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# Advances in plastic to fuel conversion: reactor design, operational optimization, and machine learning integration

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Plastic waste management is a pressing global problem that requires sustainable solutions to mitigate environmental harm. To this end, pyrolysis offers a practical method for converting waste plastics into valuable resources such as oil, gas, and char. This review comprehensively examines plastic pyrolysis, focusing on reactor diversity, operational variables, and the integration of machine learning (ML) techniques for process optimization. Understanding the reactor designs is crucial for tailoring pyrolysis processes to achieve specific product yield and composition targets. For example, a fluidized bed reactor offers continuous productivity and efficient mass transfer, whereas fixed bed pyrolysis reactors are suited for secondary pyrolysis reactions. Similarly, vacuum pyrolysis reactors operate under reduced pressure to minimize undesired reactions, and conical-spouted bed reactors display effective blending capabilities. Operational parameters such as residence time, temperature, and pressure significantly influence pyrolysis outcomes. Longer residence times and lower temperatures favor oil production, whereas higher temperatures promote gas formation. Optimal parameter settings can enhance pyrolysis efficiency and maximize product yields while ensuring environmental sustainability. ML emerges as a powerful tool for predictive modeling, interpretation, and optimization of pyrolysis processes. ML algorithms like neural networks and support vector regression techniques enable relatively accurate forecasting of product yields and properties, and can help researchers gain insights into complex pyrolysis kinetics for further tuning of process parameters to achieve desired outcomes. Overall, the synergistic integration of reactor design, operational parameters, and machine learning techniques can improve product yield and quality, minimize environmental impact, and advance sustainable plastic waste management efforts while promoting a circular economy model.

## 1. Introduction

Municipal solid waste (MSW) production is growing due to global economic expansion, growing population, and urbanization,[1] with plastic wastes (PW) from common-use plastics like polyethylene (PE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC), and polyethylene terephthalate (PET), contributing significantly. Among them, PE makes up approximately 40% of the PW, specifically in urban areas.[2] Since plastics find widespread use in packaging,[3] their demand continues to grow that stresses waste disposal systems and natural environments.[4] While plastics have undoubtedly brought immense convenience, their resistance to degradation upon disposal has resulted in extensive accumulation of PW which puts the biosphere at risk. According to reports, the annual plastic debris produced worldwide has surpassed 4.9 trillion kg per year with 9% recycling.[5,6] The rest is either incinerated or landfilled, and both means of disposal come with substantial environmental disadvantages. Landfilling is both time-consuming and leads to the release of microplastics/nanoplastics into the atmosphere, while PW disposal through incineration emits high level of toxic gases.[7,8] Therefore, it is imperative to investigate practical, economical, and eco-friendly ways to manage waste plastics.

The waste-to-energy strategy presents an exciting opportunity to repurpose PW into valuable fuels and chemicals through thermochemical transformation *via* incineration and pyrolysis.[9] Here, both incineration and pyrolysis involve the use of heat to destructively transform the waste and offer greater flexibility and time efficiency.[10] However, incineration operates at extremely high temperatures of greater than 850 °C and generates concentrated ash as a by-product which results in significant emissions of hazardous chemicals and greenhouse gases;[11] hence, incineration is less desirable. Similarly, the process of hydrothermal conversion through liquefaction

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typically takes place within the temperature range of 200–370 °C while maintaining a pressure of 4–20 MPa.[12] When approaching near-critical temperatures (up to 500 °C), catalytic enhancement is necessary for efficient reforming and gasification to achieve reasonable rates and selectivity.[13] Temperatures exceeding 500 °C often lead to the occurrence of homogeneous gasification and thermolysis. Gasification utilizes MSW as a feedstock for high chemical conversion, rather than as a fuel, eliminating the need for burning. Instead of being incinerated, MSW can be converted into a clean and valuable syngas through gasification.[14] This clean syngas can then be utilized to generate energy and produce valuable products such as chemicals, transportation fuels, fertilizers, and electricity. Gasification complements recycling efforts by segregating metals, glass, and other non-gasifiable materials from the waste stream prior to entering the gasification process.

Pyrolysis, on the other hand, exhibits better efficiency at treating plastic waste due to higher energy recovery and a lower carbon footprint.[10,15] The United Nations framed the Sustainable Development Goals (SDGs) in 2015 to establish a comprehensive framework to address environmental, social, and economic challenges related to plastic pollution.[16] Several SDGs (6, 11, 12, 14, and 15) contribute directly or indirectly to efforts aimed at managing PW. Specifically, SDG 11 promotes efforts to improve strategies for managing waste, such as PW disposal and recycling while SDG 12 aims to significantly lower the amount of waste generation through prevention, reduction, recycling, and reuse. In addition, SDG 14 aims to conserve and significantly utilize marine resources, which includes addressing marine pollution, including plastic pollution.

Pyrolysis operates at 300–1000 °C in an oxygen-deficient environment to break the lengthy polymer chains of PW and transform them into shorter-chain petrochemicals along with various valuable commodities, like gasoline, kerosene, and diesel, oil, and other distillation products.[17] The use of catalysts during pyrolysis lowers the pathway's energy requirements and boosts the overall efficiency while enhancing both the product quality and yield over non-catalytic pyrolysis processes. Commonly used catalysts for pyrolysis include HZSM-5, HY and Hb-zeolite-based catalysts (acid catalysts), as well as solid super acid catalysts like $ZrO_2/SO_4$ and Pt- stabilized $ZrO_2/SO_4$, and aluminium oxide-$Al_2O_3$. These catalysts address the challenges associated with thermal pyrolysis, such as high temperature and lengthy reaction time. However, they are challenging to maintain due to significant carbon deposition and are not economically suitable for industrial-scale usage, but they can be cost-effective for PW conversion to desirable liquid fuels.[18] Importantly, pyrolysis process specifics like the choice of reactor can have a significant impact on the mixing of catalysts with PW, reaction rates, and residence times, as well as product yield and quality. Common reactors used in laboratory-scale experiments include fixed bed (FiBR), fluidized bed (FBR), conical spouted bed (CSBR) and vacuum pyrolysis reactors. Usually, reactor runtime parameters like feedstock used, feed rates, mixing, temperature, and pressure influence product yield. For example, when LDPE and PET were pyrolyzed with HZSM-5 in the presence of $N_2$ at a heating rate of 80 °C $min^{-1}$ for 30 min, 51.7 wt% of liquid products were obtained.[19] On the other hand, when HDPE underwent pyrolysis in a BR using silica-alumina for 60 min at a heating rate of 30 °C $min^{-1}$, 77.4 wt% liquid products were obtained.[20]

Despite these advancements, significant challenges remain in optimizing the pyrolysis process to maximize yield and efficiency. These challenges include the precise control of reaction parameters, effective mixing of catalysts, and real-time adjustments to changing conditions. This is where machine learning (ML) can play a pivotal role.[21] ML algorithms can analyze vast amounts of data from historical and real-time sensor readings to dynamically adjust process parameters, ensuring optimal performance under various conditions. By iteratively adjusting parameters based on learned patterns, ML models can enhance reactor productivity and product quality.[22] The ability of ML algorithms to predict the outcomes of complex pyrolysis reactions can help researchers and industry professionals fine-tune process parameters, leading to more efficient and effective plastic waste conversion.[23]

The novelty of this review lies in its comprehensive examination of the latest advancements and emerging trends in converting plastic waste into fuel through pyrolysis-based technologies. It consolidates information on non-catalytic and catalytic pyrolysis from the available literature to explore their potential integration with ML techniques for process optimization. In the wake of growing PW pollution and environmental damage, this effort presents some insight into the current state of PW management within a circular economy framework. Furthermore, the inclusion of life cycle assessment (LCA) and techno-economic analyses (TEA) provides valuable insight into the environmental and financial implications of pyrolysis-based PW management. By addressing these key areas, the aim is to advance circularity in PW management practices through innovative techniques and contribute to long-term environmental sustainability.

## 2. Pyrolysis

Pyrolysis is usually classified as thermal pyrolysis (non-catalytic) and catalytic pyrolysis, as shown in Fig. 1.[24]

### 2.1. Thermal pyrolysis

Thermal pyrolysis aims to enhance PW recycling by heating the raw material in an inert environment[25] to promote plastic decomposition. Due to inert conditions, plastics decompose at high temperatures from 400–450 °C to 700–800 °C. Experimental studies of converting PE, PS and PP wastes into liquid hydrocarbons have shown that pyrolysis can operate at temperatures up to 900 °C.[26] Mixed waste plastics have low thermal conductivity, therefore, heat losses need to be accounted for while treating them. Since catalysts are not used in this process, the temperature, energy requirements and operational costs are higher. Furthermore, longer hydrocarbon chains are produced with this method compared to catalytic pyrolysis.[27] The factors that lead to the additional breakdown of these lengthy hydrocarbons, resulting in a significant decrease

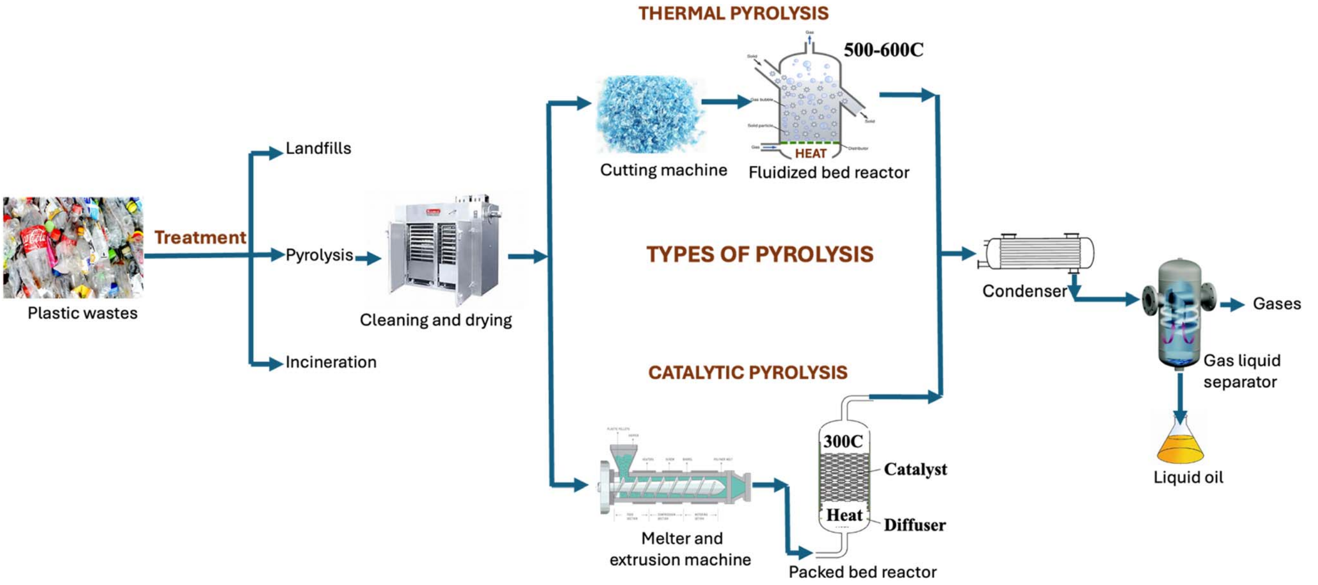

Fig. 1 Schematic representation of the thermal and catalytic pyrolysis pathways to convert plastic waste to end products.

in boiling points for improved product output and residence time, are not considered in non-catalytic pyrolysis. The pyrolysis process is known for its limited heat recovery during combustion. The majority of the liquid materials produced by thermal pyrolysis predominantly contain hydrocarbons with higher boiling points. The conversion of pyrolysis products into oils and other useful products either requires a catalyst or additional treatment processes such as separation. Refining is necessary to enhance the usability of gaseous products obtained through thermal pyrolysis for operating fuel purposes, with regards to quality of yield.[28] An overview of the effect of multiple parameters on thermal pyrolysis of plastics is given in Table 1.

The products recovered from these waste materials rely on the types of plastics involved and the process conditions employed. It has been noticed that pyrolysis of PE in mixed PW produces many unstable solids with high viscosity, known as low-grade yield.[49,50] The non-catalytic degradation of PE yields a relatively higher quantity of alkenes and dialkenes, highlighting its potential as a substitute fuel source. Pyrolysis of LDPE at 430 °C, yielded liquid of approximately 76 wt%.[51] The yield was slightly reduced to 75 wt% at 450 °C.[51,52] Pressurizing the BR between 0.8–4.3 MPa during pyrolysis of LDPE at 425 °C increased the gas yield even at lower temperatures.[53] The research revealed a liquid oil yield of 90%, accompanied by 10 wt% and 0.5 wt% of gaseous products and char respectively, indicating that pressure influences pyrolysis outcomes. A thermal pyrolysis study performed on HDPE at 400–550 °C revealed that the maximum liquid output of 79 wt% occurred at 550 °C.[54] Additionally, the product fraction exhibited a significant presence of wax within the range of 500–550 °C. The pyrolysis oil that produced had a dark brownish color and boiling range between 82 and 352 °C, indicating that it included a variety of components, including diesel, kerosene, and gasoline. The oil production of PET is slightly greater compared to PE and PP during the same operating.[55] The liquid and gaseous yields from PET pyrolysis range from 23–40 wt% and 52–77 wt%, respectively.

Another study conducted on pyrolysis of PP in a micro steel reactor at 250–400 °C indicated the highest oil yield at 70 wt%, with a total conversion rate of approximately 99% at 300 °C.[56] In contrast, raising temperature to 400 °C resulted in total conversion to decrease to 94% and residue to increase to 6 wt%. This implies that coke production became more pronounced at elevated temperatures. In contrast, the PP pyrolysis conducted at 380 °C produced an increased liquid yield of 80 wt%, with 7 wt% of gaseous products and 13 wt% residual product.[57] Similarly, the yield increased up to 82 wt% when PP pyrolysis was performed at 500 °C.[55] Thus, raising the temperature above 500 °C caused the liquid yield to decrease. This was demonstrated in PP pyrolysis that at 740 °C in a BR, yielding 48.8 wt% liquid, 49.6 wt% gaseous products, and 1.6 wt% char.[26] Pyrolysis of PVC within a temperature range of 225–520 °C, and a heating rate of 10 °C min$^{-1}$ under pressure of 2 kPa resulted in a liquid yield of 0.5–13 wt%, with a maximum tar content of 20 wt%. HCl was the principle product obtained (58 wt%) from pyrolysis of PVC.[58]

Economically, thermal recycling can have a substantial impact due to heating, while environmentally, it carries significant implications.[59] In conclusion, thermal pyrolysis presents a viable method for recycling plastic waste into valuable hydrocarbons, though it is associated with higher energy consumption and operational costs due to the lack of catalysts. Further research into optimizing process parameters and reactor designs could enhance the efficiency and yield of thermal pyrolysis, making it a more competitive option for large-scale plastic waste management.

### 2.2. Catalytic pyrolysis

Catalytic pyrolysis offers several advantages over thermal pyrolysis, such as degradation at lower temperatures, high

Table 1 Product yields obtained from thermal pyrolysis of various plastic feedstocks under different operating parameters[a]

| S. no. | Feedstock | Pyrolysis type | Reactor used | Heating rate (°C min$^{-1}$) | Residence time | Temperature (°C) | Pressure (atm) | Product yield (wt%) Liquid | Gas | Solid | References |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | HDPE | Slow pyrolysis | FiBR | 5 | 120 min | 500–800 | — | 70 | 36 | 2–8 | 29 |
| 2 | HDPE | Fast pyrolysis | Batch | 35 | 60 min | 450 | — | 74.5 | 5.8 | — | 30 |
| 3 | HDPE | Fast pyrolysis | CSBR | — | 0.016–0.032 s | 500 | 1 | 31.5 | 1.5 | — | 31 |
| 4 | HDPE + pine sawdust | Fast pyrolysis | FiBR | 25 | — | 500 | — | 22.5 | 69.7 | 7.3 | 32 |
| 5 | HDPE + rice straw | Fast pyrolysis | Batch | 20 | — | 500 | — | 28 | 12 | 50 | 33 |
| 6 | HDPE + sugarcane bagasse | — | FiBR | — | 45 min | 400–700 | — | 59 | 20 | 21 | 34 |
| 7 | LDPE | — | Rotary kiln | — | 20–60 min | 400–550 | 1 | 60–70 | 10–20 | 10–20 | 35 |
| 8 | PE | Slow pyrolysis | FiBR | 5–10 | 10–60 min | 350–550 | 1 | 50–80 | 5–10 | 10–40 | 36 |
| 9 | PET | Slow pyrolysis | FiBR | 5 | 15 min | 450–500 | 1 | 20 | — | 7 | 37 |
| 10 | PET | Fast pyrolysis | Microwave | 12 | 25 min | 350–400 | 1 | 25–35 | 40–50 | 20–30 | 38 |
| 11 | PP | Fast pyrolysis | Two stage tube reactor | 10 | 0.2–3.2 s | 800 | — | — | 75.1–77.2 | — | 39 |
| 12 | PP | Fast pyrolysis | FBR | 10 | 45 min | 450–550 | 1 | 30–40 | 25–35 | 25–35 | 40 |
| 13 | PP | Fast pyrolysis | Vacuum | 5–20 | 13 min | 425–500 | 1 | 80.1 | 6.6 | 13.3 | 41 |
| 14 | PP | — | Rotary kiln | — | 30–60 min | 400–500 | 1 | 65–75 | 10–20 | 5–20 | 42 |
| 15 | PS | Slow pyrolysis | FBR | 3–9 | 1–10 s | 450–600 | 1 | 60–80 | 10–20 | 5–20 | 43 |
| 16 | PS | Fast pyrolysis | Auger + FBR | 10–30 | 1 s | 300–500 | — | 86–99 | 4.8–13.8 | — | 44 |
| 17 | PS | Fast pyrolysis | CSBR | 2.5–20 | 0.1 s | 500 | 1 | 70.6 | 4.3 | — | 45 |
| 18 | PVC | — | FBR | — | 30–120 s | 300–450 | 1 | 60 | 20 | 20 | 46 |
| 19 | LDPE + PVC | Fast pyrolysis | Auger + FBR | 30 | 10 min | 300–500 | — | 21 | 70 | — | 47 |
| 20 | PE + PET | Fast pyrolysis | Two stage thermal pyrolysis reactor | 10 | 2–6 s | 600–800 | — | — | 61–65 | 8 | 48 |

[a] HDPE: high density polyethylene; LDPE: low density polyethylene; PE: polyethylene; PET: polyethylene terephthalate; PP: polypropylene; PS: polystyrene; PVC: polyvinyl chloride; FiBR: fixed bed reactor; FBR: fluidized bed reactor; CSBR: conical spouted bed reactor.

selectivity, quicker cracking of polymers, shorter residence time, inhibition of undesirable product formation, higher yield, and the production of liquid products with lower boiling points. By employing catalytic pyrolysis, it is possible to enhance yield of output and selectivity while reducing the temperature for pyrolysis. The lower reaction temperature is attributed to the decreased activation energy of the pyrolysis reactions, which leads to reduced energy requirements. Catalysts are employed to lower the pathway's energy requirement. Additionally, a catalyst can promote the production of lower hydrocarbons, petroleum range, and gaseous products. They play a vital role in reducing the temperature and residence time needed to break down wax vapors and particles into gaseous and liquid fractions. Catalysts can increase the selectivity of the required functional groups within a range of specific carbons.[60]

The implementation of efficient pyrolysis depends on various crucial factors, including the selection of catalysts, the design of the pyrolysis reactor, and the optimization of process parameters.[60] In addition to these, the effectiveness of catalyst is determined by the acidity of the catalysts which enhances the cracking process of plastics.[61,62] During the original phase of catalytic pyrolysis, the external surface of catalyst undergoes thermal cracking. Subsequently, the internal pores in the catalyst serve as pathways for the targeted movement and breakdown of bigger molecules into smaller molecules. This observation indicates that the decomposition of high olefin molecules primarily transpires on the catalyst's exterior surface, whereas further degradation and the selection of products occur within the internal pores of catalyst.[20] Zeolite materials, particularly ZSM-5, are widely used for industrial applications in the catalytic pyrolysis of plastics. This is due to their exceptional cracking activity, high selectivity towards aromatic hydrocarbons in the gasoline range, and other advantageous factors including cost-effectiveness and commercial availability.[63,64] Highly acidic catalysts like those based on zeolites accelerate the production of gaseous products, thereby decreasing oil yield. On the other hand, mild and less acidic catalysts, like clay catalysts, are likely to have the opposite effect.[65] The impact of various catalysts and operating parameters on the yield of pyrolysis products is given in Table 2.

A study was conducted to examine the catalyst acidity on distribution of pyrolysis products from HDPE in an SBR operating at 430 °C.[76] Three different catalysts, SA-1, ZSM-5 and SA-2, were used, along with 10 g of HDPE blended with 1 g of catalyst. The acidity of the catalysts was observed using $NH_3$ temperature programmed desorption, and it was found that SA-1 has the highest acidity, followed by ZSM-5 and SA-2. The experimental results indicated that the yield of liquid was the highest for SA-2 with 74.3 wt%, followed by SA-1 with 67.8 wt%, and lastly ZSM-5 with 49.8 wt%. The less acidic catalyst (SA-2) produced a higher quantity of liquid oil, while having strong sites of acidic nature, ZSM-5 produced a lower liquid yield and a higher gaseous product yield.

Secondly, the pore structure of the catalysts also influences the pyrolysis process. Micropores on the catalyst improve the yield of oils, while mesopores increase gaseous product yield.[77] The size of higher hydrocarbons prevents them from entering the micropores, resulting in improved oil quality and quantity.[78] In addition to this, the reactivity of the catalyst can be enhanced within particular ranges of temperatures. In an experiment conducted by using PP HDPE for pyrolysis in an FBR operating at 500 °C, the results showed a higher yield of liquid oil compared to the previous studies.[79] Liquid yield obtained from PP pyrolysis was 90 wt%, while HDPE pyrolysis resulted in approximately 85.0 wt% of liquid oil. This highlights the importance of temperature in maximizing the effectiveness of the catalyst and optimizing the yield of liquid products in plastic pyrolysis.

Three primary benefits are accounted for PW catalytic pyrolysis. Firstly, by choosing catalysts depending on their pore arrangement and pH values, the yield and distribution of products can be controlled. This allows for the adjustment of product yields to meet specific requirements.[80] Studies have distinguished oils obtained from noncatalytic and catalytic pyrolysis processes, demonstrating that zeolite catalysts' presence causes the production of oil, primarily containing petrol fraction carbons, $C_7$–$C_{12}$, while the noncatalytic process yields diesel fraction, $C_{13}$–$C_{20}$ and heavier fractions, $C_{21}$–$C_{40}$ as well.[81] Secondly, the choice of catalyst can inhibit or reduce the formation of unwanted substances during pyrolysis reaction. For instance, ZSM-5 has been proven effective in lowering the quantity of solid residue, sulfur, phosphorous, and nitrogen in the output oil.[82] Lastly, the employment of catalyst in the pyrolysis process increases its efficiency. By reducing the activation energy required for these reactions, the catalyst accelerates chemical reactions and plastic decomposition. This leads to a higher conversion rate of PW, as pyrolysis can proceed at lower temperatures in comparison to noncatalytic pyrolysis.

Research has revealed that the employment of catalysts like ZSM-5 reduced the energy of activation by 40 kJ $mol^{-1}$, thereby improving the efficiency of the process.[77] A diverse category of catalysts has been employed in the conversion processes of PW to fuel, encompassing various types such as clay catalysts (like kaolin), zeolites, and metal oxide catalysts.[83,84] It is essential to investigate the activity and function of these catalysts under realistic conditions, that are often governed by the reactor type chosen for pyrolysis. These reactors, along with the operating parameters, play a crucial role in determining the yield and quality of the products obtained from the pyrolysis process.

### 2.3. Effect of feedstock on pyrolysis products

The pyrolysis product distribution varies significantly between thermal and catalytic methods, influenced by the specific plastic feedstocks used. In thermal pyrolysis, which is generally conducted at elevated temperatures, typically ranging from 400 °C to 900 °C, longer hydrocarbon chains are formed, often resulting in higher energy consumption due to the lack of catalysts. For example, thermal pyrolysis of HDPE typically yields heavier hydrocarbons in the $C_{13}$–$C_{20}$ diesel range, whereas catalytic pyrolysis of the same feedstock favors lighter fractions, such as $C_7$–$C_{12}$.[81] The incorporation of catalysts like ZSM-5 and HY-zeolite lowers the energy barrier of reactions,

Table 2 Product yields obtained from catalytic pyrolysis of various plastic feedstocks under different operating parameters[a]

| S. no. | Feedstock | Catalyst (catalyst to feed ratio) | Pyrolysis type | Reactor used | Heating rate (°C min$^{-1}$) | Residence time | Temperature (°C) | Pressure | Product yield (wt%) Liquid | Gas | Solid | References |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | HDPE | ZSM-5 (1 : 10) | Slow pyrolysis | Semi batch | 4 | 60 min | 430 | — | 49.8 | 44.3 | 5.8 | 10 |
| 2 | HDPE | HY zeolite | Fast pyrolysis | Confined CSBR | 15 |  | 550 | 1 atm | 49 | 70 | — | 66 |
| 3 | LDPE | NiFeAl (2 : 1) | Fast pyrolysis | Microwave-assisted | 15 | 10 min | 700 | 1 atm | 1.28 | 60.72 | 38 | 67 |
| 4 | LDPE | HY zeolite (1 : 1) | Fast pyrolysis | Two-stage electric furnace | 3–20 | 30 min | 400 | 1 atm | 62.1 | 33.1 | 4.8 | 68 |
| 5 | LDPE | Zn + ZSM-5 (1 : 20) | Slow pyrolysis | High pressure stirring micro reactor | 3 | 30 min | 420 | 4 bar | 49.5 | 46.4 | 4.1 | 69 |
| 6 | LDPE | Fly ash (1 : 10) | — | Batch | — | — | 500 | — | 16 | 30 | 54 | 70 |
| 7 | PE | MFI (1 : 50) | Slow pyrolysis | Batch | 3 | 100 min | 350 | 1 atm | 77.4 | 22 | — | 20 |
| 8 | PE | Fly ash (1 : 20) | — | Semi batch | — | 30 min | 700 to 800 | 1 atm | 71.36 | 17.7 | 10.86 | 71 |
| 9 | PE | ZSM-5 (1 : 10) | Slow pyrolysis | Continuous microwave-assisted | 5 | 90 s | 500 | 1 atm | 33.2 | 17.6 | 40.5 | 60 |
| 10 | PE | Ni/ZSM-5 (1 : 4) | Fast pyrolysis | Rotary kiln | 5 | 10 min | 500 | — | 43.3 | 48.7 | 8 | 72 |
| 11 | PP | HZSM-5 (1 : 5) | Fast pyrolysis | FiBR | 50 to 85 | 10 min | 450 to 550 | 1 atm | 35.9 | — | — | 73 |
| 12 | PP | Kaolin clay (1 : 3) | Slow pyrolysis | BR | 5 | 15 to 45 min | 350 to 550 | 1 atm | 79.9 | 18.67 | 1.48 | 74 |
| 13 | PP | $Na_2CO_3$ | — | SBR | — | 30 to 40 min | 500 | 1 atm | 63 | 25 | 12 | 53 |
| 14 | PS | Bentonite clay | Fast pyrolysis | BR | 10 | 10 min | 500 | 50 bar | 88.1 | — | — | 62 |
| 15 | HDPE + LDPE + PP | Fe + HZSM-5 | Fast pyrolysis | Batch + FiBR | 10 | 22 h | 350 | 1 atm | 76 | 24 | 0.0 | 61 |
| 16 | LDPE + PP + PVC | CaO | Fast pyrolysis | Auger reactor + FiBR | 20 | 10 min | 300–500 | — | 31.36 | 67.98 | 1.41 | 44 |
| 17 | LDPE + PET | HZSM-5 | Slow pyrolysis | Microwave-assisted catalytic pyrolysis reactor | 8 | 30 min | 550 | 1 atm | 51.67 | 32.3 | 16 | 19 |
| 18 | PE + PP + PS + PET | Y-zeolite (1 : 1) | Fast pyrolysis | Two stage FiBR | 10 | 30 min | 500 to 600 | 1 atm | 70 | 25 | 4 | 75 |

[a] HDPE: high density polyethylene; LDPE: low density polyethylene; PE: polyethylene; PET: polyethylene terephthalate; PP: polypropylene; PS: polystyrene; PVC: polyvinyl chloride; FiBR: fixed bed reactor; FBR: fluidized bed reactor; CSBR: conical spouted bed reactor.

facilitating the generation of shorter hydrocarbons with enhanced selectivity and yield.[60]

Feedstock-specific responses to pyrolysis conditions further illustrate these differences. At 430 °C, thermal pyrolysis of LDPE yields 76 wt% liquid hydrocarbons, while HDPE pyrolyzed at 550 °C produces 79 wt%, indicating a trend toward waxy hydrocarbons.[51] In contrast, catalytic pyrolysis of HDPE with ZSM-5 significantly enhances gas yields to 74.4 wt%, with the remainder comprising lower boiling-point liquids.[54] Furthermore, PP consistently yields higher liquid outputs under both thermal and catalytic pyrolysis, with the catalytic process improving selectivity for lighter, more desirable hydrocarbon fractions.[56]

Overall, catalytic pyrolysis of plastic feedstocks, such as HDPE, LDPE, PP, and PET, proves more effective for generating lighter hydrocarbons with increased selectivity compared to thermal pyrolysis. This efficiency is largely due to the reduce activation energy and optimized reaction pathways facilitated by the presence of catalysts, positioning catalytic pyrolysis as a more targeted and energy-efficient approach for plastic waste valorization.

# 3. Reactors

## 3.1. Types

The type of reactor significantly influences the blending of plastics and catalysts, as well as the residence time, heating rate, and effectiveness of the reaction in order to produce the preferred product. Many plastic pyrolysis experiments at the laboratory level have been conducted using FBRs, FiBRs, vacuum pyrolysis reactors, and CSBR.

**3.1.1 Fixed bed pyrolysis reactor.** FiBRs are chiefly utilized as a secondary reactor due to the seamless transfer of products from primary reactions, and typically accommodate both the liquid and gaseous feed. The process operates by a steady flow of heat from the vessel walls to the substrate at a constant rate, resulting in thermal decomposition. In contrast to the FBR, the introduction of fluid from the bottom of the vessel is not necessary.[85] The catalyst in a FiBR is usually pelletized and is densely packed inside a stationary bed. An investigation on various PW, including PET, PS, PP, and PE, revealed that 450 °C was the ideal pyrolysis temperature using a FiBR, with aromatics, alkanes, and alkenes as the major constituents of pyrolysis gas.[86] The highest yield of 81% oil with 13% gas, and 6% char was obtained with PS.[87] In another study, PET was used to produce gasoline using a FiBR operating at 500 °C, with a heating rate of 10 °C $\text{min}^{-1}$, and utilizing $N_2$ as the purge gas.[88] It was observed that only 23 wt% was liquid yield, compared to a significantly higher gas yield of 77 wt%, with approximately 50% of the oil consisting of benzoic acid. The acidic nature of pyrolysis oil has been proven to be corrosive and decreases the oil quality. PET pyrolysis products have 87% volatiles, whereas other types of plastic have over 90% volatiles. Another study investigated the impact of temperature on product composition with the first-stage reaction carried out at 500 °C, followed by second-stage catalytic pyrolysis reaction at 400 °C to 500 °C.[89] It was studied that the liquid yield decreased to 57 wt% whereas the gas content increased to 43 wt%. Although the catalyst reduced the volume of liquid, it also enhanced its quality and increased the aromatic content.

**3.1.2 Vacuum pyrolysis reactor.** Vacuum pyrolysis differs from fast pyrolysis due to the utilization of lower heating rates, with the goal to improve pyrolysis oil yield. The main advantage of operating pyrolysis in a vacuum environment is the reduction in the amount of time vapors spend in the system, thus limiting any additional reactions that may occur in the vapor phase. This allows for the use of larger particles compared to traditional fast pyrolysis, as the heat transfer requirements are lower. Additionally, the inert gas is not required in vacuum pyrolysis. A pilot-scale vacuum pyrolysis reactor with 3 ton per h capacity was developed and operated at 20 kPa and 450 °C. Molten salts were utilized to supply heat to the reactor, which were heated through the combustion of non-condensable gases.[90] Vacuum pyrolysis of PP was performed at 425 °C, heating rate 15 ° C $\text{min}^{-1}$, and residence time 6 h. The results show that temperature had the most while time had the least influence. The gas displayed more breaking than noncondensable gas because of the longer residence period, which suggested a lower liquid yield. In the actual experiment, the pyrolytic oil value was 28.6%, compared to the theoretical forecast of 27.3%.[41]

**3.1.3 Fluidized bed reactor.** FBRs are specially designed for fast pyrolysis process to obtain a continuous product, as they can provide high temperature, uniform heat, good flexibility, and control over reactions.[91] Moreover, the heat transfer in a typical FBR exceeds ten times the heat transfer of a molten tube or tubular reactor.[90] PE and PP yield waxy products between 400–500 °C and liquid and gaseous products at temperatures above 700 °C.[92] The waxy product and heavy oil can be fed for naphtha crackers to regenerate ethylene and propylene for synthesizing new polyolefins. Several monomers can be recovered from pyrolysis in FBR to form specialized polymers. The use of $Ca(OH)_2$ catalyst in an FBR during PET pyrolysis produces CO, $CH_4$, and mostly aromatics, leading to a high yield of benzene.[93] Furthermore, a significant yield of waxy solid, along with oil, gas, or monomers is generally obtained at 450 °C, depending on the polymer and parameters used.[94] The pyrolysis of polyoxymethylene in an FBR produced 28.6 vol% $H_2$ when the bed was heated to 370 °C. However, the $H_2$ production efficiency dropped if the temperature was greater than this. The presence of metal oxides affects the reaction process during polyoxymethylene decomposition, causing fast breakdown of intermediates to $CO_2$ and steam at 590 °C. Despite the formation of these additional byproducts, the ratio of $H_2$ to CO remains within 2.3–2.8 at 370–590 °C. This ratio is assumed to be useful for commercial applications.[95]

**3.1.4 Conical spouted bed reactor.** CSBRs offer significant advantages in pyrolysis due to their effective blending capability, allowing them to handle a wide range of particle sizes and densities. They excel at heat transfer between phases and show minimal issues with defluidization, even when processing sticky solids—an issue often challenging for fluidized bed reactors. However, CSBR operation still presents several technical difficulties, such as catalyst feeding, entrainment, and product separation (solid and liquid), which have limited their widespread industrial adoption.[96] HDPE pyrolysis in a CSBR typically results in product fractions classified as $C_1$–$C_4$ gases, $C_5$–$C_{11}$ gasoline, $C_{12}$–$C_{20}$ diesel, and $C_{21+}$ wax.[97] In a specific thermal pyrolysis experiment, HDPE pellets of 4 mm in diameter, were continuously fed at 1 g min$^{-1}$ at 500 °C to 700 °C with nitrogen as the fluidizing agent. The key gas products identified were ethylene, propylene, and 1-butene, especially prominent at 700 °C.[98] The process was further refined by feeding 1 g min$^{-1}$ of HDPE with a nitrogen flow rate of 10 L min$^{-1}$, four times the necessary rate for minimum spouting. Under these conditions, the minimum temperature for stable CSBR operation was determined to be 520 °C, as defluidization occurred at lower temperatures due to slow polymer degradation, which led to accumulation within the reactor bed.

HDPE pyrolysis was conducted in a CSBR using an HY zeolite catalyst at 500 °C, yielding a gasoline fraction ($C_5$–$C_{10}$) of 68.7 wt%.[99] The resultant gasoline had a high octane rating with a RON of 96.5, meeting standard gasoline quality requirements. Another investigation focused on the yield and properties of waxes produced from the pyrolysis of HDPE, LDPE, and PP in a CSBR at temperatures between 450 °C and 600 °C.[100] This study demonstrated CSBR's adaptability in handling sticky solids, particularly suited for low-temperature pyrolysis, where wax production is favored. The yield of wax was found to decrease with rising temperatures as the waxes cracked into smaller molecules, forming liquid and gaseous products. HDPE and LDPE yielded similar wax fractions of around 80 wt%, while PP produced a significantly higher wax yield at lower temperatures, reaching approximately 92 wt%.

### 3.2. Operating parameters

In the case of pyrolysis, the feedstock plays an crucial role in determining the distribution of products and setting constraints on conversion time and expected outcomes. Moreover, the type and distribution of resultant products are directly affected by the purity of the raw material. The operating parameters of pyrolysis, such as residence time, temperature, and pressure, significantly influence the efficiency and outcomes of the process. Understanding and optimizing these parameters is essential for maximizing product yield, quality, and overall process efficiency.

**3.2.1 Residence time.** Residence time, typically referring to the duration that gas-phase products remain in the reactor during plastic pyrolysis, is a key factor influencing pyrolysis outcomes. It plays a crucial role in controlling product distribution and directly impacts the yields of liquid, gas, and char.[101] Longer residence times allow for more extensive thermal degradation and secondary reactions, which can enhance the conversion of feedstock into desired products. For example, studies on isothermal HDPE pyrolysis conducted in a thermogravimetric analysis setup within the 500–600 °C range found that the generation of aromatics and residual char was insignificant when compared to the production of non-condensable gases and liquids.[102] The amount of non-condensable gases was found to rise with residence time, indicating that extended exposure to high temperatures promotes further breakdown of intermediate products into gases.[103]

The formation of pyrolysis oil and liquid fraction relies on the time and is not directly related to the rise in temperature, as demonstrated in the study on linear LDPE pyrolysis.[104] It was demonstrated that the proportion of condensable liquid in pyrolysis is directly proportional to the residence time. It was found that PET had a higher percentage of conversion with a longer retention time.[102] A study conducted on the impact of time on the distribution of products from thermal cracking of HDPE in an FBR from 650 °C to 850 °C disclosed that residence time had a significant impact on the distribution of pyrolysis products. At 640 °C, the primary product produced was wax, with yields ranging from 79.7 wt% at 0.8 s to 68.5 wt% at 1.5 s. Gas yields varied between 11.4 wt% at 1 s and 31.5 wt% at 1.5 s under these conditions. Higher gas yields were found at 780 °C, with 86.4 wt% gaseous products and 9.6 wt% liquid at 1.34 s. At 850 °C, the residence time had a more significant effect on the gaseous composition. Yields of methane and hydrogen rose with residence time, reaching 22.2 wt% and 3.6 wt%, respectively, while ethene ($C_2H_4$) yield peaked at 40.5 wt% at 0.86 s. It was observed that pyrolysis performed best between 750 °C and 780 °C with a longer residence period. Under these circumstances, the cold gas efficiency was 96%.[101] Longer residence time allowed for secondary reactions to occur, which resulted in the conversion of oil to gas and char, according to research on the effect of residence time on the disintegration of LDPE and PS. At 450 °C, LDPE yielded 91.1 wt% oil and 8.70 wt% gas at zero residence time. As the residence time increased to 120 minutes, the oil yield decreased to 61 wt%, and the gas yield increased to 28.5 wt%. Even at zero residence time, PS was entirely broken down into liquid, char, and gaseous products.[53]

**3.2.2 Temperature.** The thermal degradation of polymeric materials is a complicated phenomenon that includes various chemical reactions and physical stages, including heat and mass transfer.[105] The principal degradation characteristics of the PW are governed by temperature, which regulates the breaking process of carbon chains in plastics. Higher temperatures typically accelerate the molecular vibration, weakening the van der Waals forces between molecules and causing them to fragment and evaporate from the surface.[106]

Studies have found that the impact of temperature outweighed the effects of product distribution, polymer type, and concentration at higher temperatures.[89] It was also observed that the majority of the product obtained was in solid form below 700 °C, while the primary product was in the gas phase at higher temperatures.[107] For instance, HDPE undergoes degradation when exposed to temperatures greater than 325 °C, and complete breakdown occurs at 467 °C and higher.[108,109] The degradation process is accelerated by higher heating rates, leading to an increased reaction rate. In contrast, LDPE begins to degrade at 360 °C.[109] It was observed that PP degrades at temperatures below 400 °C, indicating a lower degradation temperature compared to PE.[110] PS is known to begin breaking down at the lowest temperature of all conventional plastics, around 300 °C, which is even lower than the initial degradation point of PET.[53] Consequently, it may be said that the pyrolysis temperature is a major factor in both inducing and regulating carbon chain breaking.

It was observed that temperatures above 600 °C did not result in the production of wax, unlike the lower temperatures during PE pyrolysis.[111] This implies that the heavier wax compounds were disintegrated into lighter molecules. With the increase in temperature, the percentage of gas also increases. Higher temperatures promote the production of gas *via* molecular breakdown and generate a variety of smaller organic molecules. Furthermore, the higher energy levels lead to a higher occurrence of secondary reactions, resulting in a decrease in the amount of oil and wax as the temperature rises. A similar pattern was noted with temperature, increasing gas production and the amount of heavier hydrocarbon components in the products.[112,113] It was discovered that as the temperature increased, the cracking process decreased due to a lack of residence time. Consequently, large molecular chain chemicals and aromatics in the form of wax were present in the oil product.

**3.2.3 Pressure.** Pressure is another important parameter that affects the pyrolysis process, although it has not been extensively documented in the literature due to most experiments being conducted under atmospheric pressure conditions. However, studies have shown that varying pressure can significantly influence product distribution, particularly at lower temperatures. An investigation on the impact of pressure on HDPE pyrolysis in a continuous stirred tank reactor revealed that as the pressure increased from 0.1 to 0.8 MPa, the gas production also increased.[114] Specifically, at 410 °C, the gas production rose from 6 wt% to 13 wt%, whereas at 440 °C, it increased from 4 wt% to 6 wt%. These findings indicate that pressure has a more significant influence at lower temperatures, and its effect decreases as the pressure increases. Therefore, pressure is considered a time-dependent factor in pyrolysis.

Continuous pyrolysis of waste tires under different conditions, such as 25–50 kPa (near vacuum) and 425–500 °C, in a CSBR showed an increased yield of a liquid product with diesel-like physico-chemical properties.[64] A positive impact was reported on the porous structural properties of the residual carbon black. The decrease in pore blockage led to an increase in the surface area of the carbon blacks produced. This influence on the porous structure is attributed to two aspects: the support of vacuum in devolatilization and the diffusion of volatiles inside the particle, as well as the reduction of carbon material deposition on the porous structure due to vacuum. Furthermore, operating under vacuum resulted in a rise in gas yield while the amount of $C_{10}$ single-ring aromatic hydrocarbons decreased. This reduction in pyrolysis products can be ascribed to the adverse impact of the vacuum on their cyclization and aromatization processes. The rise in gas yield is a result of Diels–Alder processes that attenuate olefin condensation and generate aromatic compounds.[115]

### 3.3. Catalysts

The choice of catalyst plays a vital role in enhancing the efficiency and selectivity of the pyrolysis process. It directly impacts the product yield and quality, making it essential to select an appropriate catalyst based on the desired outcomes. By leveraging advancements in catalysts, the pyrolysis process can be further optimized, paving the way for more sustainable and efficient waste-to-fuel conversion methods. An overview of various types of catalysts is given in Fig. 2.

**3.3.1 Clay catalysts.** In clay catalysts, the customizable porous network is achieved by the introduction of pillars between the layers of the structure, resulting in a two-dimensional network with interconnected micropores. Micropores in clay catalysts are generally larger than those in zeolites.[116] Clay is moderately acidic and not conducive to excessive cracking and H-transfer reactions, which helps in yielding a higher amount of liquid with a maximum composition of heavy hydrocarbons. An analysis conducted on the pyrolysis of HDPE, LDPE, PP, and PS using bentonite clay pelletized at 700 °C showed that all the plastics yielded 86 to 90 wt% of liquid products, predominantly hydrocarbons of petrol-range for PS and aliphatic hydrocarbons of diesel range for the other plastics.[62] Furthermore, pyrolysis of PP at a low temperature of 350 °C using kaolin clay resulted in a yield of 79.9 wt% of liquid, mainly consisting of hydrocarbons of automobile fuel range.[74] Clay catalysts generate less coke compared to zeolites and can be used for multiple steps.[117]

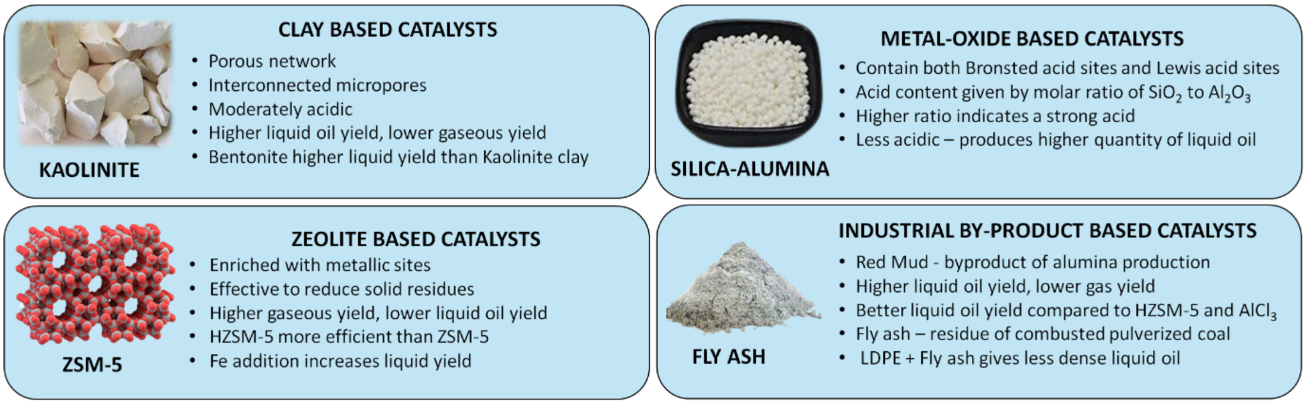

Fig. 2 Characteristics of major types of catalysts used for pyrolysis of plastic waste.

**3.3.2 Zeolites.** Zeolites are extensively utilized in the catalytic degradation of plastics due to their unique acidic properties and porous structures, which enable the selective breakdown of polymer chains into fuel-like hydrocarbons. Different types of zeolites, such as HZSM-5 and HY, enable selective cracking of polymers, producing hydrocarbons in the gasoline and diesel range, as well as valuable gaseous products like ethylene and propylene. An experiment on the catalytic conversion of LDPE using a BR and FBR involved thermal cracking in the BR, followed by passing the generated vapors through an FBR containing the HZSM-5 catalyst (10 wt%).[118] The pyrolysis process executed between 425 °C and 475 °C showed that using zeolite as a catalyst in catalytic reforming significantly increased the gas fraction, reaching approximately 74.4 wt%, while the liquid yield was about 22.0 wt% when operated at the highest temperature. Consequently, the outcome strongly aligned with catalytic direct degradation, resulting in a higher production of gaseous products when the HZSM-5 catalyst was employed.

Zeolites are typically enriched with metallic sites that enhance the efficiency and selectivity of the catalyst. Hydrogenation or dehydrogenation reactions are facilitated by the metallic sites, while cracking and isomerization reactions are catalyzed by the acid sites.[4,36] The metals typically loaded onto zeolite catalysts include noble, transition, and a few alkali metals.[119] Among the transition metals, iron (Fe) shows significant potential for converting PW into fuels due to its cost-effectiveness and high catalytic activity in cracking polymers. The addition of iron onto zeolite is effective for the pyrolysis of many polymers like PE, PS, and mixed PW, resulting in increased yield of oil and production of aromatics.[119,120] On loading 5% of Fe onto HZSM-5 in a continuous-stirred microwave pyrolysis reactor and batch microwave pyrolysis, the yield of liquid products improved from 60% to 76%, and increased the quantity of hydrocarbons in the fuel range ($C_6$–$C_{20}$) from 47% to 66%.[121] This improvement is due to the decrease in activation energy required for pyrolysis by the Fe/ZSM-5 catalyst, resulting in lower pyrolysis temperature and energy consumption.[61]

In HDPE pyrolysis, $SiO_2$ to $Al_2O_3$ ratio for HZSM-5 zeolite impacts the yield fraction of the product obtained.[94] A high $SiO_2/Al_2O_3$ ratio indicated a less acidic zeolite. Compared to the highly acidic catalyst with $SiO_2/Al_2O_3 = 30$, the less acidic catalyst ($SiO_2/Al_2O_3 = 280$) showed less efficiency in breaking down waxes, leading to higher quantities of $C_{12}$–$C_{20}$ and lower quantities of lighter olefins. The lighter olefins yield dropped from 58.0 wt% to 35.5 wt% when the $SiO_2/Al_2O_3$ ratio increased from 30 to 280, while the yield grew from 5.3 wt% to 28.0 wt% for $C_{12}$–$C_{20}$ fractions.

**3.3.3 Metal oxide catalysts.** Metal oxide catalysts are increasingly used in the catalytic degradation of plastics due to their ability to facilitate polymer breakdown through redox reactions and surface acidity. Silica alumina catalyst (SAC) catalyst is known for its amorphous and acidic nature and contains both Brønsted acid sites, which contain hydrogen atoms that are ionizable, and Lewis acid sites, which accept electrons. Acidic content is given by the molar ratio of $SiO_2$ to $Al_2O_3$, with a higher ratio indicating a stronger acid.[76] Unlike zeolites, metal oxides promote oxidative pathways, which can lower the activation energy required for polymer degradation and yield liquid hydrocarbons with fewer carbon residues. These catalysts favor the formation of mid-range hydrocarbons suitable for fuels while also producing valuable gaseous products such as hydrogen and methane. PP pyrolysis at 380 °C using the gaseous and liquid phase of silica alumina catalyst showed that a larger proportion of gaseous products (35 wt%) yielded in the vapor phase of the catalyst. In contrast, the liquid phase catalyst produced a relatively higher (68.8 wt%) yield of liquids due to the disintegration of wax residue into lighter hydrocarbons.[76] This is attributed to the disintegration of wax residue into lighter hydrocarbons in the liquid phase. Under the same operating conditions, HDPE pyrolysis in a SBR operating at 430 °C with SA-2 catalyst showed that LDPE produced a higher liquid oil yield (80.2 wt%) compared to HDPE (77.4 wt%) due to the weaker structure caused by branched chains.[51]

A high thermal stability and tunable acidity of metal oxide catalysts make them suitable for large-scale plastic conversion processes, supporting sustainable fuel production from plastic waste.

**3.3.4 Industrial byproduct based catalysts.** Fly ash, a residue obtained by the combustion of pulverized coal, is utilized for catalytic processes due to its unique composition of $SiO_2$, $Al_2O_3$, and $Fe_2O_3$.[71] Before being used, fly ash requires pretreatment and synthesis, followed by calcination at an elevated temperature to enhance its surface area.[71] According to a study, the employment of this catalyst in the pyrolysis of LDPE results in a lighter-colored oil compared to catalyst-free pyrolysis.[70] This indicates that pyrolytic oil yield of LDPE with the catalyst is less dense and contains more lighter hydrocarbon molecules. However, it is worth noting that the oil obtained has fewer useful components in comparison to the oil obtained from LDPE pyrolysis in the presence of zeolite. The pyrolysis of PE using calcined fly ash catalyst generated at 800 °C was proved to be effective, doubling the content of necessary aromatic compounds such as benzene, ethyl benzene, and xylene, in comparison to its non-catalytic pyrolysis.[71]

Red mud, a byproduct of alumina production, is commonly used in $H_2$ production due to its high content of $Fe_2O_3$. It also contains $SiO_2$, $Al_2O_3$, or $TiO_2$, which positively affect municipal PW pyrolysis. In a comparitive analysis, different catalysts were compared, and it was found that red mud produced the highest liquid content (65 wt%) and the lowest gas content (30 wt%) compared to HZSM-5 and $AlCl_3$ catalysts.[113] Similarly, in another study, the pyrolysis of PS with red mud resulted in 90 wt% oil production.[122] These findings indicate that red mud is a better catalyst for obtaining higher percentages of liquid products and minimizing gas production from polymers.

## 4. Applications of ML for optimal reactor performance

Industry 4.0 leverages ML to manage complex queries through implicit and automatic learning that advances autonomously

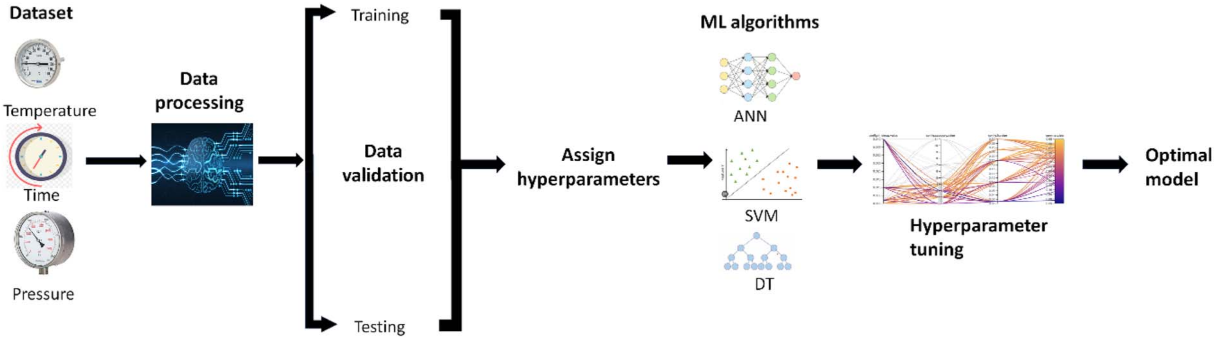

Fig. 3 Machine learning workflow for optimizing plastic waste pyrolysis.

without requiring explicit pre-programming.[123] In the context of pyrolysis, ML algorithms forecast the amounts of various pyrolysis products, including char, pyrolysis oil, and gas, along with their chemical composition and physical characteristics. These forecasts can assist researchers and industry professionals in enhancing pyrolysis procedures to attain the required yields and compositions of products, and customize the process parameters to fulfil needs. In the realm of ML model development, neural network (NN) and support vector regression (SVR) techniques has been widely used for the purpose of modeling PW pyrolysis.[124,125] In order to create ML models, it is essential to identify the input and output variables. Various ML studies have explored different input variables pertaining to PW pyrolysis.[126,127] ML modeling studies focus on analyzing pyrolysis kinetics to predict the decrease in weight and determine the activation energy of PW during pyrolysis. The input parameters are generally set as time, temperature and pressure, and the output is yield. The workflow for ML based optimization of pyrolysis products is given in Fig. 3.

### 4.1. ML prediction, interpretation, and optimization

SVR, NN, Gaussian Process (GP), and decision tree (DT) have been used to forecast the distribution of liquid and gas produced by plastic pyrolysis. It was observed that DT outperformed the others with a test of $R^2 > 0.85$ for liquid yield. The forecast of the characteristics of other products was improved by additional training, with $R^2$ values between 0.61 and 0.94.[124] In the microwave-assisted co-pyrolysis of PS and rice husk, the oil yield rose up to 70 wt% with PS to rice husk ratio of 5 : 1. In addition, ML used to examine the impact of different plastic to biomass ratios on the yield, and conversion, yielded a notable $R^2$, ranging from 0.81 to 0.94.[128] SVR and GP models forecasted gas production during the pyrolysis of packaging waste, where inputs included the type of PW, temperature, heating rate, and quantity and type of catalyst. The SVR model achieved an $R^2$ value of 0.89, while the GP model performed better with an $R^2$ value of 0.93.[126] In another study, the XGBoost model was developed to forecast the yield from PW, generating $R^2$ values between 0.86 and 0.90. A minority for Gaussian noise regression was used in order to solve the data uncertainty and increase forecast accuracy. The Shapley additive explanations approach improved ML model interpretation, revealing that pyrolysis temperature and biomass to plastic ratio were critical factors influencing oil production.[129]

An exhaustive model was created to accurately forecast the yields on co-pyrolysis of PW and biomass with approximately 95 data points using NN and XGBoost, with a high prediction accuracy of up to 0.96 $R^2$. Shapley additive explanations was employed in conjunction with the established ML models to analyze the effect of various factors on the yields from co-pyrolysis. The findings demonstrated that the percentage of PW was the primary reason influencing the yield of products.[127] Several ML techniques used to improve the co-pyrolysis of biomass and PW indicated the GP model exhibited the highest performance, yielding testing $R^2$ values of 0.98, 0.93, and 0.95 for oil, char, and gas predictions, respectively. Additionally, a multi-objective particle swarm optimization algorithm used to identify the ideal raw material composition and operating parameters to scale up the pyrolysis oil yield while reducing char and gas output successfully attained a significant oil yield ranging from 70.9% to 75.3% during co-pyrolysis through optimization.[130] A hybrid NN-genetic algorithm model introduced to forecast and improve oil yield from pyrolysis of PE and PS illustrated that NN models can forecast oil production, composition, and percentage with error of less than 8%. Furthermore, through NN-genetic algorithm optimization, the maximum oil yield of 82.3 wt% and the highest ratio of styrene to aromatics (55.2 wt%) were attained at 525 °C with 10 wt% PS.[125] It was further emphasized that lower temperatures, higher PS mass fractions, and reduced flow rates of carrier gas were desirable to produce light oil from co-pyrolysis.

ML techniques have been employed for forecasting, analysing, and enhancing the output of desired products with excellent quality in PW pyrolysis, and exploring the pyrolysis kinetics.[131] A study using thermogravimetric analysis and NN modelling to examine the thermal pyrolysis behaviour of HDPE, the weight loss, activation energy, and pre-exponential factor could all be predicted accurately, with an $R^2$ of more than 0.99 and a relative error of 6.8%.[132] In another study, the co-pyrolysis of oily sludge and HDPE on conversion and degradation reactions was examined, which indicated synergistic effects between the two, enhancing the conversion, and accelerating the degradation reactions due to significant $CH_3$ radicals generated by HDPE pyrolysis. Additionally, the researchers developed two NN models to anticipate the interactive impact and activation energy, achieving high testing $R^2$ values of 0.99 and 0.92, respectively. The NN model was later developed to optimize pyrolysis conditions, to achieve highest synergistic effect and reduce the activation energy. The model determined that the optimal conditions for the highest synergistic effect of 90.6% at 480 °C, a heating rate of 10 °C per minute, and biomass to plastic ratio of 0.7, with the experimental validation error of 6%.[133] The tree-based kinetic Monte Carlo model was made using parameters regulating Bayesian optimization to simulate the PS pyrolysis routes. The research revealed that styrene monomer might be recovered as feedstock for styrene polymerization by improving its yield and selectivity during PS pyrolysis, with peak styrene yield of 77.3 wt% attained at 600 °C.[134]

### 4.2. ML-aided characterization of pyrolysis oil

ML techniques are effective instruments that can assist in the analysis of products derived from PW pyrolysis, particularly when dealing with bio-oil containing complex compositions. Gas chromatography-mass spectrometry and ML techniques were successfully used to predict and analyze the liquid products, such as hydrocarbons resulting from plastic pyrolysis post ozone treatment by building an NN model and using spectral data of polar and non-polar phases as inputs to predict the fuse index.[135] A rapid characterization technique was introduced that combined attenuated total reflection Fourier transform infrared spectroscopy with ML in order to identify the markers of bio-oil produced during pyrolysis. Principal component analysis reduced initial data dimensionality from 7469 to less than 20, significantly enhancing prediction accuracy, with $R^2$ values improved from 0.62–0.93 to 0.05 to 21 for the prediction of various components of bio-oil.[136] Plastic pyrolysis oil and coconut oil were combined with diesel to assess their possible use in a diesel engine, with NN model created to forecast the fuel performance and emission parameters. The investigation showed that the NN model could forecast the experimental findings with accuracy ranging from 90% to 93.5% after hyperparameter adjustment.[137]

## 5. Circular economy

While pyrolysis appears effective at PW management, the techno-economic and life cycle analyzes are critical for its success. LCA assists in analyzing decisions from the standpoint of their impact on the environment.[138] TEA can help reduce costs associated with the process and enhance the efficiency of the supply chain. This evaluation helps in establishing a robust strategic framework for the chemical and fuel production from pyrolysis of post-consumer PW. Since the PW problem has grown significantly in recent years, there is a collective effort by each country to contribute to reducing plastic pollution through targeted strategies, missions, and policies.

The circular economy (CE) concept aims to maintain a continuous flow of substances in the supply chain to decrease the use of finite resources, and is designed to enhance product lifespan by means of improved product design and services to shift waste from the end to the start of the supply chain.[139] It promotes efficient resource use, reduces environmental impact, and creates regenerative industrial systems which lead to cost savings, supply chain resilience, reduced greenhouse gas emissions, and increased innovation and job opportunities. Overall, CE represents a cultural shift towards new production and consumption methods, requiring a holistic and systemic approach.[140]

### 5.1. Life cycle assessment

PW pyrolysis offers the potential to minimize PW accumulation and offset the dependency on fossil fuels. Despite these advantages, it is essential to evaluate the potential of pyrolysis in inhibiting PW's impact on the environment compared to present fossil fuels production.[141,142] Recently life cycle studies on plastic-to-plastic conversion *via* industrial pyrolysis applications demonstrate that advanced recycling can result in 5–126% decrease in emissions of greenhouse gas throughout the complete life cycle compared to regular polyolefin manufacturing.[143] Some studies have measured the climate impacts and fossil depletion associated with various recycling processes of various types of plastics, such as PE, PET, PP, and PS. Among the various chemical recycling techniques, depolymerization tends to offer the greatest benefits, accomplishing net climate effects ranging from −7.2 to −0.5 kg $CO_2$-eq. per kg of feedstock, based on the feed and size of the plant.[143–145]

Several LCAs have assessed the environmental impacts of thermal degradation of PW[146,147] and noted the release of greenhouse gases during pyrolysis. As a result, it is necessary to focus on converting pyrolytic gases into valuable chemicals to minimize carbon emissions and subsequently mitigate environmental consequences.[148] In a study, carbon footprint of pyrolysis setup was examined by employing system expansion to distribute emission loads to individual products.[149] Their findings revealed that greenhouse gas emissions linked to some olefins and aromatic mixtures were lesser than those originating from fossil sources. However, the emissions from naphtha and diesel products did not fare well compared to those from fossil sources. To improve the environmental friendliness and cost-effectiveness of plastic waste pyrolysis, the utilization of solar energy as the heat source for feedstock has been proposed.[150]

### 5.2. Techno-economic analyses

The return on investment (ROI) and overall capital investment (OCI) are key factors in assessing the efficiency of a post-consumer waste pyrolysis plant.[151] A TEA evaluation of molten solar salt pyrolysis of PW was conducted and determined that for an 8000 ton per year plant, the OCI was expected to be 3.63 million USD with an ROI of 27.6%, utilizing the pyrolysis gas to power the plant.[150] Scaling the capacity to a 16 000 ton per year plant could increase the OCI to USD 6.44 million with an ROI of 49.1%. If the energy source used is concentrated solar power, the OCI would increase by 20%, while the ROI would decrease by 11%. On comparing various reactors through a techno-economic analysis, it was concluded that the ROIs of a bubbling FBR at 740 °C is 21.7% and a circulating FBR at 840 °C is 29.5%. Both these values are larger than a rotating cone reactor at 625 °C with an ROI of 14.2%.[152]

### 5.3. Global policies and challenges in plastic waste management

Despite the promise of pyrolysis and other advanced recycling technologies, significant challenges remain in addressing PW management. These challenges include the complexity and variability of plastic materials, economic feasibility, scalability of recycling technologies, and the environmental impact of waste processing. Additionally, the global trade in plastic waste complicates efforts to implement consistent and effective policies. Various regions and countries have developed strategies to mitigate these challenges and transition towards a circular economy.

The National Recycling Strategy 2021 builds upon the collective efforts initiated by stakeholders in the recycle system under the National Framework for Advancing the U.S. Recycling System 2019. The U.S. Environmental Protection Agency aims to address significant recycling challenges nationwide, and establish a more robust and economic-friendly MSW recycling system. This strategy marks the first time that the agency considers the climatic impacts of material production, use, and disposal, as well as concentrate on the health, environmental effects of waste management in disadvantaged communities, demonstrating the agency's dedication to environmental justice. The key objectives include increasing the collection of recyclable materials, enhancing recycling infrastructure through funding, design, and processing efficiencies, reducing contamination in the recycled materials stream through public education, and fortifying the U.S. recycling system.[153]

According to the European Strategy for Plastics (COM/2018/028) in a CE 2018, Europe generates a 25.8 million tons of PW annually.[154] This strategy also highlights the issue of microplastics, which are released into the environment, and aims to ensure that all packaging is recycled, in line with Vision 2030. This strategy promotes a circular approach that prioritizes the utilization of safe and sustainable reusable products over single-use plastics. The strategy also includes specific requirements such as a complete ban on the production and marketing of specific products, waste reduction, development of PW management systems, and pollution prevention. The Resources and Waste Strategy of UK, released in 2018, builds upon the objectives drafted in the 25 Year Environment Plan and outlines the policies necessary to achieve its goals. The strategy encompasses five key strategic ambitions include working towards eradicating food waste sent to landfills, doubling resource productivity, striving to ensure that all packaging material brought into the market is recyclable or reusable, eliminating avoidable waste of all types, and eradicating avoidable PW.[155]

The Swachh Bharat Mission, initiated by the Indian government in 2014, aims towards establishing storage facilities for effective management of PW.[156] The waste-to-wealth objective of the mission aims to discover, develop, and implement technologies that can convert waste into energy, recycle materials, and extract valuable resources. Additionally, the mission focuses on identifying and supporting the advancement of modern technologies that promise to create a clean and sustainable environment. The mission complements the Swachh Bharat and Smart Cities projects by establishing CE models that are economically feasible for waste treatment, thereby enhancing waste management practices in India. These initiatives have had significant positive impacts on the economy, environment, and public health, which is evident from the accomplishment of SDG 6.2 that was realized eleven years earlier than the designated timeframe.[157] China, prior to implementing its National Sword policy and banning the import of low-quality PW in 2017, used to import significant amounts of PW to meet its domestic demand at a low cost. Despite this, China only had a recycling rate of 25%, leading to significant environmental problems. The Chinese import ban had a global impact on the PW trade and resulted in the diversion of PW to new Southeast Asian export destinations.[158] The Japanese government has development of the Plastic Resource Recycling Strategy, which focuses on the 3Rs (reduce, reuse, recycle) for plastic and promotes the use of recycled materials and bioplastics. Additionally, the government plans to address marine plastic pollution by tackling issues like illegal dumping, microplastic contamination, and ocean litter retrieval and disposal. Furthermore, the government is actively promoting the Plastics Smart campaign, which aims to raise awareness about the marine plastic litter problem, eliminate littering, and reduce the use of disposable plastics.[159]

In October 2018, the National Solid Waste Management Department of Malaysia implemented 18 regulations for the import of PW, which involved waste recycling plants to categorize PW, maintain proper documentation, and pay levies for PW imports. The Ministry of Housing and Local Government built a waste-to-energy facility in Malaysia to eliminate the use of landfills and proposed the construction of incineration plants in each state of Malaysia to convert PW into environmentally friendly energy. The issue of PW imports has been addressed globally through the Basel Convention that aims to restrict the import of PW into Malaysia and ensure that plastic trade is conducted with the "Prior Informed Consent" process to stop the disposal of PW in developing countries. To align with the principles of the CE and the integrated hierarchy, a model for PW management is suggested. This model offers a sustainable approach that aligns with the "New Plastics Economy" initiative supported by the UN Environmental Programme. The model emphasizes the recovery of fossil energy based PW through recycling procedures to produce raw materials and develop alternative plastic materials.[160]

The UAE government had announced prohibition of plastic bags starting January 1, 2024. The government emphasized the need for transition to environment-friendly and multiple-use alternatives in all stores permanently.[161] This federal ruling surpassed the regulations introduced in Dubai and Abu Dhabi, which included a nominal charge on plastic bags and a ban on most plastic bags, respectively. In Abu Dhabi, the implemented ban resulted in 90% reduction of single-use plastics. The UAE, set to host the United Nations Climate Summit COP28 in November 2024, is committed to achieving carbon neutrality by 2050. Furthermore, starting January 1, 2026, the importation of plastic cutlery, drinks cups, styrofoam, and boxes will also be banned.[162] The initial success in the usage of single-use plastic bags was reported by South Africa and Botswana after implementing SUPB levies. However, these levies were later reduced due to lobbying from the plastic industry. As a result of the 2008 plastic bag ban, Rwanda witnessed a significant decrease in plastic imports under HS Code 3926, going from 5000 to 175 tons between 2004 and 2016. Kenya's ban on SUPBs led to a decrease in their usage and a rise in the adoption of reusable bags. Despite these achievements, the effectiveness of plastic restrictions in Africa is hindered by a lack of substitutes, smuggling, and the influence of the plastic industry. Although quantitative data is being gathered throughout Africa, it is challenging to evaluate its overall efficacy due to limited enforcement, monitoring, and assessment of these policies as well as the fact that most African governments have just recently adopted them.[163]

The diverse policies and strategies adopted by different countries and regions reflect a global commitment to tackling the plastic waste crisis. While challenges persist, these policies aim to enhance recycling infrastructure, promote sustainable practices, and mitigate environmental impacts. Continued international cooperation and innovation are essential to achieving a sustainable and circular approach to plastic waste management.

## 6. Conclusions

The catalytic pyrolysis of PW can be leveraged to simultaneously mitigate the growing plastic pollution and generate valuable fuels and chemicals through careful selection of catalysts and operating conditions. Here, clay catalysts are found to promote liquid products with a higher fraction of diesel-range hydrocarbons whereas zeolite catalysts (like ZSM-5) promote gaseous products *via* cracking for industrial applications. Moreover, the effectiveness of catalytic pyrolysis depends on the process parameters, of which temperature, residence time, and reactor design are critical. While FBRs show better feedstock-catalyst mixing properties along with good heat and mass transfer characteristics that enables higher product yields and selectivity, vacuum pyrolysis reactors are preferred due to their slower heating characteristics for a higher oil yield. On the other hand, fixed bed reactors can be added as a secondary reactor for enhanced product yield and improved overall effectiveness. However, higher conversion requires optimal reactor parameters like residence time, temperature, and pressure that can be determined from the application of ML techniques to existing reactor data.

ML techniques are valuable tools that can be leveraged to accurately predict product yields, compositions, and properties, enabling researchers and industry professionals to fine-tune process parameters to attain desired outcomes. Here, NN, SVR, DT, and GP emerge as popular ML algorithms for pyrolysis modelling, prediction of critical runtime process parameters with high confidence ($R^2 > 0.8$), and characterization of product yields. Specifically, NN has proven to be one of the best technologies to optimize the yield since it is capable of handling large data sets.

As the concept of circular economies gets realized globally, all participating countries must focus on strategic planning and missions to reduce environmental pollution. The use of techno-economic and life cycle analyzes on PW pyrolysis can provide critical insights into the overall process economics and carbon footprint that can benefit decision makers. The establishment and implementation of synergistic policies as part of a robust strategic framework to control plastic pollution will be beneficial both to humans and the planet.

## 7. Future scope

While catalytic pyrolysis offers numerous advantages over thermal pyrolysis, ongoing research is necessary to address challenges and explore new opportunities. One major area of focus is the issue of catalyst deactivation, and carbon deposition. Over time, catalysts can lose their activity due to the accumulation of carbon deposits, which hinders their effectiveness. Research should aim at developing more robust and regenerable catalysts that maintain their activity over extended periods. Additionally, there is a need for the development of economical and environmentally friendly catalysts that can be produced at larger scales. The incorporation of catalytic pyrolysis with other advanced technologies holds significant promise for improving product quality and process efficiency. For instance, coupling pyrolysis with membrane separations could enhance the separation of valuable products from the pyrolysis mixture, leading to higher purity and yield. Similarly, catalytic upgrading processes can be employed to further refine pyrolysis products, converting them into high-value chemicals and fuels. Ongoing research efforts should focus on addressing challenges related to heat and mass transfer. Improved reactor designs and advanced computational models can help in understanding and enhancing these parameters, leading to more efficient and scalable systems. The application of AI and ML in optimizing pyrolysis processes presents another exciting avenue for future research. These technologies can be used to analyze large datasets, predict outcomes, and optimize parameters in real-time, thereby improving the efficiency and yield of the pyrolysis process.

Countries around the world must also develop and implement better policies to support these technological advancements. Policies that promote research and development, provide funding for green technologies, and incentivize the adoption of sustainable practices are essential. Furthermore, public education and awareness campaigns can play a crucial role in the successful implementation of these technologies. By addressing current challenges and exploring new technologies, we can enhance the efficiency and effectiveness of plastic waste management. With the support of robust policies and international cooperation, these advancements can contribute significantly to a greener, more sustainable future.

## Nomenclature

| | |
|---|---|
| BR | Batch Reactor |
| CE | Circular Economy |
| CSBR | Conical Spouted Bed Reactor |
| DT | Decision Tree |
| FBR | Fluidized Bed Reactor |
| FiBR | Fixed Bed Reactor |
| HDPE | High Density Polyethylene |
| HZSM | H form Zeolite Socony Mobil |
| LCA | Life Cycle Assessment |
| LDPE | Low Density Polyethylene |
| ML | Machine Learning |
| MSW | Municipal Solid Waste |
| NN | Neural Network |
| OCI | Overall Capital Investment |
| PE | Polyethylene |
| PET | Polyethylene Terephthalate |
| PP | Polypropylene |
| PS | Polystyrene |
| PVC | Polyvinyl Chloride |
| PW | Plastic Wastes |
| ROI | Return on Investment |
| SAC | Silica-Alimina Catalyst |
| SBR | Semi-Batch Reactor |
| SDG | Sustainable Development Goals |
| SVR | Support Vector Regression |
| TEA | Techno-Economic Analysis |
| ZSM | Zeolite Socony Mobil |

## Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

## Conflicts of interest

There are no conflicts to declare.

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