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Elevation of pyrolysis from a random to a product-selective process through the selection of reaction conditions

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This review redefines waste plastic pyrolysis as a controllable process governed by underlying reaction mechanisms rather than a purely thermal decomposition route, positioning it as a tunable platform for chemical production. It demonstrates that product distribution is governed by the interplay of reaction conditions, reactor design, catalyst chemistry, and vapor-phase transformations, rather than the polymer structure alone. A key transition from radical-dominated thermal cracking to catalyst-mediated ionic pathways is established. In this transition, catalysts suppress uncontrolled free-radical reactions and promote selective carbocation-driven mechanisms. Importantly, catalysts are reconceptualized as post-cracking molecular architects that primarily act on pyrolysis vapors. In addition, their direct secondary transformations, such as β-scission, isomerization, aromatization, and hydrogen transfer, are directed toward targeted hydrocarbons. Acidic catalysts favor aromatic formation, basic catalysts promote olefin generation *via* hydrogen abstraction, and metal catalysts regulate hydrogenation-dehydrogenation reactions, improving product stability and selectivity. Reaction engineering parameters, including temperature, heating rate, and reactor configuration, critically control heat- and mass-transfer, vapor residence time, and the extent of secondary cracking. Catalyst morphology further influences diffusion and reaction pathways, where microporous structures enhance gas formation, while mesoporous and hierarchical catalysts enable higher liquid yields with reduced coking. Overall, this review highlights that the selective production of fuels and chemicals from plastic waste is achieved through coordinated control of kinetics, reaction mechanisms, and transport phenomena. This establishes pyrolysis as an engineered and scalable route for sustainable resource recovery and circular chemical manufacturing.

1. Introduction

Development of economical and eco-friendly methods for the disposal of waste is one of the primary tasks of science and scientists. Several persistent wastes, including glass, metals, and plastics, make their way to the trash on a daily basis, increasing the bulk of solid waste.[1] The use and production of non-biodegradable plastics have tremendously increased due to the rapid growth in population and changes in lifestyle. Among plastics, large quantities of waste polyethylene and polystyrene are produced due to the tremendous use of these plastics in household and industrial packaging. In many cases, high-density polyethylene has replaced metals and, in some cases, wood. Large-scale production and consumption of plastics result in the production of large quantities of plastic waste.[2] This tremendous increase in the quantity of plastic waste is polluting the oceans, rivers, and other water bodies, in addition to the sewerage system and soil. There are various approaches for the disposal of waste plastics. One of the best approaches is tertiary recycling, which is carried out using pyrolysis. Pyrolysis of waste plastic is an eco-friendly and economic method for disposal. It is associated with the recovery of a wide range of hydrocarbons, including aromatics, cyclic hydrocarbons, paraffin, and olefins.[3] Pyrolysis results in the cracking of the macromolecular skeleton of the plastic. This leads to the formation of gaseous, liquid, and residual products.[4] In addition to cracking, pyrolysis also involves recombination and quenching reactions through cyclization, aromatization, and the formation of multiple-bond functionalities. Pyrolysis is initiated at elevated temperatures and results in the formation of a broader range of compounds. Therefore, in many cases,

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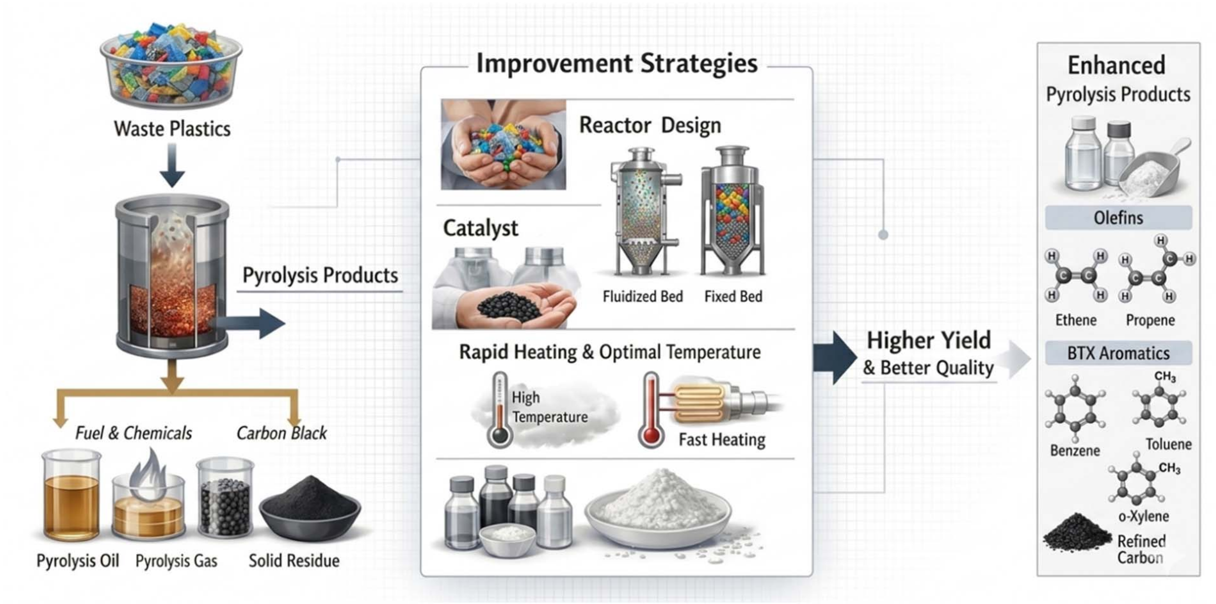

Fig. 1 Strategies for enhancing the oil yield and product selectivity: catalysts, reactor design, heating rate, temperature, and additives.

simple pyrolysis is not useful for the recovery of value-added chemicals from waste plastics.

Valorization and upgradation of the product of pyrolysis of waste plastics is one of the hot topics in pyrolysis science.[5] The yield of pyrolysis, as well as the quality of the products, can be improved using several strategies. These include the use of catalysts, reactor design, rate of heating, and heating temperature, in addition to the use of additives (Fig. 1). It has been observed that catalytic pyrolysis narrows the range of products or increases the concentration of compounds. This makes it easier to recover useful chemical feedstock. Plastic-derived oil has become one of the important resources. It is obtained by the pyrolysis of waste plastics.[6] The pyrolysis of waste plastics gives oil, gas, and char as the major products. The relative quantities of these fractions may vary with variations in the plastics, the rate and range of heating, the heating temperature, and the reactor and catalyst. It has been observed that waste plastic oil may pass through multiple reactions after its formation. Major reactions of the plastic-derived oil are polymerization and oligomerization, which result in unwanted changes in both the physical and chemical properties of the oil.[7] These include changes in viscosity and volatility, which are responsible for reducing the quality of the oil. These changes and transformations arise due to the presence of unquenched free radicals and other reactive moieties. Stability of the plastic-derived oil is necessary for its use as a resource. Stability is also needed for the uninterrupted conversion of the waste into oil, storage of the oil, and maintaining noncorrosive and nondestructive use of the plastic-derived oil as a resource.[8,9] Stability of the product oil may be achieved through conversion of the polymeric waste into the most stable compounds, such as benzenoids and alicyclic compounds. Other approaches include the use of quencher and stabilizer chemicals and blending of the plastic-derived oil with stable oils.[10] While considering the quality of plastic-derived oils, in addition to the post-pyrolysis activity, the chemical nature and relative concentration of various chemicals are also important. The quality of the oil may also be correlated to the carbon number in the individual oil molecules. For example, oils containing C_5 to C_8 hydrocarbons fulfill the criteria of gasoline or petrol, above which the oils fall into the kerosene and diesel oil category.[11] The presence of aliphatic, alicyclic, and aromatic compounds or hydrocarbons in the plastic-derived oil is primarily attributed to the nature of the plastics used. It is also influenced by reaction conditions, including catalyst and reaction parameters.[12–14] For the preparation of enhanced-quality plastic-derived oil through pyrolysis, two processes are more important: the cracking and reforming processes. Excessive and faster cracking reactions may favor the formation of excessive quantities of gases and char. However, the use of catalysts, appropriate reactor design, and suitable pressure may favor the formation of oils through secondary, tertiary, and even onward reactions between the products formed by the cracking process.[15,16]

The catalysts used in pyrolysis processes have multidimensional roles. They manipulate the activation energy needed for the cracking of plastics. This addresses the energy requirement and saves additional use of power or thermal energy.[17,18] In a great many cases, specifically solid catalysts, the transfer of energy for cracking and quality-enhancing reactions is facilitated by the catalyst. The active sites of the catalysts are responsible for shaping the molecules, *i.e.*, as cyclic aromatic, straight chain, or branched, due to the highly interactive polar sites.[19] The activity of these sites may vary with temperature due to changes in vibrational energy and the frequency of the vibration. In a strict sense, this behavior facilitates adsorption and desorption of the reactants and products, the extent of cracking, and the capacity of cracking. It also facilitates the arrangements and rearrangements of the reactive species into

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stable and more useful moieties.[20] The catalysts may also play a role in quenching radicals and active moieties. This helps in avoiding post-pyrolysis reactions, ensuring the stability of the plastic-derived oil, and improving the yield of oil.[21,22] The catalyst plays a role in facilitating cracking, reforming, reducing the energy input, selecting the product fraction, enhancing the quality and yield of the product fractions, and ensuring stability of the oil product.[23] The cracking efficiency and mechanism of the cracking may vary according to the chemical nature of the catalyst, the morphology of the catalysts, and the mode of application of the catalyst.[24] Regarding the mode of application, gases and liquid catalysts may be adjusted by selecting the environment, *i.e.*, pressure and temperature, while for solid catalysts, extra measures are needed.

In the case of non-catalytic pyrolysis, the free-radical mechanism is predominant. This mechanism involves the abstraction of hydrogen and the breakage of the carbon–carbon bond. Under suitable conditions, these cracking reactions may be followed by reforming as secondary reactions, or by more cracking reactions termed secondary and tertiary cracking, or pyrolysis.[25,26] These random cracking reactions are also associated with the formation of excessive quantities of coke. In the case of catalytic pyrolysis, the mechanism of cracking predominantly shifts to the ionic modes.[27] However, the free radical reactions are still there, in addition to the ionic and polar mechanisms. But here, the catalyst may play a role in quenching the free radicals. This is why the oil produced by catalytic pyrolysis is more stable compared to oil produced by non-catalytic pyrolysis.[28,29] Chemical and morphologically active catalysts are highly efficient because the porous and mesoporous nature of these catalysts increases the contact time. This results in efficient contact and efficient transfer of heat, which causes the effective cracking as well as reforming of the products of the catalytic pyrolysis.[30,31] Although the mode of placing or contacting the catalyst is also important. One aspect that is most important for discussion is that pyrolysis products, rather than plastics, are transformed into value-added products. The use of catalysts improves the yield and economy of the process. Plastics have been pyrolyzed using a variety of catalysts. These include zeolites with acidic and basic nature, metals, oxides of metals, carbonates, and salts.[32,33] The most commonly used catalysts include zeolite catalysts with an acidic nature.[34] These catalysts mainly operate through the carbocationic mechanism of cracking. Clays are also included among the catalysts of choice for the processing of mixed plastic waste.[35] This is because, in the case of PVC and some of the nitrogenous polymers, corrosive gases are formed, which are absorbed by the clay catalyst, protecting the reactor.

This review focuses on integrating the factors responsible for the nature, yield, and stability of the products of waste plastic pyrolysis. It is also oriented to identify and address the factors that tune the process of pyrolysis into a product-selective rather than random reaction. The most common factors that will be critically discussed for acquiring selectivity range from the composition of the waste to the nature of the catalyst, temperature, reactor design, and selection of the mechanism of the reaction.

2. Process parameters governing product distribution in plastic pyrolysis

Waste plastic is usually composed of a mixture of plastics. Plastic obtained from municipal waste is mainly composed of polyethylene, polypropylene, and polystyrene, and a small fraction of other plastics.[36,37] Each of these plastics is made of a hydrocarbon skeleton and its pyrolysis gives products that are predominantly composed of hydrocarbons. The pyrolysis of these plastics may result in the formation of liquid, gas, and solid products (Fig. 2). The relative quantity of each of these products depends upon the experimental conditions, such as the temperature, rate of heating, reactor type, and the nature and mode of the application of the catalyst. The solid product of pyrolysis of waste plastic is usually composed of char, and the gas is composed of a mixture of hydrocarbon gases, in addition to variable quantities of hydrogen.[38,39] The liquid products of pyrolysis include hydrocarbons of C_5 and onward, with a composition that can be separated based on the boiling point in a distillation process.

The gaseous or liquid products may be used for three purposes: (i) utilization as fuel, (ii) monomer recovery, and (iii) chemical feedstock. Utilization as a fuel is one of the simplest and easiest routes for the valorization of waste plastics and needs no extra measures for value addition. However, it needs improved conversion rates and efficiencies to lower the cost in terms of time and energy. Utilization of the products of pyrolysis as fuel may need increased selectivity in terms of gas or liquid production.[40] This may be achieved by approaches such as adjusting the temperature and the nature of the reactor. The temperature may be low, moderate, or high. Each of these temperatures may further be characterized based on the rate of heating, *i.e.*, slow heating and fast heating. This may lead to the classification of pyrolysis as slow, fast, and flash pyrolysis.[41,42] The quantity of gas products may increase with an increased rate of heating. Slow pyrolysis may produce a larger quantity of char, followed by the liquid and smaller quantities of gases.[43] However, the gas produced in slow pyrolysis is mainly composed of hydrocarbons, while the gases produced in fast and flash pyrolysis are mainly composed of hydrogen.[44,45] The quantity of gases can be increased by altering the reactor design *i.e.*, pyrolysis under reflux conditions may alter the quantity of gaseous products.[46] The nature of the reactor and reaction process may also affect the % conversion of waste plastic.[10] The nature of the reactor may determine the rate of heat- and mass-transfer, continuity, residence time, process, and mode of application of the catalyst, in addition to determining how the process can be scaled up.[47,48] The reactors may range from fixed-bed to fluidized-bed, rotary kiln to auger, distillation type, and autoclave type. The most used reactors for the pyrolysis of waste plastics are discussed here.

Fixed-bed reactors can be used for the pyrolysis of liquid and gaseous feed and are a secondary reactor.[49] These may be the reactors of choice for specific and selective conversions, including conversion of high naphtha, monomer recovery, and conversion of pyrolysis-derived products into chemical

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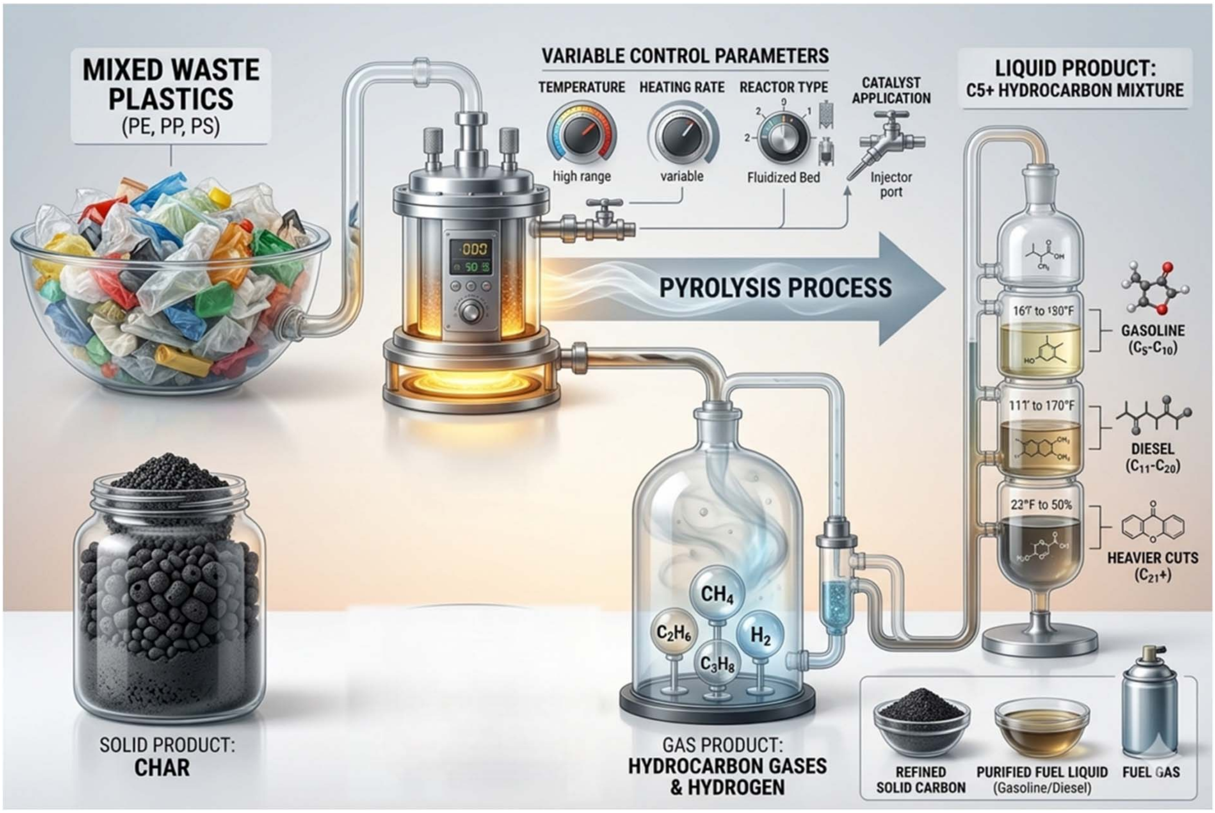

Fig. 2 Pyrolysis of waste plastics and their product distribution to solids, liquids, and gases.

feedstock. The heat-transfer mechanism involves a contact process, *i.e.*, flow of heat from the walls of the container to the feed.[50] Fixed-bed reactors operate in the range of 400–500 °C, and the nature of the products varies according to the nature of the feed and temperature range, with yields as high as 87%.[51–53] Fluidized-bed pyrolysis is used for fast pyrolysis due to its capacity to provide high temperature and uniform heating.[54] It is used for the pyrolysis of plastics as well as biomass, and is operated in the range of 400–900 °C.[55,56] A conical or spouted bed reactor is characterized by its effective blending efficiency and can handle a wide range of loads of different densities and particle sizes, in addition to facilitating heat transfer and having the capacity to handle sticky and difficult feeds.[57,58] It may convert polyethylene into fuel-range hydrocarbons ranging from gasoline to diesel, and can be operated in both low- and high-temperature ranges, according to the requirements. Its main advantages include reduced pyrolysis, resulting in kinetic selectivity of products, in addition to the capacity to handle feeds of larger particle sizes. Quantitative data on the products yielded from the plastics are summarized in Table 1.

Table 1 Summary of the typical wt% ranges for liquid, gas, and solid (char)

Plastic type	Catalyst	Temperature (°C)	Liquid (% wt)	Gas (% wt)	Char (% wt)	Ref.
PS		425	97	2.5	0.5	59
PS	FFC	400	90	6	4	60
HDPE	FFC	500	88	9.9	1.3	61
PP and HDPE	—	300	69.82	28.84	1.34	62
		350	80.88	17.24	1.88	
HDPE	Clinoptilolite, HZSM-5, and FCC	450	74.5	5.8	19.7	63
HDPE	F9 and silica/alumina (SA)	500	85	10	5	64
LDPE	—	500	80.41	19.43	0.16	65
LDPE	HZSM and HUSY zeolites	550	93.42	6.36	0.22	66
PP	Silica–alumina (SA-1 and SA-2) and zeolite ZSM-5	380	80.1	6.6	13.3	67
PE	Silica–alumina	200–600	93	7	0	68

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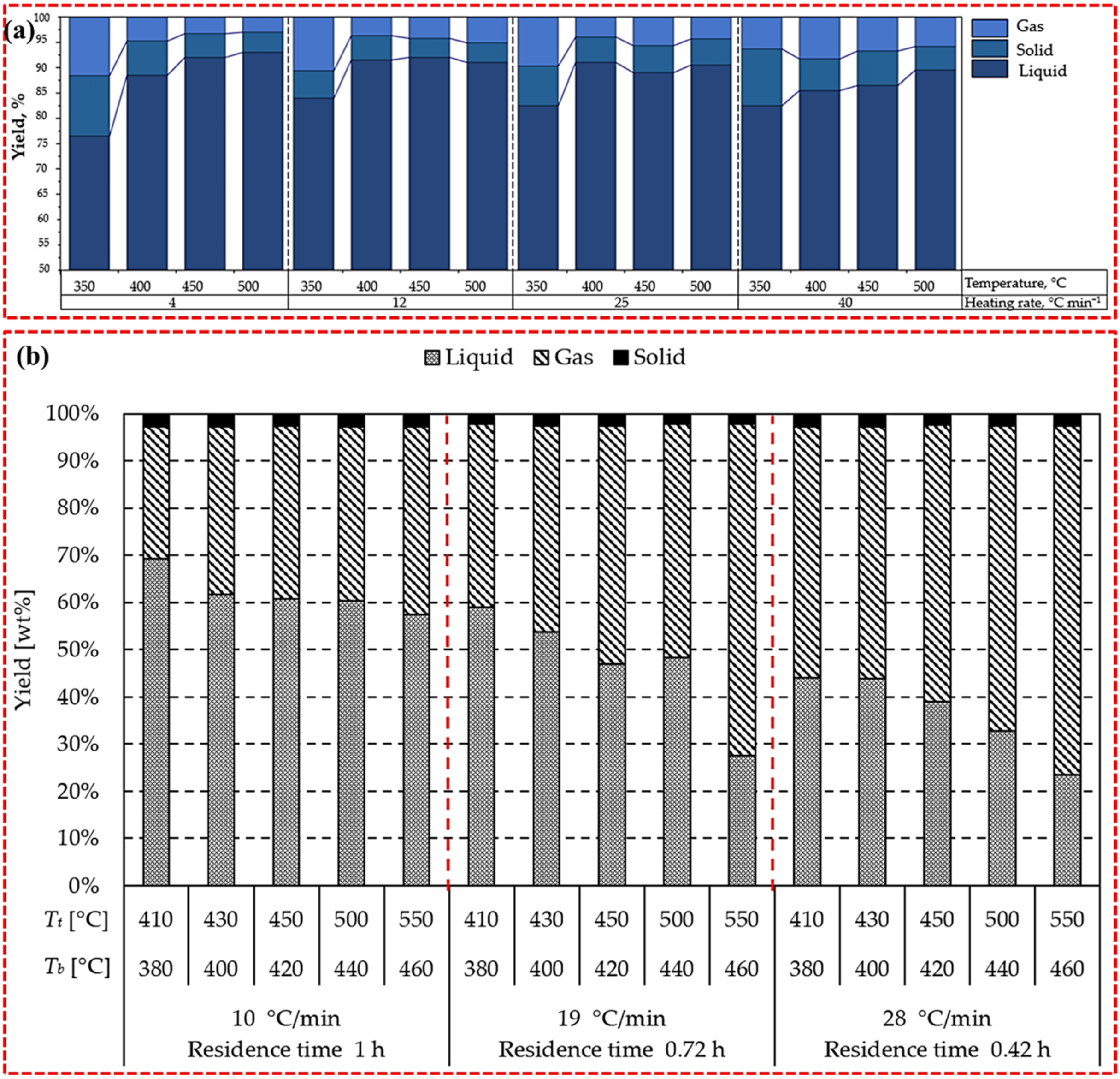

Fig. 3 (a) Results obtained for the four heating ramps (4 °C, 12 °C, 25 °C, and 40 °C min^{-1}). Reproduced from MDPI ref. 71, which is open access and permits unrestricted use of materials under the terms of the Creative Commons CC-BY. (b) Influence of the heating rate and temperature on the pyrolytic-process yield. Reproduced from MDPI ref. 74, which is open access and permits unrestricted use of materials under the terms of the Creative Commons CC-BY.

2.1. Effect of temperature and rate of heating

The temperature and heating rate are dominant parameters controlling the yield and composition of pyrolysis products.[69] In general, the liquid oil fraction is maximized at intermediate temperatures, beyond which further increases favor gas and char.[70] For example, Gonzalez-Aguilar *et al.* showed that pyrolysis of expanded polystyrene (EPS) yielded 76.5–93.0 wt% liquid oil as the reaction temperature increased from 350 °C to 450 °C (Fig. 3a). It was reported that increasing the heating rate above an optimum (12 °C min^{-1}) caused oil yields to decline, despite initially promoting oil formation. A similar study found that when EPS was pyrolyzed at 350–450 °C, the process produced a high liquid yield ranging from 76.5% to 93.0%. Increasing the heating rate from 25 °C min^{-1} to 40 °C min^{-1} had only a small effect on liquid production at lower temperatures. However, at 400 °C, the higher heating rate (40 °C min^{-1}) resulted in slightly more gas formation and a corresponding decrease in liquid yield compared with the lower heating rate (25 °C min^{-1}).[71] Similarly, Onwudili *et al.* found that LDPE produced maximal oil yield at 425 °C while beyond that point, oil declined as the amount of char and light gases increased. In contrast, PS yielded the most liquid around 350 °C but exhibited a dramatic rise in solid char at 450–500 °C (up to 30 wt%). These trends highlight that higher temperatures (450–500 °C) tend to push more products towards non-condensable forms, and moderate temperatures (400–450 °C) tend to favor oils. The product distributions at 500 °C were also measured, and it was found

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Table 2 Comparative analysis of the fixed-bed, fluidized-bed, and spouted/conical-bed reactors based on studies

Types of reactors	Functions	Advantages	Disadvantages	Ref.
Fixed bed reactor	The feedstock is placed in a stainless-steel reactor externally heated by an electric furnace. The system is flushed with inert gas (N_2 or Ar) to maintain an anaerobic atmosphere throughout the process. During pyrolysis, gases and vapors are discharged, while chars are typically removed after the process is completed. Fixed-bed reactors operate at low heating rates	1. Best suited for laboratory-scale studies due to simple design 2. Simple and robust design with low operational complexity 3. Consistent and reproducible product outcomes 4. Catalyst mechanical wear is minimal	1. Poor heat transfer leading to temperature gradients 2. Difficult char removal from the reactor 3. High carbon conservation (char formation) 4. Long solid residence time (minutes to hours) 5. Difficult to scale up for industrial applications 6. Catalyst regeneration requires process shutdown	108 and 109
Fluidized bed reactor (bubbling)	The reactor consists of a two-phase (solid fluid) mixture, created by passing pressurized fluid through solid particles. High heating rates and intense mixing of feedstock characterize these reactors. This reactor type is considered a successful solution for waste polymer pyrolysis and biomass fast pyrolysis	1. Excellent heat and mass transfer properties 2. Uniform temperature distribution (isothermal conditions) 3. Suitable for studying the fast pyrolysis behavior of solid particles 4. Enables analysis of secondary oil cracking at longer residence times 5. Widely used in laboratory studies to investigate temperature and residence time effects 6. Easily scalable to industrial levels	1. Challenges in handling heterogeneous municipal solid waste (MSW) 2. Feedstock must be finely ground to achieve fluidization 3. Char separation from bed material is problematic 4. Higher catalyst attrition and dust generation 5. Gas bypassing (bubbling) can reduce conversion efficiency	110 and 111
Spouted bed reactor (conical)	The reactor offers excellent solids movement, resulting in high interphase heat-transfer rates, making it ideal for flash pyrolysis. The conical spouted bed reactor is suitable for continuous operation, which is particularly important for large-scale biomass pyrolysis. Successfully implemented for the pyrolysis of polymers, including polystyrene, polyethylene, polypropylene, and PET. Waste plastics melt upon feeding and, due to cyclic movement, provide uniform coating around sand particles, reducing de-fluidization problems	1. Lower bed segregation and particle attrition compared with bubbling, fluidized beds 2. Ideal for irregularly textured particles, fine particles, sticky solids, and broadly dispersed particles 3. Excellent gas flow flexibility, allowing short gas residence times 4. Spout action reduces agglomerate formation 5. Can handle larger particle sizes without pre-grinding 6. Decouples gas and solid residence times, reducing secondary reactions	1. Limited data available on use with mixed municipal solid waste (MSW) 2. Requires specific reactor geometry (conical design) 3. Still limited industrial-scale implementation data 4. Catalyst entrainment can be an operational challenge	112–114

that both LDPE and PS produced a reduced oil yield (LDPE oil decreased to 50%, PS char increased to 30% of feed).[72] Actually, general surveys indicate liquid yields of approximately 60–80% for mixed plastic pyrolysis, with fast (short-residence) operations reaching approximately 85% liquid at 450–600 °C.[73] Product yields are also heavily influenced by heating (or residence) rate. Reduced heating rates (prolonged residence) will permit vapor secondary cracking, usually at the cost of oil, to raise char/gas levels. Riesco-Avila *et al.* found that an oil yield of 69 wt% was maximum at moderate conditions (410 °C, 10 °

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C min^{-1} heating rate) in a mixed-plastics pyrolysis; at either higher temperatures or faster heating (shorter residence), the oil yield decreased, and the gas fraction increased. It was mentioned that changes in the heating rate (10 °C to 28 °C min^{-1}) at 380–460 °C led to a distinct decrease in the liquid yield, where heating at 10 °C min^{-1} gave 69% oil, while that at 28 °C min^{-1} produced much less oil (Fig. 3b).[74] The majority of the studies indicate that increased heating rate has a positive effect on the liquid yield up to a certain optimum rate, but extremely rapid heating decreases the oil fraction, and volatile compounds are vaporized before condensing.[75,76] This is because of the kinetic competition, where rapid heating is more conducive to complete vaporization, enhancing light gases, and slower heating gives more time for the polymer chains to crack to condensable oils. These data indicate that tight control over the temperature and heating rate is required to maximize the liquid yield. Throughout the literature, the overall trend is evident: liquid yield increases with temperature to a maximum (usually 400–450 °C), but liquid yield increases with heating rate to an intermediate maximum (usually 10–15 °C min^{-1}) and then decreases. Composition is also controlled by temperature and heating rate in terms of the product quality. Higher temperatures and longer residence times favor the formation of lighter, aromatic-rich oils, whereas lower temperatures and rapid heating promote heavier wax production. As an illustration, Onwudili *et al.* demonstrated that PS pyrolysis oil was extremely rich in aromatics (styrene, ethylbenzene, toluene) even at 350 °C and richer in char at 500 °C, whereas LDPE oil was aliphatic at 425 °C and aromatic at high temperature.[72] The quicker the heating, the lighter the product; the slower the heating, the more secondary condensation, which enhances aromatics and char.[77] Generally, the literature remains consistent that when the temperature is increased, and the heating rate is increased, the product distribution moves towards the light (gas and light oils) fractions, whereas when temperature and heating rate are moderate, the total oil yield is maximized. To avoid conceptual ambiguity, it is important to distinguish the relative roles of heating rate and final temperature under different pyrolysis regimes. In slow pyrolysis systems (*e.g.*, fixed-bed or batch reactors), the heating rate is a controllable parameter and plays a dominant role in determining product distribution. Gradual heating allows progressive bond cleavage and extended vapor residence time, promoting secondary cracking, repolymerization, and char formation.[78–81] Under such conditions, the polymer is largely decomposed by the time the final temperature is reached, and therefore, the apparent influence of peak temperature is less pronounced than that of the heating profile and residence time. In contrast, fast pyrolysis systems (*e.g.*, fluidized or spouted-bed reactors) operate under very high and often uncontrolled heating rates governed by rapid heat transfer. In these systems, thermal decomposition occurs almost instantaneously, minimizing secondary reactions, and the final reaction temperature becomes the primary parameter controlling product selectivity, particularly the distribution between condensable liquids and non-condensable gases.[78,79,81,82] This distinction highlights that heating rate and temperature should not be treated equivalently, but rather as regime-dependent variables, which is critical for rational reactor design and process optimization. Although temperature and heating are the key factors that determine the kinetic regime of the process, reactor design also affects the heat and mass transfer, which adds selectivity to the product distribution.

2.2. Effect of reactor design on oil yield, product distribution, and product nature

Pyrolysis reactor design (type and configuration) has a significant effect on the heat/mass transfer, residence time, and mixing, and therefore, the oil yield, composition, and product properties. The effects of continuous fluidized reactors (bubbling or conical-spouted beds), fixed-bed reactors, batch reactors, and vacuum or rotary design differ. A more detailed examination of reactor design reveals that each configuration imposes distinct heat- and mass-transfer characteristics, which directly govern reaction kinetics and product selectivity. Fixed-bed reactors operate under relatively low heating rates and longer vapor residence times, favoring secondary cracking, condensation, and the formation of heavier liquid fractions and char.[83] In contrast, fluidized-bed reactors provide excellent gas–solid contact, rapid heat transfer, and uniform temperature distribution, enabling fast pyrolysis conditions that enhance the production of lighter hydrocarbons and gaseous products.[84,85] Spouted-bed reactors combine the advantages of fluidization with improved handling of irregular and sticky feedstocks, offering efficient mixing and reduced agglomeration, which is particularly beneficial for plastic waste streams.[86] Additionally, microwave-assisted pyrolysis reactors enable volumetric heating through dielectric absorption, allowing rapid and selective heating of materials, which can reduce thermal gradients and potentially improve energy efficiency and product uniformity.[87,88] These distinctions highlight that the reactor is not merely a physical container, but a critical parameter that dictates transport phenomena and, consequently, the distribution and quality of pyrolysis products.[89,90] From a comparative perspective, reactor configuration strongly influences both conversion efficiency and product distribution. Fixed-bed and batch reactors generally maximize overall liquid yield but often produce heavier and less stable oil fractions due to prolonged vapor residence and secondary reactions.[91] In contrast, fluidized and spouted-bed reactors, operating under fast pyrolysis conditions, tend to shift product distribution toward lighter hydrocarbons and non-condensable gases, owing to rapid heating and reduced residence time.[92] Microwave-assisted systems introduce an additional level of control by selectively heating specific components, which can further modify product selectivity.[93,94] These trends are summarized in Table 2, which consolidates reported yields and clearly demonstrates the trade-off between liquid yield maximization and product selectivity toward light fractions, depending on reactor design. In general, fluidized-bed reactors afford rapid heat transfer and excellent mixing, which tends to increase gas and light hydrocarbon production, whereas fixed- and batch-bed reactors often yield heavier oils.[95] Several studies explicitly

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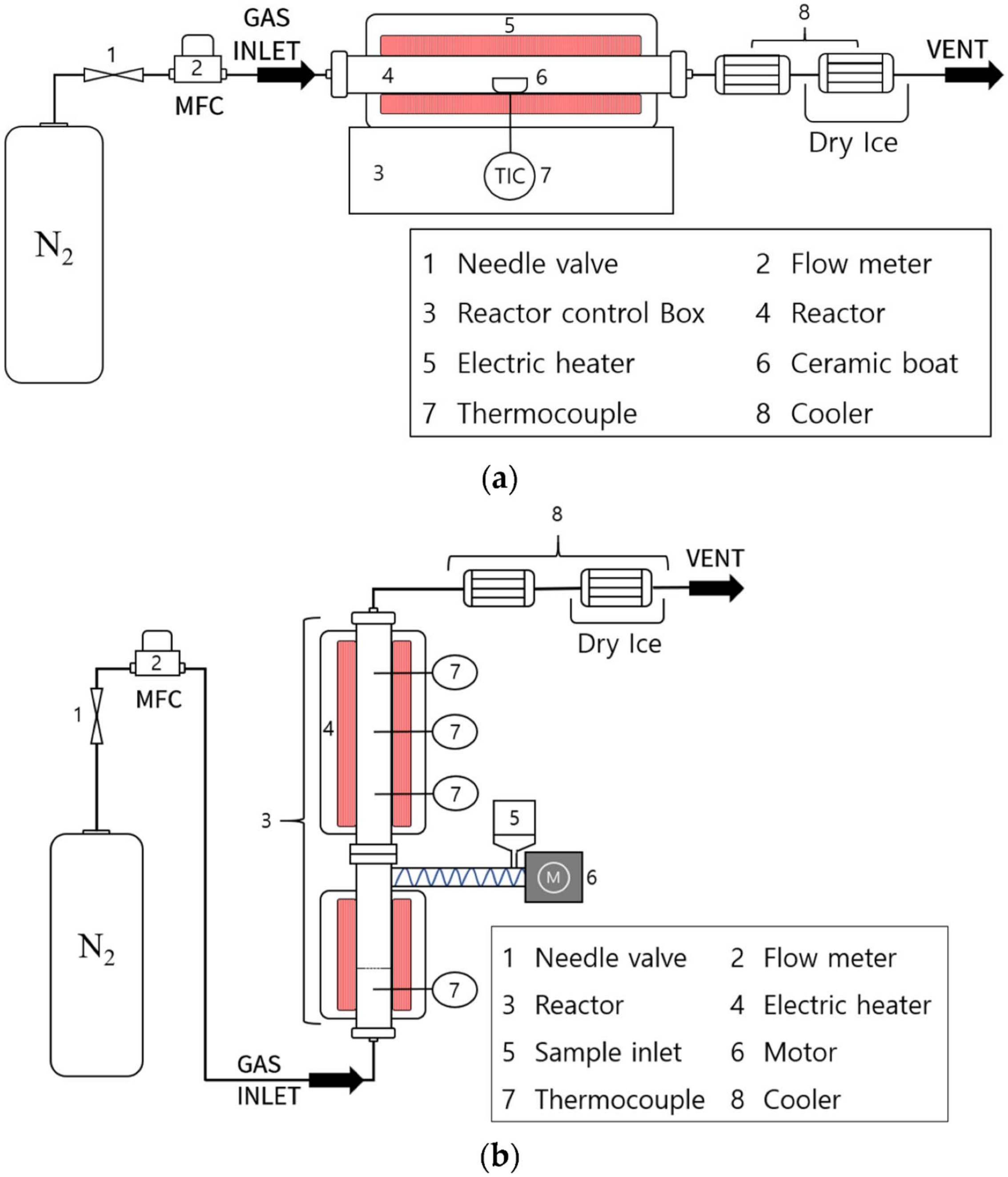

Fig. 4 Schematic of the fixed (a) and fluidized (b) bed reactors. Reproduced from MDP1 ref. 77, which is open access and permits unrestricted use of materials under the terms of the Creative Commons CC-BY.

compared reactor types. For instance, Lee *et al.* studied the pyrolysis of mixed plastics using fixed and fluidized bed reactors (Fig. 4a and b). The results showed that fluidized-bed pyrolysis of mixed plastics gave more complete conversion than fixed-bed pyrolysis; higher heat/mass transfer in the fluidized bed led to faster decomposition and increased gas yields.[77] Specifically, the oil from the fluidized bed had lower hydrogen content (higher C/H ratio), indicating heavier (more aromatic) molecules, because rapid heating cracked the chains more thoroughly. Choi *et al.* conducted a side-by-side comparison of lab-scale fluidized bed and fixed bed reactors (Fig. 5a and b) for PP, LDPE, and ABS. They reported that total oil yields were essentially the same in both reactors (*e.g.*, 61–62 wt% for PP/LDPE and 82–87 wt% for ABS), confirming that the reactor type alone did not change the overall conversion (Fig. 6a). However, the fluidized bed produced a much higher fraction of light hydrocarbons; for instance, it generated 26–38% more C_5–C_{10} light oil fraction and 8.6–38.1% more C_1–C_2 light gases than the fixed bed. Thus, the reactor design shifted the distribution within the oil phase. It was also observed that

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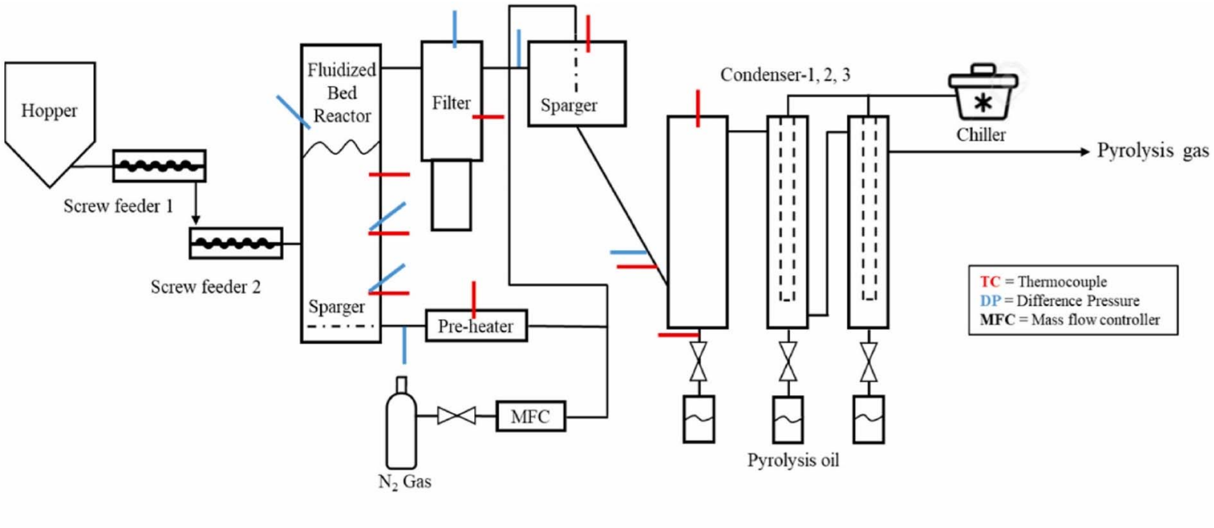
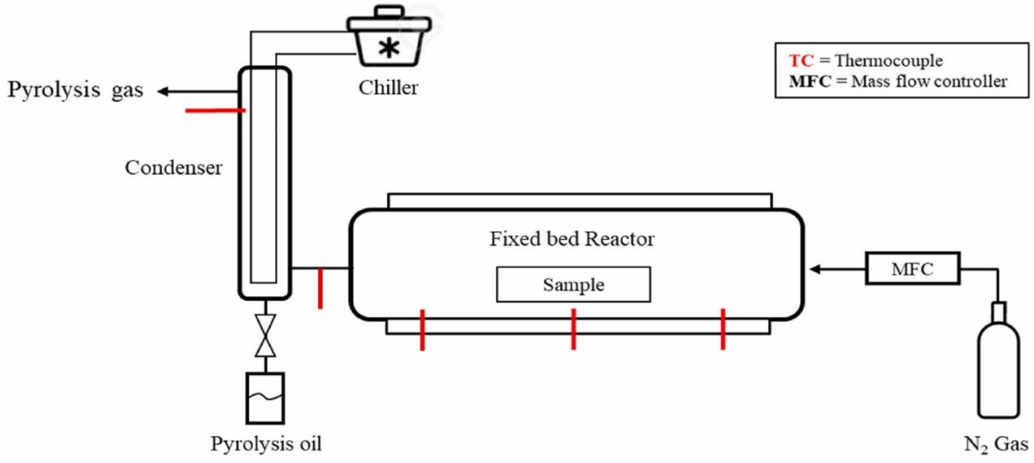


(a) Fluidized-bed reactor



(b) Fixed-bed

Fig. 5 Schematic of the (a) fluidized-bed reactor and (b) fixed-bed reactor for the pyrolysis of plastic waste. Reproduced with permission from ref. 96. Copyright 2024, Elsevier.

ABS pyrolysis in the fluidized bed yielded about 89% of products in the C_5–C_{22} range, compared to 84.7% in the fixed bed. They also noted compositional changes: ABS oil was 72% aromatics, while PP oil contained mostly paraffins and olefins.[96]

The rates of heating and residence time are also dependent on reactor design. Fluidized or spouted-bed reactors commonly allow rapid pyrolysis (short vapor residence) and continuous feeding, which improves light-gas yields and inhibits secondary cracking of condensable products.[97,98] Conversely, batch or fixed beds tend to lead to a longer vapor residence, which favors heavier products or char. Paavani and colleagues examined reactor designs and found that vacuum pyrolysis reactors (lower pressure) are slow in the secondary reaction, thus preferring oil production, and fixed-bed reactors are commonly secondary reactors cracking heavier vapor.[99] On the same note, in the same study, it was established that LDPE needed a very high temperature (>520 °C) even in the fixed-bed to crack completely; at 520 °C, both the reactors yielded 67.4% heavy oil, which means that the cracking did not occur completely under mild conditions.[96] These results imply that high heat transfer (as in fluidized reactors) is needed to avoid heavy oil when processing tough polymers. Examples from the literature underscore these differences. For instance, Wang *et al.* report that using catalysts in different reactors can change yields: an LDPE/PET mix pyrolyzed in a conical spouted fluidized bed (Fig. 6b) with HZSM-5 gave only 51.7 wt% liquid, whereas HDPE pyrolysis in a batch fixed-bed with a silica–alumina catalyst produced 77.4 wt% liquid oil.[100] The fluidized-bed case had more severe

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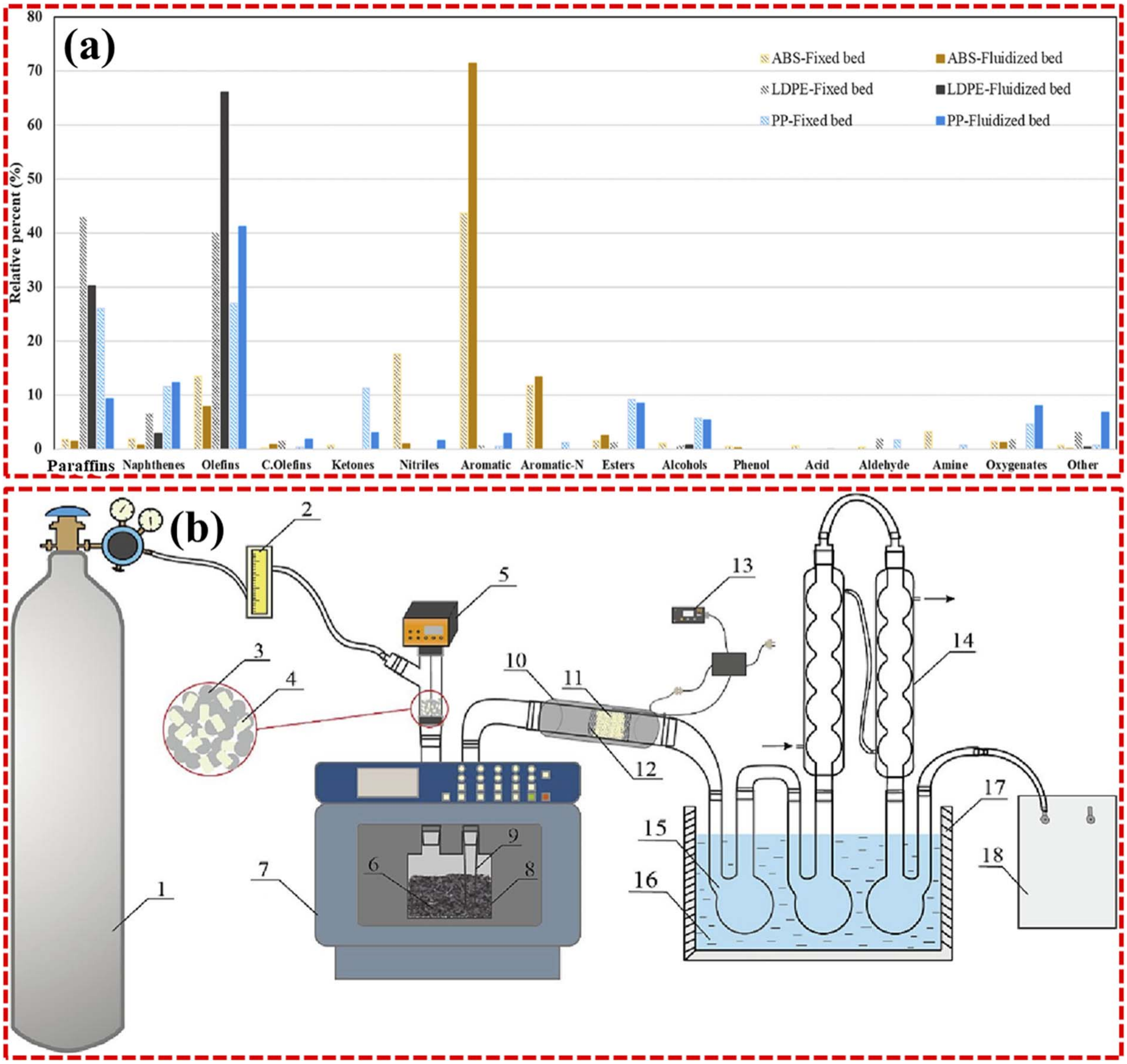

Fig. 6 (a) GC-MS comparison of the pyrolysis oils obtained from PP, LDPE, and ABS using fixed-*vs.* fluidized-bed reactors.[96] (b) Schematic of the MACFP device: (1) nitrogen cylinder, (2) gas flowmeter, (3) LDPE pellets, (4) PET pellets, (5) feeder, (6) microwave absorbent bed, (7) microwave device, (8) quartz reactor; (9) downdraft tube, (10) electric heating belt, (11) ex-catalytic bed, (12) quartz wool, (13) temperature controller, (14) spherical condenser, (15) condensate bottle, (16) 4 °C ice-water, (17) water channel, and (18) gas bag. Reproduced with permission from ref. 100. Copyright 2024, Elsevier.

secondary cracking (lower liquid). Likewise, Lee *et al.* noted gas yields were higher in the fluidized bed, and the continuous fluidized reactor gave a higher gas fraction under equivalent conditions.[77] In general, fluidized beds (including spouted and fast-bed designs) tend to reduce liquid yield relative to fixed beds under identical conditions but produce oils richer in light fractions and often with higher olefin/aromatic content, whereas fixed beds maximize overall oil, but the oil may contain more heavy compounds. Literature consistently shows reactor design is a key determinant of pyrolysis performance. Fixed and batch reactors tend to maximize oil yield but with heavier components, whereas fluidized and high-heat-transfer designs favor light fractions and gases.[101,102] Vacuum or staged reactors can suppress secondary cracking to improve yield. These effects are validated quantitatively; similar feeds in different reactors give different light-oil fractions (often tens of % differences) and different gas/oil splits. Practical reactor selection thus depends on the desired outcome; if maximizing total oil is the goal (*e.g.*, fuel production), slower, low-pressure systems may be preferred. If maximizing light hydrocarbons or specific chemical products is sought, fluidized or microwave-enhanced reactors are advantageous. In addition to the previously described passive effect of reactor design, the active insertion of a catalyst allows control of the reactive pathway and provides a more effective means to achieve selective products. In catalytic pyrolysis, reactor configuration becomes even more critical due

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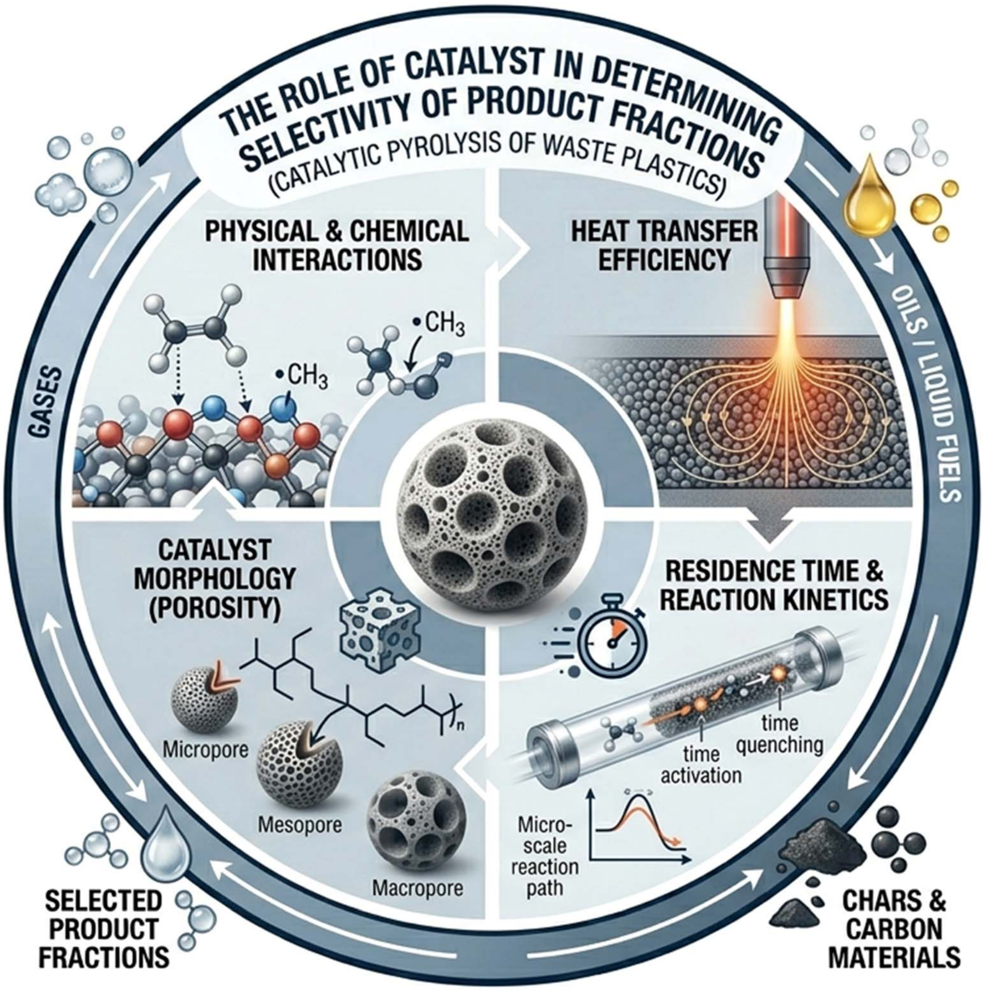

Fig. 7 Role of the catalyst in pyrolysis.

to the interaction between thermal decomposition and catalytic upgrading pathways. Two primary approaches are commonly employed *e.g.*, *in situ* catalysis, where the catalyst is directly mixed with the plastic feedstock within the reactor, and *ex situ* catalysis, where pyrolysis vapors are subsequently passed through a secondary catalytic reactor.[103] *In situ* systems promote immediate interaction between evolving intermediates and catalyst surfaces but may suffer from catalyst deactivation due to coke deposition and mass transfer limitations.[104] In contrast, *ex situ* configurations decouple thermal cracking from catalytic upgrading, allowing independent optimization of both steps.[103,104] Various two-stage reactor designs have been reported, including fluidized bed-fixed bed, fixed bed-fixed bed, and spouted bed-fixed bed systems, where the first stage generates pyrolysis vapors and the second stage selectively upgrades these vapors into targeted products, such as aromatics or light olefins.[104,105] These configurations provide enhanced control over vapor-phase reactions, improved catalyst utilization, and greater flexibility in tuning product selectivity, highlighting the importance of reactor engineering in catalytic plastic pyrolysis.[106,107] A comparative summary of fixed-bed, fluidized-bed, and spouted/conical-bed reactors based on the studies is provided in Table 2.

2.3. The role of the catalyst in determining the selectivity of the product fractions

Catalytic pyrolysis of waste plastics is optimized to enhance the yield or control the nature of product fractions. Catalytic activity is influenced by the catalyst's heat-transfer properties, particularly its thermal conductivity and heat capacity (Fig. 7). The catalytic cracking of plastic-derived hydrocarbons is predominantly governed by the acidic properties of the catalyst, particularly the presence of Brønsted and Lewis acid sites. These acidic sites facilitate the formation of carbocation intermediates, which drive β-scission, isomerization, and aromatization reactions, thereby directing product selectivity toward light olefins and aromatic hydrocarbons.[115–117] It facilitates the cracking of molecules through the efficient heat-transfer properties of the catalyst through radiation or convection process, or it helps in reforming and quenching of reactive moieties through thermal exchange and manipulation of thermal equilibria.[118] Catalysts may also alter the nature of products or the

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Table 3 Representative experimental studies on plastic pyrolysis. Yields and conditions vary; catalysts and process design can significantly shift the product distributions

Plastic type	Catalyst	Catalyst : feed (ratio)	Reactor type	Temp (°C)	Char/coke (wt%)	Gas (wt%)	Oil yield (wt%)	Major products of oil (%)	Ref.
LDPE	HZSM-5 (Zn- and P-modified)	1 : 2	Two-stage fixed bed	500	1.5	42.6	55.9	87.4% aromatics with benzene, toluene, ethylbenzene, and xylene of 75%	188
LDPE	HZSM-5	1 : 2	Semi-batch	500–650	—	61.4	59.9	65.9% mono- and poly-aromatics	207
	HY					67.1	67		
	MCM-41					20	78.4		
LDPE	Equilibrium FCC (USY and spent)	1 : 2	Semi-batch	350	5.5	70.7	23.9	—	198
PP					3.4	49.4	47.1		
LDPE (with H_2)	Ni-loaded zeolite (*e.g.* Ni/ZSM-5)	10 : 1	Batch	350	—	58	25	97.75–99.69% hydrocarbons with gasoline (C_5–C_{12})	208
PP and PE	Red mud-based adsorbent	130 g : 630 g	Vertical fixed-bed		420	—	45–55	>70% hydrocarbons: C_5–C_{20} and naphtha range: 78.57%	209
HDPE	MCM41 and ZSM-5	2 : 1	Fixed bed reactor	360	—	70	83.15	95.85% aromatic consisting of 97.72% gasoline	210
LDPE	AC2	0.6, 1.3, 1.5, 2, 2.5, and 2.71	Facile fixed-bed tube	500	4.3	23.7	72.0	Paraffins: 82.9 and aromatic: 14.6	211
EPS, PE, HIPS, and PP	—	—	Nabertherm horizontal furnace	500	—	33	66.0	100% aromatic compound: Styrene (C_8H_8) 69.88% and benzaldehyde 18.82%	212
PVCPET				475	34.6 11.4	65.1	5.8		
HDPE	ZSM-5/SiC		Downstream quartz	350–450	—	—	46.3	>22% gasoline aromatics	213
Television and PC monitor and refrigerator plastics	Y Zeolite and ZSM-5	1 : 1	Fixed bed	500	13.8	16.2–69.8	84 and 77.5	Highest aromatic concentration: Benzene, ethylbenzene, and toluene	214
PP, LDPE and HDPE	Bentonite clay		Bench scale fixed-bed	700	—	—	61–96.53	Hydrocarbon, styrene (20.12%), and 2,4-dimethyl-1-heptene (15.08%)	215
HDPE	—	—	Fluidized bed reactor	780	—	78.8–86.4	9.6	Hydrocarbon (gas) C_2H_4: 41.9 and methane: 8.8–13.7	216
Polystyrene	Zeolite ZSM-5	1 : 2, 1 : 1, 2 : 1, and 3 : 1		500–600	11.4	3.6	91.2	Aromatics: benzene, toluene, and phenanthrene	217
	Y-zeolite				24	6.8	71.0		
WPP	FCC	0.1	Batch reactor	300–400	3.0	13.2	83.3	Paraffin, olefins, and naphthalene aromatics: 30.83, 44.6, and 19.44	218
HPDE	Y-zeolite		Fixed bed reactor	600	—	21	69	Aromatic hydrocarbons (80–95%)	219
	Metal promoted Y-zeolite				14–26	31–42	29–45	97–99% aromatic hydrocarbons: toluene, ethylbenzene, xylene, naphthalene, and alkylated naphthalene	
HDPE	Zeolite and FFC	20% wt : 6 g	Fixed bed	600	—	—	47.6	Gasoline-range hydrocarbons (C_8–C_{12}): 30–35%	220
LDPE				500			69.9		
PP				550			65.3		
PLA				400			72.8		

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Table 3 (*Contd.*)

Plastic type	Catalyst	Catalyst : feed (ratio)	Reactor type	Temp (°C)	Char/coke (wt%)	Gas (wt%)	Oil yield (wt%)	Major products of oil (%)	Ref.
PS	Natural zeolite	1 : 1	Small pilot-scale	450	33.2	12.8	54	Aromatics: ethylbenzene: 80%, styrene: 15.8%, and alpha-methylstyrene: 38.3%	221
	Synthetic zeolite				27.2	22.8	50		
LDPE	CAT-2	1 : 10	200 mL stainless steel batch	460	—	49	51	100% gasoline range (C_7–C_{12})	222
PP						42	58		
WPP	Kaolin	1 : 2	Vertical tube	500	1.7	17.55	80.75	74% aliphatic	223
	Hematite				2.76	27.33	70		
	White sand	1 : 1			2.76	29.24	68		
LDPE, HDPE, PP, and PS	Z-503		Fixed bed	>405	—	—	55.1–68.2	Paraffins 60.09%, paraffins 73.2%, aromatics 51.41%, and aromatics 97.25%	224
PET/LDPE (CPW1)	Spent FCC (USY zeolite-based)	1 : 1 (2 g : 2 g)	Two-stage fixed-bed reactor	500	4.8/5.2–5.9	43.8–47.1	42.8–45.5	Aromatics + alkanes	225
PA6/LDPE (CPW2)					0/5.2–5.4	33.1–33.7	60.7–61.1	Caprolactam-derived + aromatics	
LDPE	H-ZSM-11 zeolite	(10 mg : 1 g)	Fixed bed (quartz tube pyrolyzer)	500–700	0	80.8	37.5–61.1	—	226
WEPS	ZSM-5 ammonium powder	20 : 1	Multilayer catalytic bed	550–650	0.08–0.62	11.3–24.4	75.1194.37	Low amount aromatics: BTE of 11.38% and the highest amount of styrene 84.74%	227
	Mn/Ni/ZSM	2 : 1	Horizontal tubular	550	14.5–12.9	22.4–35.8	51.6	15.8, *n*-Olefin ratio: 19.5%	228
	Ce/Ni/ZSM-5			550	11.5–10.4	73.1–80.5	9.7		

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selectivity of product fractions through the manipulation of the residence time, the activity of the moieties (through quenching and reactivation by the presence of active sites), or the morphology of the catalyst (*i.e.*, porosity, *e.g.*, meso-, nano- or micro-porosity of the catalyst) that catalyzes the cracking and reforming process.[119–121] The catalyst may also modify the short-range thermal equilibrium, which may help in the selection of products. The chemical nature of the catalyst may also help in cracking as well as reforming through physical and chemical interactions.[24] Adsorption and adhesion are the major physical processes that alter the heat-transfer mechanisms, thermal equilibrium, and mode of interactions, *i.e.*, abstraction of electrons, offering the surface for stability of active moieties such as ions and free radicals, in addition to the quenching of moieties into stable products.

The catalyst may also act through its basic nature. Solid base catalysts help in cracking, lowering the activation energy, and abstraction of hydrogen from larger molecules.[122] In the case of base-catalyzed cracking of petroleum and macromolecular hydrocarbons, the production of olefins is one of the dominant phenomena.[123] This encourages the conversion of heavy naphtha and macromolecular compounds into lighter naphtha and gaseous molecules. The role of base-catalyzed cracking through the abstraction of hydrogen has been reported by Lemonidou *et al.* for the cracking of hydrocarbons over calcium aluminate.[124] It was reported that the oxygen of the peroxide reacts with hydrogen, causing and initiating cracking. To make the best use of the catalyst, it is very important to understand the mechanisms that differentiate thermal cracking from the catalyst effects that are the subject of this section. Table 3 presents a comparative analysis of the reported studies on plastic pyrolysis.

3. Mechanistic control of plastic cracking pathways in pyrolysis

3.1. Transition from radical-dominated to catalyst-mediated cracking

In non-catalytic pyrolysis of plastics, the reaction is driven by high-temperature homolytic bond cleavage that generates abundant free radicals (Fig. 8). Polymer chains undergo random C–C bond scission to form alkyl radicals, which propagate chain cracking *via* β-scission (a radical reaction where a C–C bond breaks at the beta-position relative to the radical center, producing a small radical and an olefin) and hydrogen-transfer steps.[125] For example, reactive molecular dynamics of polypropylene (PP) pyrolysis show that random main-chain homolysis predominates initially, with resulting radicals yielding ethylene, propylene, methane, *etc.*, *via* further H-abstraction and β-scission.[126] This radical chain mechanism is inherently unstable and self-accelerating; any new radical formed rapidly reacts further, leading to broad product distributions and limited selectivity. In contrast, catalytic cracking (especially over solid acids) shifts the dominant mechanism away from uncontrolled radical propagation. Brønsted (proton donating) and Lewis acid sites (electron pair-accepting) on catalysts protonate or polarize C–C bonds to generate surface-stabilized carbocations (carbonium ions) and suppress long radical chains.[127] These ionic intermediates undergo more selective β-scission, isomerization, and cyclization: for example, zeolite Brønsted sites convert polyolefin backbones into alkoxy or alkyl–zeolite carbocations that crack into smaller alkanes/olefins.[128,129] In this way, catalysts effectively quench free radicals by providing alternate pathways (ionic or hydrogen-

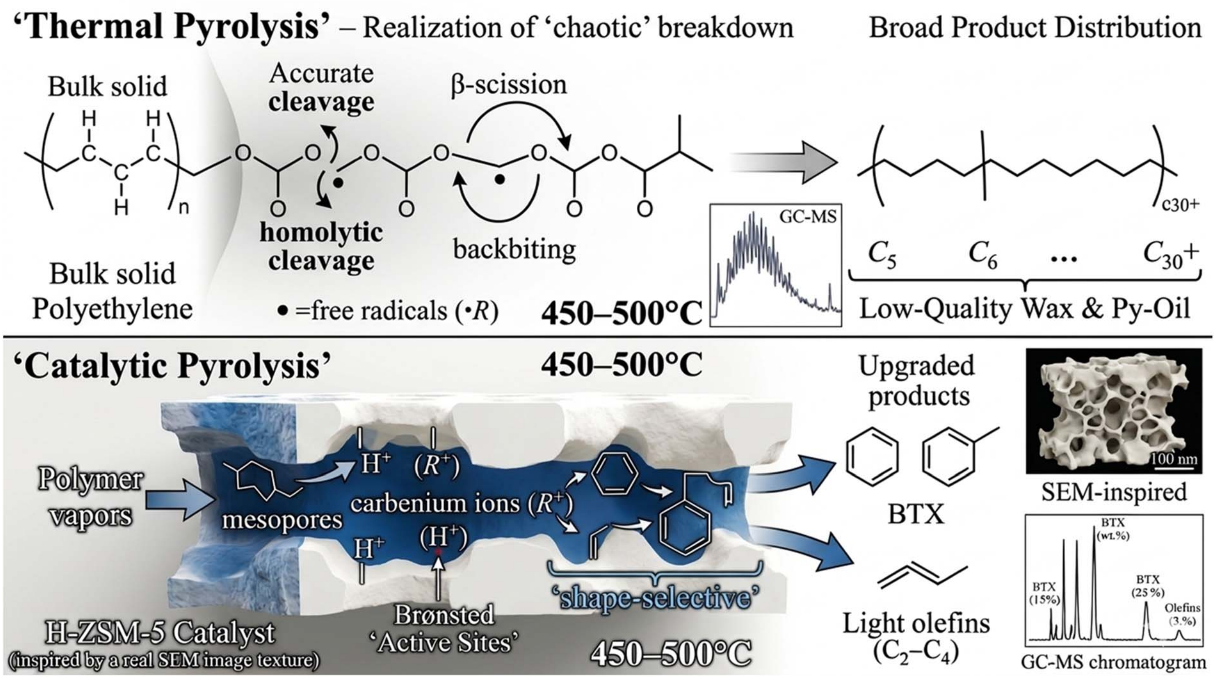

Fig. 8 Transition from thermal to catalytic pyrolysis.

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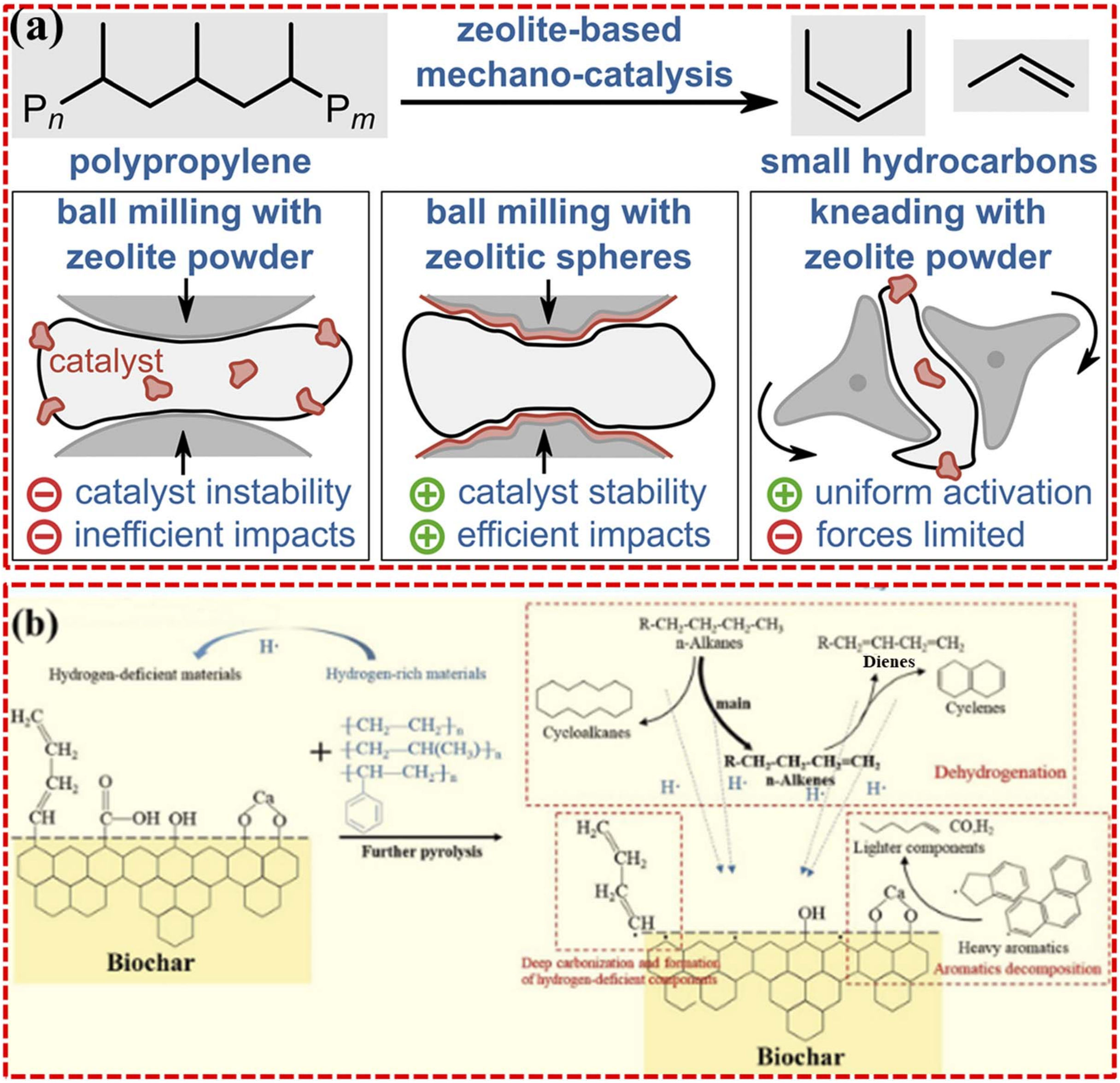

Fig. 9 (a) Mechano-catalytic polypropylene conversion and homolytic C–C bond cleavage generating radical intermediates. Reproduced from the Royal Society of Chemistry ref. 131, which is open access and permits unrestricted use of materials under the terms of the Creative Commons CC-BY. (b) Catalytic pyrolysis of polyolefin plastics by a biochar catalyst. Reproduced with permission from ref. 132. Copyright 2025, Elsevier.

transfer) and lower-energy intermediates. Valizadeh *et al.* reported that introducing acid or even basic catalysts consistently transforms polymer pyrolysis from a free-radical regime to a carbonium-ion-dominated regime, altering kinetics and product pathways.[130]

Notably, recent studies emphasize that radical and ionic mechanisms can coexist under catalytic conditions. For example, in zeolite-catalyzed pyrolysis, one may generate radical cations (species with both radical and positive character) stabilized by the zeolite electric field.[131] In mechano-catalytic polypropylene conversion, mechanochemical degradation proceeds *via* homolytic C–C bond cleavage, generating radical intermediates, whereas the introduction of Brønsted-acidic zeolites shifts the mechanism toward carbocationic pathways (Fig. 9a). Notably, radical-driven scission dominates in the absence of catalysts, while zeolite acidity promotes ionic cracking routes. In another study, Liu *et al.* also report that biochar-based catalysts catalyze both radical generation and ionic reactions, and their catalyst Brønsted and Lewis sites facilitate carbocations and hydride-transfer (transfer of a hydride, H^-, between molecules), but free radicals are still generated and are partly intercepted by hydrogen transfer (Fig. 9b).[132] Thus, catalytic pyrolysis often features mixed mechanisms: free radicals are rapidly intercepted at acid sites, yet can form transiently. Overall, catalysts suppress the uncontrolled propagation of radicals (by converting them into more stable carbocations or quenching them *via* hydrogen

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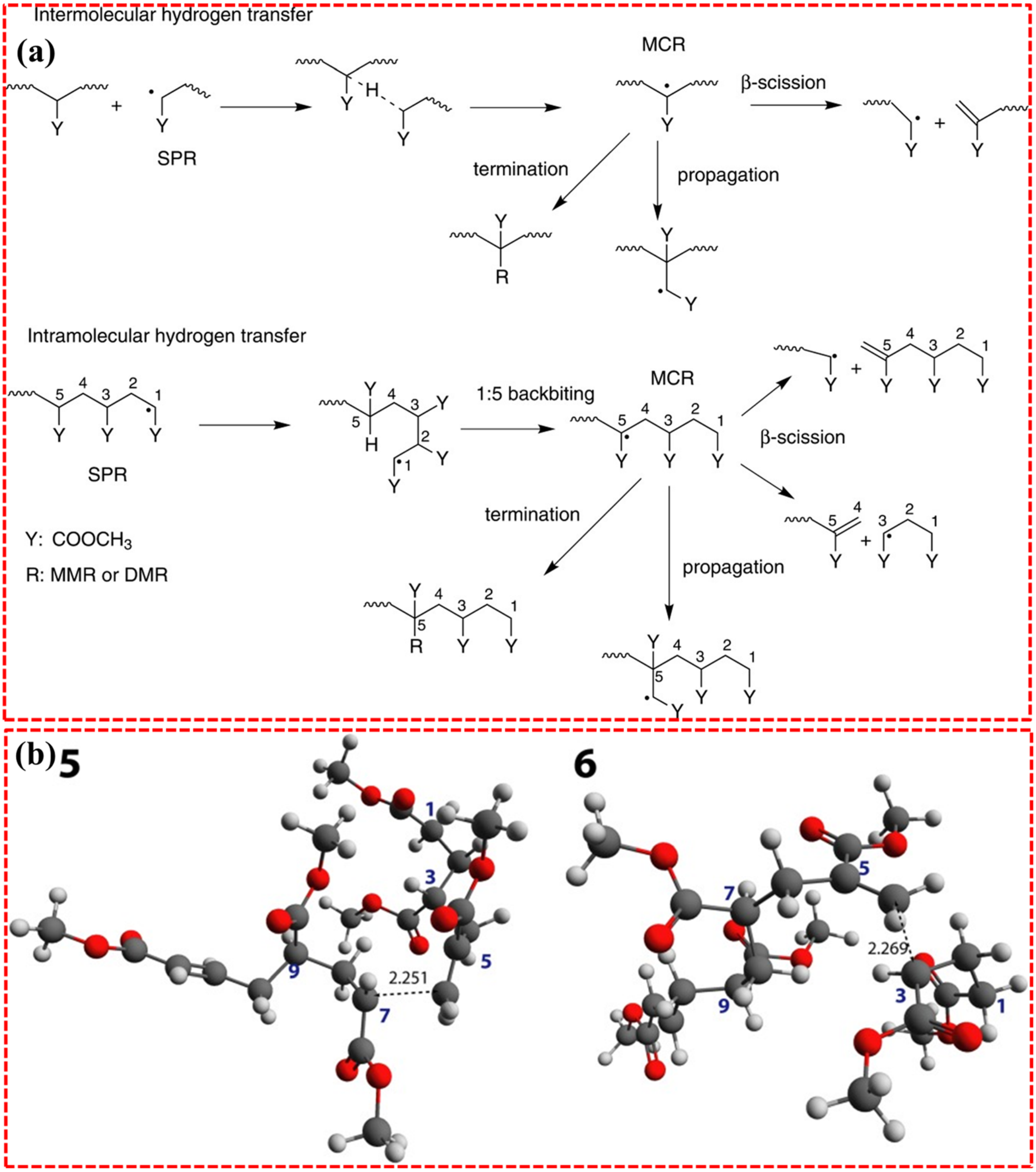

Fig. 10 (a) Intermolecular and intramolecular hydrogen transfer reactions in the spontaneous thermal homopolymerization of methyl acrylate. (b) Transition states of the β-scission reactions from 6DMCR5. 5: transition state of L-side β-scission and 6: transition state of R-side β-scission. Reproduced from John Wiley and Sons ref. 140, which is open access and permits unrestricted use of materials under the terms of the Creative Commons CC-BY.

transfer), thereby steering the cracking chemistry toward more selective ionic pathways.

More importantly, various catalysts modulate this transition in different ways. Classical carbocation β-scission and aromatization reactions are preferentially catalyzed by strong Brønsted acids (*e.g.*, H-ZSM-5), whereas dehydrogenation/hydrogenolysis (cleavage of C–C or C–heteroatom bonds by hydrogen) and hydrogen-transfer reactions are catalyzed by Lewis acids or metal catalysts (*e.g.*, Ni, Ru). Pathways may also be shifted by using base catalysts, which are known to shift even simple sites (*e.g.*, alkaline oxides), and move pyrolysis towards carbonium-ion chemistry. Weakly acidic catalysts, on the other hand (high pores), retain more of the radical character and produce heavier waxes.[133] The mechanistic shift from a radical-dominated regime (in pure thermal cracking) to catalyst-mediated ionic pathways is well established. Recent studies

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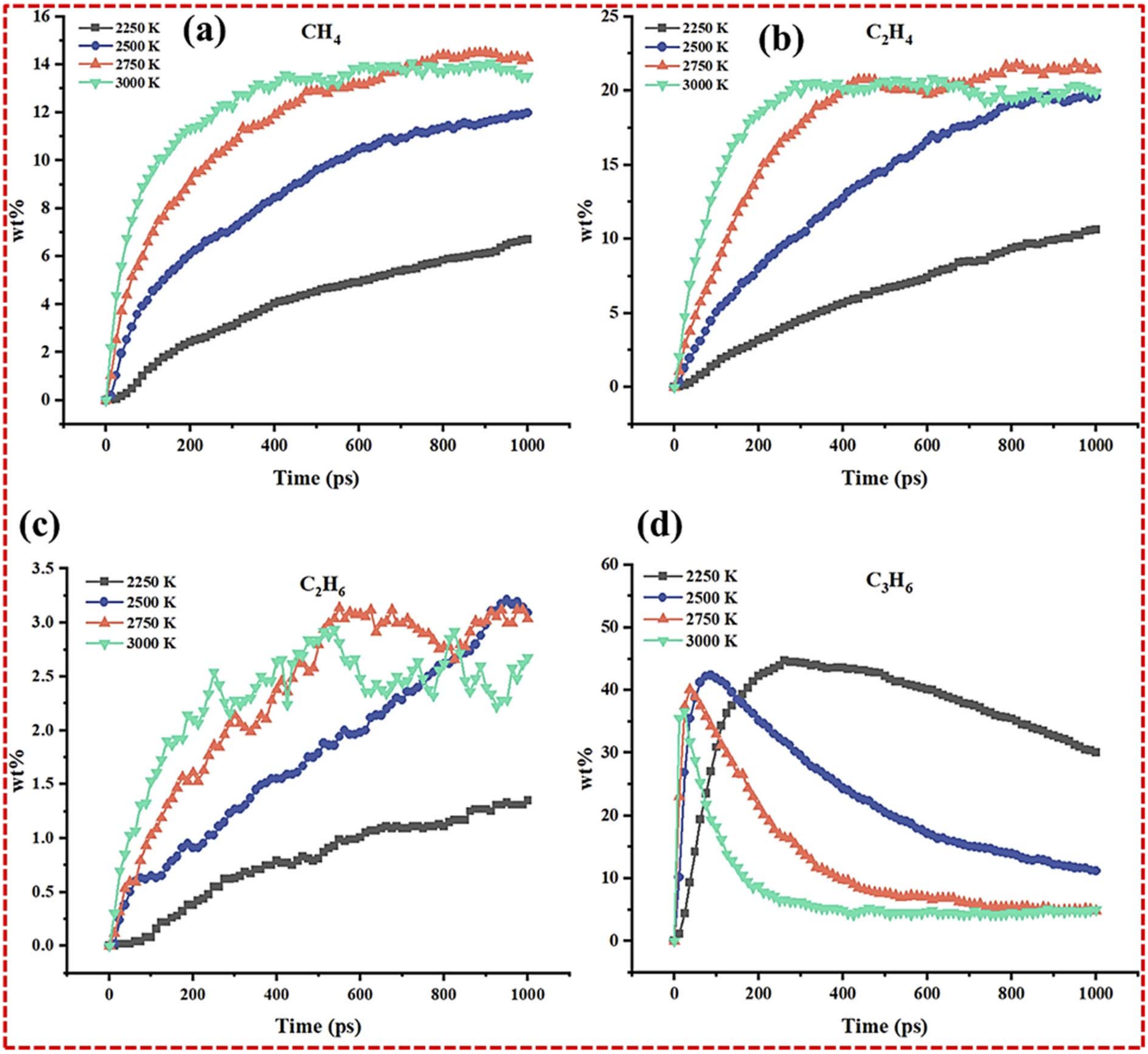

Fig. 11 Evolving trends of wt% for major gases with time during PP pyrolysis obtained from the ReaxFF MD simulation at 2250–3000 K: (a) CH_4, (b) C_2H_4, (c) C_2H_6, and (d) C_3H_6. Reproduced with permission from ref. 126. Copyright 2025, Elsevier.

consistently show that solid catalysts intercept radical chains either by forming surface-stabilized carbocations or by hydrogen-transfer, yielding qualitatively different degradation pathways. The dominant reaction mechanism in plastic pyrolysis is closely associated with characteristic product distributions. In thermal pyrolysis, governed by free-radical pathways, the product spectrum is typically broad, consisting of a mixture of waxes, long-chain aliphatic hydrocarbons, and light gases, with liquid yields commonly in the range of 60–80% under moderate conditions but with limited selectivity.[134,135] In contrast, catalytic pyrolysis, driven by carbocation-mediated mechanisms over acidic catalysts, enhances selectivity toward lighter and more valuable products. Strong Brønsted acidity promotes β-scission and aromatization, leading to increased formation of light olefins (C_2–C_4) and aromatic hydrocarbons such as BTX, often at the expense of heavy wax fractions.[136,137] The exact distribution depends on catalyst properties and reactor conditions, but catalytic systems generally exhibit reduced wax formation, higher gas yields, and improved chemical specificity compared to purely thermal processes.[134] However, the nature and extent of this molecular-level change are not universal; they are highly dependent on the molecular structure of the polymer being processed, as will be discussed next.

3.2. Chain-scission selectivity and polymer chemistry

The intrinsic chemical structure of each polymer strongly dictates its preferred cracking mode. Polyethylene (PE) and polypropylene (PP), both aliphatic polyolefins, undergo largely random C–C chain scission. Mechanistically, thermal PE pyrolysis is initiated by random homolytic C–C bond cleavage along the backbone, producing primary and secondary alkyl radicals.[138,139] Those radicals undergo β-scission and 1,5-hydrogen transfer (backbiting) steps to yield a statistical distribution of alkanes and alkenes (Fig. 10a and b).[140] In

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simulations of HDPE and LDPE pyrolysis, each C–C bond appears equally likely to break at high temperature, consistent with a random-scission model (polymer degradation where chain breaks occur at random positions along the backbone).[126] Similarly, PP, with its methyl-branched backbone, also degrades by random main-chain scission. Recent molecular dynamics simulations of PP pyrolysis confirm that random backbone cleavage dominates the initial step, and the resulting tertiary radicals rapidly undergo β-scission into propene, ethylene, methane, and other light fragments. Empirically, both PE and PP yield broad, waxy product mixtures dominated by C_1–C_4 hydrocarbons, reflecting these non-selective chain-break events (Fig. 11a–d).[126]

By contrast, polystyrene (PS) follows a depolymerization (unzipping) pathway. In PS, cleavage of the chain end yields a resonance-stabilized benzyl radical that preferentially ejects a styrene monomer. Mechanistically, the benzylic C–C bond readily homolyzes, and the benzyl radical readily de-propagates (β-scission) to release styrene; this process repeats down the chain. The result is high selectivity for the monomer. For example, experimental pyrolysis of PS (especially under conditions minimizing secondary reactions) produces the styrene monomer as the major product, often exceeding 50–80% of the total yield.[141] Polystyrene depolymerization under thermal conditions predominantly yields styrene monomer with only minor oligomeric byproducts, owing to a radical unzipping mechanism that favors monomer recovery.[142–144] In other words, PS pyrolysis follows chain-end scission to monomer, unlike the random scission of polyolefins.

Heteroatom-containing polymers diverge further due to their polar bonds. For example, polyvinyl chloride (PVC) first undergoes rapid dehydrochlorination: labile C–Cl bonds eliminate HCl in a zipper sequence, forming conjugated polyene sequences.[145,146] These polyenes then often crack and form aromatic and charred residues in a separate high-temperature stage. PVC pyrolysis occurs in two steps: first, autocatalytic HCl loss from C–Cl sites, then backbone scission of the resultant polyene.[147] Similarly, polyethylene terephthalate (PET) contains polar ester linkages that thermolyze to yield oxygenated fragments. Pyrolysis of PET routinely produces aromatic acids and CO/CO_2; for example, one study found benzoic acid as the dominant product (75% of the vapor) from PET fabric decomposition.[148] In general, cleavage of PET ester bonds gives mono- and di-oxygenated compounds (benzoic acid, acetaldehyde, CO_2, *etc.*) rather than the olefins typical of polyolefins. Polyamides (nylons) also contain strong amide bonds; pyrolysis normally produces nitriles, amines, and other nitrogen compounds. As a matter of fact, traditional pyrolysis is not a clean process for polyamides, as reported by Jiang *et al.*; when pyrolyzing nylon-6, the resulting NH_3/NO_x gases are problematic, and the process is usually unsuccessful in general.[149] The chemistry of the polymer backbone, bond strengths, substituents, and polarities dictate chain scission selectivity. PE and PP, with non-polar C–C/C–H bonds, crack randomly along the chain. PS, with its benzylic resonance, preferentially unzips to styrene. Polymers bearing polar groups (PVC, PET, PA) undergo directed bond cleavage (dehydrohalogenation, ester or amide breakdown), producing characteristic functional products (HCl and polyenes for PVC, benzoic acid for PET, caprolactam/amine for PA) instead of a broad alkane distribution. These quantitative and mechanistic differences have been confirmed in recent studies of mixed plastic pyrolysis and fundamental decomposition kinetics, underscoring the need to tailor cracking strategies to polymer chemistry. Knowledge of these polymer-specific scission modes is important because catalysts do not act on the solid polymer but on the vaporized intermediates, a novel concept that envisions their role as a post-cracking molecular sculptor.

4. Catalyst-induced product shaping rather than polymer cracking

Catalytic pyrolysis of plastic waste can be viewed not as the direct breakdown of polymer chains on a surface, but rather as post-cracking molecular architecture (the targeted chemical modification of volatile intermediates after they have been thermally generated from the polymer) of the volatile products formed by thermal depolymerization. In this paradigm, the polymer is first thermally cracked to a mixture of free radicals and low-molecular-weight fragments (vapors), and these vapors, not the solid polymer, undergo the bulk of catalytic transformation.[150] For example, tire-derived pyrolysis vapors are rich in reactive radicals that undergo chain scission, hydrogen abstraction, and aromatization before quenching into liquid oil.[151,152] Catalysts follow the path of post-cracking catalysts, which produce distributions of products by surface reactions of those vapors instead of cracking the polymer backbone itself. Such catalysts represent a new class of molecular architectures for enhancing plastic pyrolysis. Through vapor-phase reactions, catalysts will be able to selectively direct chemistry to the desired products (aromatics, olefins, stable hydrocarbons) rather than just catalyzing the rupture of polymers. In this way, surface acid/base and metal sites influence the isomerization, hydrogen-transfer, and stabilization reactions that shape the final oil and gas composition.[153] Recent studies explicitly highlight that catalysts interact primarily with pyrolysis vapors. For instance, upgrading of polyethylene vapors over zeolites increased gas and BTX yields, whereas thermal pyrolysis alone produced much more of the heavy waxes.[153] In short, catalysts in plastic pyrolysis act downstream of polymer cracking, selectively driving rearrangements, hydrogenation/dehydrogenation, and radical quenching to engineer the oil and gas products.

4.1. Catalysts as post-cracking molecular architects

Catalysts influence the fate of pyrolysis vapors through several complementary surface-mediated mechanisms. First, catalysts provide surfaces for aromatization and isomerization: unsaturated fragments in the vapor can cyclize and dehydrogenate on acid sites to form aromatics. For example, mechanistic studies on model pyrolysis vapors show that long-chain olefins break into smaller olefins on a ZSM-5 surface, which then undergo oligomerization, cyclization, and hydrogen-transfer to yield benzene, toluene, and xylenes (BTX) (Fig. 12). In one model

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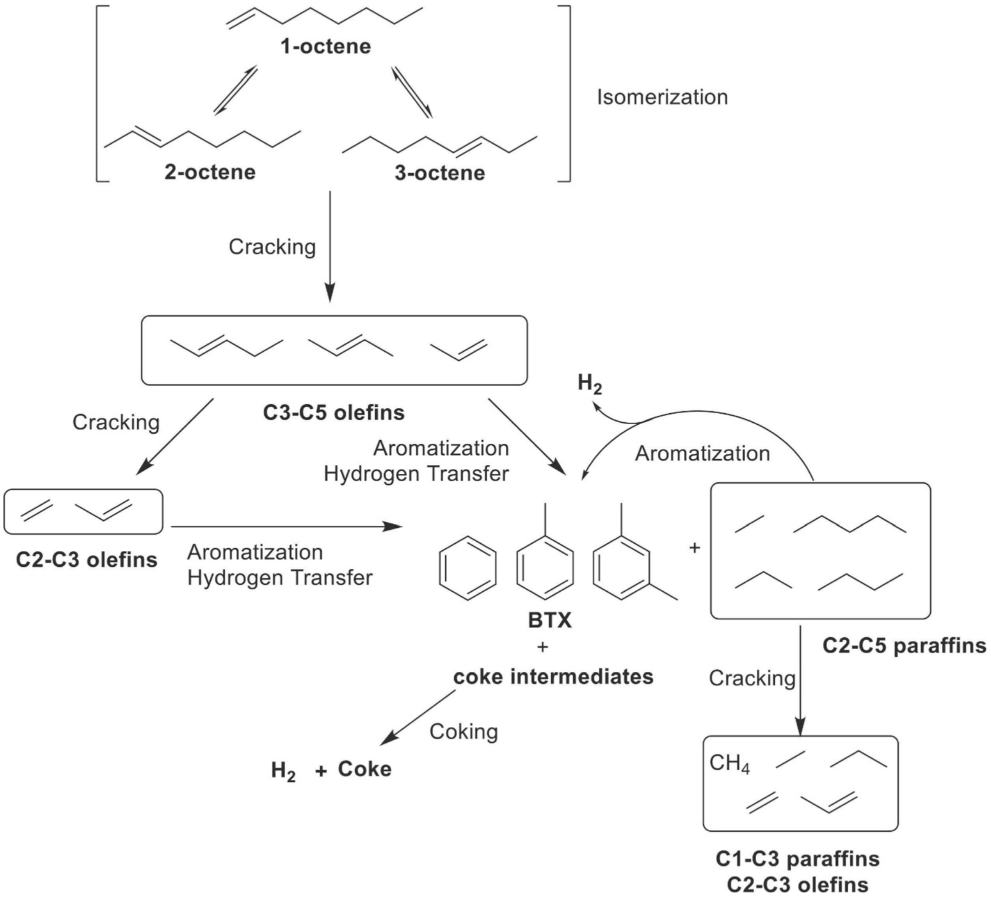

Fig. 12 Proposed reaction network of 1-octene over ZSM-5. Reproduced with permission from ref. 153. Copyright 2023, Elsevier.

compound experiment, 1-octene over ZSM-5 cracked into smaller olefins, which are further isomerized and cyclized into BTX aromatics (with coke and H_2 as byproducts).[153] Likewise, strong Brønsted-acid catalysts such as HZSM-5 dramatically enhance rearrangements. Synthesized ZSM-5 (microporous and highly acidic) showed increased cracking and isomerization of plastic vapors, breaking large molecules into smaller fragments and dramatically raising aromatic oil yield. In general, acid sites create carbocations from olefinic or paraffinic fragments, and these carbocations undergo β-scission and cyclization on the catalyst surface to form aromatics.[154] In short, the catalyst surface acts as a template and proton source for converting linear pyrolysis fragments into branched and cyclic products with high aromatic content.

Second, catalysts mediate hydrogen transfer and radical quenching. Pyrolysis vapors contain radicals and unsaturated fragments, and catalyst surfaces can often supply or abstract hydrogen, *via* adjacent acid/base sites or metal hydrides, quenching radical chains. This hydrogen transfer both stabilizes the intermediate and alters selectivity. For instance, the mechanistic study cited above reported that hydrogen transfer on zeolite occurs concurrently with cyclization; the octene-derived olefins that cyclize into BTX also release H_2 (Fig. 13a).[153] More broadly, metal-containing catalysts (*e.g.*, Ni, Pd, and Ru) can activate hydrogen or induce dehydrogenation. In a hydrogen-free Ni/ZSM-5 system, polymer C–C bonds were dehydrogenated at Ni sites, forming C═C bonds and releasing H atoms, which then saturated other fragments on the acid sites.[155] Those released hydrogen atoms contribute to the thermal decomposition and can saturate neighboring radicals, essentially quenching them and preventing polymerization or coke formation. Conversely, Lewis-acid or radical sites can abstract hydrogen from pyrolysis intermediates to form olefins. For example, basic oxide catalysts (MgO and CaO) remove H as protons, increasing unsaturation. In all cases, the net result is that radicals in the vapor phase encounter a catalyst surface that either donates or withdraws hydrogen. This interrupts radical recombination (the coupling of two radicals to form a stable covalent bond) and shifts the product slate. For example, one pyrolysis study found that *in situ* catalysis, where vapors immediately encounter acid, substantially increased alkane yields due to hydrogen transfer compared to *ex situ* cracking (Fig. 13b and c).[156] The surface thus acts as a radical quencher (a species that terminates radical chains by donating hydrogen or capturing radicals): donating H or capturing radicals to stabilize them as lower-reactivity species, which suppresses runaway polymerization/coking in the pyrolysis oil.

Finally, catalysts stabilize the liquid oil through surface interactions that neutralize reactive species. Many catalysts have functionalities that react with labile byproducts to remove

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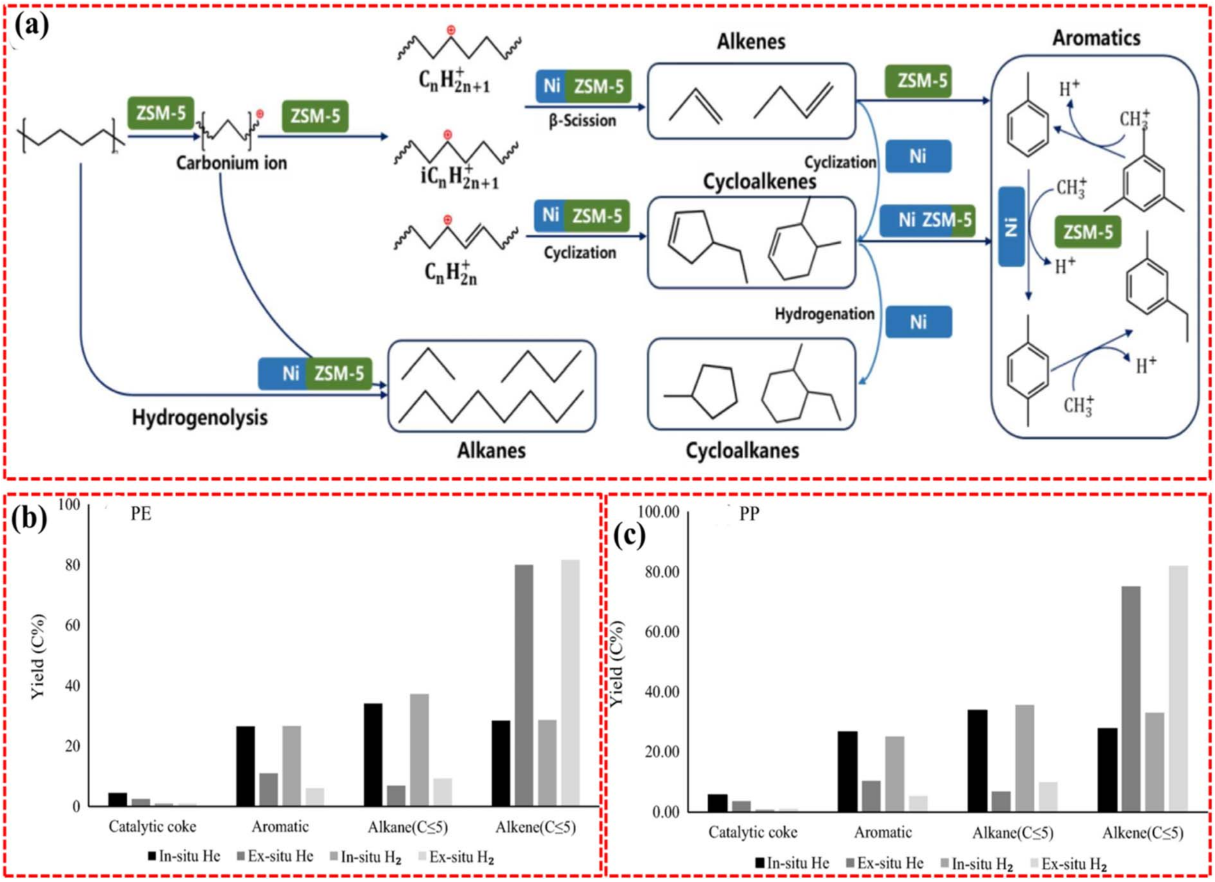

Fig. 13 (a) Main reaction pathways of LDPE conversion into aromatics over 5Ni/ZSM-5(130). Reproduced with permission from ref. 153. Copyright 2023, Elsevier. Product distribution during the catalytic pyrolysis of (b) PE and (c) PP. Reproduced with permission from ref. 156. Copyright 2017, Elsevier.

them or convert them to inert species. For instance, basic sites (such as CaO and MgO) strongly interact with acidic and oxygenated compounds in the vapor. CaO catalysts have been reported to take up CO_2 and H_2O, which are generated during the pyrolysis process, and to decarboxylate organic acids, thus lowering the acid content in the oil and enhancing its stability. In a single experiment, the PET pyrolysis reaction was significantly enhanced by the addition of CaO, which facilitated decarboxylation reactions, a vivid illustration of surface chemistry cleaning up the vapor.[157] Likewise, the surface areas and functional groups of activated carbon and other mesoporous supports can be involved in weak acid-base or redox reactions. These surfaces are likely to inhibit the formation of char; mesoporous catalysts used in pyrolysis upgrading have a lower likelihood of forming carbon, and this enhances the heating value of biofuels. In practice, catalysts can adsorb small radicals or oxygenates, which will provide more time or reactive handles to stabilize the oil molecules. As an example, MgO surfaces trap CO_2 (to form magnesium carbonate) and H_2O, which is effectively the mopping up of unstable species.[158] These surface interactions can also block sites prone to coking: as observed, open mesopores act as highways for large molecules to exit, reducing micropore-coke build-up.[159] In summary, catalysts stabilize the pyrolysis oil by interacting with and removing harmful fragments (acids, peroxides, radicals), so that the condensed oil is richer in stable hydrocarbons and poorer in reactive condensable byproducts.

Overall, this post-cracking molecular architecture perspective is underpinned by literature showing that plastic vapors are the primary reacting species on catalysts. Catalytic studies consistently report that solid catalysts do not noticeably depolymerize the bulk polymer directly but instead refine the thermal oil. For example, tire pyrolysis followed by zeolite upgrading increased light gases and aromatics primarily by secondary cracking of vapors. Similarly, ethylene- and propylene-rich aliphatic vapors from polyolefins are readily aromatized or oligomerized on ZSM-5 surfaces. In all these cases, catalysts act after the polymer has cracked. This insight shifts focus onto designing catalysts whose pore structure, acidity, and redox function can optimally react with small radicals and olefins. In the following sections, we will examine how different catalyst chemistries and structures steer these vapor-phase transformations towards the desired products. The way in which the catalyst transforms pyrolysis vapors by aromatization, hydrogen transfer, or radical scavenging is largely dependent on their chemical nature, as described below.

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4.2. Chemical nature of catalysts (acidic *vs.* basic *vs.* redox)

The intrinsic chemical character of the catalyst, *i.e.*, acidic, basic, or redox-active, dictates the mechanistic pathways accessible to pyrolysis vapors. Strong acid sites, typically in zeolites or acidic aluminosilicates, promote carbocation chemistry in the vapor phase. Olefinic fragments can be protonated on Brønsted acid centers to form carbenium ions, which then undergo β-scission, hydride shift, and cyclization.[160] This leads to intense cracking and aromatization. For instance, hydrothermal cracking of polyolefin vapors over H-ZSM-5 was reported to produce abundant aromatic hydrocarbons *via* acid-catalyzed rearrangements.[154] In their study, Jia *et al.* found that introducing mesopores into H-ZSM-5 (a hierarchical acid catalyst) dramatically increased mono-aromatic yield; acid sites on the zeolite mouths catalyzed fragmentation of even very large biomass-derived molecules, doubling aromatic selectivity relative to purely microporous H-ZSM-5.[159] On strongly acidic zeolites, such as H-ZSM-5 or ultrastable Y (USY), secondary reactions such as alkyl transfer (movement of an alkyl group from one molecule to another, *e.g.*, alkylation of aromatics) and oligomerization also occur, further enriching aromatic content. In short, acidic catalysts follow a classical carbonium ion mechanism, protonation of paraffins/olefins to form C^+, then β-scission and cyclization to smaller olefins and aromatics. The net effect of acidity is therefore to favor aromatic and iso-paraffinic products at the expense of linear olefins.

Basic sites on oxides (MgO, CaO, metal hydroxides/carbonates, mixed oxides) drive fundamentally different chemistry. They tend to abstract hydrogen atoms from hydrocarbon fragments, leading to dehydrogenation and olefin formation. In practice, base catalysts are found to be highly selective for light olefins and even aromatic formation, but *via*

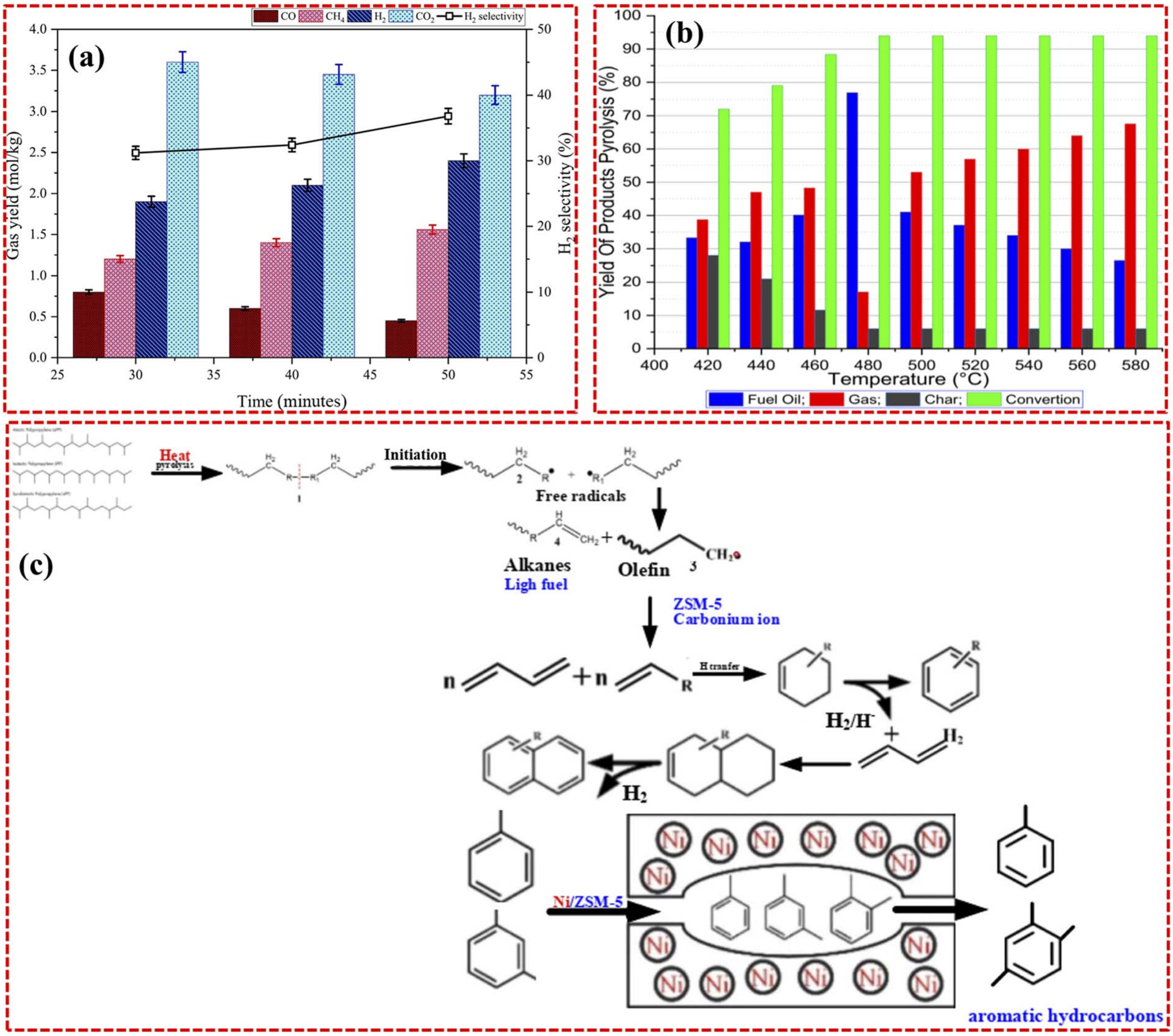

Fig. 14 (a) Effect of reaction time on the gas yield and H_2 selectivity. Reproduced from Elsevier from ref. 164, which is open access and permits unrestricted use of materials under the terms of the Creative Commons CC-BY. (b) Effect of temperature on the Ni/ZSM-5 bifunctional catalytic pyrolysis products. (c) Reaction mechanism of the catalytic pyrolysis of PP with a Ni/ZSM-5 catalyst-fixed bed. Reproduced from Elsevier from ref. 165, which is open access and permits unrestricted use of materials under the terms of the Creative Commons CC-BY.

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a different route.[161,162] In one example, Du *et al.* demonstrated that the introduction of CaO to the pyrolysis of PET significantly enhanced the production of benzene through decarboxylation reaction, which implied that the basic catalyst not only eliminates acidic oxygenates but also facilitates the C–H abstraction reaction to produce aromatic rings.[157] The weakly basic catalysts form partially oxygenated compounds (aldehydes, ketones), and strong bases prefer the formation of hydrocarbons by eliminating CO_2/H_2O. Basic sites can mechanically deprotonate –OH or –COOH groups; however, in hydrocarbon vapors, they mainly abstract H and stabilize carbanions. Pyrolysis of basic oxides, therefore, tends to produce higher quantities of aliphatic unsaturated hydrocarbons (olefins) and can be used to stabilize oil by radical-scavenging reactive radicals. Moreover, simple catalysts are more coking-resistant in comparison with strong acids. Bases also counteract acidic products in co-pyrolysis systems, such as CaO, which is known to fix CO_2 and decarboxylate acids to ketones, which reduces the number of acids in the oil directly.[163] In short, simple catalysts direct chemistry to hydrogen abstraction (forming C=C) and deoxygenation (CO_x elimination) to yield olefin-rich, relatively stable oils.

Metals (especially Ni, Cu, Fe, Pt, and Ru, *etc.*) add hydrogenation/dehydrogenation and reforming capabilities. They are commonly employed in H_2 (hydrogenolysis) or can produce H_2 *in situ* (through dehydrogenation). As an example, Ni-impregnated catalysts significantly enhanced the dehydrogenation of pyrolysis vapors in tire or plastic pyrolysis; Ni-loaded zeolites enhanced the total aromatic yield by promoting the release of H_2.[150] In another experiment, Ni/SiO_2 was the most effective catalyst to generate hydrogen-rich gas from mixed plastics (Fig. 14a), which was employed with Ni having a high hydrogenation/dehydrogenation capacity.[164] Unsaturated fragments are mainly hydrogenated by other metals, such as Pt or Ru (usually on supports such as C or Al_2O_3), to produce alkanes, and long chains are broken into gasoline-range fuels. To illustrate, a bifunctional Ni/ZSM-5 catalyst yielded 77 wt% liquid fuel from PP (Fig. 14b), which suggested that Ni facilitated the transfer of hydrogen and aromatization at the same time (Fig. 14c).[165] On a broader scale, the choice of Ni and Co in plastic pyrolysis is made due to their ease in facilitating CH activation and hydrogenolysis (cleavage of C–C bonds by molecular hydrogen). Copper is also interestingly active; $CuCO_3$ was reported to provide 94% yield of liquid from PE, which indicates that it is highly hydrogenated on the surface.[166] In tandem systems, a large-pore metal catalyst is frequently employed to fractionate heavy fractions, then an acid catalyst is used to refine products. As an example, a relay catalyst bed of Al_2O_3 (a large-pore metal oxide) followed by ZSM-5 reduced the range of products to C_5–C_{12} alkanes/olefins (77% selectivity).[167] In such sequences, the metal oxide provides an initial cracking (with some hydrogen transfer), and the zeolite finishes by aromatizing or further cracking. In summary, metal catalysts bring hydrogen into play, either supplying H_2 to saturate bonds or abstracting H to generate it, effectively performing hydrodeoxygenation and hydrocracking. The result is often higher alkane fractions and more controlled reforming of aromatics, in contrast to purely acid or base catalysts. Redox-active catalysts (*e.g.*, Fe_2O_3) can also capture heteroatoms (Cl and Br) and facilitate dehydrogenation/aromatization, but the dominant effect is hydrogen management and chain reforming.

In comparing these three classes, some general principles emerge. Acidic catalysts favor carbocation pathways and thus yield the most aromatics (often producing coke as well), basic catalysts favor hydrogen abstraction and olefins (with oxygenates removed), and metals bridge the gap by adding a strong hydrogenation/dehydrogenation dimension. For example, zeolites such as H-ZSM-5 will crack and cyclize vapors into BTX, whereas MgO tends to give ethylene/propylene and stability *via* CO_2 release. Ni-loaded catalysts can pull H out of hydrocarbon fragments, pushing reactions toward saturation and aromatics. The different types of catalysts thereby leave a chemical imprint on the product slate: carbocations → aromatics, hydrides/oxides → alkenes (and deoxygenation), metals → mixed hydrogenation/reforming. It is possible to design plastic pyrolysis to favor benzene/toluene/xylene over olefins and paraffinic fuels by choosing and mixing these catalysts. The chemical nature of the catalyst determines which reaction takes place, but the physical structure and the time at which the vapour contacts the catalyst define the extent and selectivity of the reaction, especially secondary cracking.

5. Morphology and residence-time-driven selectivity

In addition to chemistry, the physical structure of the catalyst and its time-dependent location in comparison to the feed also have strong effects on the selectivity of the products. Porosity and residence time define the extent to which exhaust vapors are cracked and the molecules that escape as oil.

5.1. Porosity-controlled secondary cracking

The pore structure of the catalyst (micropores *vs.* mesopores *vs.* hierarchical) serves as a molecular sieve that discriminates the extent of secondary cracking. Microporous catalysts (pore width <1 nm, *e.g.*, H-ZSM-5 and zeolite Y) are highly confined, and only small fragments can diffuse through.[168,169] As a result, large vapor molecules that enter the micropores tend to crack excessively. In practice, this leads to over-cracking (excessive fragmentation beyond the desired product range) and high gas yields. For example, an *ex situ* pyrolysis of PE over a microporous zeolite produced 80% C_2–C_4 olefins (gas range) and only 7% alkanes, whereas for the *in situ* case, less over-cracking was observed, giving 28% olefins and 34% alkanes.[156] The dominance of light olefins in the *ex situ* (microporous) case indicates that the micropores force heavy fragments to fragment until they are small enough to exit. Studies on polyethylene pyrolysis found that microporous zeolite catalysts greatly increase gas yields compared to non-catalytic pyrolysis, precisely because of their shape-selective cracking.[4] Moreover, coke tends to form inside micropores, quickly deactivating such catalysts. As noted, purely microporous zeolites generate toxic coke trapped in the pores and exhibit limited stability.[170] In short, microporous catalysts maximize cracking (often past the point of useful

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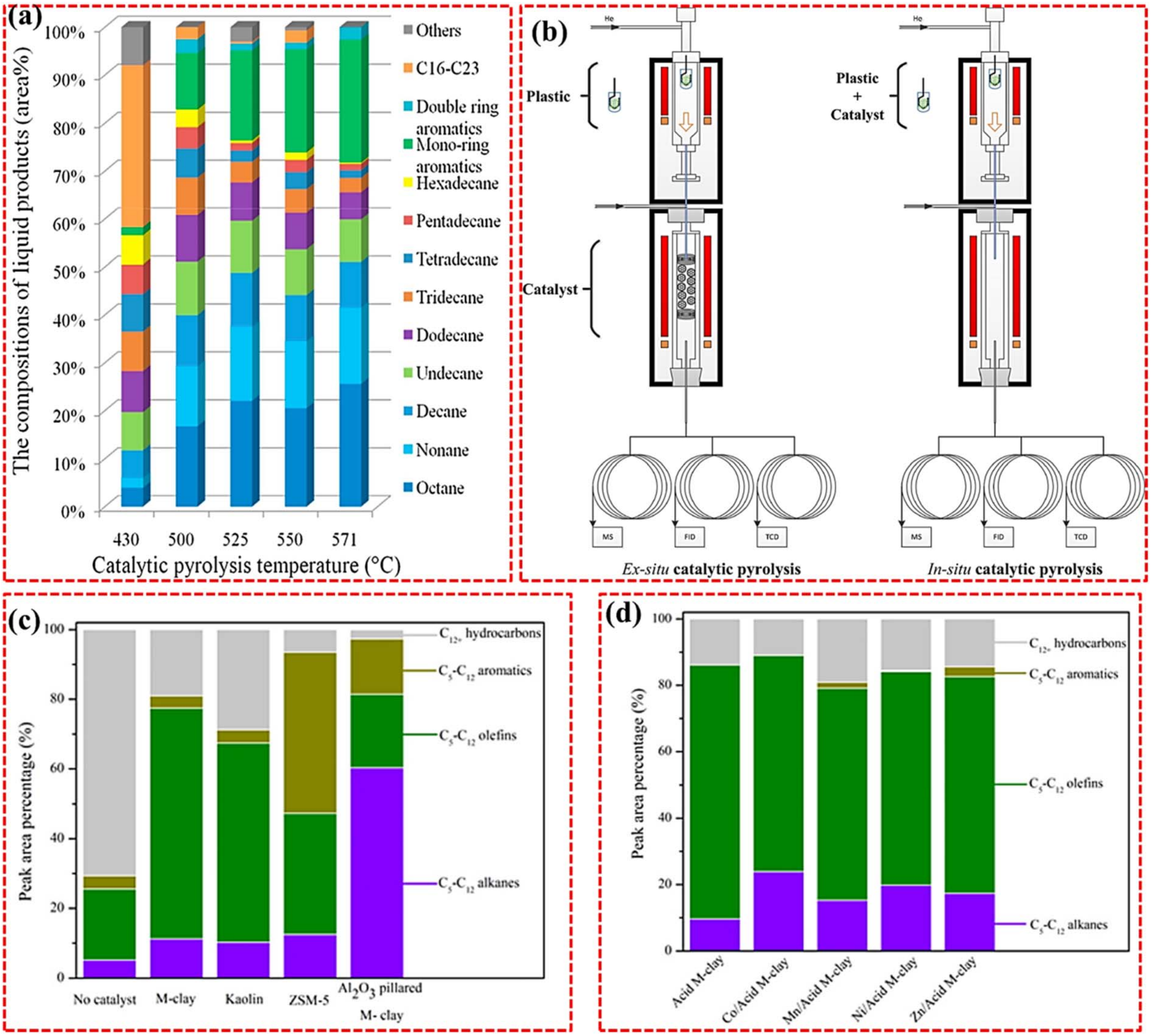

Fig. 15 (a) Compound distribution changes along with different catalytic pyrolysis temperatures with a fixed catalyst/reactant ratio of 2. Reproduced with permission from ref. 174. Copyright 2019, Elsevier. (b) Configurations of *in situ* and *ex situ* pyrolysis in a tandem micro-pyrolyzer with online GC/MS-FID-TCD. Reproduced with permission from ref. 156. Copyright 2017, Elsevier. (c) Product distribution for the *in situ* catalytic cracking of LDPE over clay-based catalysts compared with the reference material ZSM-5. (d) Product distribution for the *in situ* catalytic cracking of LDPE over modified M-clay catalysts. Reproduced with permission from ref. 167. Copyright 2021, Elsevier.

fuel) and thus are associated with light gases and low liquid yields.

Mesoporous catalysts (pore width 2–50 nm) have much larger channels. These allow bulkier molecules to access active sites and escape before over-cracking,[171] which results in enhanced oil stability and higher liquid yield; moreover, the oil contains larger, more saturated hydrocarbons. Mesopores significantly reduce coking by providing more volume for coke precursors to deposit away from the active sites.[172,173] Consistent with this, mesoporous catalysts have been highlighted for improving bio-oil quality by reducing carbon formation. For plastic pyrolysis, mesoporous supports tend to produce heavier oil with high alkene/paraffin content. For example, activated carbon (highly porous) used in LDPE pyrolysis yielded 72% alkanes and 28% aromatics at high temperature, compared to zeolitic catalysts, which yield more aromatics (Fig. 15a).[174] The larger pores also favor secondary reactions at milder rates, and molecules can reside for longer in the mesopores without immediate cracking, allowing beneficial transformations (such as oligomerization to stable oligomers). Overall, mesoporous catalysts temper the severity of cracking and thus help preserve liquid hydrocarbons. Their looser environment is sometimes described as broadening the reaction zone and homogenizing product distribution.

Hierarchical catalysts are materials that contain a combination of both micro- and meso-pores. Micropores are highly aromatic-selective, strongly acidic, and shape-selective, whereas diffusive and stable mesopores enhance diffusion and stability.[175,176] It is found in the literature that hierarchical zeolites are much more efficient in plastic or biomass pyrolysis

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than their purely microporous counterparts. As an example, Jia *et al.* found that desilicated (mesoporous) ZSM-5 yielded twice as much mono-aromatic compound as conventional ZSM-5 during the pyrolysis of wood, and it produced significantly less coke in the micropores.[159] In practice, hierarchical catalysts provide moderate selectivity and yield high-quality liquid fuels (monoaromatics and gasoline-range hydrocarbons) without debilitating deactivation. The open mesopores serve as highways that allow large pyrolysis fragments access to active sites and subsequently escape before over-cracking, and the micropores within continue to catalyze cyclization and aromatization of the intermediates. This dual porosity eliminates excessive deep cracking of the gas, thereby increasing the yield of the aromatic liquid and catalyst life. Beyond pore structure, the relative location of the catalyst to the pyrolysis zone (*in situ* or *ex situ*) offers another crucial temporal control over the products.

5.2. Catalyst placement and temporal control

Along with morphology, the positioning and timing of catalysts strongly affect product outcomes. Two contrasting modes are *in situ* (catalyst mixed with or placed directly inside the pyrolysis reactor, so vapors contact it immediately upon formation) *versus ex situ* catalysis (pyrolysis vapors pass into a separate secondary reactor containing the catalyst, separating thermal cracking from catalytic upgrading). In an *in situ* configuration, the catalyst is intimately mixed with or located inside the pyrolysis reactor, and vapors encounter the catalyst immediately upon formation.[177,178] In *ex situ* setups, the pyrolysis vapors pass into a second reactor (often a packed bed) containing the catalyst, so primary cracking is separated from catalytic upgrading.[177,178] These arrangements yield different selectivity. Xue *et al.* studied a tandem micro-pyrolyzer to investigate the effects of plastic type, catalyst, and feedstock contact mode, as well as the type of carrier gas, on product distribution (Fig. 15b). It was found that *in situ* catalytic pyrolysis of PE produced significantly more aromatics and paraffins, whereas *ex situ* operation produced mostly olefins. Quantitatively, *ex situ* over ZSM-5 gave 80% alkenes and only 7% alkanes (mostly gas) with just 11% aromatics, whereas *in situ* gave only 28% alkenes, 34% alkanes, and 27% aromatics.[156] The explanation is that *in situ* contact promotes secondary hydrogen transfer and aromatization inside the catalyst (rich H from β-scission saturates olefins), while the *ex situ* process results in rapid thermal cracking with less hydrogen environment.[179,180] In practice, *in situ* tends to maximize aromatic and paraffinic products but at higher catalyst loading/cost, whereas *ex situ* can preserve more liquid yield but with lighter composition.

Staged or multi-zone systems (sequential exposure to different catalysts or conditions) are another option for control beyond a single stage. In this case, various catalysts or conditions are used sequentially. A very popular method is two-stage pyrolysis, where the initial step involves a thermal or mild catalytic process to depolymerize the product before a second catalytic step to upgrade. As an example, Dai *et al.* applied a relay system of Al_2O_3 (large-pore cracking) followed by ZSM-5 (acid aromatization) to the LDPE vapors. This synergy resulted in a focused C_5–C_{12} liquid fraction (77% of products) with streamlined distribution produced by the Al_2O_3 cracked polymers entering ZSM-5 micropores (Fig. 15c and d).[167] That is, the slate of products was sharpened using two catalysts in series. The other method is segmented co-pyrolysis, whereby the feeds or catalyst beds are physically divided. Tian *et al.* showed a two-stage system in segments, biomass + LDPE, where $FeCl_3$ catalyzed biomass vapors, and MCM-41 catalyzed LDPE vapors. This produced 72.0 wt% mono-aromatic hydrocarbons in the final oil, approximately 13.5 percentage points better than that obtained by traditional mixed pyrolysis, and significantly less wax byproducts were formed.[181] They, in effect, staged the catalysts, hence every feed was upgraded into favorable conditions, thus significantly enhancing the quality of the oil. More generally, staged systems, such as dual-catalyst beds, concentric reactors, or temporal pulsing of catalysts, permit fine-tuning of contact time with each type of catalyst. The char can be suppressed by short residence in the primary vapor with a weak catalyst, after which longer contact with a second catalyst can be used to effect aromatization.

Altogether, *in situ* contact can be effective by placing the catalysts and timing, and *ex situ* can be advantageous with fewer catalysts by forming olefins. Sequential bed, as well as zoned reactor arrangements, have been demonstrated to dramatically enhance selectivity. As an example, a two-step reaction involving Al_2O_3 followed by ZSM-5 gave a high-quality C_5–C_{12} fuel with a selectivity of 77%,[182] and a pyrolysis segmented reaction gave 72% mono-aromatics.[181] These strategies starkly differentiate this review from prior work by emphasizing that timing and staging of catalyst–vapor interactions are as important as the catalyst chemistry itself. These engineering decisions on catalyst shape and position determine the consequences of secondary reaction, which are the key factor in long-term oil stability and catalyst lifetime, as discussed next.

6. Secondary reactions governing oil stability

Secondary reactions after primary pyrolysis profoundly affect the stability and quality of the resulting oil.[183–185] Ongoing radical-driven chemistry in the vapor or liquid phase can convert desirable products into heavy residues. Aromatization of intermediate olefins catalyzed by acidic sites can be beneficial, producing stable monoaromatics that improve oil quality and value.[186] In contrast, oligomerization and uncontrolled polymerization lead to heavy polyaromatics and waxes (oil aging), reducing fuel quality.[187] Dimerization (joining two identical or similar molecular fragments) of radical fragments can likewise cause a rise in viscosity and gum formation. Notably, catalysts or additives, such as hydrogenation or stabilization of products to preserve them in more stable forms, can suppress active radicals. The overall effect will be determined by the ratio of these pathways. In pyrolysis investigations of plastics, a keen design of catalyst and reaction control (temperature, residence time) has been demonstrated to direct secondary chemistry to desirable aromatics and eschew undesirable coke

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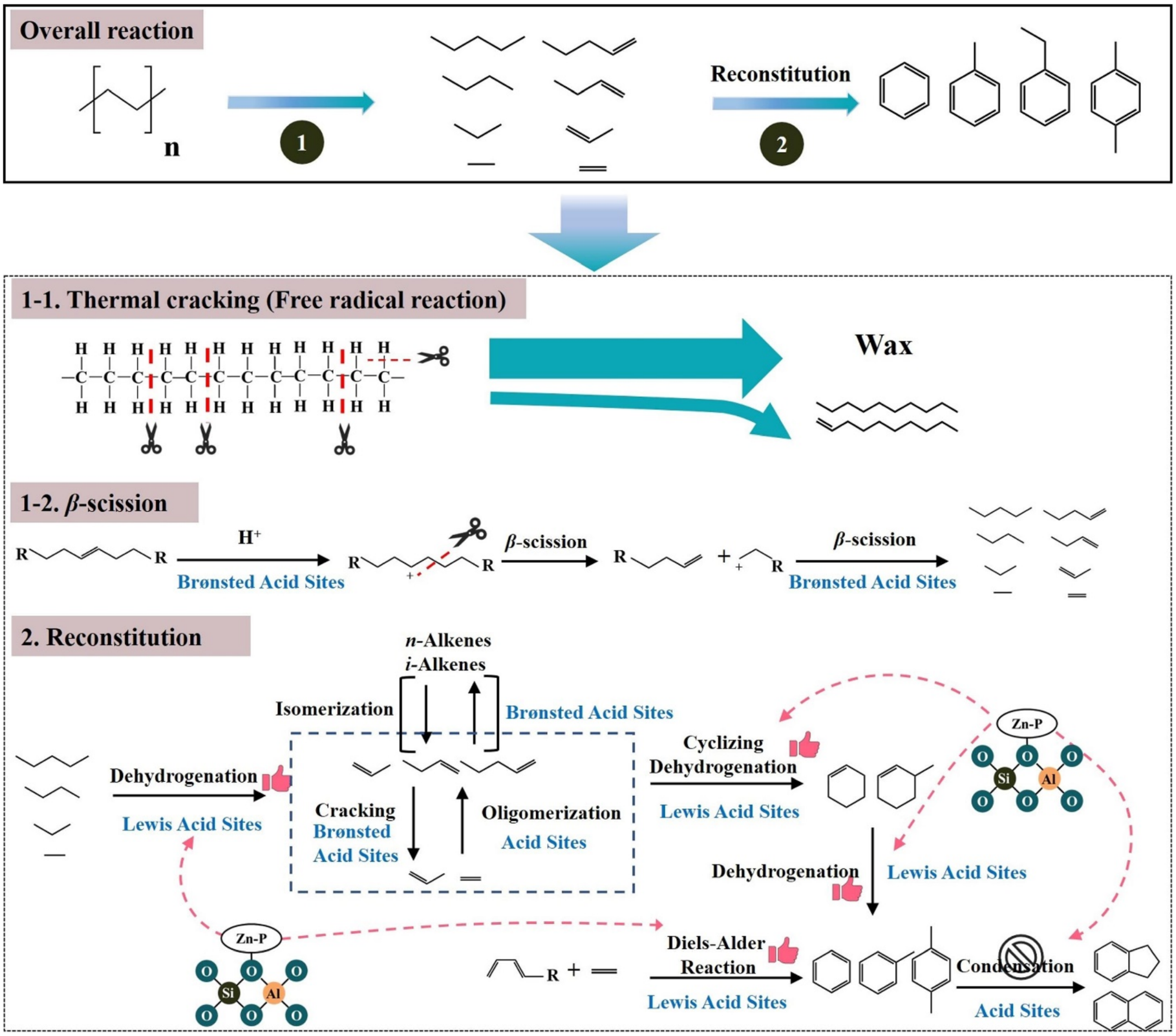

Fig. 16 Proposed mechanism of the catalytic pyrolysis of LDPE over Zn–P/HZSM-5. Reproduced with permission from ref. 188. Copyright 2024, Elsevier.

precursors. Below, we summarize key findings from recent studies on these secondary reactions.

6.1. Beneficial *vs.* detrimental secondary reactions

Selective aromatization of pyrolysis vapors is often a goal. For example, using tuned zeolite catalysts (*e.g.*, Zn- and P-modified HZSM-5) achieves very high monoaromatic yields. Zhang *et al.* showed that adding Zn and P to HZSM-5 in LDPE pyrolysis (500 °C) gave 55.9 wt% liquid oil with an outstanding 87.4% of that in monocyclic aromatics (BTEX fraction 75%). The Zn species increased Lewis acidity (promoting aromatization) while P neutralized excess Brønsted acidity, suppressing coke and polyaromatics (Fig. 16).[188] In general, catalysts with strong acidity and shape selectivity crack long chains into smaller fragments that readily cyclize to aromatics. By contrast, non-selective or overly acidic catalysts can drive heavy oligomerization. In one study, severe coking on an HZSM-5 catalyst was shown to block pores and acid sites, causing a collapse in aromatic production and a rise in waxy residues.[189] Similarly, the high-acidity catalysts tend to produce unwanted poly-aromatic byproducts (even naphthalene and anthracene) *via* uncontrolled oligomerization and hydrogen-transfer reactions.[190] In contrast, milder catalysts or supports (*e.g.*, mesoporous MCM-41 with only moderate acidity) can favor liquid yields by limiting secondary cracking. Liu *et al.* found that MCM-41 gave the highest oil yield (78.4% oil at 650 °C) in LDPE pyrolysis, whereas strong acids (ZSM-5, HY) produced much more gas and only 32–35% oil (with ~66% gas). MCM-41 moderate acidity and high surface area suppressed excessive cracking/oligomerization, whereas ZSM-5 drove further breakdown into light gases, and the oil was rich in aromatics, up to 65.9% at 500 °C.[191]

Even after condensation, residual radicals and unsaturated molecules in pyrolysis oil can recombine. Over storage time, these free radicals, *e.g.*, alkyl and olefinic fragments, undergo dimerization and polymerization, causing viscosity increases,

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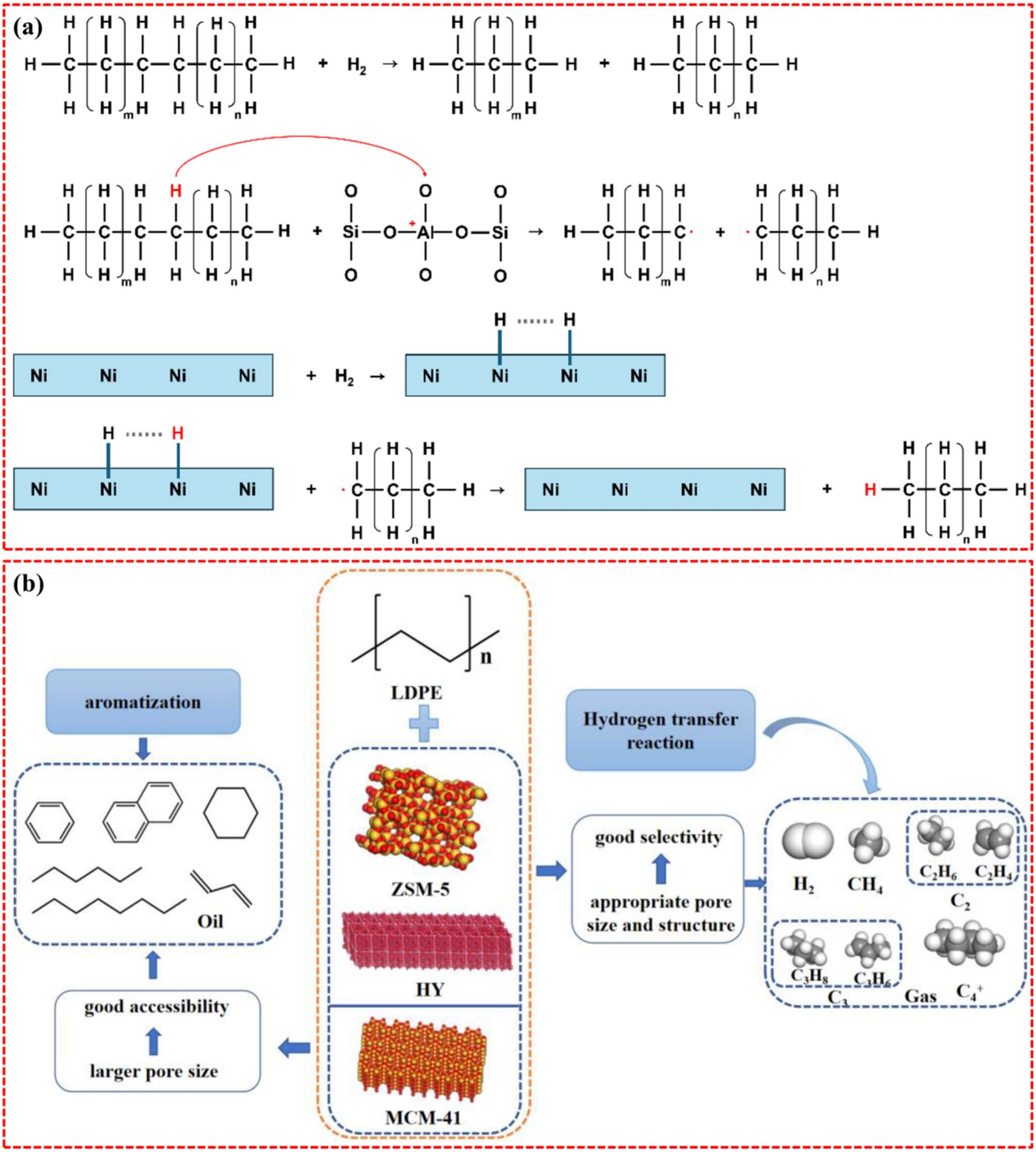

Fig. 17 (a) Suggested PE degradation mechanism using zeolite and nickel nanoparticles (red symbols: atoms or electrons involved in reactions). Reproduced from MDPI from ref. 193, which is open access and permits unrestricted use of materials under the terms of the Creative Commons CC-BY. (b) Schematic of catalyst participation in the LPDE pyrolysis reaction pathways. Reproduced from MDPI from ref. 191, which is open access and permits unrestricted use of materials under the terms of the Creative Commons CC-BY.

gum formation, and phase separation.[192] In bio-oil studies (analogous to plastic oil), aging is traced to polymerization and cross-linking of unstable components. For plastics, similar chemistry applies to olefinic fragments, which can couple or cyclize over hours day^{-1}. Catalytic stabilization can mitigate this.

Catalysts, especially bifunctional metal/acid systems, can actively stabilize fragments. For example, Ni-containing zeolite catalysts introduce hydrogen-transfer pathways. Cho *et al.*

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reported that Ni/zeolite catalysts adsorb H_2 and saturate radical intermediates, and the Ni sites facilitate hydrogen absorption, while the zeolite component stabilizes carbocation/radical species during pyrolysis (Fig. 17a). Ni/zeolites offered much higher liquid yields (almost full conversion) at 350 °C under 20 bar H_2 than in the absence of H_2.[193] This means that hydrogenation reduces the free radicals to stable alkanes. Equilibrium FCC catalysts, on the same note, tend to generate less coke as the sites of added metals encourage the enhancement of hydrogen-transfer to stabilize fragments.[194] Conversely, radicals are not controlled in purely thermal pyrolysis, resulting in fast oil aging. In fact, it was mentioned in one of the reports that even the strong radical scavengers did not have any significant impact on the aging of bio-oil, which highlights the importance of catalytic quenching *in situ* during pyrolysis.[192] To conclude, it has been demonstrated that the addition of hydrogen donors or catalysts that have hydrogenation activity (*e.g.*, Ni or Ru) or moderate acid strength can trap radicals and enhance oil stability, but the absence of such quenching results in further oligomerization and coke formation.

These effects are demonstrated in several experimental reports. As an example, Liu *et al.* evaluated LDPE pyrolysis with ZSM-5, HY, and MCM-41. They found that ZSM-5 (strong acid) maximized aromatic content up to 65.9% aromatics in the oil at 500 °C, but also cracked more into gas (only 38% oil yield), while MCM-41 (weaker acid) gave 78% liquid yield (with only 22% gas) and lower aromatics, reflecting reduced secondary cracking (Fig. 17b).[191] In a similar way, PE was pyrolyzed with modified HZSM-5 (with P, Zn) to give 87% monoaromatics (primarily BTEX) selectivity in the liquid; the added P was needed to suppress excess acid sites and reduce heavy coke formation.[188] Conversely, Daligaux *et al.* demonstrated that repeated LDPE runs over typical ZSM-5 resulted in heavy coking that bridged the catalyst and reverted the products to uncondensed waxes rather than aromatics.[189] These conditions indicate a fine line: catalysts that are selected correctly will result in positive secondary reactions (aromatization and hydrogen transfer), whereas uncontrolled conditions will result in harmful oligomerization and dimerization. The dark side of these reactions is coke formation, which inactivates catalysts and is a significant issue in plastic-to-oil pyrolysis.

6.2. Coke formation and catalyst deactivation

Excessive secondary reactions and long vapor residence exacerbate coke deposition and catalyst decay. Long residence time at high temperature allows primary pyrolysis fragments to recombine into solid carbon. For example, Bahlouli *et al.* demonstrated that with an equilibrium FCC catalyst at 350 °C, LDPE pyrolysis (over 2 min) yielded only 5.5 wt% coke, whereas PP (with its methylated structure) gave even less (3.4 wt%). Although these cokes were moderate, they accumulated in the reactor and deactivated the acid sites.[195] In contrast, if vapor is held even longer (as in large batch reactors), far more aromatics polymerize. Oil shale studies similarly report that vapor residence of 3–5 s causes polyaromatic condensation and coke formation.

Catalyst acidity critically controls coke formation. Strong Brønsted sites promote hydrogen transfer and polycondensation, forming hard coke. Spent FCC catalysts (with moderate acidity) produced more hydrocarbons and less coke than fresh zeolites, and softer acidity and larger pores inhibited polymer condensation.[194,196] It has been noted that FCC catalysts minimize coke because their non-zeolitic components modulate acidity. By contrast, pure zeolites (*e.g.*, fresh ZSM-5) easily deactivate. Bahlouli *et al.* showed that heavy coke on ZSM-5 blocks pores and halves the number of acid sites, causing a sharp drop in aromatics. Coke on ZSM-5 was found to consist mostly of trapped polyaromatics (hard coke) that require high-temperature oxidation to remove.[195] Thus, reducing catalyst acidity or using metal-doped catalysts has been shown to slow deactivation. In addition to their role in cracking and product shaping, catalysts are also subjected to deactivation phenomena, primarily due to coke formation, which significantly influences long-term process performance. Coke is formed through the progressive transformation of reactive intermediates such as olefins and aromatics into polyaromatic hydrocarbons, which subsequently deposit on the catalyst surface.[197] This behavior is particularly pronounced in zeolite-based catalysts, where strong Brønsted acidity promotes aromatization and polycondensation reactions, while the microporous structure restricts diffusion, leading to pore blockage and loss of active sites.[197] The deposited carbon species may be broadly classified as soft coke, which is hydrogen-rich and relatively reactive, and hard coke, which is more condensed, graphitic, and responsible for irreversible deactivation.[198] The nature and extent of coke formation depend strongly on process conditions, where higher temperatures, longer vapor residence times, and higher acidity generally enhance coke deposition,[199,200] whereas optimized catalyst morphology (*e.g.*, mesoporous or hierarchical structures) and controlled reaction environments can mitigate these effects.[201] Therefore, catalyst deactivation is not only a function of catalyst chemistry but also of the interplay between reaction conditions, transport limitations, and vapor-phase chemistry, which must be carefully controlled for sustained catalytic performance.

Heteroatoms in the plastic feedstock (chlorine, sulfur, nitrogen, or metals) can poison catalysts or generate coke precursors. Notably, PVC contamination releases HCl during pyrolysis, which can chlorinate and deactivate acid sites. Nielsen *et al.* stressed that residual chlorine in pyrolysis vapors can deactivate catalysts during upgrading and corrode equipment.[202] Even at pilot scale, trace metals (from dyes and fillers) bind to active sites and favor carbon deposition. It is also noted that contaminants (*e.g.*, sulfur or chloride) further increase coking on spent FCC catalysts. Practically, such poisoning may have to be limited by pre-treatments (washing and pre-cracking). To conclude, coke formation and catalyst deactivation are hastened by longer vapor residence, strong acids, and feed impurities. To sustain the stability of oil, short residence times, moderate acidity, and clean feed are key control strategies. In addition to chemical and morphological variables, the energy-transfer mode (microwave or supercritical fluid heating) can be considered a chemical variable that affects radical

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concentration and resultant product distribution without affecting the bulk temperature.

7. Energy input as a chemical variable

Pyrolysis chemistry can be directed by the mode of heating. Conventional convective heating transfers heat through reactor walls, and the thermal gradients are usually large. Conversely, new energy sources (microwaves, supercritical fluids) can provide very dissimilar thermal and radical conditions. These influence non-uniform heating and reactive species density, changing cracking directions. We explain below how microwave-assisted pyrolysis (MAP) and supercritical water (SCW) modify the chemical kinetics, in terms of the heat flux (power input) and ensuing radical concentration, as opposed to bulk temperature.

Microwaves can heat dielectrics volumetrically, and hotspots and plasmas can be produced in seconds. This contrasts with slow thermal diffusion in a heated bed. Undri *et al.* found that HDPE pyrolyzed by microwave produced significantly more light olefins (C_1–C_4) and less heavy wax than pyrolysis by conventional heating, due to the rapid process of primary bond scission by the microwaves.[203] Traditional pyrolysis non-uniform heating produces local high-temperature spots (cracking to gases and coke) and low-temperature spots (remaining wax).[204] MAP has better heat transfer and uniformity of reactor temperature by heating inside with a high heat flux; plastic quickly reaches the target temperature and has very little thermal lag. An example of this is illustrated in a study where activated carbon susceptors were used as the microwave power increased (40 W to 80 W), the temperature of the HDPE increased (651–1471 °C) in seconds, and the gas yield increased 16–84%. The carbon felt emitted plasma discharges under MW, causing local surface temperatures of 750 °C within 0.5 s.[205] These intense hotspots greatly increase radical concentrations, so that even very heavy chains crack. The outcome is an oil/gas distribution that is biased toward light gases and monomers (*e.g.*, ethylene through free-radical cleavage). Practically, microwave heating will prefer short-chain hydrocarbons and aromatics, and conventional heating produces more mid-range waxes. Therefore, the large heat flux in MAP (high power input) yields a very dissimilar radical pool compared to that of slow, homogeneous heating.

The introduction of high-pressure water changes heat and mass transfer essentially. SCW is a uniform, high-heat-capacity medium that is even capable of being a carrier of radicals. Popelier *et al.* discussed the effect of supercritical water in decreasing coking and enhancing liquid output in polyolefin pyrolysis.[206] They note that SCW dissolves and dilutes radical fragments, inhibiting bimolecular condensation, and water also supplies hydrogen radicals to stabilize intermediates. In an SCW environment, heat is supplied more uniformly and rapidly by the fluid, so secondary condensation (coke) is suppressed. Essentially, SCW pyrolysis sees continuous extraction of heat and products into the dense phase, unlike dry pyrolysis, where retained vapors encourage secondary polymerization. As a result, coke formation is minimal in SCW processes.

Both microwave and SCW emphasize energy flux over mere temperature set points. A system at 500 °C achieved by slow external heating contains fewer instantaneous radicals than one at 500 °C reached by a rapid, concentrated power input. Microwaves can deposit kilowatts per liter in milliseconds, whereas electric furnaces supply far less. Hence, MW and SCW tend to produce higher transient radical densities (and hence different product selectivity) than conventional heating at the same nominal temperature. Novel heating modes alter cracking pathways, MW-induced hot spots favor deep free-radical cracking to light olefins and aromatics, while the solvating, hydrogen-rich SCW medium suppresses condensation and yields more stable oil. These non-uniform heating effects must be considered as a chemical variable in reactor design and catalyst selection.

8. Conclusion

This review developed a multi-dimensional, mechanistically consistent structural overview of waste plastic pyrolysis as a chemical process that is multi-dimensional in nature and design-oriented, as opposed to a traditional thermal degradation system. The main finding is that product selectivity is not a natural product of a polymer degradation process but a manageable activity of reaction pathways, catalyst characteristics, and process engineering variables. On the basic level, thermal pyrolysis occurs through random homolytic cleavage of C–C bonds, which produce highly reactive radical species that freely propagate chain reactions. This naturally causes extensive product distributions, low selectivity, and reduces the stability of the resultant oil because of continuous secondary reactions such as oligomerization and coke formation. The addition of catalysts, however, completely changes the balance of this reaction network as the reaction shifts to an ionic reaction on the surface with carbocation intermediates taking the place of free radicals as the active species. Such a shift causes a large decrease in the randomness of reactions, allowing reaction control of 1,2-scission, isomerization, and cyclization reactions that determine product composition. One of the key conceptual developments that has been emphasized in this work is the fact that most catalysts do not react with the bulk polymer phase, but with vapors obtained through pyrolysis. This post-cracking paradigm redefines catalytic pyrolysis as a two-step process: first, the thermal depolymerization, which is then followed by upgrading the volatile intermediates catalytically. In this context, catalysts act as the molecular architects, guiding the intricate chains of reactions that encompass aromatization, hydrogen transfer, dehydrogenation, and radical quenching. This architectural metaphor captures the essential paradigm shift: catalysts do not simply break bonds but actively design the molecular outcome. By steering vapor-phase intermediates through aromatization, hydrogen transfer, and radical quenching, they transform random degradation into deliberate molecular construction. As a result, chemical identity, stability, and carbon distribution of the end products are established mainly in this stage of the vapor transformation phase. The review also shows that mechanics pathways and product

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families are determined by catalyst chemistry. Carbocation-mediated cracking and aromatization are catalyzed by acidic catalysts, yielding high-value aromatic hydrocarbons, but commonly at the cost of increased coke formation. Simple catalysts can be used to perform hydrogen abstraction and deoxygenation, and prefer olefin-rich and more stable hydrocarbon streams. Catalysts based on metals add hydrogenation–dehydrogenation capability, allowing the regulation of saturation, hydrogen transfer reaction, and reforming. Incorporation of such functionalities in bifunctional or hybrid catalysts is a potent strategy toward product selectivity modification. In these processes, besides chemistry, reaction engineering parameters determine the outcomes. The kinetic regime is characterized by temperature and heating rate, in which moderate conditions are optimal for the yield of liquids, and extreme conditions are optimal for the formation of gases. The design of the reactor controls the heat- and mass-transfer, mixing efficiency, and the vapor residence time, and thus the degree of secondary cracking. As an example, fluidized-bed reactors will increase heat transfer and favor the formation of lighter products, whereas fixed-bed systems will favor high liquid yields of liquid heavy fractions. In the same way, diffusion constraints and secondary reactions are regulated by catalyst morphology, in particular, pore structure. Microporous catalysts are more likely to occur and result in over-cracking and gas formation, but mesoporous and hierarchical structures allow balanced upgrading with increased liquid yield and decreased coking. Microporous materials (pore sizes <2 nm, *e.g.*, H-ZSM-5, zeolite Y) cause excessive cracking and increased gas yields due to confinement, have low liquid yields, are prone to coking inside pores and are unstable. Mesoporous catalysts (pore size 2–50 nm, *e.g.*, MCM-41, activated carbon) facilitate rapid diffusion of large molecules to active sites and out of the pores to prevent excessive cracking, improve liquid yield and oil stability, and decrease coking by creating more space for coke precursors away from active sites. The other important consequence is the discovery that secondary reactions are the main factors of oil quality and stability. Positive routes, such as controlled aromatization, increase the fuel properties, and negative routes, such as polymerization and condensation, increase the viscosity, gum formation, and catalyst deactivation. The capacity of catalysts to suppress the reactive intermediates by hydrogen-transfer processes or surface stabilization is thus critical in generating stable and viable hydrocarbon streams. Notably, this review highlights that selectivity during plastic pyrolysis is developed because of the coordination of several variables, such as reaction mechanism, catalyst functionality, reactor configuration, and timing. *In situ vs. ex situ* catalysis, staged reactors, and custom residence-time control are other strategies that give further degrees of freedom on how to direct product distributions to the desired chemical targets. To sum up, plastic pyrolysis should be re-conceived as a catalytic reaction system, in which a tight control of reaction pathways allows heterogeneous plastic waste to be converted into value-added fuels and chemical feedstocks. This paradigm shift of uncontrolled degradation to designed molecular conversion offers a solid basis for the development of pyrolysis technologies in terms of industrialization and sustainable use in the circular chemical economy.

9. Future perspectives

9.1. Rational design of single-atom and hybrid catalysts

Future studies need to concentrate on single-atom catalysts (SACs) and bifunctional systems that incorporate acid, base, and metal functionality on the atomic scale. These catalysts are capable of selectively controlling hydrogen transfer, carbocation stability, and radical quenching, and select targeted hydrocarbons (*e.g.*, BTX or olefins) with unprecedented selectivity. This will enable the mechanistic control of catalysts that goes beyond the traditional acidity-based control by designing catalysts with tunable electronic environments.

9.2. Reactor-catalyst co-design for process intensification

One such gap is the independent optimization of reactors and catalysts. The systems of the future should move towards integrated reactor-catalyst engineering, in which the position of the catalysts (*in situ vs. ex situ*), the hydrodynamics of the reactor, and the heat transfer are optimized. More sophisticated designs, such as multi-zone, staged, or tandem reactors, can separate cracking and upgrading processes and are much more effective in enhancing yield and selectivity and reducing coke formation.

9.3. Real-time control of reaction pathways *via* process analytics

Real-time monitoring of the intermediate and reaction pathways will be made possible by the development of *in situ* diagnostic devices (*e.g.*, online GC-MS, spectroscopy, and AI-driven monitoring). This will enable the dynamic control of variables, such as temperature gradients, residence time, and catalyst exposure, making pyrolysis not a fixed reaction but a feedback-controlled chemical reaction.

9.4. Tailored strategies for mixed and contaminated plastic waste

The majority of existing research works are on individual polymers, and waste streams are heterogeneous. Future efforts should come up with a way to deal with the irregularity of feedstock, such as PVC, PET, and multilayer plastics, by developing adaptive catalytic systems that can handle heteroatoms (Cl, N, O) and avoid corrosion or deactivation. This involves the use of bi-functional catalysts that can crack and decompose contaminants at the same time.

9.5. Product-oriented pyrolysis for the circular chemical economy

The future of pyrolysis is the change in the production of fuels to the recovery of chemical feedstock. The focus of research should be on high-selectivity pathways to monomers (*e.g.*, styrene), olefins, and aromatics so that they can be combined with petrochemical value chains. This demands process design

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principles that focus on desired end-products instead of maximum conversion and places pyrolysis in line with the principles of the circular economy and sustainable chemical production.

Conflicts of interest

The authors declare that they have no conflicts of interest.

Data availability

No new data were generated or analyzed in this study.

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