suitable reactor for a large-scale operation in terms of the economic point of view.^[115,119] There are some difficulties in using fluidized-bed reactors, however: the raw material provided to the reactor must be tiny, so it can float in the fluid, and separating the char from the bed material is difficult. Thus, this type of reactor is seldom used in large-scale projects.^[120]

A recent study by Al-Salem et al. reported the recovery of wax from virgin LDPE, HDPE, and plastic solid waste (PSW) using a fixed-bed reactor.^[121] The highest wax yield (64.5 wt%) was obtained from LDPE at 500 °C and 32 wt% from HDPE at the same temperature; however, a low wax yield (9.25 wt%) was achieved using the PSW at 700 °C. Similarly, pyrolysis of HDPE employing a fixed bed reactor at 500 °C with a heating rate of 10 °C min⁻¹, 20 min residence time using nitrogen gas as a carrier gas, gives the highest liquid yield of 95 wt%, low gas yield and no residue without catalyst, while 85 wt% have been achieved using the Y-zeolite catalyst.^[103] Li et al. recently published an investigation into the influence of the thickness of the fixed bed reactor during the pyrolysis of HDPE.^[122] More wax yield was observed in a thin bed (11.4%) than for the thick bed (5.6%) at 425 °C. As the temperature increased from 450–550 °C, the wax yield increased in both beds, but again stronger so in the thick bed.

2.1.4.3. Rotary Kiln Reactors

The rotary kiln reactor is more efficient than the fixed-bed reactor in heating the feedstocks. Its slow rotation of an inclined kiln enables good mixing of wastes and yields uniform pyrolytic products.^[27] Rotary kiln reactors are widely used, typically for conventional pyrolysis (slow pyrolysis), usually performed at 500 °C with a residence time of 1 h. Proceeding with a slow heating rate, significant product portions of char, liquid, and

gas are the result.^[123] Rotary kiln reactors have many unique advantages over other reactor types such as good mixing of wastes, flexible adjustment of residence time, larger channel for the waste stream allowing feeding of heterogeneous materials, thus, preventing extensive pre-treatment of wastes, and simple maintenance.^[33,120]

2.1.4.4. Stirred Tank Reactors (STRs)

STRs are the most frequently applied reactors for the pyrolysis of waste plastic and biomasses. They are designed featuring a heat transfer medium like hot oil (Nano fuel process) with good temperature control and are easy to construct and operate. Catalysts are frequently added directly to the plastic waste, or upgrading can take place in a separate vapor upgrading tower (Thermofuel). The stirrer facilitates better heat transfer to the melt, uniform heat distribution, and scrapes char deposits from the reactor walls, which would otherwise act as heat insulators.^[124] Char, spent catalysts, and/or contaminants are generally removed from the bottom of the reactor (Nano fuel, Thermofuel, Royco), except in the Hitachi process, which vacuums char from the bottom through a vertical vacuum line. One of the main disadvantages of stirred tank reactors is that they require frequent maintenance and so require a large infrastructure. They also have a low conversion rate per volume and poor agitation.^[125]

2.1.4.5. Conical Spouted Bed Reactors (CSBRs)

Conical spouted bed reactors (CSBRs) provide good mixing with the capability to handle large particle size distributions and larger particles with differences in particle densities.^[112] They also allow high heat transfer between phases and avoid defluidization caused by melted plastic in the fluidized bed reactor.^[32] Spouted bed reactors have been applied successfully for pyrolysis of polymers like PS, PE, PP, and PET due to their low bed segregation and low attrition in comparison with bubbling fluidized beds.^[120] The CSBR design is relatively simple, and it is suitable for the pyrolysis of waste plastics without segregation of the wastes.^[126] The CSBR is suitable for the pyrolysis of waste plastics without defluidization. The cyclic movement of the particles in the spout enhances the breakage of any incipient agglomerate particles.

However, a variety of technical challenges during the operation of this reactor have been encountered, such as catalyst feeding, catalyst entrainment, and product (solid and liquid) collection that make it less favorable.^[112] Additionally, its design requiring many pumps to be used, making it unfavorable due to the high operating cost involved.

The FCC catalytic pyrolysis of HDPE using a CSBR results in the total conversion of 50 wt% of gasoline C₅–C₁₁ and 28 wt% of olefins (C₂–C₄).^[127] Similarly, HDPE pyrolysis was reported by Elordi and coworkers in a pilot plant unit equipped with a CSBR at a temperature range of 500 to 700 °C.^[128] The use of the CSBR minimized the secondary reaction of forming aromatic fuels in a

short residence time of the volatiles. A high yield of waxes (C₂₁₊) up to 67 wt% was obtained at 500 °C, whereas increasing the temperature to 700 °C resulted in 39 and 33 wt% of gases (C₄–) and gasoline fractions (C₅–C₁₁), respectively.

2.1.4.6. Microwave-Assisted Technology

The recent interest in microwave technology offers a new technique for waste recovery through a pyrolysis in an efficient thermochemical process to produce oil, syngas, and char.^[119,129,130] In this process, a highly microwave-absorbent material such as particulate carbon is mixed with waste materials.^[32] The microwave absorbent absorbs microwave energy to create adequate thermal energy to achieve the temperatures required for extensive pyrolysis to occur. Microwave heating is one of the best alternatives to conventional heating because it provides homogeneous and volumetric heating.^[131] Microwave radiation offers several advantages over the conventional pyrolysis method, such as increased production, rapid reaction as well as uniform and rapid internal heating of large biomass particles, better product selectivity, immediate response for rapid start-up and shut-down, high energy efficiency, no need for agitation, and controllability and cost-effectiveness.^[14,120] Unlike conventional methods, microwave energy is supplied directly to the material through molecular interaction with the electromagnetic field. Thus, no time is wasted to heat the surrounding area.^[132] Despite the advantages of microwave heating, there is also a major limitation preventing this technology from being widely explored on an industrial scale, namely the absence of sufficient data to quantify the dielectric properties of the treated waste stream.^[129] Microwave ovens and synthesizers can raise the temperature as high as 1000 °C due to the microwave absorbing materials or receptors, which include graphite and metal oxides. It was used for the pyrolysis of plastics mixed with aluminum for the recovery of metals and oil. The recovery of fuel products from the sludge is also easy due to microwave-induced pyrolysis.

The efficiency of microwave heating depends heavily on the dielectric properties of the material. For instance, plastics have a low dielectric constant, and mixing with carbon as the microwave absorber during pyrolysis may improve the energy absorbed to be converted into heat in a shorter time.^[115,133]

In a microwave-assisted pyrolysis, rice straw and sugarcane bagasse were co-pyrolyzed with PE and PS using an HZSM-5 catalyst. High yield of liquid oil, 82 and 98 wt% was achieved from PE and PS, which was higher than that from the straw (26 wt%) and bagasse (29 wt%). Unsaturated and aromatic dominant yields were observed with a high calorific value (43 MJ kg⁻¹), low viscosity (1 cP), density (0.850 g cm⁻³), and flash point (70 °C). The oxygen content of the upgraded bio-oil biomass-plastics was < 5%.^[134]

Finally, each of the reactor types and designs has its own advantages and disadvantages, as summarized in Table 3.

Table 3. The advantage and disadvantages of the reactors in pyrolysis.

Reactor	Advantage	Disadvantage	References
Batch	appropriate for thermal pyrolysis easy-to-control operating parameters	slow process inconsistency in products from batch to batch high labor costs per batch not preferable for catalytic pyrolysis due to slow mixing of catalysts with plastics difficult for large-scale production	[112]
Semi-batch	flexibility in adding the feedstocks suitable for thermal pyrolysis easy-to-control operating parameters	high labor cost per batch not preferable for catalytic pyrolysis due to slow mixing of catalysts with plastics more suitable for small-scale production	[113–115]
Fixed-bed	simple, reliable and proven for fuels that are relatively uniform in size and have a low content of fines contains gas cooling and cleaning system	not suitable for irregularly sized and shaped feedstock particles limited accessibility of available catalyst surface area low heating rate non-uniform temperature inside the sample, thus feedstocks are decomposed at different temperatures	[33,112]
Fluidized-bed	Better mixing of catalyst with fluid, providing uniform temperature distribution more flexible, allows frequent discharging of feedstocks suitable for large-scale operation suitable for catalyst regeneration formation of uniform product spectra	high cost of operation separating the char from the bed material is difficult only used for tiny feedstocks	[82,115,135,136]
Rotary kiln	enables good mixing of wastes heterogeneous material or feedstocks can be used simple maintenance	slow process significant char formation low heating rate	[27,33,123,136]
Stirred Tank	good temperature control easy to operate and construct better heat transfer to the melt uniform heat distribution	requires frequent maintenance low conversion rate per volume poor agitation	[36,137]
Conical spouted bed (CSBR)	provides good mixing, thus able to handle large-sized particles and mixtures with difference in particle densities good heat transfer between phases simplest CSBR design, usable for pyrolysis of all waste plastics without need for separation avoid defluidization	difficulties in catalyst feeding, entrainment and product collections complicated design that requires many pumps, thus high operating cost	[32,112,126,138]
Tubular	consist of various tubes with fixed wall heated externally simple and safe coke and gas can be obtained continuously suitable to use for both thermal and catalytic pyrolysis process lower labor cost, shorter processing time, stable operation stable	requires extensive pretreatment of MSW small channels for the passage of feedstock erosion of the reactor due to the presence of sand and other solid contaminants present in the feedstock heat transfer co-efficient is not well defined requires sophisticated control systems	[27,139]
Multi-step	combine two or more stages potential to control different condition sets per stage allow to run pyrolysis independently produced HCl gas can be separated from volatile value products at different stages short residence time	–	[27,140]
Plasma	convert waste into synthetic gas good heat transfer controlled process temperature, high process rate produced syngas has an optimal composition obtained products are harmless to human health and the environment	high energy demand (required temperature of 1000 °C) low reaction volume only applied for hazardous waste economically not favorable for MSW	[27]
Microwave	provides homogeneous and volumetric heating rapid reaction and cost-effective good product selectivity pyrolysis of mixed plastics possible can generate high-quality fuel products	absence of sufficient data to quantify the dielectric properties of waste streams requires very fine feedstock particles to obtain high heating rate reduce secondary cracking solid laden vapor has to be removed rapidly from reactor	[14,115,129,132,133,136,141]

2.1.5. Pressure

Pyrolysis of waste plastics takes place under atmospheric pressure or in vacuum environments. Though only little investigation has yet been conducted with respect to the effect of pressure on the pyrolysis plant, the operating pressure has a

significant effect on the production of gases by decreasing the pyrolytic liquids. Applying high pressure to the process enables the formation of low molecular weight products. Like for residence times, the influence of pressure is mostly evident at higher temperatures, that is, strongly temperature-dependent. Furthermore, the rate of carbon-carbon double bond (C=C)

formation has relation with the applied pressure. At high pressure and temperature, large-chain hydrocarbons are further cracked down to fractions instead of escaping, since the boiling point of the pyrolytic products under pressurized conditions is increased. As a consequence, pyrolysis under pressurized conditions requires more energy for further hydrocarbon cracking. It was also found that the use of high pressures increases the yield of non-condensable gases and decreases the yield of liquid products.^[30,142,143] The co-pyrolysis of LDPE between 2 and 10 bar indicated that increasing the pressure resulted in increasing the yields to a nearly tripled yield of gas and pyrolytic liquid. Furthermore, the high pressure (10 bar) resulted in the formation of lighter/shorter hydrocarbons due to cracking reactions through chain scission steps.^[144]

Mahari et al. investigated the effect of a N₂ atmosphere and vacuum environment on the pyrolysis of waste polyolefins (WP) and waste cooking oil (WCO) under microwave co-pyrolysis.^[145] A higher liquid oil yield (28–62 wt%) was observed in the vacuum environment than in the N₂ atmosphere (25–50 wt%) from the pyrolysis of WP:WCO (1:1). The negative pressure of the vacuum pump forces the gases to be sucked from the area of the low-pressure reactor (60 kPa) to the areas of the high-pressure outer environment (101 kPa) in 3–5 min at a lower temperature of 130 °C. However, the pyrolysis of volatiles started after 10–15 min and >310 °C under the N₂ atmosphere. Similarly, Lam et al. studied the pyrolysis of waste plastics and WCO mixtures in a microwave vacuum pyrolysis by applying an activated carbon reaction bed.^[146] The synergistic effect between the waste plastics and WCO generated nearly 84% liquid oil with a high heating value (49 MJ kg⁻¹). The volatiles components tend to form faster in the microwave vacuum pyrolysis (at 120 °C) than in the conventional microwave pyrolysis (320 °C). The boiling and melting points of the waste plastics WCO were decreased in the vacuum environment.

2.1.6. Type and Rate of Fluidizing Gas

Fluidizing gases are used in the transport of vaporized compositions without taking part in the pyrolysis reaction. Different types of fluidizing gases (also called carrier gases) are employed in the pyrolysis process, such as nitrogen, hydrogen, helium, argon, ethylene, propylene, etc. The carrier gases have different effects based on their molecular weight.^[147,148] The lighter gases can produce a high amount of condensed liquid oil product. The use of H₂ produced the highest liquid yield of 96.7 wt%, while without any carrier gas, only 33.8 wt% liquid was formed in the pyrolysis of PP. The reactivity of the fluidizing gas also influenced the coke formation. Using H₂ as carrier gas yields a very minimal coke formation, followed in this effect by ethylene, helium, and propylene. Carrier gases that have the same molecular weight have different effects depending on their reactivity. For instance, ethylene, which has the same molecular weight as dinitrogen, produces a higher amount of liquid and lower amounts of char than nitrogen because it shifts the equilibrium towards the liquid product.^[148] Nitrogen gas is frequently used as a fluidizing gas by many researchers in the

pyrolysis process due to its availability and it being safer to handle than the other reactive gases such as hydrogen and propylene, which are flammable and thus hazardous. Even though helium is good in producing high-yield oil next to hydrogen, it is less readily available and more expensive than nitrogen. In addition to the type of carrier gas, the flow rate also influences the pyrolysis and cracking reactions in certain reactors. The carrier gas carries the cracking fragment gases away from the reactor, which in turn reduces the chance of secondary reactions.^[149] Lin and Yang studied the product distribution of PP using a HUSY catalyst and nitrogen gas at a temperature of 360 °C depending on the flow rate.^[90] They confirmed that the rate of degradation starts to drop rapidly at the lowest flow rate of 300 mL min⁻¹. Applying a lower flow rate of gases results in a long residence time for the production of the primary products due to the formation of coke precursors (BTX). Therefore, a lower fluidizing rate causes a long residence time in the pyrolysis process. Low gas residence time also enhances the formation of primary products such as aliphatic and light olefins and low yields of secondary reaction products (aromatics). On the other hand, longer gas-residence time enhances secondary reactions, which lead to less oil and more gas product. At a flow rate of 900 mL min⁻¹, gasoline fuel and C₁–C₄ gas fractions have been formed in advanced yields. Hence, the type and rate of fluidizing gas are also very important factors in pyrolysis as they influence product distribution.^[148]

Williams and Slaney investigated the thermal pyrolysis of PE, PP, PS, PVC, and PET wastes individually, held for 60 minutes under N₂ and H₂ pressure at 500 °C.^[51] The reaction of PE and PP in both nitrogen pyrolysis and hydrogen liquefaction conditions produced a high oil yield (93 and 95%) with lower concentrations of gas and no solid residue. PS liquefaction also produced 71 wt% oil from pyrolysis and 77 wt% in hydrogen liquefaction conditions, but also showed a significant amount of solid residue. PVC could not be completely pyrolyzed due to problems of corrosion of the reactor from formation of high concentrations of hydrogen chloride. However, 2 wt% oil, 38 wt% gas, and 52 wt% solid residues were produced with hydrogen liquefaction. PET also showed a high conversion to a solid residue under nitrogen pyrolysis conditions with a yield of 53 wt% with consequent production of 15 wt% oil and 32% of gas. Under hydrogen liquefaction conditions, the yield was 41 wt% solid residue, 27 wt% oil, and 32% of gas. Abbas-abadi et al. studied the effect of carrier gases such as H₂, He, N₂, ethylene, propylene, argon, and the absence carrier gas on the pyrolysis of HDPE.^[150] They found that 95.1%, 4.5% and 0.4% of condensed product, gas and char yields were obtained respectively under H₂ carrier gas. Similarly, 93.7%, 3.4% and 2.9% using He, 91.2%, 4.1% and 4.7% using N₂, 94.1%, 4.5% and 1.4% ethylene, 88.2%, 9.5% and 2.3% using propylene and 87.6%, 5.6% and 6.8% using argon of condensed, non-condensed and char products were obtained. Finally, the quantity of condensed products sank to 42.3%, while the amounts of non-condensed and char products were raised to 36.4% and 6.8%, respectively, without any carrier gas. The fuel yields obtained from the thermal and catalytic pyrolysis of

Table 4. Catalytic pyrolysis products of waste polymers using different parameters.

Plastic	Reactor	Process parameters Catalyst	Temp. [°C]	Pressure [atm]	Heating rate [°C min ⁻¹]	Duration [min]	Yield [wt%]			Ref.
							Oil	Gas	Char	
PS	Tubular	Al-Al ₂ O ₃	500	–	–	600	92.69	7.31	0.0	[87]
LDPE	Fixed-bed	bentonite	700	–	10	–	87.0	–	–	[151]
LDPE	Batch	HUSY	550	–	5	–	61.6	34.5	1.9	[69]
HDPE	Batch	HUSY	550	–	5	–	41.0	39.5	1.9	[69]
HDPE	–	Zeolite-Y	450	–	–	60	81.00	17.50	1.50	[65]
HDPE	Fixed-bed	bentonite	700	–	10	–	88.7	–	–	[151]
HDPE	Semi-batch	FCC	450	1	25	60	91.2	4.1	4.7	[150]
HDPE	Semi-batch	FCC	420	1	25	–	89.1	6.7	4.2	[150]
PS	Batch	Zn	500	–	–	150	96.73	3.27	0	[115]
PS	Semi-batch	FCC	400	1	7	–	90	6	4	[152]
PS	Fixed-bed	bentonite	700	–	10	–	88.5	–	–	[151]
PP	Semi-batch	FCC	400	1	7	–	85	13	2	[152]
PP	Semi-batch	FCC	450	1	25	–	92.3	4.1	3.6	[148]
PP	Fixed-bed	bentonite	–	–	10	–	90.5	–	–	[151]
PC	Fixed-bed	ZSM-5	500	–	–	–	57.47	19.06	23.47	[153]
PC	Fixed-bed	silicalite	500	–	–	–	58.32	20.32	21.36	[153]
PC	Fixed-bed	$\gamma < M > \text{-} > \text{Al}_2\text{O}_3$	500	–	–	–	38.49	22.07	39.45	[153]
LDPE	Microwave	ZSM-5	450	–	–	10	32.58	65.77	1.81	[154]

“–”: Data not available.

Table 5. Thermal pyrolysis products of waste polymers under different parameters.

Plastics	Reactor	Process parameters		Heating rate [°C min ⁻¹]	Duration [min]	Yield [wt%]			Ref.
		Temp. [°C]	Pressure			Oil	Gas	Char	
LDPE	Batch	425	0.8–4.3 MPa	10	60	89.5	10	0.5	[21]
LDPE	Batch	430	–	3	–	75.6	8.2	7.5	[155]
PS	Batch	425	0.31–1.6 MPa	10	60	97	2.50	0.5	[21]
LDPE	Vacuum	500	–	–	–	96	2.7	1.0	[33]
HDPE	Vacuum	500	–	–	–	97.7	0.9	0.8	[33]
PP	Fixed-bed	700	–	–	–	84.4	15.3	0.2	[33]
PP	Vacuum	500	–	–	–	95	3.5	<0.1	[33]
HDPE	Fluidized bed	650	–	–	20–25	68.5	31.5	0	[156]
PS	Fluidized bed	600	–	–	–	98.7	0.65	<0.2	[80]
PET	–	500	–	–	–	15	53	32	[157]
PET	–	500	1 atm	6	–	38.89	52.13	8.98	[158]
PET	–	500	1 atm	8	–	34.16	57.72	8.12	[158]
PVC	Vacuum	520	2 kPa	10	–	12.79	0.34	28.13	[159]
PP	Horizontal steel	300	–	20	30	69.82	28.84	1.34	[79]
PP	Batch	380	1 atm	3	–	80.1	6.6	13.3	[160]
LDPE	Micropyrolyzer	574 ± 22	–	10	30	84	14 ± 1	1.75	[161]
PP	Micropyrolyzer	574 ± 22	–	10	30	68	1.64	31 ± 3	[161]
PS	Microwave	–	–	–	8–10	88	10 ± 0.009	2 ± 0.01	[131]
HDPE	Two-stage micropyrolysis	625	–	10	–	62.7	34.3	3.0	[162]

“–”: Data not available.

HDPE, LDPE, PP, PS, PET, PVC and PC under different parameters are summarized in Tables 4 and 5.

As shown in Tables 4 and 5, LDPE, HDPE, PP, and PS have the capability of producing the highest yield of fuel oil and a lower amount of gas in a pyrolysis. Conversely, PET produces the highest yield of gases, more than liquid oil. PVC produces the lowest oil yield among all plastics. Feedstocks with higher H/C ratios are generally easier to convert to hydrocarbons and produce less coke, whereas feedstocks with lower H/C ratios (e.g., <1) may produce large quantities of coke during zeolite upgrading, leading to rapid catalyst deactivation (Table 6).^[163] Singh et al. studied thermal pyrolysis of HDPE, PP, PS, PET, and the mixed plastics in a semi-batch reactor at 450, 500, 550, and 600 °C.^[164] The maximum liquid yield of HDPE was 89.5 % at

Table 6. Elemental analysis of pyrolytic liquids in comparison to conventional diesel.

waste/ Plastic	Element [wt%]				H/C ratio	Reference
	C	H	N	S		
PS	91.60	8.07	–	0.15	1.06	[113]
PP	85.52	14.40	–	0.31	2.03	[113]
PE	80–85.4	14.4–15.5	–	–	–	[157]
PVC	48.1	6.75	<0.01	<0.01	–	[166]
PET	62.5	3.8	<0.01	<0.01	–	[167]
Diesel	85.3	14	ND	0.5	–	[166]

550 °C, and 86.5 % from PP at 500 °C. A maximum of 84 % liquid yield was obtained at 500 °C for PS, whereas PET yielded only 28 % of liquid at 400 °C and the mixed plastic produced a

maximum of 80.5% liquid yield at 500 °C (Figures 5a–5e). Miandad et al. also studied the pyrolysis of PS, PE, PP, PET, and their mixtures at 450 °C.^[165] Their study showed that 80.8, 13 and 6.2% of PS and 42, 54.5, and 3.5% of PP oil, gas and residue were produced, respectively. In contrast, pyrolysis of PE produced 62, 25 and 13% of gas, wax and char, respectively. The mixtures of PS/PP, PS/PE, and PP/PE gave 25, 54, and 24% of oil, 69.9, 38.3, 51.2% of gas and 5.1, 7.7 and 24.8% of char, respectively. The mixtures of PS/PP/PE also produced 49, 47.1 and 3.9% of oil, gas, and char, respectively. Finally, the mixture of the four feedstocks, PS/PP/PE/PET, yielded 40% of oil, 42% of gas, and 18% of char, as shown in Figure 5f.

3. Types of Pyrolysis Oils and their Properties

The oil derived from the condensation of pyrolytic gases possess almost similar properties to that obtained from solid feedstocks. Both have a high calorific value that allows them to be used in various gas engines for electricity generation without further treatment. Moreover, it is less stable for long-term storage as it is intricately mixed with oxygenated compounds.

This oil can be further processed to obtain polymer-derived gasoline, diesel as crude oil is refined in the refineries. To improve the yield of liquid hydrocarbon products from the pyrolysis of polymer feedstocks, a lower temperature, higher heating rate, and shorter gas residence time operating process should be applied.^[168]

The produced liquid oils from different feedstocks have different physical and chemical properties such as viscosity, density, flash point, and pour point. Table 7 shows the physical properties of liquid oils produced from different types of plastic wastes through pyrolysis.

The quality of the pyrolytic oil is low, and further processing is required. The quality of the crude oil is improved through further refining processes which produce to polymer-derived gasoline or diesel, as demonstrated in Figure 6.^[170] Hydrocracking of LDPE using different catalysts produces light hydrocarbons (C₅–C₁₂), namely gasoline, and heavy oils (diesel). 68.40% and 31.60% yields of gasoline and diesel have been obtained using the Ni/Z (Z=natural zeolite) catalyst, respectively, further, 64.90% and 35.10% using NiMo/Z, 67.60% and 32.40% using Co/Z and 71.49% and 28.52% using CoMo/Z of gasoline and diesel yields, respectively.^[170] In contrast, thermal

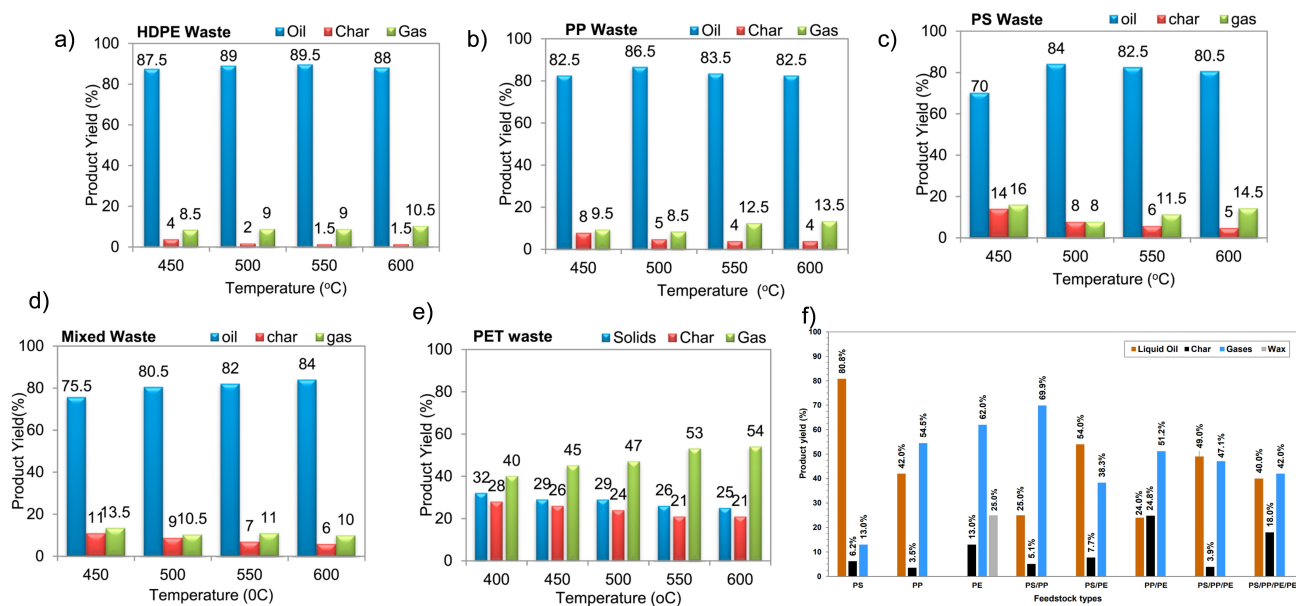


Figure 5. (a–e) Product yield analysis of individual and mixed plastic waste at different process temperatures; (f) effect of thermally activated natural zeolite (TA-NZ) on pyrolysis product yield. Reproduced with permission from Refs. [164] and [165]. Copyright 2017 and 2019, Elsevier.

Table 7. Physical properties of liquid oil produced from different types of plastic waste.

Waste/Plastics	Flash point [°C]	Pour point [°C]	Water content [ppm]	Ash [wt %]	Viscosity [cst 50 °C]	Density [kg m ⁻³]	Cetane rating	Sulphur [wt %]	CV [MJ kg ⁻¹]	Ref.
HDPE	48	-15	-	-	1.63	0.79	-	-	45.86	[51]
LDPE	41	-	0.3	0.4	-	0.779	-	-	30–39	[77,130]
PP	30	-39	0.13	0.01	2.27	0.792	56.8	0.01	53.4	[77]
PS	26.1	-67	0.67	0.006	2.27	0.96	12.6	0.01	50.4	[115]
PVC	40	-	-	-	-	0.84	-	-	21.1	[159]
PET	-	-	0.46–0.61	0.02	-	0.90	-	-	28.2	[79]
Gasoline	42	-	-	-	1.17	0.780	-	-	42.5	[169]
Diesel	52	6	0.05	0.01	1.9–4.1	0.85	40–55	0.05	43	[169]

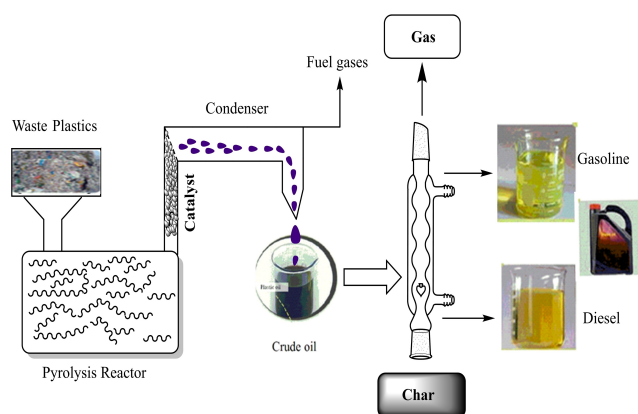


Figure 6. Pyrolysis process of generating fuel oil from the waste plastics.

pyrolysis of LDPE and PP produces 21.30% and 58.00% yields of gasoline and 67.76% and 36% of diesel, respectively.^[171] Ajibola et al. used a Zeolite Y kaolin deposit for the pyrolysis of waste LDPE in a stainless steel bed reactor at a temperature of 300 °C.^[172] Long-chain hydrocarbons (C_8 – C_{29}) were obtained with alkene and aromatic dominance with 56% of gasoline fractions (C_6 – C_{12}), 26% gasoline and kerosine (C_{13} – C_{18}), 10% fuel oil (C_{18} – C_{23}), and 8% residue ($C_{>24}$). Such pyrolytic waste plastic products are cleaner, free of sulfur compounds, and have a properties similar to conventional diesel; the densities of the lump liquid oils derived from PP and HDPE are reported to be 0.86 g cm^{-3} and 0.89 g cm^{-3} and the API gravities gravity (API = American Petroleum Institute) were 33.03 and 27.48, respectively. These values are comparable with the density and API of diesel-range (C_{12} – C_{16}) hydrocarbons. The kinematic viscosities of PP and HDPE-derived liquid products were $4.09 \text{ mm}^2 \text{ s}^{-1}$ and $5.08 \text{ mm}^2 \text{ s}^{-1}$, respectively. When these values are compared with the viscosities of petroleum fuels, they meet the specifications of premium fuels. Other parameters like ash content, heat value, water content, flash point, and cetane number of the pyrolysis products of the waste plastics are in line with conventional diesel and gasoline.^[79] However, waste plastics of PET and PVC are challenging for pyrolysis; low yield oils are obtained, and the fuels obtained from these plastics had the lowest calorific value below 30 MJ kg^{-1} due to the presence of benzoic acid in PET and chlorine in PVC that deteriorated the fuel quality.^[147]

4. Depolymerization and Pyrolysis Reaction Mechanisms

Basically, condensation of organic polymer materials such as PET, nylons, polyesters, PCs and polyamides can easily be depolymerized into their corresponding monomers through reversible reaction, namely, glycolysis, hydrolysis, and alcoholysis. However, chain growth organic polymers such as HDPE, LDPE, PP, PS, and PVC cannot be reversed to their monomers;

instead they have to undergo thermal hydrocracking and catalytic cracking to free radical fragments.^[9]

The plastic pyrolysis mechanism can be categorized into end-chain scission or depolymerization, random-chain scission, chain stripping, and cross-linking.^[173] The pyrolysis reaction models of PE can be described by the “contracting sphere” model, whereas that of polypropylene can be described by the “contracting cylinder” model.^[38] Highly aromatic oils are obtained from PS and PVC, while oxygenated oils that result from carboxylic acid and carbonyl compounds are produced from PET.^[51] In general, catalytic and noncatalytic pyrolysis are different in terms of reaction mechanisms, degradations, and other aspects from plastic to plastic. The detailed mechanisms are categorized into initiation, propagation and termination steps.

In the initial step, homolytic C–C bond cleavage by either random or end scission results in the formation of two radicals followed by intramolecular/intermolecular hydrogen transfer to form stable secondary or tertiary radicals. Following, the radicals undergo C–C rupture through β -scission to form olefins and other radicals. Finally, at the termination step, disproportionation takes place to form olefins, alkanes or bimolecular coupling among the radicals.^[174]

4.1. Polyvinyl Chloride (PVC)

The production of PVC globally is estimated to be 44.3 million metric tons per year which accounts for nearly 12% of the total plastic demand.^[175] PVC decomposes at a lower temperature than the other plastics. Different models have been proposed to elucidate the mechanism of PVC breakdown. The decomposition of PVC happens through a series of reactions, a model for which has been proposed as three consecutive processes: 1) conversion of PVC into intermediates and HCl; 2) decomposition of intermediates into polyene chain and other volatiles; and 3) decomposition of polyene into toluene (and other aromatics) and chars.^[176,177]

PVC contains a high Cl percentage (57 wt%) and a high amount of additives such as plasticizers, stabilizers, flame retardants, and fillers.^[178] Chlorine is removed from the polymer either by nucleophilic substitution with OH^- or by an elimination reaction (dehydrochlorination) (Figure 7). As the pyrolysis temperature increases, BTX aromatics, which are fundamental petrochemicals, can be formed under pyrolysis conditions by the Diels-Alder reaction and dehydrogenation from polyene as shown in Figure 8.^[179] The degradation of PVC with precipitated silica (silica ppt) as a catalyst was investigated by Nasir et al. using a fluidized bed reactor.^[182] In the first step, HCl was removed due to the C–Cl bond breakage. In the second step, the C–C bonds of the remaining organic part were cleaved by C–C bond scission. As a result of HCl removal, conjugated polyenes are formed which subsequently pyrolyze to aliphatic and aromatic hydrocarbons. The maximum degradation temperature of PVC was reduced due to the high surface area and pore size of the catalyst.

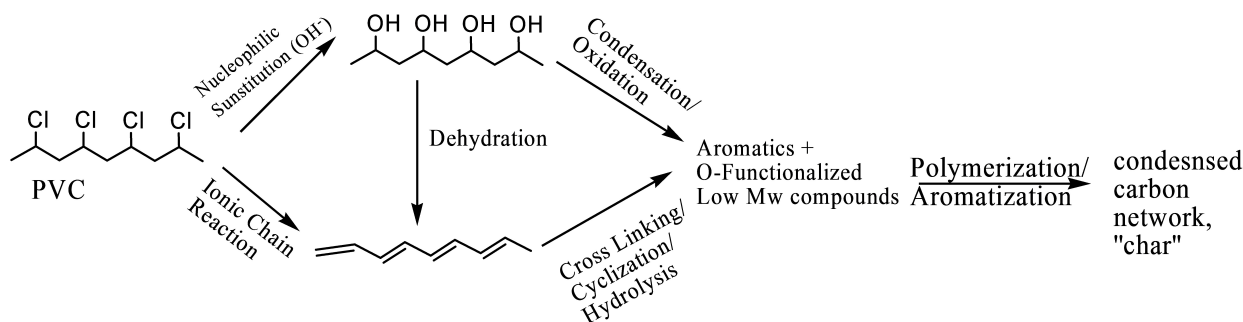


Figure 7. Assumed reaction pathway of PVC decomposition in subcritical water. Reproduced with permission from Ref. [180]. Copyright 2015, Elsevier.

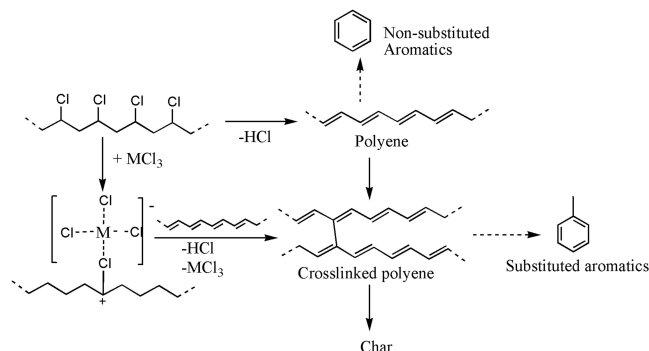


Figure 8. Reaction scheme of PVC pyrolysis in the presence of Lewis-acidic metal chlorides yielding aromatic compounds. Reproduced with permission from Ref. [181]. Copyright 1998, Elsevier.

4.2. Polyolefins (LDPE, HDPE, and PP)

Polyolefins are among the most-used thermoplastics today. They can be fabricated in different grades with varied properties as ultra-high molecular weight polyethylene (UHMWPE), HDPE, and LDPE. They have high resistance to solvents, alkali, acids, and good dielectric and barrier properties.^[185]

HDPE, LDPE, and PP are hydrocarbon-based polymers, consisting of carbon and hydrogen, which have similar properties to hydrocarbon fuels, their calorific values being close to those of liquefied petroleum gas (LPG), gasoline and diesel. Polyolefins (LDPE, HDPE, PP) are the major type of thermoplastic polymers used throughout the world for different applications such as bags, toys, containers, pipes (LDPE), housewares, industrial wrappings and film, gas pipes (HDPE), battery bags, automotive parts, electrical components (PP). Thermal cracking of PE and PP typically takes place at high temperatures (> 700 °C) to produce an olefin mixture (C₁–C₄) and aromatic derivatives, primarily BTX.^[44] Oil products of PE-type plastics generally have high calorific values since they contain paraffinic, olefinic, and aromatic hydrocarbons.^[78] The pyrolysis of both PE and PP occurs through the random-chain scission mechanism, and a whole spectrum of hydrocarbon products is obtained.

Polyolefins are degraded by a complex free-radical reaction mechanism to yield liquid oils, waxes, and gases.^[186] HDPE contains mostly secondary carbon atoms in its linear structure, and thus the C–C bonds have an equal chance in the random cracking during the pyrolysis, whereas the branched structures

of LDPE feature a higher amount of tertiary carbons, which tend to be involved in cracking before the bonds of secondary and primary carbon atoms. Similarly, the C–C bonds of tertiary carbon atoms in PP are less stable than the HDPE and LDPE; subsequently, smaller hydrocarbons are produced during pyrolysis.^[187] Thermal degradation of PE consists of free radical formation and hydrogen abstraction steps, as shown in Figure 9.^[19] The thermal degradation of PP occurs through random scission followed by a radical transfer process.^[188]

Based on the radical chain reaction, the depolymerization reaction (Figure 10) takes place through chain initiation (A),

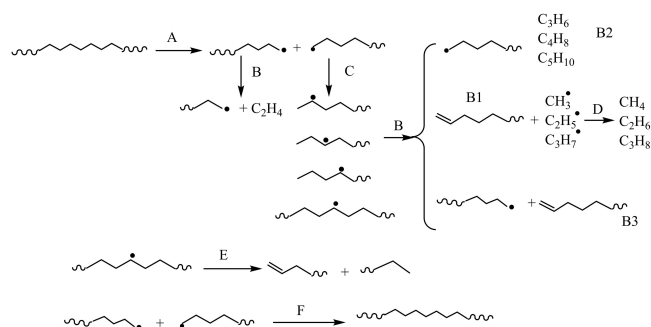


Figure 9. The mechanism for thermal cracking of PE in a semi-batch reactor under atmospheric pressure (A: C–C scission; B: β -scission; C: intramolecular hydrogen transfer; D: H-abstraction; E: β -disproportionation; F: chain termination). Reproduced with permission from Ref. [171]. Copyright 2015, American Chemical Society.

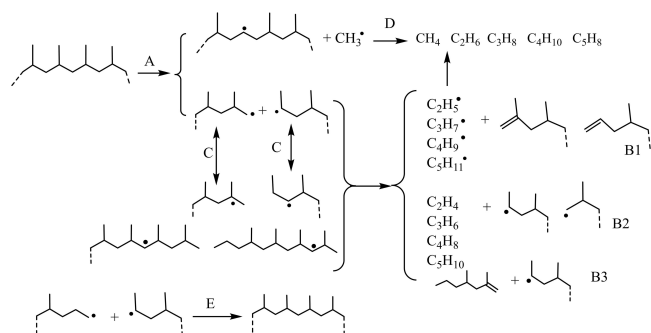


Figure 10. Mechanism for thermal cracking of PP in a semi-batch reactor under atmospheric pressure (A: C–C scission; B: β -scission; C: intramolecular hydrogen transfer; D: H-abstraction; E: chain termination). Reproduced with permission from Ref. [171]. Copyright 2015, American Chemical Society.

chain reaction (B, C, D, E), and chain termination (F). The thermal degradation of PE and PP is shown in Figures 9 and 10.^[177] Levine and Broadbelt confirmed that intermolecular hydrogen transfer between radicals is the dominant reaction to form alkanes and that β -scission of radicals the dominant pathway to form alkenes.^[189] However, in PP thermal cracking products, the yield of the alkanes in the oil fraction is lower than that of alkenes, which revealed that the β -scission is the main reaction. In contrast, the thermal degradation of PE (LDPE) shows a relatively higher content of saturated gases, which indicates that the probability of the B1 reaction (Figure 9) taking place may be higher in this case.

In another study by Jing et al, a mixture of LDPE:PP (60:40) was pyrolyzed using a semi-batch reactor under atmospheric pressure applying a microwave heater.^[190] They reported that high contents and selectivity towards olefins (50.65–68.64 mol%) were achieved in the process. Based on their findings, they proposed the reaction mechanism as follows: when the temperature has increased, C–C bond cleavage occurs to generate free radicals. The unstable free radicals undergo β -scission reactions to generate small molecules of olefins and new free radicals, or the free radicals can interconvert to tertiary or secondary free radicals via intramolecular hydrogen transfer to finally form α -olefins by β -scission reactions.

The high heat transfer between the steam and the hydrocarbons inhibited the secondary reaction, and the β -scission reactions became predominant to form *n*-alkenes and α -olefins. However, as reported by Undri and coworkers, the oil produced from HDPE pyrolyzed by microwave irradiation dominantly contained aliphatic hydrocarbons and a low content of aromatic compounds.^[191] Homolytic C–C bond cleavage in HDPE forms free radicals; then, aromatization can occur by radical rearrangement or through Diels-Alder reactions. GC-MS analysis showed

that linear alkanes ($>C_{12}$) chains were dominant, and a 1-alkene fraction was also observed. The Diels-Alder reactions of the olefins (dienes and dienophiles) also take place to form aromatic compounds from the LDPE and HDPE pyrolysis.^[192]

4.3. Polystyrene

Polystyrene (PS), made of styrene monomers, is an aromatic, non-biodegradable plastic, and it is thermally cracked into aromatic hydrocarbons due to its aromatic skeleton. It is resistant to heat and has high durability, strength, and is light in weight, making it appropriate for use in food packaging, electronics, construction, medical, appliances, and others.^[130] Pyrolysis of PS produces the monomer styrene as a major component.^[193] Other identified components were toluene, ethylbenzene, propenylbenzene, propynylbenzene, and naphthalene. Fast pyrolysis gave a yield of the monomer of 75% or better, with a total yield of aromatic liquids of 83–88%, and no char was produced.^[130] The thermal scission mechanism produces radical species which continue producing dimers through an intramolecular radical transfer reaction.^[188] The proposed depolymerization mechanism of ex situ catalytic pyrolysis of PS was investigated at elevated pyrolysis temperatures. The reaction is initiated by hydrogen abstraction from the polymer chain, which produces PS fragment radicals and ethylbenzene or phenyl radical. In the following, through hydrocracking and hydrogenation and makeup reactions, benzene, ethylbenzene and ethylene are produced (Figure 11). Therefore, the aliphatic hydrocarbons obtained during ex situ catalytic pyrolysis must arise from catalytic cracking. Styrene monomers could be de-alkylated in the catalyst bed reactor to produce benzene and ethylene.^[194–196]

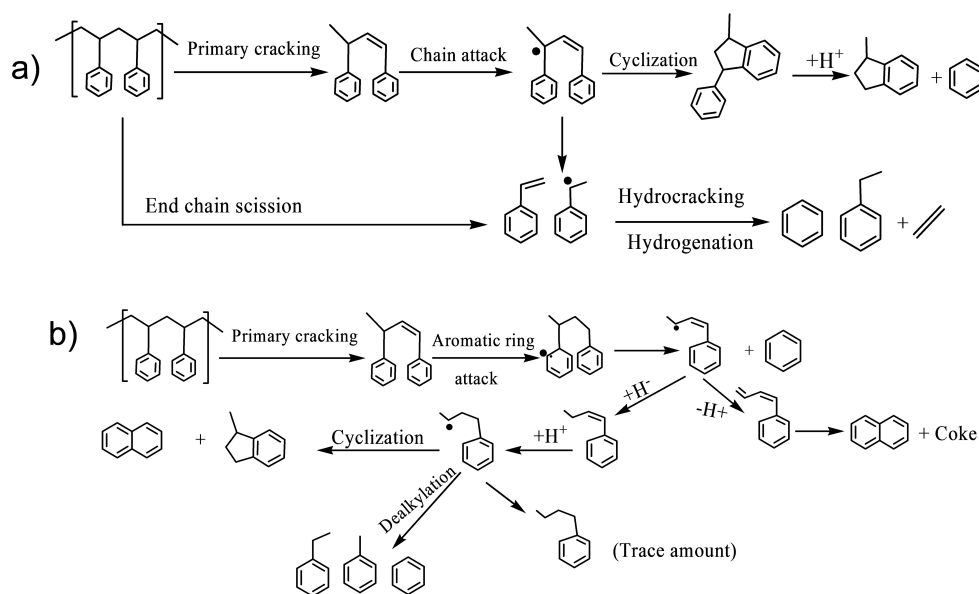


Figure 11. Proposed reaction mechanisms of PS during catalytic pyrolysis: (a) ex situ pyrolysis; (b) in situ pyrolysis. Reproduced with permission from Ref. [197]. Copyright 2017, Elsevier.

The monomer styrene is the major pyrolysis product of polystyrene, and α -methylstyrene and its dimer are other competing pyrolytic products. According to density functional theory (DFT) calculations, the bond dissociation energy (BDE) value of the C–C bond of the backbone are lower than that of the C–C_{aromatic} bonds in the branches. Furthermore, the isotactic and atactic structures are less stable than the syndiotactic form of PS. Therefore, the PS is first degraded into a methylene-end radical and a benzyl-end radical through homolytic bond cleavage with subsequent decomposition to styrene by the end-chain β -scission reaction. Alternatively, α -methylstyrene can be formed through mid-chain β -scission due to the 1,2-hydride transfer, or dimers can be formed through the mid-chain β -scission after 1,3-hydrogen transfer.^[198]

A study by Dewangga et al. confirmed that bentonite-catalyst-assisted pyrolysis of PS in a batch reactor at 400 °C and 25% catalyst load gives 88.7 wt% of liquid product, 32.24 wt% amounting to styrene.^[199] In another study, Hussain et al. also reported that thermal and clinker-catalyzed pyrolysis of PS in a batch reactor resulted in the production of a high yield of styrene.^[200] Using a Portland cement solid-base catalyst system, 94.98% conversion efficiency of polystyrene was achieved at 400 °C. In the thermal pyrolysis, the same conversion efficiency was observed at 600 °C. 42.14% (catalytic) and 63.17% (non-catalytic) of the produced oil, respectively, was styrene.

4.4. Polyethylene Terephthalate (PET)

PET is a thermoplastic polymer best known for its application in plastic bottles and containers. It is the dominant aromatic polyester produced; polybutylene terephthalate, polypentene terephthalate, and polyhexene terephthalate are of a minor, albeit as growing importance.^[167] Chemical recycling of PET on an industrial scale is not feasible due to harsh reaction conditions needed. However, chemical recycling conditions are improved by the addition of catalysts.^[201] PET, which contains oxygen and aromatic groups, is generally degraded by decarboxylation. The recombination of radicals leads to the formation of higher molecular weight products (benzene, toluene, naphthalene, and anthracene) and gaseous products (ethylene, propene, CO and CO₂) (Figures 12a and 12b).^[34] Grause et al. proposed a reaction mechanism for the ex situ pyrolysis of PET, starting with the hydrogen attached to C _{β} moving to the oxygen atom of the ester C=O bond as indicated in Figure 12a.^[202] The C _{β} –H and alkoxy C _{β} –O bonds are cleaved, and C _{α} =C _{β} and O–H bonds are formed consequently. The heterolytic bond cleavage of the alkoxy C _{α} –O bond leaves the C _{α} atom partially positively charged. Without using a catalyst, terephthalic acid and benzoic acid vinyl ester are the major products from the thermal cracking of PET. Terephthalic acid and acetophenone derived from this thermal depolymerization of PET could easily be converted into aromatic hydrocarbons during an ex situ catalytic pyrolysis with the help of HZSM-5 zeolite catalyst that has a strong de-oxygenation ability towards carboxylic and ketone groups.^[203,204] The carboxylic and ketone

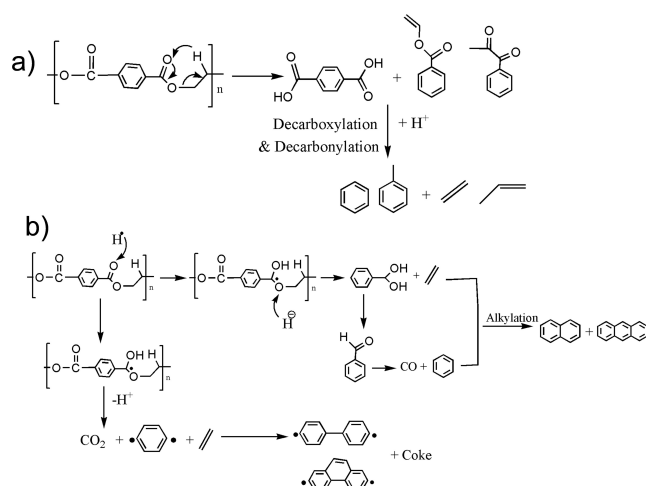


Figure 12. Proposed reaction mechanisms of PET during catalytic pyrolysis: (a) ex situ pyrolysis; (b) in situ pyrolysis. Reproduced with permission from Ref. [197]. Copyright 2017, Elsevier.

groups in terephthalic acid and acetophenone are removed in the form of CO₂ and CO during this process.

A recent study by Jia et al. reported catalytic fast pyrolysis using ZSM-5 zeolite and nickel chloride as catalysts.^[205] Thermal and catalytic fast pyrolysis was carried out using a horizontal tubular reactor under N₂ atmosphere. The wax products formed using the ZSM-5 showed low oxygen content, which indicates the deoxygenation process of PET by ZSM-5. They also proposed a decomposition pathways of PET (Figure 13): firstly, the hydrogen atom connected to C _{β} transfers to the oxygen atom located at the C=O bond. Then, scission of the alkoxy C _{α} –O and C _{β} –H bonds occurs, which results in the formation of C=C and O–H bonds. Both benzaldehyde and vinyl-containing products have been formed in both the thermal and catalytic pyrolysis process. The acid site of the zeolite catalyst contributed a proton to the C=O to form free benzene radicals and carbon oxides, which further transform to terephthalic acid and benzoic acid vinyl ester and other products (Figure 13).

Similarly, Du et al. studied the pyrolysis of PET to terephthalic acid and benzoic acid vinyl ester and other products using ZSM-5 and CaO catalysts.^[206] The catalysts enhance deoxygenation reactions. Pure benzene could be obtained from

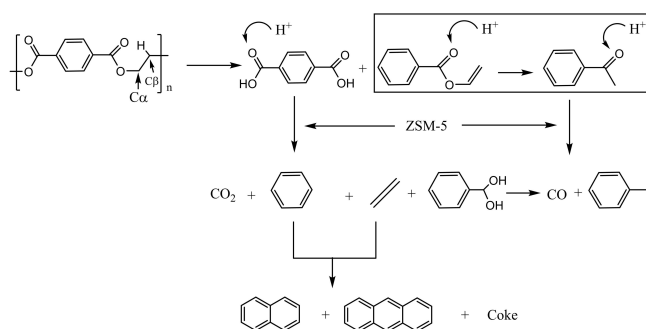


Figure 13. Possible decomposition pathways during PET pyrolysis. Reproduced with permission from Ref. [205]. Copyright 2020, MDPI.

slow heating in the absence of catalyst, while catalytic pyrolysis produced aromatic hydrocarbons.

The pyrolysis of PET using a CSBR has also been reported as a suitable process. However, defluidization, which is caused by agglomerates, has been reported using fluidized bed reactors. The main pyrolysis products of PET are gases, solids, and heavy oxygenated compounds.^[207]

4.5. Polycarbonate (PC)

PC is one of the most versatile engineered thermoplastic polymers and generally falls into two categories depending on it containing aliphatic or aromatics chains. The poly(bisphenol A carbonate) (PC) is among the most common aromatic-rich polymers and is used in a variety of optical and technical applications.^[208,209] PC is a rigid polymer of low polarity with excellent insulating properties which is also widely used in construction due to its excellent optical properties.^[210]

The pyrolysis of PC results in the formation of its monomers, basically bisphenol A (BPA), and a series of aromatic compounds of phenolic origin. Such phenolic compounds are generally very important as colorants, antioxidants in the food industry to increase shelf-life, and in medicine, specifically in protecting against several pathological disturbances, such as atherosclerosis, brain dysfunction, and cancer. Additionally, polyphenols may be used for the production of paint, paper, cosmetics, and in wood adhesive (resins) applications. Thus, PC degradation receives great interest.^[153,208,211,212] Gases such as carbon dioxide and methane and liquid fuels like toluene and benzene are also produced during the pyrolysis process.^[213] The decarboxylation reaction takes place at higher temperatures (> 500 °C). The scission reaction of the carbonate bond leads to PC decarboxylation, which results in the formation of phenol end polymers due to the higher activation energy of the scission reaction. Therefore, phenol and substituted phenols (4-methyl and 4-ethylphenol) are formed at elevated temperatures. The initial scission starts at the hydroxyl end, while CH₃ migration needs even more energy. However, no volatile products have been observed below 500 °C except for *p*-isopropylphenol and phenolic dimers (Bisphenol A). Thus, the decomposition reaction starts at the hydroxyl or phenyl chain ends. The *p*-isopropyl phenol product degrades early due to the homolytic fission at the isopropylidene group followed by H abstraction (Figure-14a and 14b).^[209]

PC has a high content of additives, and the pyrolysis results in the formation of a large volume of chars and gases, which are highly contaminated due to the additives. Therefore, hydrolysis of PC at a high temperature is applied to obtain high yields of BPA, phenol, and 4-isopropenylphenol.^[210]

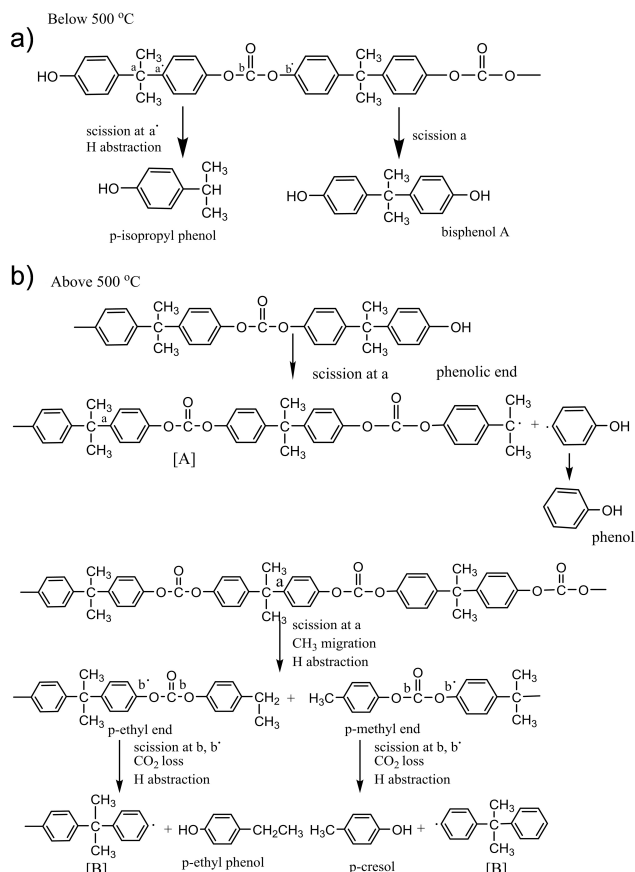


Figure 14. Suggested mechanistic steps for the pyrolysis of PC. Reproduced with permission from Ref. [209]. Copyright 2018, Elsevier.

5. Composition and Importance of Char and Gas Byproducts

5.1. Char Formation and its Application

Choosing the right reactor types and working parameters can improve the yield of oil and gas; however, carbon-rich residues called pyrolytic char are commonly left in the reactor. The amount of the chars is maximal at slow pyrolysis or low-temperature pyrolysis, slow heating rate, and long residence time. Pyrolysis of waste plastics such as PE and PP at high temperatures produces a very low amount of chars. For example, the pyrolysis of PE and PP at 668 °C and 746 °C produces 2–4 wt% and 0.7–2 wt% of char, respectively.^[82] The char byproduct is mainly composed of a carbon-rich matrix that contains almost all the inorganic compounds previously present in the raw waste plastics, which are generated from the additives and many condensed byproducts produced during the pyrolysis process dispersed throughout the solid porous structure.^[136] The char byproducts may be used as fuel for cookstoves by molding it into a briquette. Some chars produced from different plastic wastes are composed of inorganic matter that may, however, hinder their use as a fuel. Chars produced from HDPE waste by fast pyrolysis are composed of 42.62%, 3.06%, 0.43%, and 1.8%, of carbon, hydrogen, nitrogen, and

sulfur contents, respectively, with a calorific value of 4,500 cal g⁻¹. These chars have the potential to be used as road surfacing and as a building material, increase soil organic matter, as available mineral nutrients could be associated with the concentration and nature of dissolved organic compounds.^[82,214,215]

Additionally, well treated and upgraded chars are used as adsorbents in wastewater treatments for the removal of organic dyes and heavy metals. Some reports showed that the upgraded chars are meso- and macro-porous materials that have adsorption capacities for organic dyes like methyl blue in the range of 3.59–22.2 mg g⁻¹. Another potential application of the pyrolysis char is as a solid fuel in boilers and as a feedstock in the preparation of activated carbon.^[115,132]

5.2. Gas Formation and its Application

Pyrolysis of the waste plastics at higher temperatures and long residence times are the best conditions to maximize gas production in the process. These settings are contrary to the parameters used to maximize oil production. Overall, the amount of gases produced from the pyrolysis of polyolefins and PS plastics is quite low in the range of 5–20 wt%, and it strongly depends on the temperature, catalyst, and type of plastics used in the pyrolysis. The pyrolysis of PET and PVC plastics produced large volumes of gases in comparison to PE, PP, PS, and PC. The yield of the gas produced from the pyrolysis of PET (76.9 wt%) and PVC (87.7 wt%) waste plastics are much higher than the liquid yield at 500 °C. Since PET needs very little energy to be converted into other chemical structures, more gas can be produced. Conversely, for the pyrolysis of PVC, the dehydrochlorination step cause a high volume of gas to be released rather than the liquid product. The gas composition depends on the size and type of feedstock material, reactors and operating parameters.^[82,115,132]

The main gas compositions derived from HDPE, LDPE, PP, and PS are, principally, hydrocarbon gases such as methane (CH₄), ethylene (C₂H₄), and butadiene (C₄H₆), with trace amounts of propane (CH₃CH₂CH₃), propene (CH₃CH=CH₂), *n*-butane

(CH₃(CH₂)₂CH₃), and other miscellaneous hydrocarbons that can be used as a fuel gas due to their high calorific value (Table 8). On the other hand, pyrolysis of PC, PET, and PVC yields toxic gases such as CO₂, CO, and HCl in addition to the formation of hydrocarbon gases.^[216,217] The PVC pyrolysis releases hazardous gas and causes metal corrosion and other environmental impacts.^[204]

The gases obtained from the pyrolysis of PE and PP alone had a high calorific value between 42 and 50 MJ kg⁻¹. Thus, the pyrolysis gases have a high potential to be used as a heating source in industrial plants. Additionally, ethylene and propene gases may be used as a chemical feedstock to manufacture polyolefins if separated from other mixed gases. The gases can also be used in gas turbines to generate electricity and direct firing in boilers without further treatment.^[82,115,132,218] CO₂ and CO are produced from PET due to the oxygen present in its molecular structure (C₁₀H₈O₄)_n at an average concentration of 38.79%; the highest content of CO₂ from pyrolysis of PET was found to be 49.79%.^[219]

6. Conclusion and Future Prospects

The pervasive consumption of plastics paired with their long lifetime and the huge volumes in use causes environmental challenges. Various strategies are practiced to manage these disposals, such as recycling, landfilling, and incineration. Unfortunately, these strategies are not sufficient to effectively manage the plastic waste without releasing toxic chemicals. This unveils the importance of plastic recycling and innovative technologies to deal with this problematic surplus in an environmentally friendly manner. The pyrolysis technology is considered the best method and sustainable solution that may be economically profitable on a large scale, addressing environmental concerns regarding waste minimization, carbon sequestration, soil amendment, energy/heat supply, and value-added products. Pyrolysis technology is used to convert waste plastics into liquid oil (fuel) and other valuable byproducts such as char and gases under controlled conditions and is considered to be a relatively environmentally friendly technology when com-

Table 8. Gas composition of waste plastic pyrolysis.

Plastic	Reactor type	H ₂ [wt%]	CH ₄ [wt%]	C ₂ H ₆ [wt%]	C ₃ H ₄ [wt%]	C ₃ H ₈ [wt%]	C ₃ H ₆ [wt%]	C ₄ H ₁₀ [wt%]	C ₄ H ₈ [wt%]	CO ₂ [wt%]	CO [wt%]	HCl [wt%]	Ref.
HDPE	CSBR	0.00	0.14	0.05	0.62	0.9	7.19	0.87	4.82	–	–	–	[220,221]
HDPE	CSBR	–	0.03	0.07	0.08	0.08	0.50	0.18	0.57	–	–	–	[222]
LDPE	Fluidized bed	0.66	11.76	4.68	26.86	1.25	18.59	0.01	7.63	–	–	–	[223]
LDPE	–	0.02	0.03	0.00	0.003	0.003	0.65	1.76	–	2.90	0.00	–	[44]
LDPE	Semi batch	0.15	3.63	9.35	4.16	12.27	18.65	8.31	1.32	–	–	–	[171]
PVC	Fixed-bed	40.4	32.5	11.2	4.6	4.0	2.4	1.7	1.0	0	0	58.2	[136]
PVC	–	52.5	24.4	6.7	6.7	1.5	4.7	0.9	2.1	0	0	–	[219]
PP	–	0.01	0.04	0.11	0.05	0.1	2.73	0.23	1.29	0.64	0	–	[44]
PP	Semi batch	0.09	2.01	4.24	0.90	7.36	29.06	0.23	1.48	–	–	–	[171]
PS	–	0.0	27.4	0.0	25.0	22.5	0.0	0.0	25.1	0.0	0.0	–	[219]
PS	–	45.4	28.3	1.3	23.7	0.0	0.0	0.0	0.2	0.0	0.0	–	[219]
PET	–	12.7	7.5	0.3	4.4	0.0	0.0	0.00	0.1	33.0	41.2	–	[219]
PET	–	6.7	1.2	0.1	3.3	0.0	0.2	0.0	0.1	49.79	37.8	–	[219]
PC	Fixed-bed	0.16	2.48	–	–	–	–	–	–	11.93	3.53	–	[153]
PC	Fixed-bed	0.27	2.94	–	–	–	–	–	–	13.91	2.72	–	[153]

pared to uncontrolled incineration and landfilling practices. The pyrolysis products depend on several process parameters such as temperature, catalyst choice, heating rate, carrier gases, retention time, kind of plastics, reactor, and pressure. A yield of up to 80–90% of fuel oil by weight can be recovered from thermoplastic waste. The produced liquid oils are either gasoline or diesel fractions, which have comparative characteristics with commercial diesel or gasoline fuels. The gases recovered from the pyrolysis of waste plastics are mainly C₁–C₄ compounds for the polyolefins, and additional gases like CO, CO₂, and HCl are obtained from PC, PET, PVC. High temperature and retention time are the main limitations of the pyrolysis of plastic wastes that need to be optimized to make the process more economical and environmentally friendly. Pyrolysis chars can also be activated for use in the absorption of heavy metals, smoke, and odor, and as an input to other material productions.

Several catalysts have been studied to upgrade the quality of liquids obtained from the pyrolysis process. Specifically, exploration and utilization of naturally occurring and cheaper catalysts like natural zeolites require more research. Moreover, catalyst modification requires further attention to improve their performance to optimize the pyrolysis method. Nano-sized zeolite crystals should be investigated for their conversion efficiency and selectivity of fuels oils obtained from waste plastics. Integrating and combining catalysts to bimetallic, trimetallic, and other systems should also be studied for use in catalytic pyrolysis. Efforts should be made to lower the pyrolysis temperature in order to lower energy consumption, in addition to using the latest technologies such as plasma, microwave irradiation, and continuous systems to provide tunable and scalable pyrolysis procedures. Computer-based technologies and models, including such based on quantum mechanics, should be incorporated to investigate the detailed pyrolysis reaction mechanism of the polymers.

PP, PE, PS, and PC waste plastics are suitable for pyrolysis with a good yield of fuels, but PVC and PET are not suitable because of hazardous chlorinated gas escaping, at already a low temperature, from PVC and toxic heteroatom-containing gases produced from PET in addition to their low liquid yield. Therefore, more detailed studies are required to improve the products from these polymers, or other chemical or mechanical recycling methods should be applied for such types of plastics. Incorporating PET or PVC with biomasses during the pyrolysis process should be investigated for synergistic advantages.

Safety is one of the primary concerns during the construction and designing of the pyrolytic reactors. Therefore, reactors should be designed using standard codes so that they perform under high temperature and pressures without rupture. Finally, as municipal waste management is challenging in most urban environments and cities, responsible government should incorporate proper waste management systems in their policies.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: catalytic pyrolysis · depolymerization · fuel oil · pyrolysis · waste plastics

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