

## Pyrolysis technology for plastic waste recycling: A state-of-the-art review

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### ABSTRACT

Discarded plastics can be converted to various fuels and chemicals to generate positive economic value instead of polluting the environment. In the past few years, pyrolysis has attracted much attention in the industrial and scientific communities as a promising versatile platform to convert plastic waste into valuable resources. However, it is still difficult to fine-tune an efficient and selective pyrolysis process to narrow the product distribution for a feasible commercial production. Furthermore, traditional plastic-to-fuels technology looks like another expensive way to burn fossil fuels, making no contribution to the plastic circular economy. By learning from the developed plastic-to-fuels technology, achieving the conversion of plastic waste into naphtha or plastic monomers that can be used for new plastic manufacturing in a closed-loop way is a more promising resource recovery pathway. However, there is no comprehensive review so far about achieving plastic waste recycling/upcycling by pyrolysis. This article will provide a critical review about the recovery pathways of plastic pyrolysis based on the various products (fuels, naphtha, hydrogen, and light olefins). It will overview the recent advances regarding plastic pyrolysis process and reactor design, introduce various recovery pathways based on the pyrolysis process, summarize process optimization and catalyst development, discuss the present challenges for plastic pyrolysis, highlight the importance and significance of creating a plastics' circular economy, discuss the economic feasibility, the environmental impact, and outlook for future development for plastic pyrolysis. This review presents useful information to further develop and design an advanced pyrolysis process, with an improved efficiency, desirable product selectivity, and minimum environmental impacts. It is helpful to encourage more circular economy-oriented research aimed at converting waste plastics to naphtha and plastic monomers instead of simply producing fuels from the scientific communities of chemistry, energy, and the environment.

### 1. Introduction

Plastics are ubiquitous and have become an integral component of modern society. Growing annual demand for plastics has been observed in the last few decades, due to the ever-increasing dependency on these versatile materials used in a variety of ways, such as food packaging, hardware, electronics, and construction. This growing demand has been

accompanied by a huge amount of plastic solid waste (PSW), with 6300 Mt of PSW being generated by the end of 2015 and most of them accumulating in landfills or the natural environment (Fig. 1).

Global PSW pollution has led to serious environmental consequences both on land and in the oceans, because the PSW cannot easily be degraded in the natural environment, unlike biomass. The accompanying micro- and nano-plastic particles are threatening the ecosystem

**Abbreviations:** Psw, plastic solid waste; Voc, volatile organic compounds; Pcds, polychlorinated dibenzo-para-dioxins; Pcds, polychlorinated dibenzofurans; Pet, polyethylene terephthalate; Hdpe, high density polyethylene; Ldpe, low density polyethylene; Pe, polyethylene; Pvc, polyvinyl chloride; Pp, polypropylene; Ps, polystyrene; Pahs, polycyclic aromatic hydrocarbons; Csbr, conical spouted bed reactor; Sic, silicon carbide; (gc × gc-tofms), two-dimensional gas chromatography coupled with time-of-flight mass spectrometry; GC-MS, Gas Chromatography-Mass Spectrometer; FTIR, Fourier Transform Infrared Spectroscopy; NMR, Nuclear Magnetic Resonance; SEC, Size Exclusion Chromatography; PC, polycarbonate.

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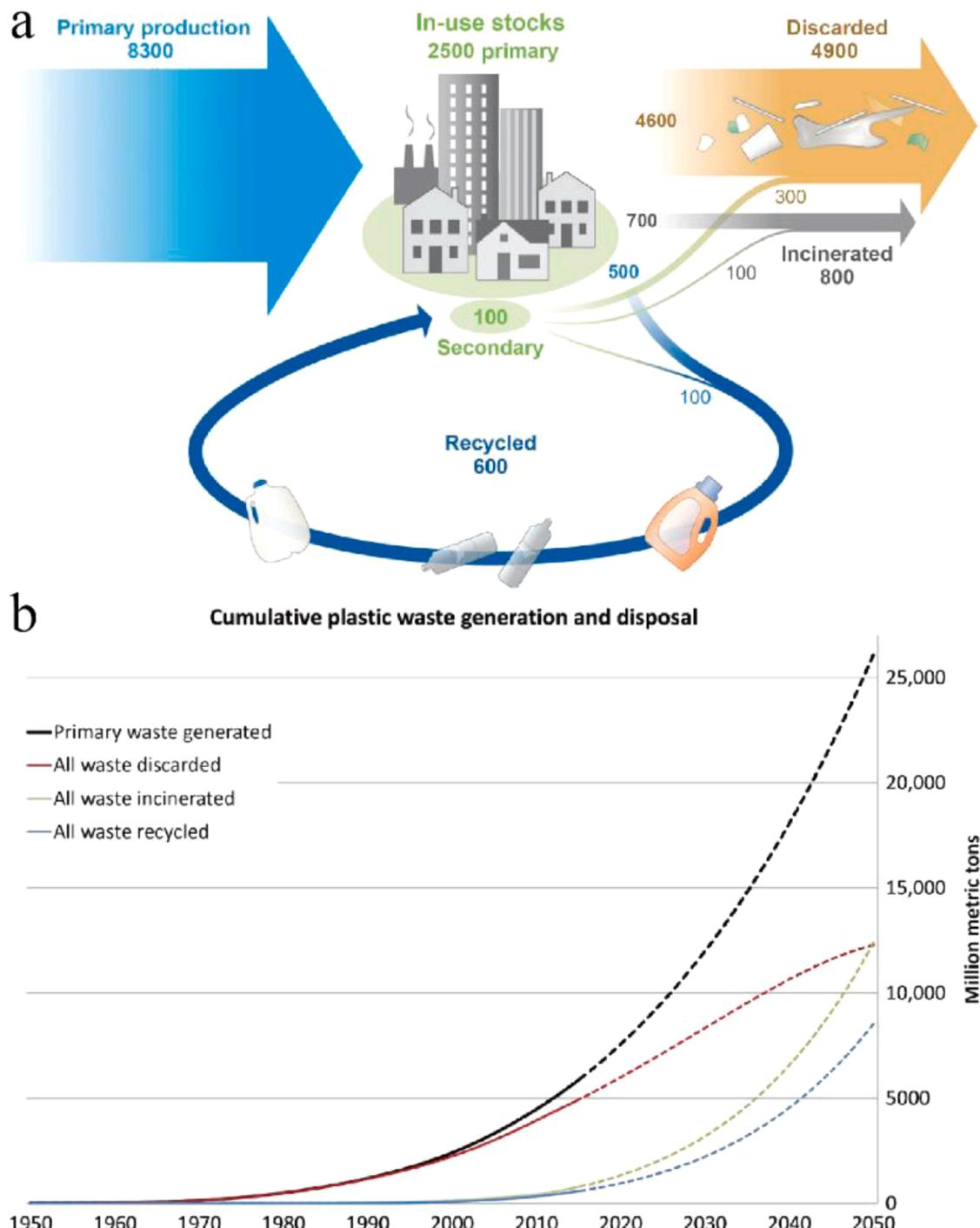
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and even human health [2,3]. Although this makes PSW disposal and management a matter of paramount importance, technological limitations pose a great constraint on the development of PSW recycling [4]. Without a bold shift in approach, PSW mismanagement may continue to worsen, thereby missing opportunities to harvest these valuable waste materials. Developing a systematic and “circular economy” manner to address PSW pollution and stop catastrophic ocean plastic pollution is imperative.

Up to date, primary, secondary, tertiary, and quaternary recycling methods for PSW have been developed, as shown in Fig. 2 [5]. Currently, primary and secondary recycling are widely applied, due to ease of

operation, which can probably obtain valuable products, but these methods can only be done with uncontaminated and single-use plastics and produce polymers which have inferior properties to virgin materials [6]. Serious contamination and a high variety in plastics in the waste stream also affect the product quality from mechanical recycling that dominates current recycling practices. Apart from mechanical recycling, current PSW recycling relies heavily on “quaternary” recycling which results in contamination of nearby landscape surfaces, as well as air pollution emissions such as volatile organic compounds (VOCs),  $\text{NO}_x$ ,  $\text{SO}_x$ , polychlorinated dibenzofurans (PCDFs), and dioxins [7]. A more promising recycling pathway, “tertiary” recycling, focuses on the



**Fig. 1.** Global primary plastics production, waste generation, recycling rate and disposal. **a.** Global production, use, and fate of plastics (in million metric tons) from 1950 to 2015. **b.** Cumulative plastic waste generation and disposal (in million metric tons). (Adapted from [1] with permission from Science).

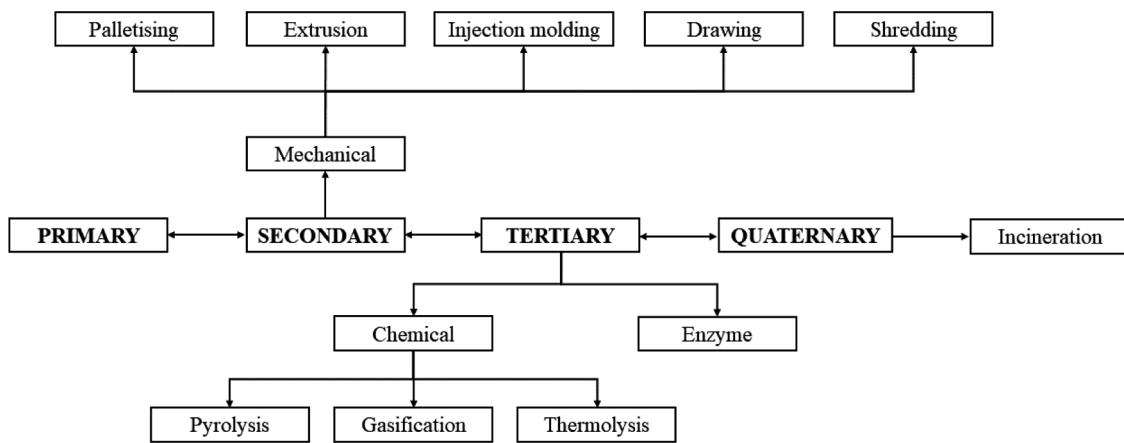


Fig. 2. Four main techniques of PSW recycling. (Adapted from [5] with permission from Elsevier).

**Table 1**  
Main features and characteristics of thermochemical techniques. (Adapted from [14]).

Process types	Incineration	Gasification	Hydrogenation	Pyrolysis
Definition and main objective	Excess burning of feedstock whilst recovering power and heat after steam generation. Air is used in abundance over stoichiometric as an oxidizing agent.	Defined as the treatment of PSW in oxygen deficient environment to produce fuel or synthesis gasses through gas reforming.	Treatment of PSW under high pressure with hydrogen media to produce high quality products, syncrude oil.	Pyrolysis is a thermal degradation in the presence of heat with a surrounding inert atmosphere, typical nitrogen or vacuum.
Main features	<ul style="list-style-type: none"> <li>Off gas is disposed with advanced electrostatic precipitators, fabric filters, scrubbers, etc. and then send back to stack.</li> <li>The most common technologies are fluidized bed combustion, moving grate, and rotary kiln.</li> <li>The produced bottom ash can be treated for recovering iron, steel, aluminum, copper, and zinc.</li> <li>Very low bottom ash, suitable for landfill.</li> </ul>	<ul style="list-style-type: none"> <li>Carbon in PSW is converted into syngas which comprises CO, H<sub>2</sub>, CH<sub>4</sub>, and light hydrocarbons.</li> <li>Residues including ash and slag can be used as construction materials.</li> <li>Scrubbing is conducted to remove particulates, hydrocarbons, etc.</li> <li>Syngas can be used for heat, energy, or electricity generation. Syngas can also be used to produce transportation fuels (e.g. Fischer-tropsch reaction, Methanol-to-Gasoline process, etc.).</li> </ul>	<ul style="list-style-type: none"> <li>Visbreaking is typically applied as a pretreatment process before hydrogenation.</li> <li>The process is still in research and development phases, requiring high cost catalysts.</li> </ul>	<ul style="list-style-type: none"> <li>The process maximizes degradation of PSW to liquid oil and gas.</li> <li>The main product, liquid oil, can be easily upgraded into transportation fuels.</li> </ul>
Main products	<ul style="list-style-type: none"> <li>High temperature flue gasses</li> <li>Energy in form of heat and power</li> </ul>	<ul style="list-style-type: none"> <li>Syngas (H<sub>2</sub> and CO)</li> <li>CO<sub>2</sub>, H<sub>2</sub>O, and methane</li> </ul>	<ul style="list-style-type: none"> <li>Syncrude</li> <li>Natural gas equivalent</li> </ul>	<ul style="list-style-type: none"> <li>CO, H<sub>2</sub>, and hydrocarbons</li> </ul>
Operating conditions	The process is operated generally under atmospheric pressure, with temperatures between 850 °C and 1200 °C.	The process is operated generally under atmospheric pressure, with temperatures between 850 °C and 1200 °C.	High pressures reaching 100 bars in some sections with reaction temperatures ranging from 350 °C to 490 °C.	Open vent pressure to slightly above atmospheric, with temperature ranging from 300 °C to 900 °C.
Main pollutants	Sulfur dioxide, nitrogen oxides, and dioxins	Tar, H <sub>2</sub> S, and HCl	HCl and residues	H <sub>2</sub> S, and HCl

depolymerization of PSW to produce fuels and chemicals that can be alternatives to petroleum-based products. Here, considerable research achievement has been accomplished, regarding the enzymatic degradation of plastics. But it was pointed out that the degradation capability of enzymes largely depends on the plastic types and given conditions [8]. Only a few plastic materials, such as polyethylene terephthalate (PET) and polyamides, can be enzymatically converted into oligomers or monomers due to the existing of hydrolysable bonds. Other common plastics which contain saturated carbon–carbon backbones cannot be broken down to desirable molecules.

Comparatively speaking, thermochemical conversion of PSW is a quite popular and promising choice for PSW recycling. Compared with biological recycling, thermochemical recycling is easier to scale up and able to treat unsorted and contaminated waste. Table 1 shows main features and characteristics of thermochemical techniques. Among thermochemical pathways, pyrolysis has gained more attention recently because it can achieve environmentally friendly conversion of PSW into highly valuable fuels and chemicals [9]. Compared to incineration and gasification, pyrolysis is carried out in the absence of oxygen so that

there would be less CO<sub>2</sub> emission and toxic pollutants can be minimized. Especially, polychlorinated dibenzo-para-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) can be mitigated largely in the pyrolytic conditions (lower than 600 °C and the absence of oxygen) [10–12]. Furthermore, pyrolysis shows specific advantages from the perspective of environmental management, operating costs, product value, and alternative energy production. Techno-economic analysis indicates that producing petroleum intermediates from PSW may have significant economic potential [13]. At this point, pyrolysis has been the focus of thermochemical recycling, and thermochemical recycling has always been at the center of PSW management when it comes to how to respond to the PSW pollution.

Current research about this topic mainly focuses on plastic pyrolysis parameters optimization, catalyst development, kinetic analysis, and reactor design, to improve product yield and selectivity [15–18]. Various catalysts, such as Al-SBA-15 [19], fly ash synthesized natural catalyst [20], zeolites (ZSM-5, Y, etc.) [15,21] and, pillared clays [22], have been developed and used to enhance the pyrolysis oil yield by reducing wax formation and obtain a potentially valuable fuels or

chemicals. Operating conditions, including the key pyrolysis temperature [23], residence time of vapors [24], and catalyst-to-reactant ratio [25], have been optimized to improve plastic-to-fuel feasibility. Typical types of reactors have been reported for plastic pyrolysis [24–26]. In terms of catalytic pyrolysis, in-situ catalysis mode and two-step system (pyrolysis-catalysis) are reported in the literature [27–29]. One challenge related to in-situ catalysis mode is that the impurities in the PSW could potentially deactivate the catalyst materials and the catalyst separation after reaction is much more tricky. In contrast, the pyrolysis-catalysis system is divided into two stages where plastic is decomposed to primary volatiles at around 500 °C, and then passes through a catalytic reforming bed at a given temperature. The advantages of two independent reactors in series are very clear, compared to the conventional one step pyrolysis/gasification process. First of all, controlling the pyrolysis temperature and reforming parameters can be addressed separately, allowing independent temperature optimization and injecting steam into the subsequent reforming reactor without affecting the pyrolysis process. Second, the catalyst is separated from the PSW pyrolysis reactor, effectively avoiding the mass and heat transfer issues posed by high plastic viscosity and making the catalyst recovery much easier. In addition, there is no contact between the reforming catalysts and PSW feedstock so that the impurities present in the PSW may no longer cause undesirable catalyst deactivation.

This review primarily introduces recent advances in converting plastics to fuels, naphtha, light olefins, and hydrogen by catalytic pyrolysis. A few review articles summarized plastic pyrolysis for fuels production in the past few years, including process parameter conditions [30], examples of plastic-to-fuel processes [9], reactor design [31], and chemistry [32]. Different from them, the scope of the article will be narrowed to focus on catalytic pyrolysis of plastics for selective

production of different valuable products and provide a state-of-the-art review of this area. Furthermore, the emerging plastic-to-naphtha and light olefins technologies that are able to contribute to the circular plastic economy will be highlighted considering that they can be used as the feedstock for new plastic manufacturing by utilizing the existing petroleum refining facilities. In addition, techno-economic and environmental considerations of PSW pyrolysis are discussed to encourage further study and investment. Overall, it will help researchers and industrial partners to fully understand what is going on for plastic pyrolysis and determine what else they can do or if plastic pyrolysis technique is worth the investment.

## 2. Conceptual design

### 2.1. Plastics

There are many different types of plastics available in the market as shown in Fig. 3. It is unfortunate that only PET, high density polyethylene (HDPE), and low density polyethylene (LDPE) have been routinely recycled, with a recovery rate not much higher than 5% [33]. Generally speaking, both proximate analysis and elemental analysis of various plastics are necessary to understand the pyrolysis process of plastics. Proximate and elemental analyses of different plastics are shown in Table 2. In terms of proximate analysis, volatile matter content plays a key role in determining the pyrolysis oil yield, where more volatile matter in a plastic lead to a higher pyrolysis oil yield. On the other hand, in order to obtain high quality petroleum-based products, carbon and hydrogen are the desirable components instead of oxygen or chlorine.

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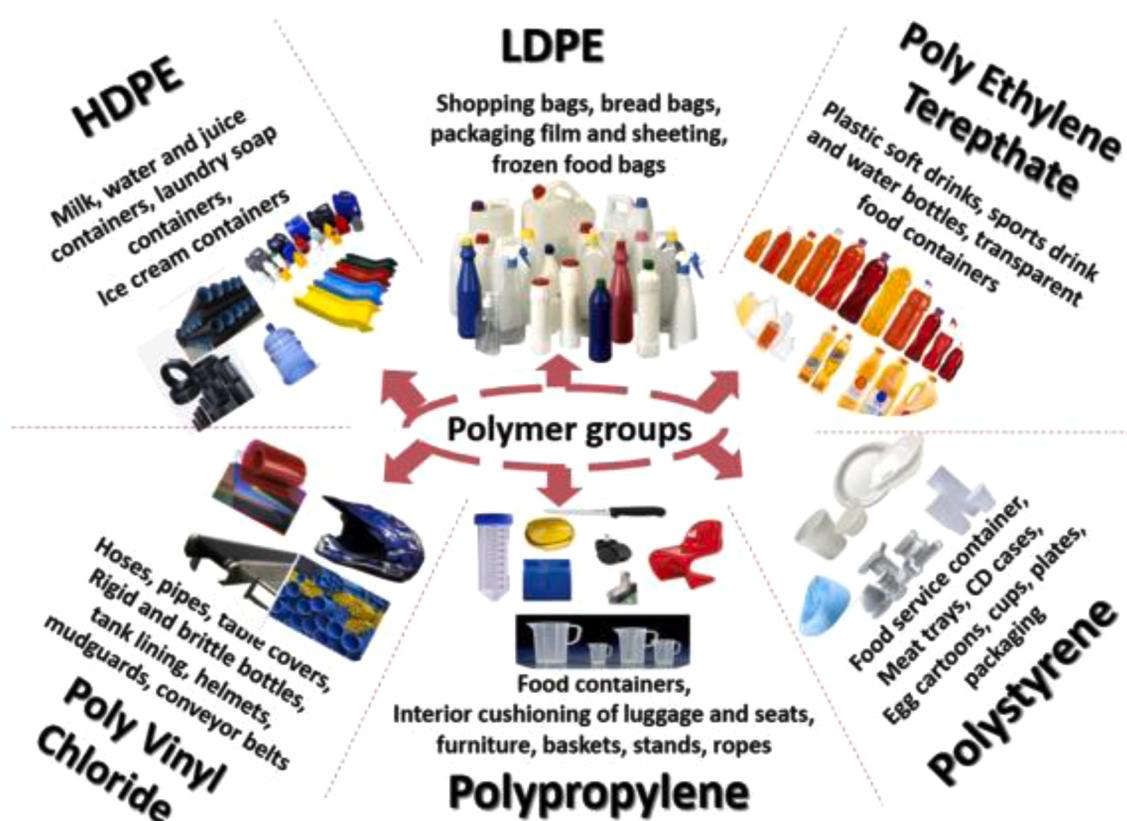


Fig. 3. Various commercial plastics and corresponding applications. (Reprinted from [34] with permission from Elsevier).

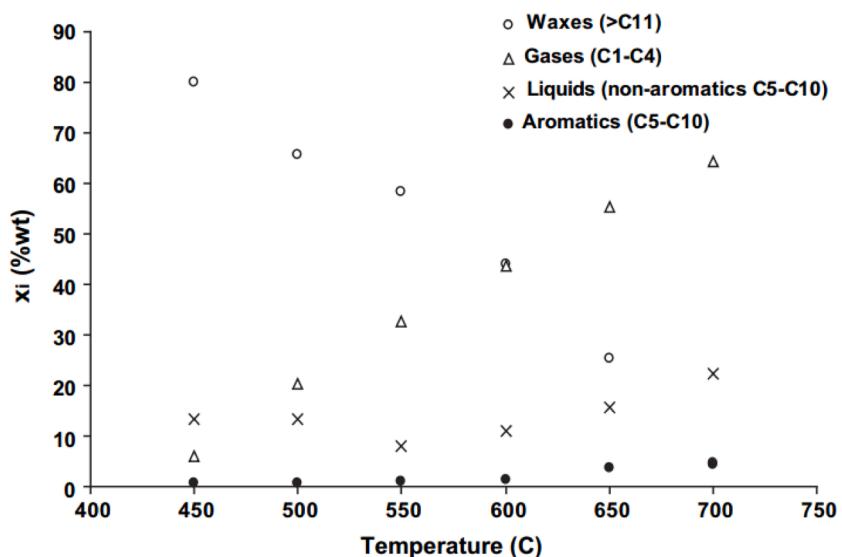
**Table 2**  
Properties of different plastics.

Plastics	SPI codes <sup>a</sup>	Chemical structure	Proximate analysis (wt.%)			Elemental analysis (wt.%)				Degradation temperature (°C)		Ref.
			FC <sup>b</sup>	VM <sup>c</sup>	Ash	C	H	O	Cl	T <sub>5%</sub> <sup>d</sup>	T <sub>max</sub> <sup>e</sup>	
PET	1		13.15	86.85	0	62.50	4.21	33.29	0	400	435	[35–37]
HDPE	2		0	100	0	85.50	14.50	0	0	415	460	[38,39]
PVC	3		2.77	97.23	0	38.40	4.90	0	56.70	270	290, 465	[31,40,41]
LDPE	4		0.02	99.98	0	85.40	14.60	0	0	375	460	[40,42,43]
PP	5		0.03	99.97	0	86.44	14.46	0	0	355	470	[40,44,45]
PS	6		0	99.80	0.20	93.63	6.36	0	0	400	435	[35,46,47]

<sup>a</sup> means codes defined by Society of the Plastics Industry.

<sup>b</sup> represents fixed carbon.

<sup>c</sup> represents volatile matter.



**Fig. 4.** Product distribution based on thermogravimetric analysis within the temperature range of 400–750 °C. (Reprinted from [6] with permission from Elsevier).

## 2.2. Pyrolysis technology

### 2.2.1. Mechanism for plastic pyrolysis

During plastic pyrolysis, long chain polymers are broken into smaller fractions, and the resulting oils and gasses are both highly valuable precursors of fuels and chemicals [9,48]. Without using any catalyst, pyrolysis of PP and PE at 500–600 °C mainly produces C<sub>20</sub>-hydrocarbons that are a solid wax product at room temperature [49]. At higher temperatures, more gas and oil products can be formed, which are composed of C<sub>1</sub>–C<sub>4</sub> olefin mixtures, C<sub>5</sub>–C<sub>20</sub> olefins and a small amount of aromatics, respectively [49]. For example, thermal cracking of PE produces a wide range of hydrocarbons that are primarily composed of gasses (C<sub>1</sub>–C<sub>4</sub>), C<sub>5</sub>–C<sub>10</sub> non-aromatic hydrocarbons, mono-aromatics, and waxes (>C<sub>11</sub>) (Fig. 4). Wax yield experiences a linear drop with the increasing temperature, while the gas yield

significantly increases. It appears that operating under higher temperatures may slightly facilitate the formation of aromatics. It is widely accepted that polyethylene pyrolysis can be illustrated by a free radical mechanism (initiation), which is followed by random scission and chain-end scission (secondary decomposition) and then recombination of different chains (termination), as shown in Fig. 5 [50,51]. Similarly, PS pyrolysis is also considered to proceed via type free radical reactions that include  $\beta$ -scission, hydrogen abstraction, hydrogen transfer, radical recombination, and disproportionation with the aromatic monomer, dimer, and trimer as the main products [52–54]. Aromatic monomers are mostly produced via unzipping reaction, where the terminal aromatic ring falls off due to the fracture of C–C linkage between two aromatic rings. It can be seen from Fig. 6 that intramolecular hydrogen transfer followed by  $\square$ -scission contributes to the generation of aromatic dimers. However, intermolecular hydrogen transfer followed by

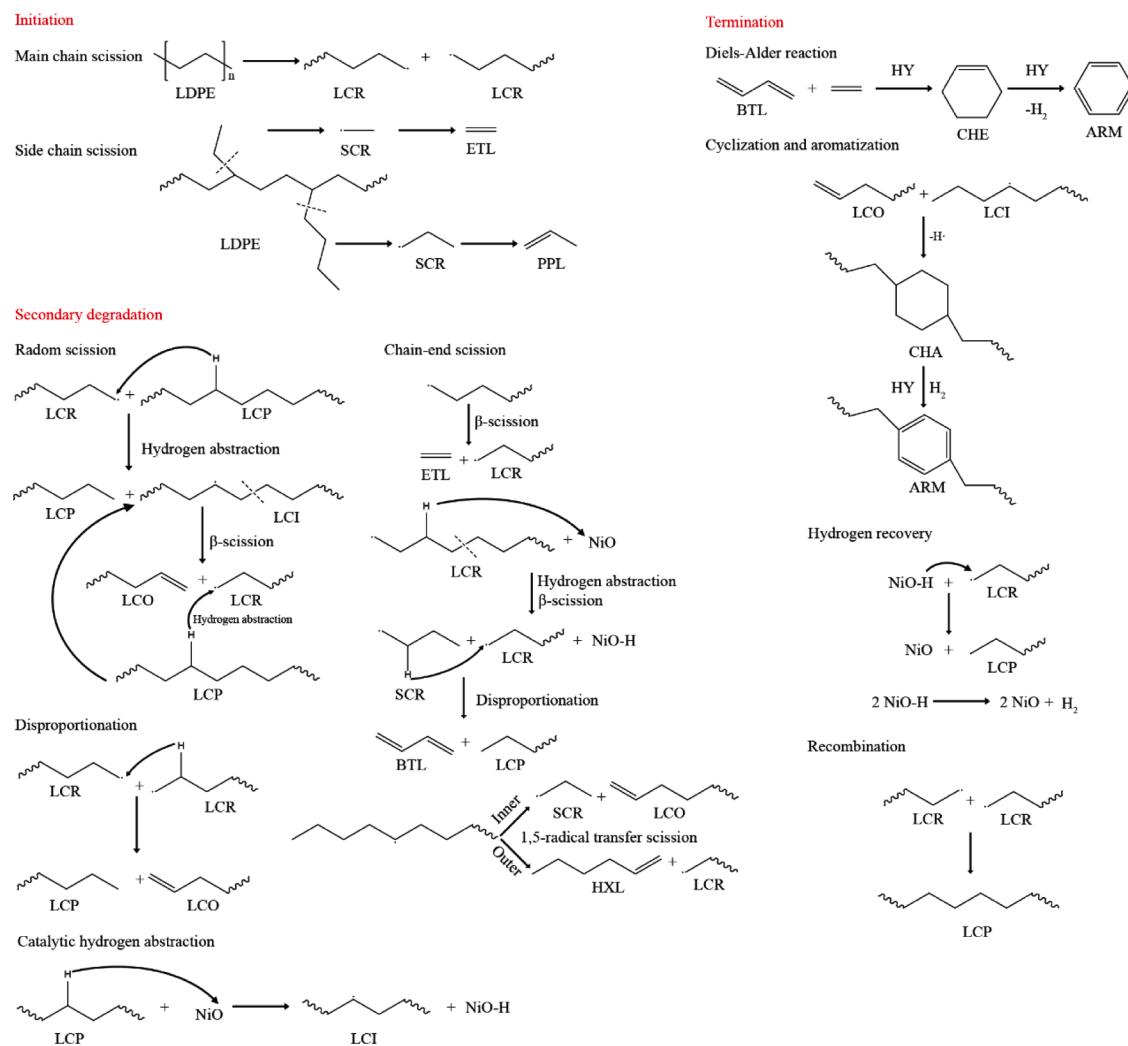


Fig. 5. Reaction mechanism of low-density polyethylene pyrolysis. (Adapted from [63] with permission from Elsevier).

$\square$ -scission gives a larger molecule containing three aromatic rings or more. On the other hand, aromatic dimers and trimers can be formed through monomer recombination or intermolecular benzyl radical addition followed by  $\square$ -scission [55,56]. However, PVC is totally different because PVC pyrolysis, without catalysts, can still obtain a high yield of liquid oil that consists of polycyclic aromatic hydrocarbons (PAHs) instead of wax [57]. It is widely accepted that poly vinyl chloride (PVC) pyrolysis can be recognized as a three-stage mechanism, including (1) dechlorination accompanied with inner cyclization; (2) aromatic chain scission; (3) release of 2–4 rings aromatics [57,58]. During the PET pyrolysis, the major thermal degradation pathway is considered to include  $\square$ -scission and retro-hydroalkoxylation, yielding benzoic acid and vinylic products, where the bridging glycol O – C bond can be cleaved and a  $\beta$ -H atom is transferred to the carbonyl O [59,60]. Furthermore, the ester groups will be released to produce a large amount of  $\text{CO}_2$ ,  $\text{CO}$ , and ethylene, in agreement with previously reported PET pyrolysis product distribution [61].

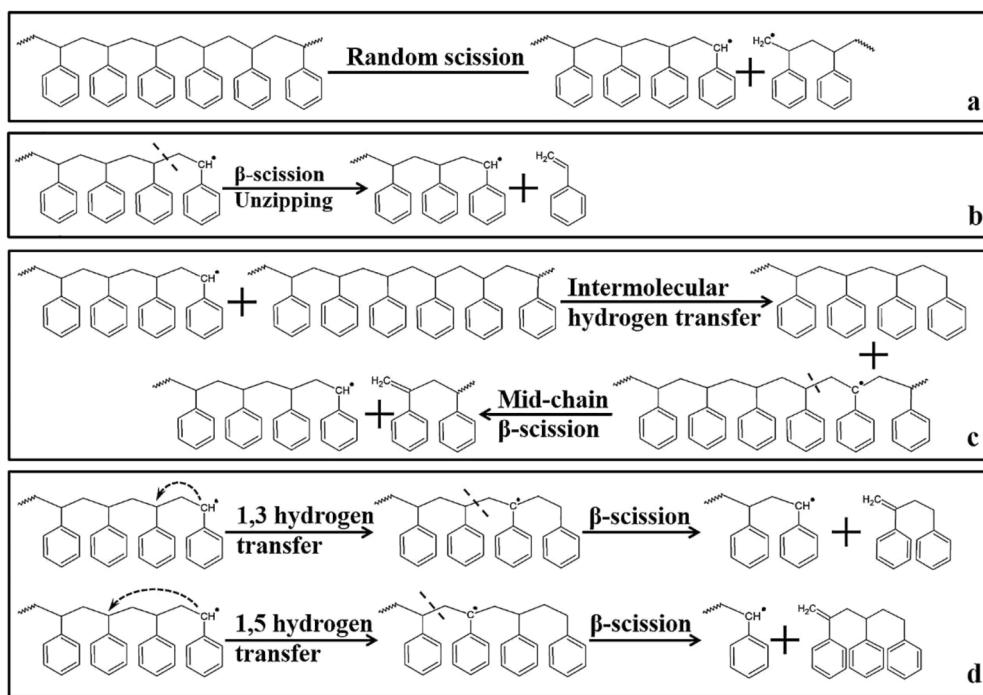
As we know, the activation energy of pyrolysis reactions will be lower if a catalyst is added, which is important for lowering energy consumption of pyrolysis by reducing reaction temperature and/or processing time. The catalyst can also facilitate the degradation of long chain polymers, and reduce or avoid wax formation [62]. In the above-mentioned polyethylene pyrolysis process, the presence of catalyst can effectively lower the required energy for cracking the C–C and the C–H bonds, thereby generating more carbonium ions [63].

Furthermore, an effective catalyst can improve the hydrocarbon distribution and selectivity, making it more suitable for upgrading to gasoline, diesel, and jet fuels.

### 2.2.2. Process and reactor design

Unlike some other solid wastes, plastics have some undesirable properties for pyrolysis, such as low thermal conductivity, sticky nature, low softening and melting temperatures. Generally speaking, in a pyrolysis process, a higher heating rate is favorable for liquid oil production, and minimizes the drawbacks of secondary reactions, which could cause the formation of more solid residues or gas products. In order to achieve the high heat transfer and avoid clogging issues easily occurring in pilot and industrial scale systems, advanced reactor designs need to be developed for pyrolyzing plastics based on the most important principle of improving the heat transfer during pyrolysis and enhancing the energy efficiency of this process.

A batch reactor can be used to easily implement a plastic pyrolysis, but a batch system can also cause some problems, such as poor heat transfer; non-continuous operations also pose a challenge for system scale-up [31,64]. Several reactor configurations have been proposed and developed to minimize heat transfer limitations and avoid common processing issues in the pyrolysis of waste plastics. The simplest approach to improve heat transfer efficiency is stirring which assures better thermal convection between the plastic feedstock and heat transfer surfaces [65]. Based on this principle, some improved designs



**Fig. 6.** Typical polystyrene pyrolysis reactions. (a) Random scission; (b) Unzipping reaction; (c) Intermolecular hydrogen transfer; (d) Intramolecular hydrogen transfer. (Reprinted from [53] with permission from Elsevier.)

have been developed, like the rotary kiln [66,67]. PSW samples are mainly heated by conduction from the reactor walls; additional heat carriers (such as metal or ceramic balls, or sand) also needs to be added to improve heat transfer inside the reactor. A helical screw plays an important role in this system, not only for conveying the PSW feedstock to the heating zone, but also evacuating any solid residue [68,69].

A fluidized bed reactor enables a pyrolysis process to be continuous, at high heating rates, and relatively short residence times, which have been widely applied in plastic pyrolysis [16,70,71]. Jung et al. [70] developed a lab scale fluidized bed reactor to pursue the high yield of aromatics at high pyrolysis temperatures (650–750 °C). The process proposed by Park et al. [16,71,72] was also used to produce aromatics from polyolefins without a catalyst, and the selectivity of aromatic hydrocarbons in the pyrolysis oil could be up to 92%. In order to effectively reduce the residence time and convert waste plastics to olefins with high yield, Milne et al. [73] designed an internally circulating fluidized bed and confirmed its effectiveness. In spite of the many advantages of fluidized bed reactors, defluidization problems caused by the agglomeration of the molten plastics and heat carriers need to be taken seriously. Once a well-fluidized bed loses fluidization partially or totally, the temperature gradient will be observed in the reactor and the contact of gas and solid particles will be affected significantly, both of which can lead to side reactions, lower product quality, and potentially reduce the process efficiency. Seville et al. [74,75] concluded that the defluidization can be attributed to an increased sintering rate and the tendency of particle to agglomerate at higher temperatures. Generally speaking, agglomeration and defluidization occurs more easily if “sticky” bed materials or feedstock are used or the feedstock contains alkali elements. It was experimentally found that the bed pressure decreased significantly due to the accumulation and growth of the agglomerates, thereby causing defluidization [76]. The inorganic compositions of feedstock were the significant influence on the bed agglomeration, and both the increase in bed particle size and temperature and the decrease of gas velocity and static bed height accelerated the defluidization. If the initial bed height is increased, the bed resistance will increase accordingly so that much more power input is needed for re-fluidizing the consolidated bed [77]. Considering that defluidization is caused by agglomeration of

bed materials coated with melted polymer, improving the contact between gas and solid phases is an effective to avoid the defluidization problems. In this regard, a conical spouted bed reactor (CSBR) combines the advantages of the spouted bed regime with those of the conical geometry to provide high heat and mass transfer coefficients between gas and solid phases, thereby avoiding the defluidization to some extent.

Another advantage of CSBR design over fluidized bed reactors is to lower the reactant residence time to about 20 ms, thus avoiding undesirable secondary reactions and alleviating coke formation [49,78]. As shown in Fig. 8, CSBR is divided into three regions, including the spout, annulus, and fountain. In order to achieve the spout status, the gas inlet diameter would be 20–30 times larger than the particle diameter, but the use of a draft tube can resolve this and affect other operation parameters, such as spouting velocity, pressure drop, gas distribution, etc. [79,80]. The design of CSBR has been further developed for PSW pyrolysis applications in the past decades. Research headed by Olazar investigated the pyrolysis of different waste plastics, confirming CSBR's suitability for PSW processing, in terms of its hydrodynamic behavior and versatility [49,61,81,82]. In the flash pyrolysis of polystyrene for monomer recovery, bed temperature and gas flow rate in the CSBR significantly affected the styrene yield, within the range from 50.8 wt.% to 70.6 wt.% [82]. The extremely vigorous mixing regime of particles inside the CSBR enables catalysts to be easily and effectively utilized in the in-situ catalytic pyrolysis of PSW. In the catalytic pyrolysis of polyolefins over HZSM-5, the resulting pyrolysis oil was composed of 60 wt.% C<sub>2</sub>–C<sub>4</sub> olefins, 10 wt.% single-ring aromatics, 15 wt.% nonaromatic C<sub>5</sub>–C<sub>11</sub> hydrocarbons, and 14 wt.% C<sub>4</sub> alkanes [83]. It was pointed out that polymer melting and catalyst coating with the melted polymer can be facilitated in a CSBR, and the high heat and mass transfer rates shortened the residence time of pyrolysis vapors to generate more primary pyrolysis products by minimizing any secondary reactions [84].

Dielectric heating enables microwave irradiation to be a fast and selective heating method, which has been widely applied in solid waste pyrolysis [85–87]. Unlike the conventional pyrolysis process, in this alternative approach, microwave-absorbing materials are preferentially heated without initially increasing the temperature of the surrounding pieces of the HDPE because plastics are transparent to microwave

irradiation. It has been found that microwave-assisted pyrolysis is able to significantly minimize side reactions, compared to conventional pyrolysis of plastic, and thereby more effectively control product distribution [88]. A few studies have also confirmed the application potential in plastic pyrolysis [87,89]. Fig. 8 shows a typical microwave-assisted pyrolysis reactor which was developed by Ruan's group [90]. Relevant process operations, optimization, and improvements have been reported [90–93]. One advantage for this microwave pyrolysis reactor is that plastic feedstock is heated by heat conduction from the high temperature SiC balls which are stirred by a shaft, effectively increasing the heat transfer efficiency and achieving fast pyrolysis. Based on a 200 kg/day lab-scale continuous microwave pyrolysis system, Ruan's group has shown that pyrolysis of 1 kg HDPE chips consumed a total of 5 MJ electrical energy [94]. At this time (2021) a California company has achieved a processing capacity of up to 1 ton/day of PSW via this microwave pyrolysis system, for recovery of fuels and naphtha from waste plastics, and has demonstrated the potential for commercial application.

Several other up-to-date plastic pyrolysis reactor designs have also been studied, to improve the pyrolysis process, and product yield and quality, such as: (a) the molten salt pyrolysis reactor, and (b) thermal plasma pyrolysis reactor. The advantages and disadvantages of these plastic pyrolysis reactors are summarized in Table 3 and different pyrolysis reactors are shown in Fig. 7.

### 2.3. Plastic pyrolysis oil characterization

Research and development of plastic pyrolysis in recent years mainly focus on maximizing the selectivity and yield of target products by innovative catalyst design, optimizing the operating conditions and reactor configurations. The most important thing is to characterize the obtained liquid product. By a detailed chemical characterization of bio-oil, it would increase the knowledge of the chemical composition of liquid product, which is necessary to optimize the process and determine its potential uses. Although progress has been made to analyze the liquid product, limited information has been obtained from traditional tools due to the large number of various compounds and coelutions in the oil. Therefore, research focus needs to be shifted to developing a systematic and comprehensive strategy to characterize the liquid product with the help of advanced instrumentation. The current pyrolysis oil characterization techniques are shown in Table 4 and the corresponding advantages and disadvantages are also listed Table 4.

The chemical profile of PSW derived oils can determine if the liquid oil can be used as gasoline, diesel, other fuels, or as chemicals. For example, with the goal of producing naphtha as a potential feedstock for virgin plastic production, more C<sub>5</sub>–C<sub>12</sub> paraffins and less aromatics are desirable in naphtha [109]. Branched hydrocarbons are essential components to improve the physical properties, such as low melting point and pour point, for using as transportation fuels [110]. The chemical composition of the liquid oil is usually characterized by the gas

**Table 3**  
Advantages, disadvantages, and real practices of various PSW pyrolysis reactors.

Reactor types	Advantages	Disadvantages	Real practice	References
Batch reactor	Simple construction and operation; Low investment	Low processing capacity; Long residence time; Low heat transfer rate	Operating condition: 3.5 L batch reactor, 100 g plastic mixture, pyrolysis temperature of 500 °C, Reaction time of 30 min Result: 65.2 wt.% of liquid yield with 69.7 of monoaromatics; a positive energy balance (+700 kJ/kg)	[24,95,96]
Screw kiln reactor	Uniform heat transfer; Controllable residence time; Simple separation of solid residue	Plugging risk; Possible heat transfer difficulties at large scales; Poor mixing at radial direction	Operating condition: the reactor size of a 26.5 mm diameter and a 500 mm length, pyrolysis temperature of 500 °C, 300 g plastic mixture/h, residence time of 15 s Result: 5.5 wt.% liquid oil and 93.2 wt.% of wax	[97,98]
Fluidized bed reactor	High heat and mass transfer rate; Scale up; Good mixing; Good control of operation parameters	Defluidization problems; High carrier gas rate; Required particle size; High investment	Operating condition: the reactor size of a 710 mm high cylinder with 58 mm of internal diameter, pyrolysis temperature of 500 °C, 2 g HDPE in total, residence time of 1.3–1.7 s Results: 40.9 wt.% of liquids (mainly composed of C <sub>10</sub> –C <sub>40</sub> linear paraffins almost without aromatics), 7.4 wt.% of wax	[16, 99–101]
Conical spouted bed reactor	Extremely short residence time; High heat transfer rate; Good mixing; Good control of operation parameters	Scale up; Bed material particle size limitation; Catalyst circulation	Operating condition: 30 g of sands, LDPE flowrate of 60 g/h; residence time of around 12 s; pyrolysis temperature of 500 °C Result: 69 wt.% of wax with the M <sub>w</sub> of 1534 Da; HHV of 35.55 MJ/kg	[26,31,78, 82]
Microwave-assisted pyrolysis reactor	Fast, selective, and volumetric heating; Easy design and operation; Convenient start-up and shutdown	Heating dependence on waste dielectric properties; The limited processing capacity due to the finite microwave penetration depth	Operating condition: 6 kg of silicon carbide balls used as the microwave absorbents, HDPE feeding rate of 2 kg/h; residence time of around 90 s; pyrolysis temperature of 500 °C Result: 33 wt.% of liquid oil (mainly composed of C <sub>6</sub> –C <sub>26</sub> n-alkanes/alkenes), 41 wt.% of wax; if a ZSM-5 catalyst is used, pyrolyzing 1 kg of HDPE requires 5 MJ electrical energy, giving a 89.6% energy efficiency. Furthermore, 6.1 MJ of electrical energy potentially produced from gas product enables this process to be energy self-sufficient.	[31,94, 102–104]
Molten salt pyrolysis reactor	High heating transfer rate; No limitation on particle size	Scale up; High operation cost	Operating condition: 13 kg of the tin and lead alloy used as the molten metal bed, 300 g of HDPE, pyrolysis temperature of 419–428 °C Result: 93.31 of liquid oil (48.8–52.1% of C <sub>4</sub> –C <sub>10</sub> , 30.9–33.6% of C <sub>11</sub> –C <sub>16</sub> , 16.9–17.9% of C <sub>17</sub> –C <sub>24</sub> almost without aromatics)	[31,105, 106]
Plasma pyrolysis reactor	High heating transfer rate; Low investment; Ultra-fast reaction velocity	Extremely high voltage; Scale up	Operating condition: 270 W direct current thermal plasma, residence time of 30 min, pyrolysis temperature of 500 °C, pressure = −0.95 bar, 15 g LDPE sample Result: 75.6 wt.% of liquid yield with aromatic monomers and dimers as the main products	[107,108]

chromatography (GC)-flame ionization detection (FID) or Gas Chromatography-Mass Spectrometer (GC-MS) analysis. Baena-González et al. [111] analyzed the composition of plastic waste pyrolysis oils by GC-MS, and intended to recover bitumen, solvents, and styrene by combining distillation and/or liquid-liquid extraction processing steps, as needed. As evaluated by GC-MS, the chemical compositions of PSW derived liquid oils vary, depending on the chemical structure of the beginning plastics. PS pyrolysis only obtained 79.5% of mono-aromatics and 11.5% di-aromatics, while the styrene content was as high as 53.5% [67]. More complicated compound mixtures were generated from polyolefin plastics pyrolysis. The liquid oil from PE pyrolysis contained 55.5% aromatic, and 43.1% aliphatic compounds, while PP pyrolysis obtained 52.9% aromatic and 44.7% aliphatic compounds [67].

However, common GC-MS technique is only able to analyze some of components in pyrolysis oil due to the insufficient resolution and the difficulty in detecting structural isomers. In this regard, two-dimensional gas chromatography (GC  $\times$  GC) coupled with time-of-flight mass spectrometry (TOF-MS) (GC  $\times$  GC-TOFMS) that uses a non-polar column to separate compounds with similar chemical structures first and a polar column for the second dimension could be one of the most attractive options. Fan et al. [112] found more than 5100 compounds in characterizing the bio-oil produced from sewage sludge pyrolysis using GC  $\times$  GC-TOFMS, which is about 10 times as many as those identified by GC-MS. Tessarolo et al. [113] studied the detailed chemical compositions of bio-oil by GC-MS and GC  $\times$  GC-TOFMS with the hope of allowing the improved usage of this attractive renewable energy source in bio-fuels. Results showed that several coelutions present in the GC-MS can be resolved by GC  $\times$  GC-TOFMS and the number of compounds identified by GC  $\times$  GC-TOFMS was much higher. Although GC  $\times$  GC-TOFMS analysis of bio-oil in biomass pyrolysis has been developed, its application in analyzing plastic pyrolysis oil is lacking.

In order to further acquire the heavy hydrocarbons distribution that can not be calibrated by GC-FID/MS and information for distinguishing hydrocarbons in the liquid oil with the extremely similar structure, Fourier Transform Infrared Spectroscopy (FTIR), Nuclear Magnetic Resonance (NMR), elemental analysis, and Size Exclusion Chromatography (SEC) can be also applied. From  $^1\text{H}$  NMR spectra, protons attached to alkanes, olefins, and aromatics can be determined, and the percentages of different chemical groups can be obtained, by integrating the  $^1\text{H}$  NMR spectra [114]. Chemical shifts, which are indicative of the functionalities of alkenes and alkanes are 4.5–6.5 ppm and 0.5–2.7 ppm, respectively. The FTIR spectral analysis can also obtain similar results to NMR. C–H stretching vibrations of the chemical functional groups  $-\text{CH}_3$ ,  $-\text{CH}_2$ , and  $-\text{CH}$  appeared at 2800–3000  $\text{cm}^{-1}$  and C=C stretching vibrations were observed at approximately 1640–1650  $\text{cm}^{-1}$ , indicating the presence of olefins. If aromatics also existed, a peak at 3000–3100  $\text{cm}^{-1}$  would appear. SEC analysis is able to acquire the molecular weight distribution information of the plastic pyrolysis oil. On average, the molecular weight of an oil fraction with a lower boiling temperature, is lower than that of a higher boiling temperature.

Currently, the most common tool used for pyrolysis oil characterization is GC-FID/MS that can provide the detailed chemical compositions and the relative contents [19,115]. Considering that GC inlet temperature and oven temperature is usually around 280  $^{\circ}\text{C}$ , the heavy hydrocarbons with high boiling point can not be detected by GC/GC-MS. Despite of this, heavy hydrocarbons have small solubility in  $\text{CH}_2\text{Cl}_2$  that is usually used as a solvent for GC analysis so that the information about larger fractions may not be obtained accurately [110]. This could limit the understanding for the pyrolysis oil by only GC/GC-MS analysis. Based on our knowledge, a PSW pyrolysis oil sample should be distilled into naphtha-range hydrocarbons (the boiling temperature  $< 170$   $^{\circ}\text{C}$ ), kerosene-range hydrocarbons (170  $^{\circ}\text{C} <$  the boiling temperature  $< 280$   $^{\circ}\text{C}$ ), diesel-range hydrocarbons (280  $^{\circ}\text{C} <$  the boiling temperature  $< 400$   $^{\circ}\text{C}$ ), and wax (the boiling temperature  $> 400$   $^{\circ}\text{C}$ ) fractions first. The relative yields of different range hydrocarbons

can be determined by simulated distillation. For those naphtha-range and kerosene-range hydrocarbons, GC-FID/MS can play a key role in analyzing the chemical compositions and determining the corresponding carbon yield. With regard to heavier compounds, FTIR, NMR, and SEC can be effectively combined to analyze the corresponding chemical properties.

### 3. PSW pyrolysis for recovery of fuels or chemicals

Since mechanical recycling of PSW is hampered by high pre-sorting requirements and decreasing product quality in each cycle, chemical recycling can tackle these challenges and has attracted much interest from scientific and industrial communities. Research and development on chemical recycling of PSW, especially pyrolysis, seem to have made significant progress. The use of pyrolysis to recycle highly valuable products from PSW around the world shows a great potential. Especially, transforming PSW to pyrolysis oil at an industrial scale, which can be fed into the current petrochemical production network as a raw material and reduce the input of fossil resources, shows higher market attractiveness. By feeding the PSW derived pyrolysis oils into the current petrochemical production network to manufacture virgin plastic products, the loop for plastic re-use can be partially closed. In this regard, chemically recycled plastics can lead to lower  $\text{CO}_2$  emissions, compared to using fresh fossil resources for plastics production.

#### 3.1. Fuels production from pyrolysis of psw

Pyrolysis of PSW to produce valuable liquid fuels suitable for transportation, is an effective pathway to optimize the PSW management towards zero landfilling, and minimize the carbon footprint of the transportation industry [116]. Commercial PSW pyrolysis plants have been built in recent years, showing the feasibility of producing transportation fuels from PSW at an industry scale. For example, a pyrolysis plant with the capacity of 5–7 tons/day PSW was designed and commissioned in South East Asia in 2014, with the aim to eliminate the PSW already in the landfill [116]. In this system, the oil yield was approximately 65 wt.% and it was demonstrated to be distilled into 27% gasoline and 70% diesel. Another batch-operated rotary kiln with a volume of 35  $\text{m}^3$  was assembled with a total processing capacity of 14 tons/day of PSW in Eastern Europe in 2015 [116]. According to the report, the top priority for successfully commercializing the product is to mitigate wax formation by using suitable catalysts, and optimizing the process. But its throughput is limited by the batch operating mode, which prevents the catalyst from working at optimized conditions. Although the produced fuel is unable to meet transportation standards, it can, at least, be used as a fossil fuel substitute. Many observations have verified that production of liquid fuels from PSW via pyrolysis is promising and commercially viable. In this regard, a great number of studies have been conducted to develop new catalysts suitable for different fuels production, and improve the pyrolysis process.

##### 3.1.1. Effects of temperature and residence time

Temperature is definitely one of the most important pyrolysis parameters for controlling the cracking reaction of PSW, since the cracking of PSW is largely dependent on the temperature ranges they are exposed to. One study indicated that 99.4 wt.% decomposition can result for a plastic mixture at 500  $^{\circ}\text{C}$  [117]. Increasing the pyrolysis temperature will promote the cracking of PSW, which in turn generates more gas and gradually eliminates wax in the products. When HDPE pyrolysis was performed in a fluidized bed reactor at 650–850  $^{\circ}\text{C}$ , the yield of the liquid (mainly composed of aliphatic hydrocarbons) was highest at 640  $^{\circ}\text{C}$  (79.7 wt%), whereas only 9.6 wt% of liquid product (high aromatic hydrocarbons) with high yields of gaseous products (86.4 wt%) was obtained at 780  $^{\circ}\text{C}$  [23]. Gracida-Alvarez et al. studied the effect of temperature on HDPE pyrolysis, and found that higher temperature was favorable for the formation of aromatics and light aliphatics and

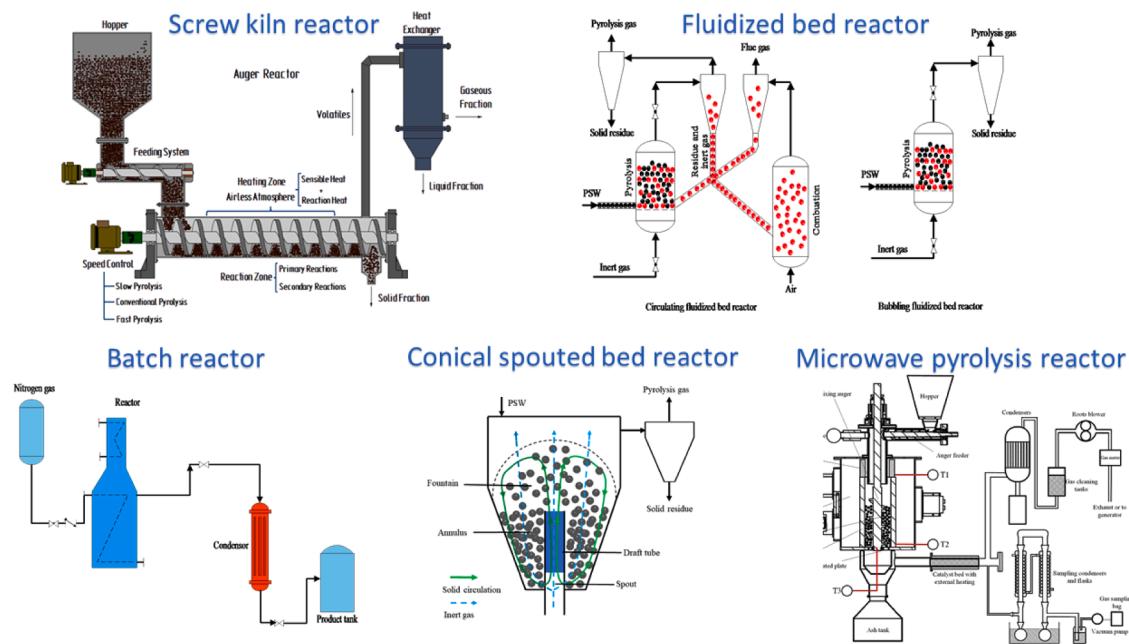


Fig. 7. Scheme of the pyrolysis process in different reactors. (Adapted from [94,97] with permission from Elsevier).

Table 4

Advantages and disadvantages of methods for plastic pyrolysis oil characterization.

Methods	Advantages	Disadvantages
GC-FID/MS	Understanding the detailed chemical compositions	Limited inlet and column temperature; Different solubility of long chain hydrocarbons in solvents
GC × GC-TOFMS	Higher resolution in the chemical compositions in the oil	Limited inlet and column temperature; Different solubility of hydrocarbons in solvents
FTIR	Obtaining chemical groups information; No requirement for oil vaporization	No information for detailed chemical compositions
NMR	Obtaining chemical groups information; No requirement for oil vaporization	No information for detailed chemical compositions
SEC	Obtaining the molecular weight distribution information; No requirement for oil vaporization	No information for chemical compositions/groups
Thermogravimetric analysis	Obtaining boiling temperature range	No information for chemical compositions/groups
Distillation, combined technologies	Accurate chemical profiles for naphtha, kerosene, diesel, and wax	High cost; Time-consuming

facilitated the degradation to diesel range aliphatics and wax [118]. In a small pilot scale batch pyrolysis reactor, increasing the pyrolysis temperature from 400 °C to 450 °C can obtain about 4% increase in oil yield, while further temperature increases could cause a decrease in oil yield [119]. It was also found that the increase of pyrolysis temperature enhanced the concentration of H<sub>2</sub> in the gas product, however, there was no effect on the formation of CO or CO<sub>2</sub> [120].

For a two-step pyrolysis-catalysis process, catalytic temperature also plays a vital role in product yield and selectivity. It is indispensable for driving the catalytic reaction to provide suitable catalytic temperature. Zhang et al.'s [121] results indicated that a higher catalytic temperature

decreased the liquid yield due to the facilitated cracking of the pyrolysis vapors toward non-condensable gasses during catalytic pyrolysis of plastic over an activated carbon catalyst. When the catalytic temperature was increased from 430 to 571 °C, approximately 20% higher selectivity of C<sub>8</sub>–C<sub>16</sub> linear alkanes was obtained, and mono-ring aromatics production also responded with a gradual increase. More gasses (mainly C<sub>1</sub>–C<sub>4</sub> hydrocarbons) were also obtained in the ex-situ catalytic reforming of plastic pyrolysis vapors, as the catalyst bed temperature increased from 500 to 600 °C [122]. This finding indicated that the catalytic temperature changed the liquid oil compositions more effectively than the catalyst type.

Residence time defined for steady-state pyrolysis system is a measure of the average time plastic feedstock spends in the pyrolysis reactor and can be calculated by considering the total gas flow in the reactor and the internal volume of the reactor. It is found to show very similar effects on the PSW pyrolysis to reaction temperatures. Generally speaking, the longer residence time could result in the over-cracking of PSW and increase the chances for secondary reactions (further cracking, isomerization, aromatization, alkylation, and hydrogenation/dehydrogenation reactions, etc.), obtaining higher yield of gas product. Mastral et al. [23] studied effect of residence time on HDPE pyrolysis and observed that the longer residence times provided enhanced yields of gaseous products. In addition, longer residence time is favorable for the evolution of aromatics [118]. More specifically, when pyrolyzing HDPE at a two-stage micropyrolysis reactor, low temperature (625 °C) and short residence time (1.4 s) produced diesel range hydrocarbons combined with gasoline and gasses; moderate temperature (650 °C) and short residence time (1.4 s) mainly produced gasoline range hydrocarbons and gasses; high temperature (675 °C) and long residence time (5.6 s) primarily produced gasses and aromatics. All in all, longer residence time tends to facilitate the secondary conversion of the primary products, and generates more stable compounds, including aromatics and non-condensable gasses. It was interesting that Mastral et al. observed the interdependence of temperature and residence time [123]. At a temperature lower than 685 °C, longer residence time inversely resulted in a higher liquid yield for HDPE pyrolysis, while at temperatures above 685 °C, the residence time had no obvious influence on the liquid and gas yields.

In order to study the effect of volatiles residence time on the products, two different set-ups were developed, a pyroprobe flash pyrolyzer that allows us to study the primary products due to near zero residence

time and negligible secondary reactions and a fluidized bed reactor where the extent of the secondary reactions is significant [124]. They found that the increase of residence time can decrease the yields of C<sub>4</sub>–C<sub>7</sub> hydrocarbons in the thermal pyrolysis of HDPE, but the yields of C<sub>4</sub>–C<sub>7</sub> hydrocarbons increased with residence time in the presence of HZSM-5 catalyst. During thermal degradation, some hydrocarbons produced by primary reactions and by tar and heavy hydrocarbon cracking can be further cracked with the increasing residence time so that the yields of C<sub>4</sub>–C<sub>7</sub> hydrocarbons decreased. However, this behavior is not detected under catalytic conditions. It was also reported that the liquid yield during LDPE pyrolysis in a closed reactor decreased from 91.1 wt.% at zero residence time to 72.4 wt.% at residence time of 60 min, and further to nearly 61 wt.% with the residence time increasing to 120 min [125].

Overall, the high temperature and long residence time would promote the cracking of polymers, leading to the production of more low-molecular-weight hydrocarbons and gas molecules, and the aromatic selectivity shows an upward trend with the increasing temperature and residence time. Basically, in order to provide maximum liquid products, the pyrolysis temperature should be precisely controlled and residence time needs to be minimized. For example, it is reported that the decomposition temperature for PP is 378–456 °C, whereas LDPE and HDPE degrade at 437–486 °C and 452–489 °C, respectively [126]. A further increase in reaction temperatures would lead to enhanced yields of gaseous products.

### 3.1.2. Effect of catalysts

In a non-catalytic pyrolysis of PSW, carbon–carbon linkage in the polymer chains can be broken randomly and no rearrangement of the fragments occurs, resulting in a wide distribution of products, such as light olefins, gasoline range, diesel range, and waxes [67,111]. Although increasing temperature can improve the share of lighter hydrocarbons, the production of desirable fuels and chemicals with high selectivity is still a great challenge. The use of a suitable catalyst with desirable properties is necessary to narrow the product distribution and enhance target product selectivity. On one hand, the addition of a catalyst can lower the decomposition temperature of the plastic; on the other hand, product selectivity can be modified towards a vast variety of valuable oils, such as gasoline [63], diesel [127], aromatics [128], and jet fuel [129], which are fairly different from the product compositions for non-catalytic pyrolysis. The product distribution from catalytic pyrolysis of plastic is controlled by catalyst properties, including acidity and pore structure, as shown in Fig. 8. With an increase of catalyst acidity, shorter-chain hydrocarbons would be generated, due to the facilitated cracking reaction.

There is no doubt that catalytic pyrolysis of plastics sometimes shows several drawbacks, which may be caused by the inherent nature of the catalysts used. For example, one main concern is catalyst deactivation. The difficulty of regenerating the catalyst poses another challenge to this technology. In some cases, catalyst structure can be completely destroyed in the catalytic process, significantly increasing the capital cost. In addition, the activity and selectivity for the catalytic process depends primarily on the catalyst type, and the corresponding reaction conditions, such as temperature, velocity, and atmosphere. In the previous studies, it was found that solid acids, used in the catalytic pyrolysis of plastics, have been recognized as the most promising candidates [19, 130,131]. Therefore, different types of solid acids used for catalytic pyrolysis of plastics are discussed below.

Zeolites are very common molecular sieves, which turns out to be one of the most suitable candidates for plastic cracking, due to the acidic properties and unique shape selectivity. Therefore, a great number of studies concerning the screening of effective zeolites, and the investigation of the corresponding catalytic fundamentals have been conducted. The need for screening zeolite catalysts was highlighted by Manos et al., who compared the catalytic performance of 4 zeolites (Ultrastable Y, Y,  $\beta$ , ZSM-5) during catalytic degradation of HDPE in a

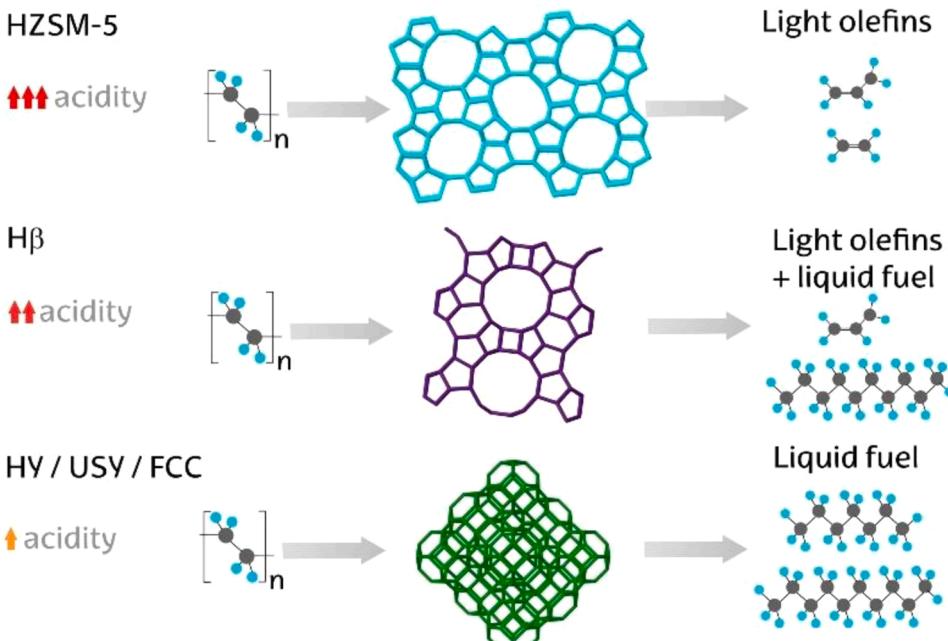
semi-batch reactor [132]. It was found that lighter hydrocarbons can be generated over medium-pore zeolites, as compared to large-pore zeolites, in the order of (lighter hydrocarbons) ZSM-5 < mordenite <  $\beta$  < Y < Ultrastable Y (heavier hydrocarbons). In addition, the same order was observed concerning the bond saturation (alkanes or olefins). This indicates that the pore structure of zeolites largely affects product distribution, especially the ratio of alkanes to olefins. US-Y, Y, and  $\beta$  zeolites mainly produced alkanes, whereas the major products were alkenes over mordenite and ZSM-5, due to rapid bimolecular hydrogen transfer reactions, which is responsible for the generation of saturated hydrocarbons [133]. A similar study was conducted by Mordi et al., who tested the catalytic activity of H-mordenite, H-Theta-1, and H-ZSM-5 in the catalytic degradation of LDPE [134]. The major degradation components were C<sub>11</sub>–C<sub>19</sub> hydrocarbons (mainly alkanes/alkenes) from H-mordenite or H-Theta-1, while the carbon chain length was no more than 14 (mainly aromatics) over H-ZSM-5. It was interesting that cracking initiation could be completed at the external surface of the zeolite catalysts, or at the pore entrance, because polymer molecules were too large to enter the pore structure and access the internal active sites.

One important finding was that zeolite catalysts tended to show higher selectivity than other catalysts, towards aromatics in most cases, especially HY and ZSM-5. The aromatic formation mechanism mainly involves two stages, one of which is catalytic cracking to generate carbenium ions by Lewis acid site reactions, or carbonium ions via protonation of hydrocarbons on Bronsted acid sites. In the next step, these intermediates were converted into aromatics via isomerization, oligomerization, cyclization, Diels–Alder, and aromatization reactions on the surface of catalysts [135]. In this regard, Akubo et al. observed in the catalytic pyrolysis of HDPE, in a fixed, two stage bed that Y zeolites with transition metal promoters produced an oil product with aromatic content of over 80% [136]. The share of aromatics was much higher than in the non-catalytic process, where the aliphatic product content was up to >99%. The single ring aromatic compounds, including toluene, ethylbenzene, and xylenes were dominate, although 2-ring and multiple aromatics were also formed. A high yield of aromatic hydrocarbons was also obtained in the catalytic fast pyrolysis of PS with HZSM-5, H $\beta$ , HY, and ultra-stable Y [137]. Ultra-stable Y catalyst showed the best shape selectivity for ethylbenzene and benzene formation, and maximized the aromatic production.

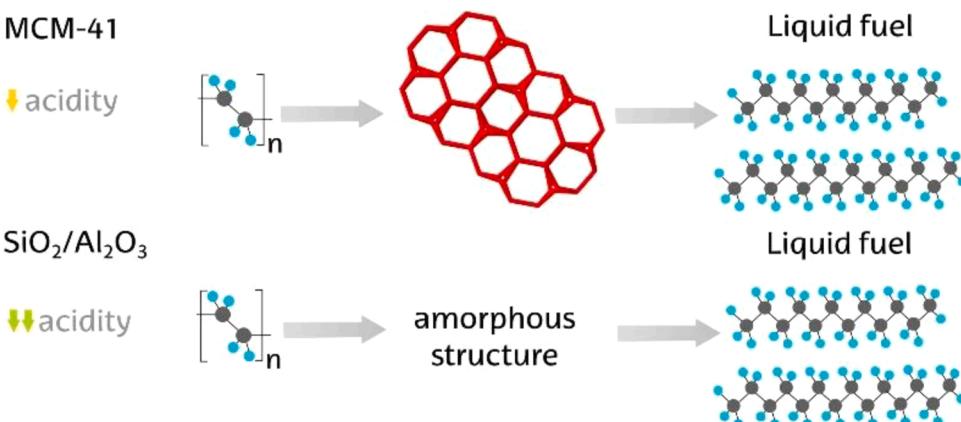
Mesoporous aluminosilicates (Al-MCM-41 and Al-SBA-15) with the tunable pore size of 1.5–30 nm allow plastic molecules or intermediates to enter the catalyst mesopores directly, mitigating the steric and diffusional hindrances, and greatly increasing the accessibility of internal acid sites. It was then used in the catalytic cracking of plastics in 1996 for the first time, which confirmed the feasibility of this type of catalyst [138]. It was proposed that the growth around micelles is responsible for the synthesis of the ordered mesoporous aluminosilicates [139]. The templates are first formed by aggregating the micelles into the hexagonal structures, and then the silica begins to condense around these templates. After calcination at high temperature, the templates are removed and the ordered mesoporous structure is formed. The uniform mesoporous distribution and ultra-high specific surface area enable it to show a higher conversion rate for polyolefins, as compared to amorphous SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> [140]. Compared to ZSM-5, the acid strength of MCM-41 was lower, leading to the lower catalytic activity for cracking of HDPE and LDPE. It was interesting that the severe steric hindrance caused by the narrow pores of ZSM-5 resulted in the lower catalytic activity for PP cracking while MCM-41 exhibited 99% conversion due to the better accessibility of acid sites located in the mesopores.

Zhang et al. [19] converted LDPE into a gasoline-type product using the shape-selective Al-SBA-15 catalyst and the results showed a great potential of Al-SBA-15 catalyst in the catalytic cracking of LDPE. When the silicon/aluminum molar ratio of Al-SBA-15 was 5, the temperature at the 50% conversion was even lower than ZSM-5, regardless of the weaker acid sites. With ZSM-5 catalyst, the product contained a large

## Zeolites



## Mesoporous catalysts



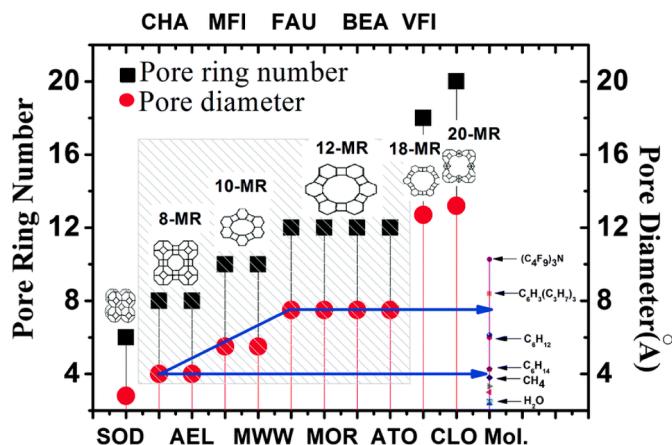
**Fig. 8.** Effect of different acid catalysts on product distribution during catalytic pyrolysis of polyolefins. (Reprinted from [31] with permission from Elsevier).

amount of mono-aromatic, such as benzene, toluene, ethylbenzene and xylenes, which was completely different from Al-SBA-15 catalyst. Al-SBA-15 gave rise to a well-defined gasoline-type product which was mainly composed of C<sub>4</sub>–C<sub>10</sub> alkenes/alkanes. The catalytic activity of Al-SBA-15 was attributed to the following features: (1) the large pore size which allowed LDPE chains to fully access the Brønsted sites of the catalyst; (2) the modulated strength of acid sites was favorable for controlling the cracking of LDPE, and generating more gas; (3) the wide-pore system improved the diffusion of gasoline-like hydrocarbons and minimized secondary cracking reactions. Similar conclusions were drawn by Soccia et al. in the catalytic cracking of LDPE over mesoporous Al-SBA-15 materials [141]. Due to the higher diffusional efficiency of reactants in the mesoporous structure of the Al-SBA-15 catalysts compared to ZSM-5, a higher selectivity of the gasoline range hydrocarbons was obtained. The density and strength of the Brønsted acid sites, pore structure, and the Al content, had a significant effect on the pyrolytic product distribution.

Although these mesoporous materials with high surface area and well-defined larger pores show great potential to process bulky plastic

feedstocks, the shape selectivity and long catalyst lifetime cannot be observed [142]. In the catalytic pyrolysis of LDPE, HZSM-5 gave a significant increase in the light olefins and aromatics by eliminating heavier hydrocarbons, while mesoporous Al-MCM-41 catalyst exhibited no shape selectivity with a wide range of hydrocarbons. To improve the shape selectivity of mesoporous materials, “relay catalysis process” was developed, in which several catalysts are used in tandem. Recently, Ratnasari et al. [143] effectively converted waste plastics to gasoline range hydrocarbons (C<sub>8</sub>–C<sub>12</sub>) over MCM-41/ZSM-5 catalysts. Pyrolysis volatiles passed through a mesoporous MCM-41 catalyst layer followed by a microporous ZSM-5 zeolite with the aim of controlling the product distribution more accurately. Highest selectivity (97.72%) of gasoline range hydrocarbons was obtained at the a MCM-41:ZSM-5 ratio of 1:1, which was higher than the single use of ZSM-5 or MCM-41. It indicated that the high surface and large pore volume were favorable for catalytic cracking of the heavy hydrocarbons in the primary pyrolysis vapors to lighter molecules, which were then easier to enter into ZSM-5 micropores for further reforming reactions.

As mentioned above, the catalytic pyrolysis of plastics over zeolites



**Fig. 9.** Relationship between molecular kinetic diameter, pore diameter and pore ring number of different zeolites. (Reprinted from [150] with permission from the Royal Society of Chemistry).

proceeds initially by the acid sites present in the outer surface or large pores, and then the smaller intermediates can subsequently enter the zeolite micropores for further cracking or other secondary reactions, which is controlled by the acidity and the pore channel architecture of the zeolites. For example, cyclohexane with a kinetic diameter of 0.6 nm is unable to enter the micropores of ZSM-5 zeolite (10 membered ring channels with size of 0.56 nm) due to steric hindrance imposed by the micropore size, but it can access the acid sites inside the micropores of Y zeolite (12 membered ring channels with size of 0.74 nm) [144]. However, the  $C_6H_3(C_3H_7)_3$  possessing approximately 0.82 nm pore channels can not enter the micropores of Y zeolite, as shown in Fig. 9. Theoretically, strong Brønsted acid sites that determines the cracking performance of zeolites are attributed to the acidic protons linked to the Si-O-Al bridge bond inside micropores [145]. Therefore, enhancing the accessibility of the zeolite acid sites could improve product distribution and catalyst lifetime in the catalytic cracking of polyolefins over zeolites. Unlike conventional zeolites which are mainly composed of micropores, hierarchical zeolites are characterized by their multimodal microporous–mesoporous–macropore pore size distribution with a considerable share of mesopores, enabling them to be more active for plastic cracking. In this regard, significant advances have come due to the application of hierarchical zeolites. Lee et al. [146] compared hierarchical ZSM-5 zeolite with conventional one in the catalytic cracking of PE, finding that hierarchical ZSM-5 showed higher catalytic activity (about 95% of conversion) due to a high external surface and a rapid mass transfer. Caldeira et al. [147] tested two hierarchical Beta zeolites obtained from reorganization of the protozeolitic nanounits and the use of a silanization agent. Both hierarchical Beta zeolites can achieve higher plastic conversion (67.3 wt.% and 97 wt.%) than the conventional Beta sample. The results obtained indicate that the HDPE cracking activity is strongly related with the acid sites within the micropores, so the overall catalytic activity largely depends on the accessibility to the acid sites. Silva et al. [148] also confirmed that hierarchical ZSM-23 demonstrated the higher conversion efficiency and lower energy level in catalytic cracking of PE compared to the microporous ZSM-23. Quantitative analysis of the accessibility of Brønsted acid sites shows that a larger number of accessible Brønsted acid sites exists in hierarchical ZSM-5 (64.3%) than the parent ZSM-5 (6.25%) [149]. It enables the decomposition temperature of LDPE to decrease to 420 °C, which is originally 453 °C with the use of parent ZSM-5.

Other materials used for catalytic cracking of PSW are clay-based catalysts. The huge reserves and low price of this type of material make these attractive to be used for catalysts in industry. These materials are found to have a naturally layered structure, between which different metal oxides can be intercalated (pillared clay). The acidity of

clays is lower than zeolite catalysts but higher than pure silica. Although less active than USY zeolite, clays led to higher liquid yield in the catalytic pyrolysis of PE at around 600 K, with gasoline range hydrocarbons being the major products [151]. Alkenes dominated in the oil product from the clay-catalyzed process, instead of aromatics. It was due to the milder acidity as compared to USY zeolite, thereby mitigating the hydrogen-transfer secondary reactions. At the same time, a smaller amount of coke was formed on the surface of clays. In the catalytic pyrolysis of PS, Kaolin was confirmed as an effective catalyst, giving a higher liquid yield than the non-catalytic pyrolysis process with aromatic hydrocarbons being the main components [152].

To further improve the catalytic performance of clays, modification techniques change the pore structure and acidity, with the aim of tuning or narrowing the resulting hydrocarbons distribution. Although kaolin catalyst has a certain cracking ability to convert polymers to diesel range hydrocarbons, the HCl modified clay can further crack the diesel fraction into shorter chain hydrocarbons ( $C_6$ – $C_{11}$ ) because HCl modification is able to create more active functional groups, resulting in stronger acidity [153]. Stefanis et al. modified the smectite clays by acid restructuring or oxide intercalation assembly and tested their performance in the catalytic cracking of PE [154]. The chemical profile and yield of liquid product both reflected that clay-based catalysts with weaker acidity mitigated the over-cracking toward small molecules, giving higher liquid product yield. Several restructured or pillared clays had different structures, leading to an activity different from each other. Most clays gave aliphatic hydrocarbons as the major products except HSA (a modified saponite clay). Li et al. [22] also developed various transition metal pillared clays to produce diesel range hydrocarbons and hydrogen from mixed plastics. The high catalytic activity of modified clays was attributed to the moderate acidity, high surface area, and uniformly dispersed metal oxide particles on the support.

In addition to these materials, fluidized catalytic cracking (FCC) catalysts composed of crystalline zeolites, acid  $SiO_2$ – $Al_2O_3$ , and binding agents are proposed as promising catalysts for catalytic cracking of plastics. Although the spent equilibrium FCC showed lower catalytic activity than the silica–aluminas, this can be compensated by using more spent FCC catalysts. Taking the economical factor into account, the negligible cost of the spent FCC catalyst enables it to be more suitable for industrial application. Rodríguez et al. [155] conducted catalytic cracking of HDPE pyrolysis waxes in a CREC riser simulator reactor, with the goal to study the effect of the FCC equilibrium catalyst properties on product distribution. As a whole, three FCC catalysts produced similar product compositions, while with less acidic catalyst the naphtha fraction contained less aromatics and more olefins. The spent FCC catalyst was also used to crack HDPE in a conical spouted bed, restricting the formation of aromatics and paraffins and giving rise to the lumps of gasoline fraction and light olefins [84]. The spent catalyst possesses meso- and macroporous pores which allow plastic molecules to diffuse for cracking and micropores in the zeolite crystals which give a higher shape selectivity to gasoline range hydrocarbons and light olefins.

Metal oxides, with a multivalent nature, and special acid–base properties, have been widely used in heterogeneous catalysis reactions [156,157]. Various metal oxides have been tested in catalytic cracking of plastics, showing potential to catalyze the thermal cracking of polymers and/or the reforming of pyrolysis intermediates in the volatiles into more stable products (Table 5) [25,158,159]. Ten years ago, Shah et al. [160] attempted to achieve the maximum conversion of LDPE into chemicals using a wide range of acidic and basic metal oxides and calcium carbide. An interesting finding is that metal oxides, such as  $MgO$ ,  $Al_2O_3$ , and  $ZnO$ , are more suitable for the production of polar and aromatic products, while  $CaC_2$  should be adopted if aliphatic products are desirable.

$Al_2O_3$  is a very common catalyst/support in the catalytic pyrolysis of solid wastes.  $Fe$ – $Ce$ – $Al_2O_3$  was used to catalytically convert polycarbonate (PC) plastic waste into aromatic hydrocarbons at 650 °C [161]. Three preparation methods, including co-precipitation,

impregnation, and physical mixing, were compared. Experimental results showed that co-precipitation gave rise to the highest content of monocyclic aromatic hydrocarbons. It was attributed to weaker acid sites, larger pore volume, higher surface area, and uniformly dispersed metal oxides. Transition metals (Fe, Co, and Ni) were able to effectively improve the basicity of the  $\text{Al}_2\text{O}_3$  support [162]. When used in the catalytic pyrolysis of PS,  $\beta$ -chain-breaking was facilitated, thereby leading to a higher selectivity of styrene monomers. Different metal species (Ni, Cu, Ce, Co, and La) were also screened in the catalytic pyrolysis of PS waste foams, at temperatures ranging from 400 to 500 °C to obtain the highest conversion of PS, and more desirable product components [163].  $\text{Cu}/\text{Al}_2\text{O}_3$  was found to be the best candidate for PS conversion, with the highest styrene yield of 63.59%.

Recently, a significant breakthrough was made in the PE conversion over  $\text{Al}_2\text{O}_3$  supported Pt catalyst [164]. PE was effectively converted to valuable long-chain alkyl-aromatics and alkyl-naphthalenes by combining exothermic hydrogenolysis and endothermic aromatization at a very

low temperature of 280 °C. Compared to the conventional long-chain alkyl-aromatic production, this one-step process is much simpler and less energy-intensive and gets rid of organic solvents used in the conventional process. More importantly, up to 80 wt.% of low-molecular-weight liquid/wax products was obtained, with negligible amounts of light gasses produced. The stability testing of  $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$  catalyst indicates that the intrinsic activity of the catalyst stays unchanged regardless of the decreasing liquid/wax yield in the second run. However, the issue for this process is the long reaction time in a batch reactor increasing the difficulty in scaling it up.

It is noteworthy that, inspired by the macromolecule deconstruction enzymes, an artificial processive catalyst ( $\text{SiO}_2$ -supported Pt nanoparticles) was designed for PE hydrogenolysis, into diesel and lubricant-range alkanes with high selectivity [165]. The key is to develop sufficiently narrow pores to enable the headfirst adsorption of a PE chain and accessibility to the active sites (Pt species) positioned near the end of the pores, selectively breaking one type of bond at a regular interval from

**Table 5**  
Effects of different catalysts on liquid yield and product distribution in the plastic pyrolysis.

Catalysts	Feedstock	Reaction conditions	Liquid yield (wt. %)	Product distribution	Refs
Natural zeolite	PS	Catalytic pyrolysis temperature of 450 °C, Reaction time 75 min	54	91% of aromatics	[166]
Spent FCC catalyst	HDPE	Catalytic pyrolysis temperature of 500 °C, feeding rate of 1 g/min, 30 g of catalyst	60	50% of non-aromatic $\text{C}_5\text{-C}_{11}$ hydrocarbons, 8–10% of $\text{C}_{12}\text{-C}_{20}$ hydrocarbons, 10% of wax	[84]
Equilibrium FCC catalysts	HDPE waxes	Catalytic pyrolysis temperature in the 500–560 °C range, catalyst/feedstock ratio fixed at 5 $\text{g}_{\text{cat}}/8_{\text{wax}}$ , contact time of 6 s	57–80	20–30% of $\text{C}_5\text{-C}_{12}$ hydrocarbons, 35–50% $\text{C}_{13}\text{-C}_{20}$ hydrocarbons, 2–10% $\text{C}_{20+}$ hydrocarbons	[155]
Conventional/hierarchical Beta Ni/Mo/Fe/Ga/Ru/Co-Y-zeolites	HDPE	Catalytic pyrolysis temperature of 380 °C, Plastic to catalyst mass ratio of 100		Around 13% of $\text{C}_5\text{-C}_{12}$ aromatics, 30% of $\text{C}_5\text{-C}_{12}$ alkanes, 25% of olefins	[147]
	HDPE	Pyrolysis temperature of 600 °C, Catalytic temperature of 600 °C, HDPE to catalyst ratio of 1:2	31–43	Around 80–95% of aromatics, 5–20% of aliphatic hydrocarbons	[136]
MCM-41 and ZSM-5	HDPE	Pyrolysis temperature of 500 °C, Catalytic temperature of 500 °C, MCM-41:ZSM-5 ratio of 1:1, HDPE to catalyst ratio of 1:2	83.15	97.72% of gasoline range hydrocarbons, 95.85% of aromatics	[143]
MgO	HDPE	Pyrolysis temperature of 500 °C, Catalytic temperature of 450 °C HDPE:MgO of 15:1	37	36% of $\text{C}_5\text{-C}_{12}$ aromatics, 38% of $\text{C}_5\text{-C}_{12}$ alkenes, 11% of $\text{C}_5\text{-C}_{12}$ alkanes	[25]
ZnO	LDPE	10% ZnO addition, 50 kPa pressure	72	56.2% of $\text{C}_7\text{-C}_{36}$ alkanes, 30% of $\text{C}_9\text{-C}_{18}$ alkenes, mainly composed of diesel range hydrocarbons	[167]
Ni/CuO	PS	Pyrolysis temperature of 390 °C, reaction time of 90 min	93.5	68.9% of aromatics, 21.29% of olefins, 2.2% of oxygenates	[168]
Sulphated ZrO <sub>2</sub>	PET	Pyrolysis temperature of 450 °C, residence time of 20 s, catalyst to plastic mass ratio of 3 wt.-%	41.4	27.5 wt.% of benzoic acid, 13.9 wt.% of other aromatic compounds	[169]
ZnO	PET	Pyrolysis temperature of 450 °C, Catalytic temperature of 700 °C PET:metal oxides of 1:20		83.9% of aromatics, 16.1% of oxygenates	[170]
MgO				38.7% of aromatics, 61.3% of oxygenates	[171]
TiO <sub>2</sub>				38.9% of aromatics, 61.1% of oxygenates	
ZrO <sub>2</sub>				43.9% of aromatics, 56.1% of oxygenates	
CaO				99.7% of aromatics, 0.3% of oxygenates	
ZnO	PS	Pyrolysis temperature of 450 °C, 60 min heating time and 1:0.2 feed to catalyst ratio	84.7	85.8% of aromatics	[172]
Kaolin clay	PP	Catalytic pyrolysis at 600 °C, plastic to catalyst ratio of 9	22	30–40% of aromatics, 25–35% of straight alkenes, 5–10% of cycloparaffins, 2–7% of straight alkanes	[153]
Fe/Al oxide-pillared clay	PE	Catalytic pyrolysis at 300 °C, Reaction time of 3 h	60	No aromatics, 100% of aliphatics	[154]
Sewage sludge derived char	PE, PP and PS	catalytic temperature at 600 °C with a residence time of 1 s	46.6	Monocyclic aromatics of up to 75.3%, styrene of 29.1%, and xylene of 12.5%	[173]
Coconut-shell activated carbon	HDPE	Feed to catalyst ratio of 1:0.6, catalytic pyrolysis temperature of 400 °C, operation time of 45 min	47.59	1.08% of cycloparaffin, 52.57% of n-paraffin, 32.18% of olefin, 4.53% of aromatic	[174]
Coconut sheath activated carbon	PS and PP	Microwave pyrolysis at 900 W and with a polymer to an absorbent ratio of 10:1, reaction time of 176 s	84.30	80.58% of aromatic content (toluene (3.39%), styrene (67.58%), ethylbenzene (1.82%) and $\alpha$ -methyl styrene (1.71%)) and 11.29% of olefinic content, 93.13 area% of jet fuel-ranged hydrocarbons, (39.11% of $\text{C}_8\text{-C}_{16}$ alkanes, 54.02% of $<\text{C}_{16}$ aromatics)	[86]
Phosphoric acid-activated biomass char	LDPE	Catalytic pyrolysis at 500 °C, catalyst to LDPE ratio of 1	75.3	65.3% of $\text{C}_8\text{-C}_{16}$ alkanes and 33.4% of aromatic hydrocarbons ( $<\text{C}_{16}$ )	[175]
Biomass-derived activated carbon/MgO	LDPE	Catalytic pyrolysis temperature of 500 °C, catalyst to LDPE ratio of 2, and char to MgO ratio of 1	72	27% of alkanes, 23.8% of alkenes, 47.5% of aromatics (mostly in the diesel range)	[176]
ZnCl <sub>2</sub> -activated biochar	PE, PP and PS	Catalytic pyrolysis temperature of 500 °C, catalyst to LDPE ratio of 1:4	51.8	43.1% of alkanes, 2.2% of alkenes, 44.7% of aromatics (mostly in the diesel range)	[177]
KOH-activated biochar	PE, PP and PS	Catalytic pyrolysis temperature of 500 °C, catalyst to LDPE ratio of 1:4	42.6		[178]

the chain end. The obtained shorter chain hydrocarbons will be desorbed, and released from the shell/core structure. This catalyst enables plastics-to-diesel/lubricant technique to be more reliable and promising.

MgO and CaO are two typical base metal oxides used in the catalytic conversion of PSW, which are effective for enhancing the cracking process and altering product distribution. In the catalytic pyrolysis of LDPE over MgO, 96.0% of gasoline-range hydrocarbons can be obtained, with 56.3% C<sub>5</sub>—C<sub>12</sub> aliphatics being the main components [25]. The possible mechanism for the MgO-catalyzed upgrading of LDPE pyrolysis vapors was also proposed in this study. As mentioned above, the polyolefin cracking can generate long and short chain radicals which are converted into stable alkanes or olefins by hydrogen transfer reactions. The first step for MgO catalyst is that the base catalyst is able to abstract the hydrogen proton attached to the long chain hydrocarbons, forming a carbanion. The obtained carbanion is easy to be fragmented into shorter chain alkenes via  $\beta$ -scission (Fig. 10). This is the reason why gasoline range hydrocarbons can be obtained in the catalytic pyrolysis of LDPE over MgO. The  $\beta$ -scission process is terminated by utilizing the proton from the MgO surface, and long chain alkanes will be generated (Fig. 10). On the other hand, the free radicals may be recombined into long chain alkanes or cracked into smaller fragments which go through cyclization and dehydrogenation to form aromatics. Kumagai et al. [158] investigated the catalytic conversion of PET over CaO, with the focus on the CaO deterioration effect. The presence of CaO significantly facilitated the decarboxylation reaction, obtaining 83.6% selectivity of aromatic hydrocarbons. However, the catalytic activity decreased gradually with repeated runs, which means the increase in oxygenates. Observed from scanning electron microscopy images, CaO was thoroughly sintered, resulting in the reduction of its basicity.

Besides these, transition metals have also been tested for catalytic pyrolysis of plastics, with different effects on the product formation. Kumagai et al. [170] studied the PET pyrolysis over various metal oxides (ZnO, MgO, TiO<sub>2</sub>, and ZrO<sub>2</sub>) using tandem  $\mu$ -reactor-GC/MS and found that benzene-rich aromatic hydrocarbons were the major products. ZnO has the strongest basicity, maximizing the decarboxylation effect and resulting in the 88.8% benzene. In contrast, MgO, TiO<sub>2</sub>, and ZrO<sub>2</sub> with lower basicity, exhibits lower catalytic performance for the decarboxylation reaction, and a higher decarboxylation temperature was also observed, compared to ZnO. In a HDPE pyrolysis-catalytic cracking process, CuCO<sub>3</sub> was used as a catalyst to achieve effective conversion of waste HDPE into liquid hydrocarbons [179]. The liquid hydrocarbon fuel collected was mainly composed of paraffins, olefins, and aromatics and applied to successfully power a petrol-engine of a bike, showing the potential to use in petrol and diesel engines. Wu et al. [180] synthesized a Ni-Ce based catalyst where the Ni-Ce core was encapsulated by a silica shell, with the hope of effectively mitigating the sintering of nanoparticles at high temperature. This catalyst showed excellent catalytic activity and coking resistance ability in hydrogen production. It was reported that sulphated zirconia was an effective catalyst for recovering benzoic acid through PET pyrolysis due to its high acidity, with up to 27–32 wt% benzoic acid yield [169]. More importantly, catalytic pyrolysis of PET in the presence of sulphated zirconia for benzoic acid production can be achieved at temperatures below 525 °C, which is much lower than the non-catalytic pyrolysis temperature (600 °C).

Carbonaceous materials derived from organic solid wastes have been recognized as a promising candidate for catalysts, or support in heterogeneous catalysis, due to excellent surface properties, such as controllable surface area and porosity, low synthesis cost, and high stability. Some researchers pay attention to this type of abundant and inexpensive material and have developed many different carbonaceous materials for use as catalysts. From literature sources regarding carbon-based catalysts used in the catalytic pyrolysis of PSW, it can be seen that organic solid wastes are the more popular feedstocks for carbon catalyst preparation in order to reduce catalyst costs. Although plastic-to-fuels technology has been developed very well, the price of plastic based liquid fuels still cannot compete with the existing petroleum industry.

Generally speaking, developing carbon materials from solid wastes would be much cheaper than any other sources, which is especially important for PSW conversion. This section of the literature review will summarize recent progress made in the development of carbonaceous materials to be used in the catalytic cracking of PSW to produce valuable fuels and/or chemicals.

Sewage sludge char from direct high temperature carbonization was used to catalyze the conversion of waste plastic mixture into an aromatic-rich oil [181]. In this study, acid sites caused by aluminum phosphate and dehydrogenation caused by  $-P=O$  and sulfides were able to promote aromatization; simultaneously, calcium oxide and iron species in the char were favorable for ring-opening reactions, thereby preventing the formation of heavy aromatics. At a temperature of 600 °C and a residence time of 1 s, 75.3% selectivity of monocyclic aromatics could be obtained. In the PET pyrolysis, a carbon-supported Pd catalyst was added to prevent the formation of hazardous materials, such as polycyclic hydrocarbons and biphenyl derivatives [182]. When the carbon-supported Pd catalyst loading ratio was 0.05, the concentrations of 2-naphthalenecarboxylic acid and biphenyl-4-carboxylic acid were reduced by 44% and 79% respectively.

Considering that biomass production and processing industry give rise to a lot of low-cost by-products, the synthesis of carbon materials from abundant biomass wastes would be feasible, cost-effective, and promising [183]. Juliastuti et al. [174] prepared an activated carbon produced from coconut shell pyrolysis and used it as the pyrolytic catalyst in a microwave-assisted pyrolysis of HDPE. Results showed that the total yield of liquid and gas could reach 99.22% and the main components in the oil were cycloparaffins and n-paraffins, accounting for 54.09%. When activated carbon was used in a microwave batch reactor for catalytic pyrolysis of PS, the highest oil yield was 93.04 wt% with aromatics being the main products [184]. Rex et al. [185] also synthesized different activated carbons from rice husk, corn husk, and coconut sheath, respectively, which were used as microwave absorbents and catalysts, simultaneously in the microwave pyrolysis of a waste plastic mixture. The product oil was mainly composed of gasoline range hydrocarbons, with the highest styrene recovery of 67.58% in this process.

Lei and his co-workers have developed H<sub>3</sub>PO<sub>4</sub>-activated biomass carbon material and studied the effect of acid concentration on heating rate and carbonization time, with the ultimate goal of optimizing H<sub>3</sub>PO<sub>4</sub> concentration to obtain the optimum activated carbon yield, and textural characteristics from biomass precursors [186]. Subsequently, they attempted to produce jet fuel range hydrocarbons from PSW over the activated carbon [121,175]. It turns out that up to 100% selectivity of jet fuel range hydrocarbons (71.8% alkanes and 28.2% aromatics) can be obtained at the optimized conditions. The acidity of activated carbon plays a critical role in determining the catalyst activity, where weak acidity is favorable for jet fuel-ranged alkane formation, and strong acidity increases aromatics. Further, increasing catalytic reaction temperature can also promote aromatization reactions, generating more aromatics, and releasing more hydrogen as well. They also combined biomass derived activated carbon and MgO as catalysts in the catalytic pyrolysis of LDPE; so, the pyrolysis vapors went through a MgO catalyst layer, followed by a biomass-derived activated carbon layer [176]. Similarly, 100% jet fuel range hydrocarbons can be obtained at the desired experimental conditions. The synergy effect between these two catalysts, was seen on the hydrogen production, with 94.8 vol% of hydrogen in the gas product. Catalyst stability testing showed that corn stover derived biochar is able to catalyze the LDPE degradation without wax formation after 20 regeneration-reuse cycles [187].

Using ZnCl<sub>2</sub> as an activation agent, enables the specific surface area of biochar to increase significantly, and the Zn species leads to more Lewis acid sites, which promotes the Diels–Alder reaction, hydrogen transfer, and dehydrogenation progress in the catalytic pyrolysis of PSW [177]. ZnCl<sub>2</sub>-activated biochar increased the selectivity of aromatics to 47.5%, with two-ring aromatics being significantly enriched. Sun et al.

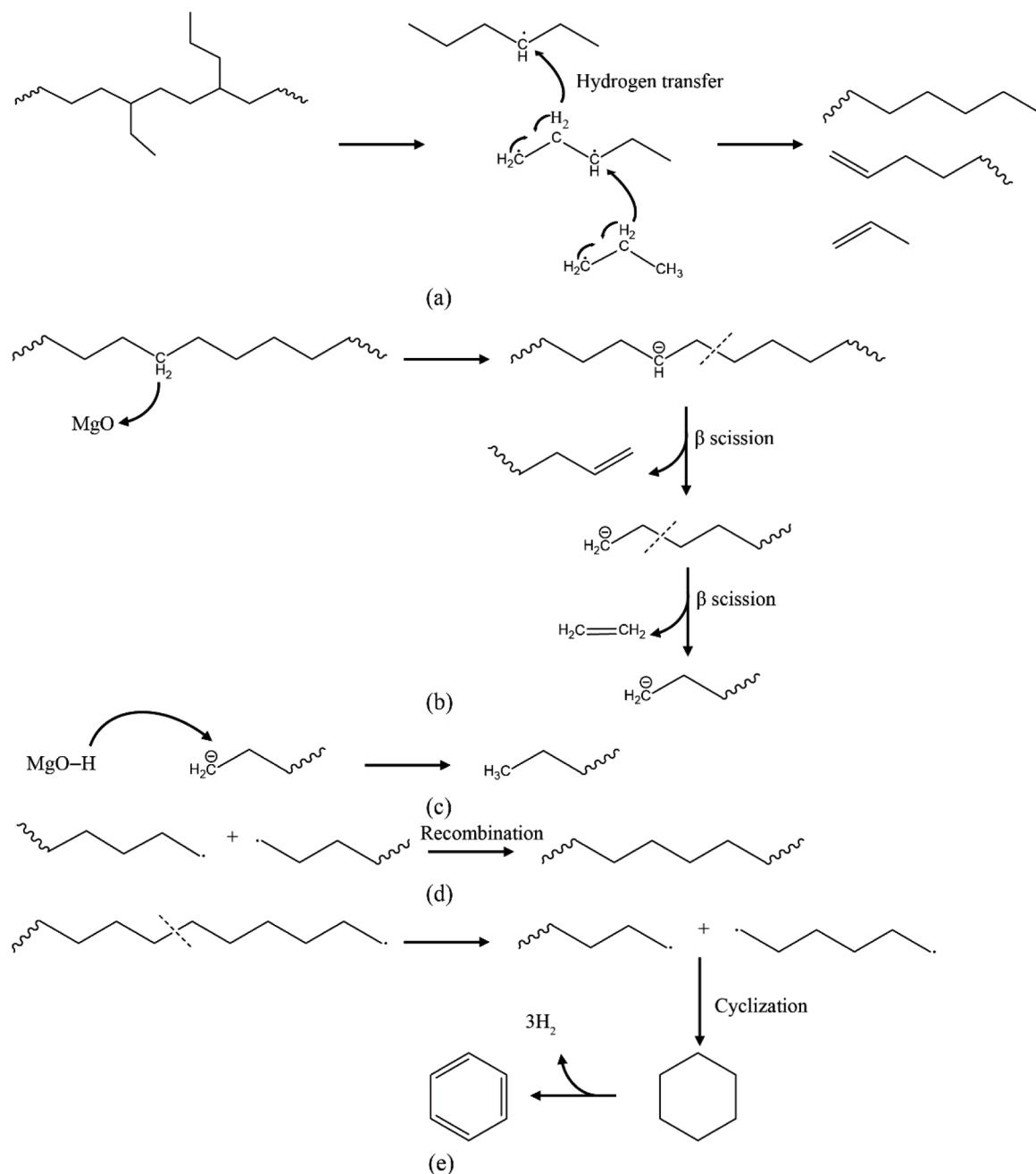


Fig. 10. The possible mechanism for the MgO-catalyzed upgrading of LDPE pyrolysis vapors. (Adapted from [25] with permission from Elsevier).

[178] investigated the effect of biochar catalysts, activated with different chemical agents ( $\text{ZnCl}_2$ ,  $\text{KOH}$ , and  $\text{H}_3\text{PO}_4$ ) on the plastic pyrolysis. Brønsted and Lewis acid sites created by  $\text{H}_3\text{PO}_4$  and  $\text{ZnCl}_2$  both facilitated the aromatization process, leading up to 66% and 47.6% of aromatics, respectively.

Catalyst deactivation is one of the barriers for the PSW pyrolysis process, which impacts the process efficiency, economics, and the optimization of operating conditions at large-scale production. It is mainly caused by coke deposition and poisoning of active sites, both of which contribute to the loss of catalytic activity in the catalytic cracking of plastics. Previous studies stress that the acidity and pore structure of cracking catalysts are two key factors to determine the deactivation resistance ability [188,189]. Therefore, the next parts will discuss the coke deposition and active site poisoning during the catalytic pyrolysis of plastics.

Coke deposition means that large-molecular-weight carbonaceous

species polymerized from the pyrolytic volatiles accumulate on the catalyst surface, thereby covering the active sites and resulting in catalytic activity loss [190]. It has been reported that olefin oligomerization and condensation reactions were the main causes for coke formation [191]. As shown in Fig. 11, catalyst deactivation caused by coke deposition takes place through several pathways. In terms of a supported metal catalyst, the first deactivation pathway is to form carbide by strong chemisorption as a monolayer or create multilayers by physisorption, hindering access to the active sites. The metal particles and other active sites can even be covered totally, which enables reactants to be inaccessible to these active sites. The blockage of catalyst pores is also able to prevent reactants from contacting the active site inside the micropores of catalysts. Generally speaking, coke properties are mainly studied from the perspective of its content, location, morphology, and chemical nature. Temperature programmed oxidation (TPO) technique is able to accurately measure the amount of coke deposited on the

catalyst surface. Barbarias et al. tested the coke amount by this technique, and found that the coke deposition rate in the catalytic reforming of HDPE pyrolysis volatiles over a commercial Ni-Ca/Al<sub>2</sub>O<sub>3</sub> catalyst varied from 0.1 to 6.1 mg<sub>coke</sub> g<sub>cat</sub><sup>-1</sup> g<sub>HDPE</sub><sup>-1</sup>, depending on the catalytic temperature, space-time and steam/plastic ratio [192].

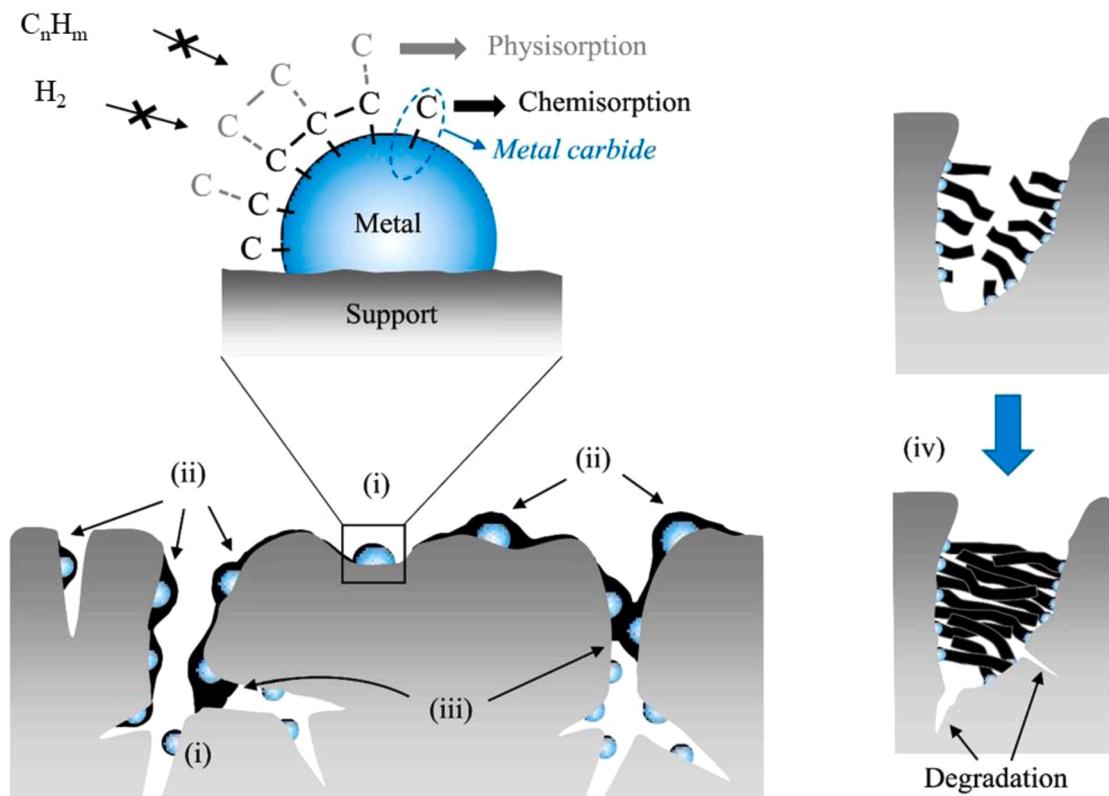
Ibáñez et al. [194] identified coke in the sequenced pyrolysis-cracking of HDPE over an HZSM-5 zeolite catalyst at a temperature of 500 °C and a continuous feed of HDPE (1 g min<sup>-1</sup>). They observed that waxes are the precursors of coke formation during the initiation period, while light olefins could lead to the steady coke formation over time on stream by condensation and oligomerization in the subsequent sections. Two types of coke were determined by TG-TPO analysis, one of which (coke I) was aliphatic hydrocarbons generated from the degradation of waxes and located on the outside of mesoporous and microporous pores. Another one (coke II) was aromatic hydrocarbons, either inside the zeolite pores or in the exterior of the zeolite pores, which were formed by degrading coke I or oligomerizing and condensing light olefins. Apart from coke I and coke II, wax itself or molten plastic could play a role in covering the active sites on the surface of catalysts. If weight hour space velocity for a continuous plastic pyrolysis is too high, wax itself or molten plastic can not be immediately cracked, momentarily or enduringly blocking the mass transfer channel. Considering that TG-TPO is not able to analyze the coke type and location, Castaño et al. [195] gave more in-depth insights into the coke formation in the cracking of HDPE in the presence of HZSM-5, H $\beta$  and HY zeolites. They observed in the Raman spectra, that a more graphite-like coke was formed as the pore size of the zeolite increased. It was found from UV-vis spectroscopy that the micropore size of the larger zeolite, condensation of higher poly-condensed aromatics, was also confirmed by solid-state <sup>13</sup>C CP-MAS NMR profiles. Although soluble coke is mainly composed of aromatics, the spent HZSM-5, H $\beta$ , and HY zeolites gave rise to different aromatic families. For example, single-ring aromatics with two or more

aliphatic chains, indane and indene, were the main components in the soluble coke, extracted from the spent HZSM-5 catalyst.

Marcilla et al. [196] studied the effect of temperature on coke formation in the catalytic cracking of LDPE over HZSM-5 and HUSY zeolites. Results showed that the higher the cracking temperature, the lower the coke content deposited on the catalyst surface. The amount of coke, using the HZSM-5 zeolite (approximately 5%) is much lower than that of HUSY zeolite (approximately 15%), which can be due to the difference of pore sizes. They also calculated the pore volumes which were inaccessible to the adsorbate (V<sub>A</sub>) and occupied by coke (V<sub>R</sub>), with the aim of determining the possible location of the coke. V<sub>R</sub>/V<sub>A</sub> ratio should be about 1 with the simple pore filling, while the ratio would be lower than 1 with the channels and intersections being blocked. It should be noted that increasing cracking temperature leads to a larger share of coke, insoluble in dichloromethane, that are chiefly poly-aromatic compounds.

Another cause of catalyst deactivation is the presence of poisons in the catalytic cracking of PSW. Poisonous materials in the feedstock would cover a part of active sites on the catalyst surface, or compete with the reactants, thus suppressing the catalyst activity. In most literature, the used feedstock is very pure plastic without any poisons, like LDPE powder, which is not a problem at all. When a huge amount of PSW needs to be handled by pyrolysis, it is inevitable to have a small amount of N and S in the PSW. The good news is that, in the catalytic cracking of plastic mixtures with 0.23% of N and 0.07% of S, over different zeolite catalysts, the presence of N and S had little influence on the catalytic cracking [197]. However, in the catalytic cracking of LDPE-lube oil mixture with 4000 ppm of S and 85 ppm of N, the presence of N and S led to lower activities, as compared to the pure LDPE pyrolysis [198].

With the catalyst deactivation being inevitable in the catalytic cracking of PSW, regeneration is able to save the catalyst replacement



**Fig. 11.** The deactivation mechanism of a supported metal catalyst caused by coke deposition. (i) carbon chemisorption or physisorption hindering the access to reactants; (ii) metal particle encapsulation or full covering of active sites; (iii) pore plugging; (iv) degradation of catalyst structure. (Reprinted from [193] with permission from Elsevier).

costs, and thus enable a more cost-effective industrial process. Catalyst regeneration largely depends on the deactivation mechanism, and cannot be implemented if an irreversible deactivation happens, such as de-alumination and zeolite amorphization [199]. As mentioned above, coke deposition is one of the main causes for catalyst deactivation in the catalytic cracking of plastics. Serrano et al. [199] explored the deactivation mechanism of nano-crystalline HZSM-5 zeolites in the catalytic cracking of PE. He observed a reversible deactivation, caused by coke deposition, and an irreversible or permanent deactivation caused by other factors. It was also found that the coke deposited on the HZSM-5 catalyst, with larger external surface area, is less aggressive and easier to remove, than the conventional microporous nano-crystalline HZSM-5. In this case, a thermal decomposition curve is an effective way to acquire information about carbonaceous deposit removal, temperature, and reaction conditions. For example, Xie et al. [200] observed that a thermal degradation curve of a used catalyst, derived from catalytic dehydration of glycerol, stayed unchanged after 500 °C, indicating coke can be eliminated at 500 °C. Kassargy et al. [201] attempted to remove coke, derived from catalytic cracking of PE by combustion at 500 °C for 3 h, and showed a positive result that the regenerated USY zeolite, after the first 8 cycles, still possessed a comparable catalytic activity to the fresh catalyst. Although the USY zeolite, after 14 cycles of regeneration, was still able to catalyze the PE decomposition, the crystalline structure was destroyed, and Bronsted sites density significantly decreased, leading to the production of the liquid hydrocarbons with higher carbon number.

Another way to determine full combustion of the coke is to detect the concentration of CO<sub>2</sub> coming out from the combustion system, when 100 vol% oxygen is used as the inert atmosphere [202]. In the thermal regeneration of a Ni-based commercial catalyst, that was deactivated in the catalytic reforming of HDPE pyrolysis volatiles, the sintering of Ni<sup>0</sup> active sites made it impossible to fully recover its initial activity, after high temperature calcination [202]. Considering that high temperature may increase the possibility of catalyst structure change, non-thermal plasma was proposed as a regeneration technique by oxidizing the coke on the deactivated catalysts at a very low temperature [203]. With the high concentration of ozone induced by plasma, 97.4% of the coke can be eliminated at 250 °C. As far as I am concerned, non-thermal plasma regeneration, almost without destroying the catalyst skeleton structure, would be very promising. If the catalytic activity can be successfully recovered by this technique, the service life of the catalysts will be largely extended in the real industry. Unfortunately, it is hard to precisely control the temperature of plasma reactor in a long-time treatment and the scaling up of the non-thermal plasma technology is a challenge requiring more input.

All in all, zeolites are the most common catalysts in the catalytic cracking of PSW due to high catalytic activity for gasoline or diesel range hydrocarbons production, although metal oxides, carbon materials, and clays show good cracking ability. In particular, hierarchical zeolites with meso/macro pores are able to improve the diffusion of polymer chains, thereby enhancing the activity and extending the catalyst lifetime. Borrowed from the petroleum industry, this type of catalyst would be the most promising candidates for large-scale production. Catalyst deactivation is mainly caused by coke deposition and poisoning of active sites, both of which contribute to the loss of catalytic activity during catalytic pyrolysis of plastics. In the future, the focus should be to design the catalyst structure and regulate the acidity to enable better production of desirable hydrocarbons and longer catalyst life.

### 3.1.3. Mass and heat transfer

Mass and heat transfer is always a big issue for the pyrolysis process, which depends on the reactor design, although few literature references have studied it. It is especially important for PSW due to the low thermal conductivity of this material. For plastic pyrolysis, particle temperature inside the reactor plays the key role because plastic cannot start to degrade until the temperature reaches a certain point. Obviously,

different mass and heat transfer rates would alter the plastic conversion process, thereby affecting the product distribution and compositions. In isothermal and dynamic experiments, PP pyrolysis shows considerable discrepancies of parameters, stemming from heat transfer limitations or complex degradation mechanisms [204]. Ceamano et al. [205] observed significant longitudinal temperature profiles inside large PE samples during pyrolysis, and stressed that PE samples should be melted and then coated onto sand particles in order to maximize the contact surface for heat transfer. They also studied the thermal decomposition kinetics of HDPE, observing two causes of discrepancies from the experimental results [206]. One of them is caused by an imperfect heat transfer between plastic particles and reactor/plastic particles. Adjusting the amount of feedstock and heating rate was able to potentially resolve the heat transfer issues. It should be noted that an excellent gas-solid contact in the spouted bed reactor was also favorable to minimize heat and mass transfer limitations, keeping the bed in an isothermal condition [207]. In addition, a two-step pyrolysis process was developed by Zassa et al. with the aim of mitigating the heat transfer limitations of a multiphase reactor system [208]. In this system, the plastic melting and pyrolysis are separated, allowing uniform melting of the polymer before decomposition. In this way, the light olefins yield was significantly improved, with up to 75 wt.% of the gas being ethylene at the optimum conditions.

Aguado et al. [209] used a conical spouted bed reactor to study the kinetics of PS pyrolysis at temperatures ranging from 450 °C to 550 °C and compared the results with data derived from thermogravimetry (TGA) and a micro-reactor with extremely high heating rate. The inevitable mass and heat transfer limitations between PS and sand at high temperatures led to the lower activation energy in the spouted bed reactor as compared to TGA. Non-crystalline PS is not able to coat the sand particles uniformly with a fine layer after the glass transition, so that higher transfer limitations would be expected. The results confirmed the highly suitable characteristics of this new reactor for PS pyrolysis, stemming from the following advantages: bed isothermicity, compatibility with particles of various sizes, excellent gas-solid contact, alleviated particle agglomeration, small segregation, and shorter residence time of the pyrolysis volatiles.

The previous reports indicate that the competition between degradation and vaporization during PSW pyrolysis should be analyzed carefully [210,211]. Generally speaking, polymer molecules are too large to vaporize, so they should be converted into small molecules before vaporization [32]. Formed small molecules that are dispersed in the bulk phase and generate bubbles would be diffused into the interface between condensed bulk and vapor phase. Finally, these small molecules are able to move through the interface into the vapor phase. In a small scale pyrolysis process, the rate-determining step in the volatilization process of polymers is the degradation process where the rate-determining step is the rate of bond rupture within the polymer molecules, since the sample size and thickness are so small that the diffusion limitation can be minimized [210]. However, in large-scale reactors, diffusional limitations during the volatilization of polymers are expected. On one hand, the surface area plays a vital role in the rate of volatilization, since the rate depends on the fraction of molecules in the surface layer that have an energy equal to or greater than the minimum kinetic energy needed to break away from the surface. On the other hand, the vaporization rate is also determined by the diffusional rate within the bulk phase that is inversely proportional to the sample thickness. It is expected that solid, liquid, and gas phases would be present simultaneously during this process. In light of the multi-phase complexity of PSW pyrolysis, an extensive detailed analysis of the characteristics of all three phases should account for the mass and heat transfer phenomena during PSW pyrolysis. However, the inherent complexity of the problem of polymer pyrolysis makes the implementation of the multi-phase simulations remarkably challenging. Unfortunately, these challenges have not been addressed, so that there is an important research gap, yet to be filled, regarding the effect of mass and

heat transfer on the degradation behavior of PSW.

One of the effective ways to investigate the heat and mass transfer is making use of dimensionless numbers such as pyrolysis numbers (Py), Biot number (Bi), Pécelt number (Pe), and Lewis number (Le) [212–215], which are useful in assessing the performance and limitations of pyrolysis reactors (Table 6). Py numbers determine whether the pyrolysis process is governed by the reaction kinetics ( $Py \gg 1$ ) or conductive/convective heat transfer in the particle ( $Py \ll 1$ ). In the case of  $Bi \gg 1$ , heat transfer through intraparticle conduction is slower than external heat transfer through convection. In contrast, the external heat transfer would dominate the pyrolysis process. If  $Py \ll 1$  and  $Bi \gg 1$  are simultaneously obtained, thermal gradients can be observed inside the particles and thus the reaction rate inside the particle is significantly lower than the surface of the particle. The case of  $Pe \gg 1$  means that convective mass transfer from the particle is much faster than the diffusion of volatilizing molecules through the reacting particle. For an analogous comparison in the heat transfer phenomena,  $Le \gg 1$  indicates that the intra-particle heat transfer occurs much faster than the mass transfer.

### 3.2. Valuable gas from pyrolysis of PSW

Apart from the production of liquid hydrocarbons by PSW pyrolysis, obtaining valuable gas byproducts, such as light olefins and hydrogen, with high selectivity, is another feasible recycling method. Apparently, light olefins can be used to produce new plastic products, creating a circular economy for plastic waste. Hydrogen produced from PSW pyrolysis can be recognized as the “blue hydrogen” or even “green hydrogen” that greatly mitigates carbon emissions as compared to fossil-based hydrogen, making a contribution to carbon neutrality. This section will discuss the production of light olefins and hydrogen from pyrolysis of PSW in detail.

#### 3.2.1. Light olefins

Light olefins, including ethylene and propylene, are the feedstock for the production of plastics and many other downstream chemicals. Advancements in the PSW-to-light olefins technology have led to a circular economy of plastics instead of linear use, enabling the PSW to stay in the economy and out of the environment. Kaminsky et al. [216] took the lead in light olefins production by pyrolysis of plastics, and successfully obtained high yields of light olefins consisting of approximately 36% ethylene, 15% propylene, 9% 1-butene and butadiene. Rather than using catalyst materials, however, their results were obtained based on the increase of temperature and the addition of steam. This example reveals how steam improve the production of light olefins during catalytic pyrolysis of PSW.

For catalytic pyrolysis of polyolefins, relatively low yields (<40 wt%) of light olefins were usually reported based on in-situ catalysis mode and the moderate catalyst temperature (around 500 °C). For example, a spent fluid catalytic cracking (FCC) catalyst agglomerated with 50 wt% bentonite can produce as low as 28 wt% of C<sub>2</sub>–C<sub>4</sub> olefins at 500 °C [84]. The same studies also assessed the use of a spent FCC catalyst at the moderately catalytic pyrolysis of PSW, finding that 21–38 wt% of light olefins were observed [217–219]. A novel catalytic reactive distillation approach based on in-situ catalysis mode was also developed to produce light olefins from HDPE [48], where the product can be collected only when the molecular weight of the pyrolysis products is low enough to exit the cooling coil as a gaseous stream. At the operating temperature of 500 °C and 1% (w/w) of HZSM-5 (catalyst to polymer ratio), almost 100% of the HDPE can be converted into gaseous products of a specific range. The product analysis shows that the volatile products fell into the range between C<sub>2</sub> to C<sub>8</sub>, with light olefins accounting for the majority (approximately 50 wt%), in particular propylene and butenes. By tuning the reaction conditions, the middle olefins within the range of C<sub>5</sub> to C<sub>11</sub> can also be produced in this system [220]. This distillation-based pyrolysis approach provides a proof of concept that promotes a circular

economy of plastics. However, as we mentioned in the introduction, the in-situ catalysis has the shortcoming that the inorganics (in particular alkalines) in the real-world PSW would physically block and chemically poison acid sites.

Based on the insufficiency of existing catalytic pyrolysis process for production of light olefins, Eschenbacher et al. [221] and Artetxe et al. [205,222] developed a two-step (pyrolysis-catalysis) system with the goal of maximizing the yields of waxes (C<sub>21+</sub>) and C<sub>12</sub>–C<sub>21</sub> hydrocarbons in the pyrolysis reactor and then effectively cracking the produced volatiles in the cracking stage. With a bare steam-treated HZSM-5, at higher temperature (700 °C), the total yield of light olefins reached 69 wt% (19% ethylene, 22% propylene, 10% 1,3-butadiene, and 18% other C<sub>4</sub> olefins) [221]. The total yield of light olefins (C<sub>2</sub>–C<sub>4</sub>) was further enhanced to 77 wt% with the yields of ethylene, propylene, and butene being 40.4, 19.5, and 17.5 wt%, respectively, at 900 °C [222]. The high yield of light olefins can contribute to regulating and controlling the temperature for each step, where the pyrolysis temperature was optimized at 500 °C to yield 93 wt % of long chain hydrocarbons and further tuning the catalytic temperature achieved the desirable outcomes. The addition of a HZSM-5 zeolite catalyst in the catalytic reforming stage was able to reduce the temperature to below 550 °C [205]. A maximum of 62.9 wt.% of light olefins can be obtained with the yields of ethylene, propylene and butene being 10.6, 35.6 and 16.7 wt%, respectively, at this condition. More importantly, the byproduct of aromatics would never go beyond 13 wt%. Similar results were also observed in the catalytic cracking of HDPE pyrolysis waxes over HZSM-5 zeolite catalysts [223]. The catalyst with a SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of 30 showed the highest light olefin yield (58 wt%), with the yields of ethylene, propylene, and butenes being 9.5, 32, and 16.5 wt%, respectively. These collective studies highlight the importance of identifying a more efficient catalyst capable of reducing reaction temperature and tuning product distribution.

Elordi et al. [78] studied the catalytic activity of HZSM-5, HY and H $\beta$  zeolite-based catalysts during catalytic pyrolysis of HDPE, with the main products being light olefins and fuel range hydrocarbons. HZSM-5 zeolite-based catalyst show a high yield of light olefins of approximately 58 wt.% once equilibrated. An important finding is that the yield of light olefins has a strong relationship with the pore size of the zeolite catalysts being used. The HZSM-5 catalyst, with the smallest pore size, gives rise to the highest yield of light olefins; then the H $\beta$  and HY zeolites obtain higher yield of light olefins due to larger pores. In addition, the components of light olefins are also affected by the catalyst pore size. The large pore size is favorable for the formation of butenes, whereas propylene and ethylene are the main components for the HZSM-5 catalyst, with the smallest pore size.

Table 6

Dimensionless numbers which are useful in assessing reactor performance and limitations. (Adapted from [32] with permission from Elsevier).

Characteristic phenomena	Dimensionless number	Values	Significance
Reaction kinetics	$Py^I = \frac{\lambda}{\rho C_p L^2 k}$	$Py \gg 1$	Pyrolysis controlled by reaction kinetics.
	$Py^{II} = \frac{h}{\rho C_p L k}$	$Py \ll 1$	Pyrolysis controlled by heat transfer.
Heat transfer	$Bi = \frac{hL}{\lambda}$	$Bi \gg 1$	Heat transfer limitation due to intra-particle thermal gradients.
		$Bi \ll 1$	Heat transfer limitation due to external convection.
Mass transfer	$Pe = \frac{PK}{D\mu}$	$Pe \gg 1$	Release of volatiles controlled by diffusion.
		$Pe \ll 1$	Release of volatiles controlled by convective mass transfer.
	$Le = \frac{\mu\lambda}{PK\rho C_p}$	$Le \gg 1$	Negligible internal heat transfer effects.
		$Le \ll 1$	Negligible internal mass transfer effects.

### 3.2.2. Hydrogen

Selective production of hydrogen by plastic pyrolysis represents an important advance, because hydrogen has a great potential to serve as a fuel in future energy supplies. Each year over 50 million tons of H<sub>2</sub> need to be produced to support the agricultural and chemical industries all over the world, 96% of which is currently obtained from steam reforming of fossil fuels [224]. Therefore, PSW-to-hydrogen technology might be able to address two global challenges: PSW pollution and H<sub>2</sub> fuel production, if this technology can be developed and advanced to the commercial stage in the near future.

Generally speaking, two fixed bed reactors for the two-stage process are easier to be designed and operated at the laboratory scale. Approximately 0.2–0.3 g H<sub>2</sub>/g plastics was obtained in such a two-stage process at the pyrolysis temperature of 500 °C and the catalytic reforming temperatures ranging from 600 °C to 900 °C [225]. Without a catalyst, the H<sub>2</sub> yield was only 0.015 g H<sub>2</sub>/g plastics, but this H<sub>2</sub> yield was significantly increased to 0.25 g H<sub>2</sub>/g plastics by using a Ni–Mg–Al catalyst. At the high reforming temperature of 800 °C, the yield of gas derived from PS decomposition was still very low (11.2 wt.% related to the mass of plastic) without a catalyst and steam; in contrast, a 94.1 wt.% yield can be obtained after adding the Ni–Mg–Al catalyst and steam [226]. Furthermore, increasing the catalytic reforming temperature and the steam injection can improve the hydrogen production. However, scaling up the fixed bed reactor could encounter the heat and mass transfer limitation due to the inherent nature of this type of reactor.

The use of fluidized bed reactors for the two stage process has been proposed. The pioneering studies conducted by Czernik and French combined two fluidized beds to achieve a continuous plastic pyrolysis-reforming process, showing clear advantages and yielding hydrogen at 80% of the stoichiometric potential, with PP as the feedstock [227]. Barbarias et al. [228] tested hydrogen production from different plastics in an original two-step reaction system, where the plastic pyrolysis was achieved at 500 °C in a conical spouted bed reactor, followed by a catalytic reforming process at 700 °C in a fluidized bed reactor. The good mixing during a conical spouted bed enables the PSW feedstock to be heated uniformly and timely, thereby minimizing a possibility of partial or incomplete pyrolysis, and the subsequent fluidized bed is favorable for improving the catalyst utilization efficiency. Based on this reactor, polyolefins gave the highest yield of hydrogen (34.8–37.3 wt%) while PS and PET were much lower, with hydrogen yields being 29.1 wt.% and 18.2 wt.% respectively. Based on these results and Table 2, it could be hypothesized that the hydrogen production is linearly associated with the hydrogen content of plastics.

Recently, co-production of H<sub>2</sub> and high-value carbon nanotubes (CNTs) by a two-stage process, has also been reported. In this process, using a proper catalyst, hydrogen can be produced with high selectivity, and carbon nanotubes will be simultaneously deposited on the catalyst. Wu et al. [229] processed real-world waste plastics through pyrolysis-reforming over a Ni–Mn–Al catalyst, with the aim of producing hydrogen and high value CNTs. The highest hydrogen yield of 94.4 mmol H<sub>2</sub> g<sup>-1</sup> plastic can be obtained in the presence of the Ni–Mn–Al catalyst and steam, and multi-walled CNTs with parallel graphene layers were clearly observed, based on SEM and TEM images. Unfortunately, the purity of the CNTs were affected by the presence of chloride in the waste plastics, even though the polyvinyl chloride content was very low (0.3 wt.%). Given the importance of steam in the catalytic reforming of plastic pyrolysis vapors, they studied the effect of steam content on the hydrogen production and the quality of CNTs from the perspective of purity [230]. For LDPE, PP, and PS, more hydrogen was produced by increasing the steam injection rate. In terms of PS, the highest CNT yield (32 wt.% plastic conversion to CNTs) was achieved when the steam injection rate was 0.25 g h<sup>-1</sup>.

Regarding the pyrolysis-reforming of PSW for clean hydrogen production with high-value CNTs as a by-product, catalyst would play a vital role in the hydrogen yield and CNTs quality. Acomb et al. [231] screened different metals supported on Al<sub>2</sub>O<sub>3</sub> at the pyrolysis

temperature of 600 °C and a reforming temperature of 800 °C. Experimental results indicated that CNTs can be formed in quantity, on nickel, iron, and cobalt based catalysts, while copper based catalyst had the opposite result, with only trace amounts of CNTs. Of the catalysts tested, Fe based catalyst gave the highest hydrogen yield. Ni–Fe bimetallic catalyst was developed and used in the pyrolysis-catalysis of waste plastics, showing a potential catalytic performance [232]. The presence of Ni and Fe was able to play a different role, where Fe showed a higher cracking ability, producing more hydrogen and solid carbon, while the Ni improved the thermal stability and graphitization degree of CNTs. The highest H<sub>2</sub> yield was 7.24 g/100 g plastic sample, with H<sub>2</sub> concentration of around 70 vol% and carbon yield was 46 g/100 g plastic sample. They compared the results with other studies, confirming the superior catalytic performance. By further comparing the carbon materials produced in different catalytic temperatures, it can be found that higher temperature is favorable for improving carbon deposition and high quality ordered carbon nanotubes should be produced at higher than 700 °C [233]. That could be due to the fact that complex carbon precursors produced at lower temperatures made the dissociation and dehydrogenation more difficult to grow graphitic layers. Ru/γ-Al<sub>2</sub>O<sub>3</sub> was found to be very effective for steam reforming of PS pyrolysis vapors to hydrogen-rich gas, and lowering the temperature by 200 K as compared to a conventional Ni-based catalyst [234]. Understandably, with a drop in reforming temperature, less thermal input would be required, leading to an increase of thermal efficiency for the whole process.

Although the above-mentioned studies have suggested that two-step process is able to produce high purity hydrogen, it has also been demonstrated that one-step (in-situ catalysis mode) process may also be promising in the catalytic deconstruction of PSW into hydrogen and high-value carbons [88]. The one-step microwave-initiated process facilitates catalytic scission of chemical C–H bonds over an active FeAlO<sub>x</sub> catalyst by generating huge temperature gap (over 400 °C) between the catalyst and substance. Therefore, a high hydrogen yield of 55.6 mmol/g plastic can be obtained, with over 97% of the theoretical mass of hydrogen being extracted from the deconstructed plastic. The results are based on very small microwave batch experiments (0.3–0.4 g plastics processed for each run), so the largely different mass and heat transfer and limited microwave penetration depth for a large scale operation could affect the process efficiency and product selectivity.

### 3.3. Naphtha production from pyrolysis of PSW

Although plastic-to-fuels technology enables the reduction of PSW, fuels are currently burned to provide heat or electricity, causing serious greenhouse gas emission. In this way, the demand for virgin plastics cannot be offset, and the virgin plastics are still produced from fossil sources. Some researchers even claim that this solution is not recycling; it is really just another expensive and complicated way to burn fossil fuels. However, manufacturers and end-users are challenged to utilize recycled plastics instead of fossil based plastics although they hope that 100% of packaging could be recyclable. As mentioned in the Introduction part, the current recycling method (melting and remolding) often encounters a challenge because the recycled plastics does not perform as well as virgin plastics. Without a bold shift in approach, it is very difficult to achieve the goal set of plastic circular economy. The good news is that emerging and scaling technology is developed to convert PSW to naphtha that gets back into circulation as a new feedstock for plastic product (Fig. 12). In the petroleum industry, naphtha-to-plastic monomers technology (steam cracking) is very mature. If we are able to produce naphtha through PSW pyrolysis and ensure it to meet the feedstock requirements for petrochemical cracking process, plastic-to-plastic chemical recycling could not only be comparable to the more prevalent technique called “mechanical recycling” but also enable the same quality to the virgin plastics, and be suitable for complicated plastic mixtures. To be honest, the PSW-to-naphtha technology is really

accelerating solutions for a more circular recycled plastics supply chain at scale.

It is known that some major companies aim to promote PSW recycling towards increasing the share of recycled plastics in the market. In this potential circular-economy, one of the most important sectors is to turn PSW into pyrolysis oil used as feedstock for new plastic products. The corresponding pilot scale results presented to consumers show that the pyrolysis oil (recycled naphtha) based plastics have the same quality and application capability as those manufactured from fossil oil. It also pointed out that this PSW recycling method is complementary to mechanical recycling, for the time being, because some sorted single-stream plastics can be recycled mechanically. For a plastic mixture which cannot be mechanically sorted efficiently, this chemical recycling for converting PSW back to naphtha for new plastic production should be more reasonable. It should be noted that this virgin-quality recycled plastic from pyrolysis to naphtha could increase availability of plastics for food-grade products, because the mechanically recycled plastics are not allowed to enter into food packaging.

Recently, Ruan's group has licensed continuous microwave-assisted pyrolysis technology [94] to a California company for converting PSW to low-carbon and low-sulfur fuels and high quality naphtha. That could be a great step to deal with the PSW by pyrolysis technology. More importantly, the system is modular, compact, and portable so that it can be fixed on small boats and large ships, making it flexible in a number of ocean cleaning scenarios. The California company has also been expanding its processing capability, currently (2021) with a capacity of 1–5 t/day PSW. Another big company in Skive, Denmark is also working hard to develop technology which can recover naphtha from PSW, with the goal of creating a circular value chain. What makes this company unique is that they designed an effective catalyst for hydrocracking of plastic pyrolysis volatiles. It turns out that the catalyst could alter the molecular structure of hydrocarbons, obtaining desirable components. This company built the first testing facility in 2014, confirming that pyrolysis of PSW to produce desirable products by the unique technology was feasible. By now, they have started the first production facility in Skive, Denmark and the factory was successfully scaled to 20,000 tons of PSW per year. In the future, they plan to build more and larger facilities across Europe, or even the world.

In order to further advance the plastic-to-naphtha technology, the

clear demand is to expand capacity and improve technologies to create a circular economy for plastics. These practical examples indicate that it is totally possible to return more PSW to supply chains than is currently in play today, giving the credit to the innovation developed and scaled by technology providers. Unfortunately, the scientific community has not yet been devoted to this technology too much. Based on current literatures, the main components of liquid oil produced from PSW pyrolysis are unsaturated hydrocarbons and aromatics [16,19,220,236]. In the petroleum industry, the steam cracking for light olefins production requires the C<sub>5</sub>–C<sub>12</sub> saturated hydrocarbons as much as possible, with a minimum amount of aromatic. It was found that in the in-situ catalytic pyrolysis of HDPE at 500 °C (Al<sub>2</sub>O<sub>3</sub> pillared montmorillonite clay and HDPE mixture with the ratio of 1:1), over 50% C<sub>5</sub>–C<sub>12</sub> alkanes and about 15% of aromatics can be obtained, with the liquid yield of 60–70 wt.% [237]. However, in light of the drawbacks of the in-situ catalysis including fast deactivation of catalyst caused by the impurities in the real-world plastics, discontinuous process, higher operation cost, and low heat and mass transfer, ex-situ catalytic reforming of plastic pyrolysis volatiles for naphtha production was developed [238]. That was an ex-situ tandem catalysis process, where the first catalytic reforming zone was intended to improve the cracking of plastic pyrolysis wax into shorter chain olefins, and the second lower-temperature catalytic reforming zone was intended for the hydrogenation process to convert olefins to alkanes without high pressure or the use of external hydrogen (Fig. 13). In the first catalytic zone, polyolefin cracking proceeded via free radicals, mainly consisting of initiation, chain propagation, and termination. Initiation reactions primarily include random cracking and end chain cracking, which break C–C bonds of the long chains of polyolefins, generating free radicals and molecules. The formation of carbenium ions in the initiation reactions was demonstrated to work by abstraction of a hydride ion on the acid site of the catalyst. Then, propagation reactions occurred, to keep the cracking reactions going, meaning that the free radicals generated during the initiation reactions, broke off during the β-scission reactions. β-scission reactions enable the large free radicals generated from the initiation reactions, to be cracked into C<sub>5</sub>–C<sub>12</sub> olefins and smaller free radicals. Finally, the chain propagation reaction is terminated by desorbing the surface carbenium ions, forming C<sub>5</sub>–C<sub>12</sub> olefins and hydrons. The main function of Al<sub>2</sub>O<sub>3</sub> pillared M-clay in the second catalytic zone would be to convert the

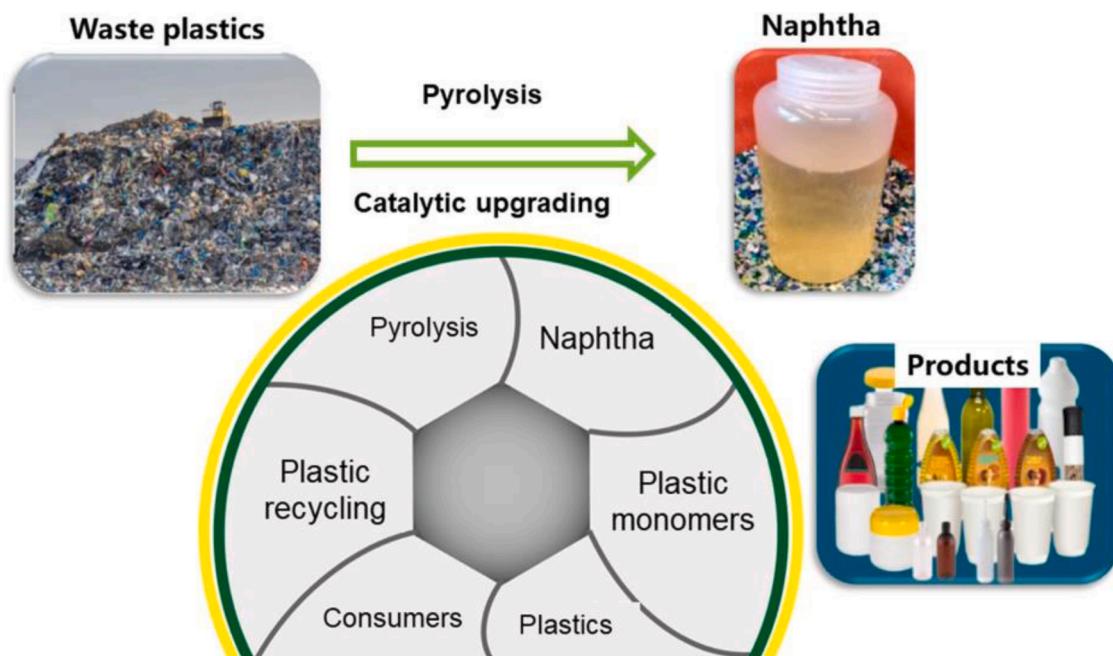


Fig. 12. Plastic-to-naphtha technology roadmap. (Reprinted from [235] with permission from Elsevier).

obtained short chain olefins to C<sub>5</sub>—C<sub>12</sub> paraffins via hydrogen transfer reactions. Most of the olefins were converted into paraffins with the simultaneous formation of aromatics. The issue for this process is that the low cracking ability of the first catalytic zone shortens the process lifetime, thereby highlighting the importance of new cracking catalysts with higher stability.

In terms of plastic-to-naphtha technology, the top priority right now should be to increase the selectivity of naphtha range aliphatic hydrocarbons by developing better cracking catalysts and simultaneously mitigate the aromatic formation. Generally speaking, aromatic formation could be promoted by a synergic effect between Brønsted acid sites (aromatization) and Lewis acid sites (dehydrogenation), while catalytic cracking process largely relies on the Brønsted acid sites [239,240]. In this regard, the isolation of Lewis acid sites will suppress the aromatic formation without affecting the catalytic cracking ability of catalysts. Further research should focus on the catalyst or catalytic system development and process optimization. This plastic-to-naphtha technology is an important strategy for a bio-based circular plastics economy. However, an effective production process for high alkane content naphtha that is able to attract industrial partners is still missing. It is also difficult to recover plastics containing oxygen or nitrogen, because the catalytic reforming process for oxygen and nitrogen removal requires higher cost. At a time when the plastic-to-naphtha technology is struggling to make money, manufacturers would like to feed clean polyolefins to existing facilities to produce high quality naphtha for downstream vendors.

#### 4. Techno-economic analysis

The costs of PSW pyrolysis recycling, which will determine if it can be commercialized in the market, can be affected by many factors, such as labor, maintenance, transportation, capital investment, electricity, heat, and other plant utilities. The techno-economic evaluation of this process is essential to reduce the underlying costs of the process and improve the corresponding supply chain. This assessment and resulting recommendations will be beneficial to establish a sound strategic design for the production of fuels or chemicals from PSW pyrolysis. The return on investment (ROI) and total capital investment (TCI) are two important factors used to evaluate the performance of a PSW pyrolysis plant (Table 7). Jiang et al. [241] conducted a techno-economic evaluation of the molten solar salt pyrolysis of PSW, and found that the TCI and ROI of a 8000 t/yr plant would be USD 3.63 million and 27.6%, respectively, with the pyrolysis gas being used to power the plant. When it is scaled up to a 16,000 t/yr plant, the TCI and ROI could increase to USD 6.44

million and 49.1%, respectively. If the concentrated solar power is used as an energy source, the TCI would present a 20% increase and the ROI would decrease by 11%. Westerhout et al. [242] compared different reactors from the perspective of the techno-economic analysis. They drew a conclusion that the ROIs of a bubbling fluidized bed reactor operated at 740 °C and a circulating fluidized bed reactor operated at 840 °C are 21.7% and 29.5%, respectively, which are both higher than a rotating cone reactor operated at 625 °C with the ROI of 14.2%. They also estimated the TCI for a 50,000 t/yr pyrolysis plant would be between USD 7.84 and 11.2 million. The specific production cost of the plastic oil was estimated, based on a plastic-to-heavy fuel plant with a capacity of 100 kg PSW/h [13]. At this scale, the cost of plastic based heavy fuel oil was about £0.87/kg, which is much higher than the price of the market product, whereas the value can be reduced significantly by further scaling up, showing improved economic feasibility. If the processing capacity of the pyrolysis plant is able to reach 100,000 kg/h, it will be profitable within a year.

A waste HDPE refinery for processing 500 tons/day was designed, and the corresponding techno-economic analysis was conducted [243]. As shown in Fig. 14, the products obtained from the refinery process, with four sections, would include plastic monomers (ethylene and propylene), aromatics, low- and high-molecular weight hydrocarbon (MWHC) mixtures. According to the capital cost estimation, including the fixed capital investment, total project investment and total installed cost, and indirect costs (engineering, consulting, construction, etc.) are the highest for both the base and heat integrated cases. In this study, the net present value (NPV) obtained from discounted cash flow analysis was used as an indicator to estimate the economic feasibility of the HDPE refinery process. Results showed that the heat integrated refinery had the NPV of 383.1 MM USD while the NPV of the base case was 366.75 MM USD. Sensitivity analysis was also conducted to study the effect of ten parameters (total project investment, internal rate of return, corporate tax rate, HDPE cost, electricity cost, ethylene price, propylene price, aromatics mixture price, low MWHC price, and high MWHC price) on NPV. It was found that the NPV decreased with the increase of the HDPE cost, electricity cost, and federal + State corporate tax linearly. More importantly, when the HDPE cost goes beyond 460 USD/tonne, the NPV would be negative, enabling the project to be economically unfeasible. However, it was suggested that the HDPE refinery process, with economic sustainability, was quite promising.

As described in the study by Larrain et al. [244], PSW pyrolysis can be classified into open-loop and closed-loop recycling processes. A closed-loop recycling process represents a plastic-to-naphtha technology as naphtha is a feedstock for new plastic production; while an open-loop

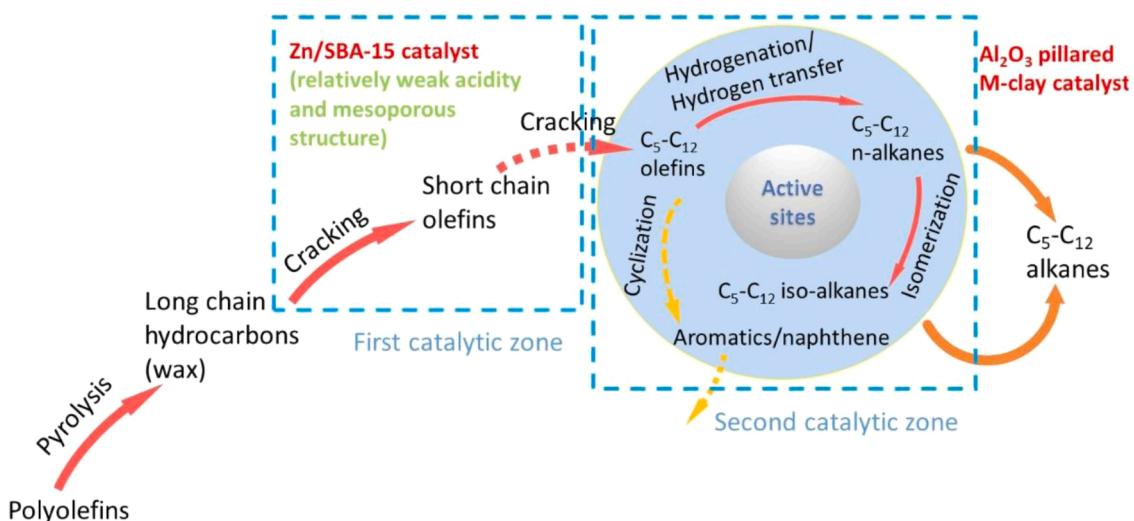


Fig. 13. Reaction mechanism for catalytic reforming of HDPE pyrolysis volatiles by a tandem catalysis. (Reprinted from [238] with permission from Elsevier).

recycling process means that PSW will be converted into waxes used for other applications. They compared the economic performance of the two processes. The economic assessment indicates that open-loop recycling presents a better economic performance when compared to close-loop recycling, with the higher price of output product. To enable these recycling processes to be feasible and cost-effective, the minimum PSW processing capacity for open-loop and close-loop recycling should be 70,000 t/year and 115,000 t/year, respectively. The supply of PSW feedstock must be ensured as well.

Designing for circularity has gained wide interest in the plastic industry, requiring manufacturers and users to rethink how to recycle PSW. Recovering ethylene monomer via pyrolysis of polyolefins is an emerging field, which follows the principles of a circular economy. Somoza-Tornos et al. [245] explored the economic benefits of this technical route in the chemical industry. The main contributors to the capital cost of the PE-to-ethylene process include the installation of the pyrolysis reactor (accounting for 12%), the compressors of the main process (accounting for 18%), the energy used for the refrigeration cycle (accounting for 32%), and the heat exchanger network (accounting for 15%). Economic assessment results showed that ethylene recovered from PE pyrolysis was able to offer a highly competitive cost of 0.386 €/kg that is much lower than the standard naphtha-based cost (0.835 €/kg). They drew a conclusion that converting waste PE to ethylene via pyrolysis seems feasible based on the proposed market assumptions in this assessment.

## 5. Environmental considerations

Life cycle assessment (LCA) plays an important role in identifying the environmental impacts of a product throughout its life cycle [247,248]. This tool can be used to compare different life cycles for alternative products and processes. As shown in Fig. 15, four stages (the goal and define the system boundary, mass and energy flows, life cycle impact assessment for all processes, and sensitive analysis) need to be implemented. The final results obtained are beneficial to the product improvement and to minimize the underlying impact of the process. Alston et al. [249] evaluated the environmental impact of the pyrolysis, incineration, and landfill of waste electrical and electronic equipment, containing up to 25% plastics via LCA analysis. They found that the main impact for landfill was in terms of requirements for huge land space and pollutants emission. In addition, persistent organic pollutants, such as polycyclic aromatic hydrocarbons and polychlorinated biphenyls, can be released from landfilling [250]; what is worse is that pollution and soil contamination may serve as breeding ground for pests and diseases

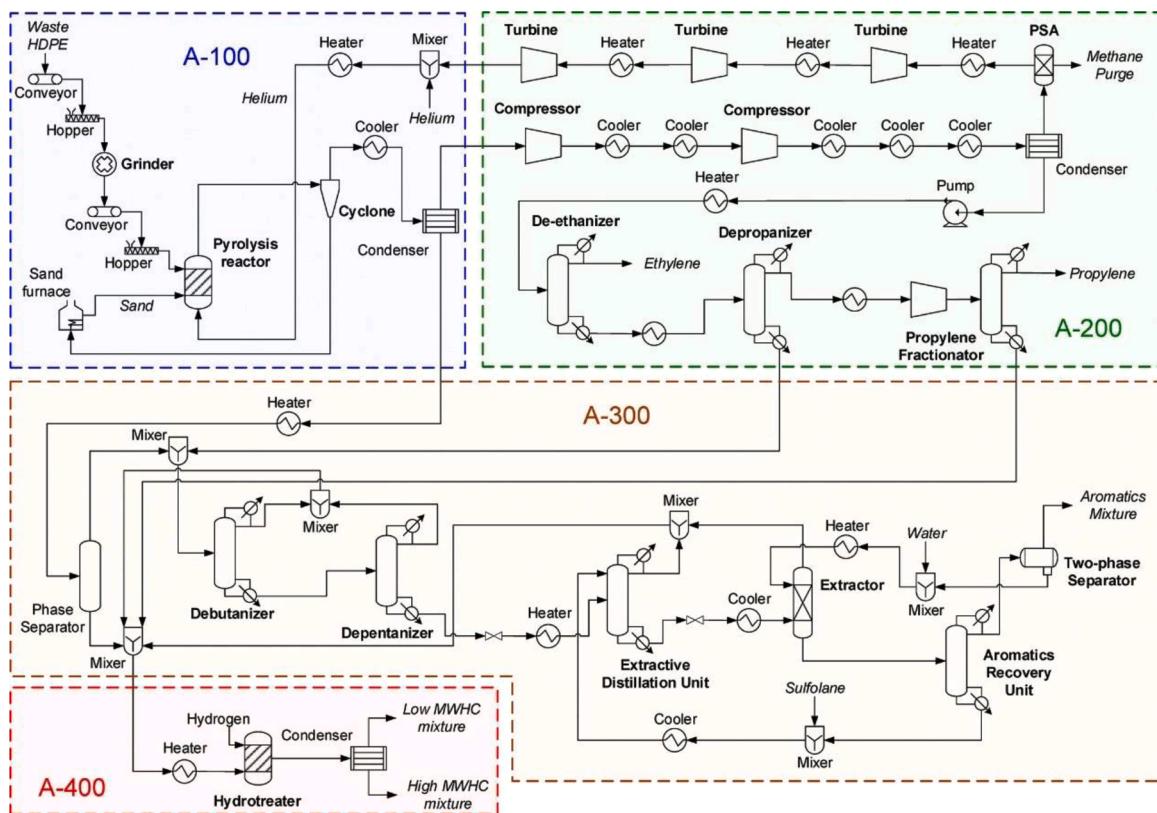
[251]. However, pyrolysis can significantly reduce the greenhouse gas emissions, pollutants emission, and requirement for landfill space; it also provides much greater resource savings than landfill and a comparable level to those for incineration [252,253]. According to an LCA study, integrating carbon nanotubes production to the plastic pyrolysis process is favorable for further reduction of climate change impact, fossil depletion, radiation potentials, and human toxicity [254]. Furthermore, a higher PET share in the PSW feedstock, can increase the impact to the environment.

Greenhouse gas (GHG) emissions are the major environmental burden for PSW pyrolysis. Many years ago, the first study of GHG emissions from PSW pyrolysis was conducted, based on a British Petroleum polymer cracking process (BP process) with a mixture of polyethylene terephthalate (PET) and polyolefins as a feedstock [255]. This study found that the GHG emissions were 1.7 kg CO<sub>2</sub> equiv/kg plastics, which was lower than other processes, such as landfill, combustion, and hydrocracking. Similar results that the pyrolysis process produced less GHG emissions were obtained from other studies [256,257]. These studies also pointed out that GHG emission savings can be improved by suppressing the use of fossil based raw materials. Iribarren et al. [258] conducted the LCA of a pyrolysis process, coupled with catalytic reforming, and targeting gasoline and diesel production within the cradle-to-gate scope. In this study, the GHG emissions were 2.44 kg CO<sub>2</sub> equiv/kg gasoline. On the other hand, Gracida-Alvarez et al. [259] analyzed the life cycle carbon footprint of a HDPE refinery design in detail, and provided the effect of regional electricity grids on GHG emissions. This study indicates that the proposed refinery process of HDPE is able to produce high quality plastic monomers and aromatics with less GHG emissions as compared to those from fossil oil, assuming American average grid electricity.

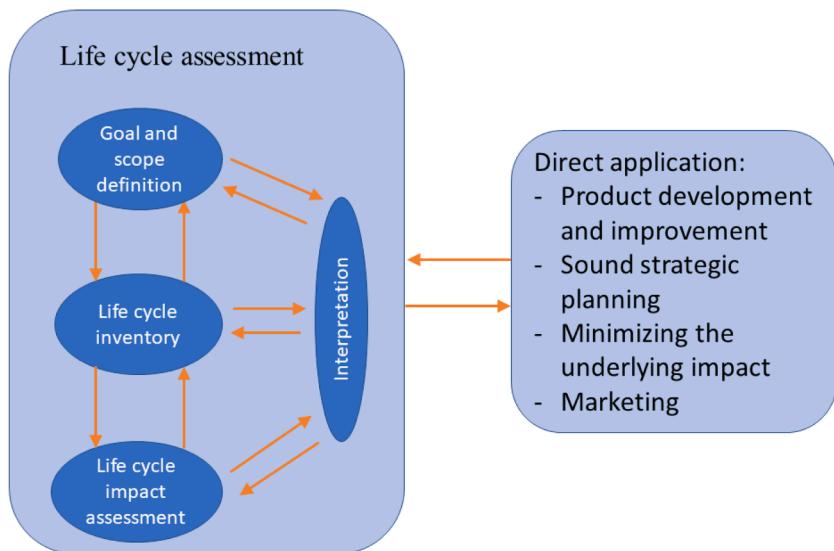
Apart from the emissions in the pyrolysis process, the GHG emission during the conversion of plastic pyrolysis oil, is another aspect for environmental considerations. By comparing the GHG emissions of fuels obtained from PSW pyrolysis and crude oil refinery, Gracida-Alvarez et al. found that pyrolysis fuels caused 8% lower emissions per megajoule [260]. A similar conclusion was also observed in another study [261]. Life-cycle GHG emissions of plastic-derived ultralow sulfur diesel were reduced by 1% to 14%, compared to petroleum diesel, depending on the co-product utilization technology. But the study by Kalargaris et al. showed that all measured emissions (NO<sub>x</sub>, HC, CO, CO<sub>2</sub>) experienced an increase with the addition of plastic pyrolysis oil in the diesel fuel [262]. In this regard, creating a circular economy by converting PSW into naphtha or light olefins could significantly reduce the GHG emission.

**Table 7**  
Literature reports on economic evaluation of pyrolysis of PSW.

Reactors	Products	Plant scale (ton/yr)	TCI (USD million)	ROI	Production cost (USD million/yr)	Refs
Molten salt reactor powered by pyrolysis gas	Pyrolysis oil/wax	4000	3.63	10.7%	1.76	[241]
	Pyrolysis oil/wax	8000	4.41	27.6%	2.51	
	Pyrolysis oil/wax	16,000	6.44	49.1%	3.55	
Molten salt reactor powered by concentrated solar power	Pyrolysis oil/wax	4000	4.34	9.4%	1.74	[242]
	Pyrolysis oil/wax	8000	5.40	24.1%	2.38	
Bubbling fluidized bed	Pyrolysis oil/wax	16,000	8	41.2%	3.34	[242]
	Ethylene and propylene	50,000	8.2	21.7%	4.3	
	Ethylene and propylene	50,000	10.4	14.2%	5.4	
Rotating cone reactor	Ethylene and propylene	50,000	7.3	29.5%	4.5	
Fluidised bed reactor	Pyrolysis oil/wax	7000	5.40	25%	2.9	[13]
	Pyrolysis oil/wax	70,000	15.1	50%	5.7	
	Pyrolysis oil/wax	700,000	91.8	100%	34	
Fluidised bed reactor	Gasoline/diesel	10,000	16.0	4.17%	5.9	[246]
	Gasoline/diesel	60,000	42.4	23.8%	29.3	
	Gasoline/diesel	120,000	63.3	35.7%	56.2	



**Fig. 14.** The detailed HDPE refinery process. A-100 represents pyrolysis section. A-200 represents monomer separation section. A-300 represents aromatics extraction section. A-400 represents hydrotreatment section. (Reprinted from [243] from permission from ACS Publications).



**Fig. 15.** The life cycle assessment framework.

## 6. Challenges

From an industrial level, many start-ups have been taking action on the PSW pyrolysis technology, and have built several promising facilities, with the hope of keeping more PSW out of landfills and our environment. In the scientific community, the constantly updated plastic decomposition/reforming mechanism and advanced catalysts/systems demonstrate the potential feasibility of high-quality products produced from PSW. The coming years will tell whether the pyrolysis technology is able to make a real change for PSW recycling/upcycling. To achieve

breakthroughs and advance the plastic pyrolysis technology into the commercial stage, continued efforts are suggested to address the following challenges.

- (1) Theoretically, the pyrolysis system and technology can be customized to produce a product based on the needs of customers, ranging from heavy oil to gasoline, naphtha, or jet fuels. However, the real world PSW is extremely complicated, probably containing pigments, dyes, coatings, paper, metal foils, glass and metal fragments etc., which might affect the quality and purity of

fuels. Accepting the fact that mixed PSW will, in reality, normally contain some level of PVC, more advanced systems are required to separate the PVC from the real-world plastic mixture or remove the hydrochloric acid in the final liquid product. In this regard, the scientific and industrial community has been developing commercial PVC and other impurities removal system based on multi-spectral sorting machinery with artificial intelligence. For other potential contaminants in the real world plastic waste that can not be identified by the spectroscopic technology, a variety of technologies can be applied to further purify the plastic waste, such as air separation systems, hydrocyclones for separating liquid from solid, and integrated water/acid/alkaline/solvent washing systems.

- (2) In terms of catalyst material, what restricts its development is the steric and diffusional hindrance of the large polymer molecules within the zeolite micropores, which is inspiring new consideration for mesoporous or hierarchical materials, such as MCM-41 and SBA-15. Although hierarchical zeolites are expected to improve the catalytic activity and product selectivity by tailoring the porosity and acidity, increasing catalyst stability and regeneration-reaction cycles is still a great challenge. In cases where mesoporous materials show superior diffusion to micro-porous counterparts, evidence of longer lifetime for mesoporous materials during catalytic pyrolysis of PSW is generally lacking.
- (3) The high percentage of olefins in the pyrolysis oil also limits the economic feasibility, whether used as fuels or a raw material for new plastics manufacturing. When the pyrolysis oil is planned to be used in the transportation fuel industry, an excessive amount of olefin is not permissible since they may lead to the formation of unwanted gums inside engines. With regard to the steam cracking in the petroleum industry, the most desirable compositions are C<sub>5</sub>—C<sub>12</sub> paraffins, with less amounts of olefins and aromatics. Until now, there are no reports for producing plastic-derived naphtha with the same quality as fossil naphtha. So, selective production of naphtha-range alkanes, with minimal amounts of olefins and aromatics, can be considered a significant step forward for PSW pyrolysis. But continued research efforts may achieve expected results by developing promising catalysts. If plastic-based naphtha can be used as an alternative to fossil naphtha for plastic monomers, without any changes needed in the existing petrochemical infrastructure, pyrolysis is expected to open up new possibilities for closed-loop recycling PSW on a large scale. In light of the production of plastic-derived naphtha, PE and PP could be the most attractive feedstock because catalytic cracking of PE and PP with the linear molecular structure is favorable for paraffinic naphtha production, but aromatic plastics will mainly produce aromatics. Certainly, advanced collection and sorting systems may be possible to separate PE and PP out from plastic mixture, but processing industrial plastic waste, such as automobile units and agricultural films, which are mostly composed of PE and PP, into naphtha is more promising and cost-effective.
- (4) Another option for PSW pyrolysis is to maximize the light olefins and/or hydrogen, which is absolutely advantageous over incineration or direct landfill. However, unlike the plastic-to-naphtha technology, this strategy is unable to match the current facilities in the petrochemical industry. It requires a big capital investment, making marginally profitable PSW recycling even less practical. Although researchers have verified the feasibility of hydrogen production from PSW via pyrolysis, some issues, such as expensive catalysts, the hydrogen storage dilemma, and

hydrogen separation, are still hampering this potential industrial application. Therefore, compared to plastic-to-fuels or naphtha technologies, valuable gas production seems to be less popular for investors, partners, and customers due to the need of developing new downstream process (separation and purification of the complicated gas).

- (5) Besides, it should be noted that converting aromatic PSW back to aromatic monomers by pyrolysis, is also highly recommended for a circular economy. In this pathway, the selective decomposition of aromatic PSW into desirable monomers requires an effective and unique catalyst, which facilitates the cleavage of C—O or C—C bonds between aromatic rings. Recently, Jing et al. [263] provided the first example of selectively producing aromatic monomers from PS, PET, PC, or their mixtures, via catalytic hydrogenolysis, achieving 75–85% monomers yield. But this process involved an expensive catalyst (Ru/Nb<sub>2</sub>O<sub>5</sub>), high hydrogen pressure, and toxic octane as a solvent. If the recommended pyrolysis-catalysis process can obtain the similar results, it should be quite promising and favored by the industry from the standpoint of process economic and environmental consideration. Additional research and development are needed to further develop new catalysts and optimize the process, in order to make it suitable for commercial grade aromatic monomers production from aromatic plastic wastes.

## 7. Concluding remarks and outlook

This review shows that research in catalytic pyrolysis of plastics is very attractive, especially in recent years when the government and the public are aware of the hazards of ever-increasing plastic pollution. Although encouraging progress has been made, recent changes in the collection and sorting of complex PSW and longer-term trends in the demand for creating a plastic circular economy require further developments in the areas of the plastic pyrolysis oil characterization, reactor designs, and catalysts. From the perspective of oil characterization, distillation coupled with a combination of GC-FID/MS, FTIR, NMR, SEC is recommended to strengthen fundamental understanding of complicated pyrolysis oil product.

Although different reactors have been developed, there is no direct way to compare their performance based on the current studies. Heat and mass transfer limitation should be evaluated by establishing accurate kinetic models, which allow to successfully simulate the real temperature and product distributions, to better describe the three-phase nature of PSW pyrolysis. It should be noted that a two-step process composed of pyrolysis followed by catalytic reforming is expected to open up new possibilities for large-scale treatment of PSW, since it allows a higher activity and product selectivity. After much effort is focusing on the catalyst development and process optimization for high quality fuel production, the plastic-to-fuels technology has been demonstrated in the commercial stage, which will provide a reference for the development of plastic circular economy.

Recently different studies have been conducted on catalyst development for PSW pyrolysis, but the catalyst lifetime and detailed coke formation mechanism are unclear during the process. Firstly, it is important to make use of extensive product information (dry gas, liquified petroleum gas, gasoline, diesel, and wax) for evaluating catalyst performance based on the carbon efficiencies of each group. Secondly, in-depth characterization should be performed for analyzing the structure changes and macromolecule species present in the structure with time on stream. Furthermore, the identification of initiator fragments for coke formation by in-situ reaction monitoring would enable the analysis of coke species evolvement.

In order to create a plastic circular economy by recovering raw materials from PSW pyrolysis for manufacturing new plastic products, an important field of research calls for more input. That is to develop advanced catalysts and processes to convert PSW to naphtha, light olefins, and aromatic monomers as alternatives to the current fossil resources for new plastic production. Future development of selectively catalytic pyrolysis of PSW would greatly benefit from more in-depth knowledge of fundamental mechanisms. This urges us to place more emphasis on experimental studies to go beyond observational findings toward efforts that address how changes to each catalyst characteristic (acid/active site distribution, pore connectivity, framework architectures, etc.) alter the reaction pathways and its corresponding impact on product selectivity. In light of the complexity of the polymer chains pyrolysis, the model compounds, for example eicosane, can be used for reaction mechanism explanation. In situ characterization techniques would capture the reaction intermediates that are useful information for determining reaction pathways and increase our understanding of catalyst deactivation as well. Regarding the steric and diffusional hindrance of the polymer chains during catalytic reactions, the effective solution for further improving the performance of hierarchical zeolites is to finely balance the interplay between the catalytic active sites located in the micropores and the accessibility of these sites provided by the mesopores. It is also necessary to develop a reliable strategy to evaluate the effectiveness of hierarchical zeolites by comprehensively considering the influence of absolute porosity values and active sites. These insights will guide us to predict the chain length distribution of products and fine-tune the catalyst structure to meet different product demands.

On the other hand, the solution to a complicated PSW mixture is suggested to be separated into polyolefins, aromatic plastics, and others, and then a proper waste plastics decontamination process may be implemented to meet the requirement for the target downstream application of pyrolysis oil. In this regard, polyolefins are suitable for naphtha and light olefins/hydrogen production, while aromatic plastics should be targeted to produce aromatic monomers. However, if the PSW mixture sorting is not realistic or economical, the mixture of naphtha, light olefins, and aromatic monomers can be directly produced from the plastic mixture, following by an aromatic extraction process to separate aromatic monomers from naphtha.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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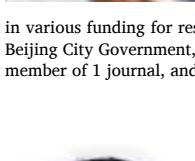
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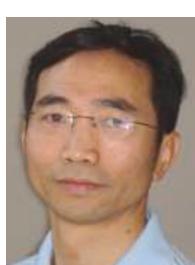
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