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Pyrolysis of waste plastics for alternative fuel: a review of key factors

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Plastic is a threat to the environment since it does not biodegrade, but it also has the potential to become a substantial resource to produce alternative energy sources, creating a multibillion-dollar untapped market. Every year, millions of tons of plastic are produced, resulting in a significant rise in plastic waste, which causes ecological and environmental problems. According to estimates, only around 10% of this waste plastic is now recycled. Plastic waste may be handled in two ways: recycling or converting it into energy. The first alternative, recycling, has several challenges, including the need for labor-intensive processes and concerns about water pollution, which may threaten its long-term sustainability. As a result, the second technique for turning waste plastic into energy has been developed, enhanced, and extensively researched. Pyrolysis is a technique that involves heating plastics at temperatures ranging from 455–700 °C without oxygen. This process yields high-calorific fuel that can be utilized as an alternative fuel. This study explores the thermal and catalytic cracking processes involved in waste plastic pyrolysis, focusing on crucial factors such as temperature, time, feedstock, reactor type, and catalyst that impact results such as oil production, gases, and heat. Furthermore, the study investigates the properties of the liquid oil produced and offers suggestions for enhancing the liquid fuel yield for each kind of plastic.

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Sustainability spotlight

This study emphasizes the long-term potential of turning waste plastics into high-calorific oil by pyrolysis, providing a possible avenue for addressing plastic waste's increasing environmental and ecological problems. The study advances energy recovery from waste plastic by improving the pyrolysis process, which includes optimizing aspects such as temperature, time, and catalyst selection. This approach reduces plastic's environmental impact while utilizing an unexplored resource, aligning with worldwide initiatives to promote sustainable waste and energy management. The work promotes numerous UN Sustainable Development Goals, including SDG-7 (affordable and clean energy), SDG-12 (responsible consumption and production), and SDG-13 (climate action).

1. Introduction

The production of alternative fuels has vital significance in response to growing energy needs and the subsequent impact on fossil fuel reserves and limited natural resources.^{1,2} This effort includes carefully harnessing non-biodegradable waste materials, thereby realizing their significant energy value.^{3,4} One important aspect of this need is the pyrolytic conversion of waste plastic, providing an alternate oil product suitable for deployment as an alternative fuel in diesel engines and as a possible source of electrical power generation.^{5,6} Local governments across the globe confront formidable challenges in effectively managing the growing issue of waste plastic disposal.⁷ Due to its widespread use in packaging and as a medium for transporting liquids, plastic is essential to the

safe and effective movement of these goods. However, the rapid rate of urbanization has made it necessary to move landfills to remote, more difficult-to-reach places, which has resulted in higher transportation logistics costs. Consequently, this voluminous plastic waste's mechanized handling and processing of this voluminous plastic waste have emerged as a pressing imperative. Notably, it is noteworthy that an annual quantity of approximately 280 million metric tons of plastic waste is generated globally,^{8,9} a fact graphically illustrated in Fig. 1.^{10,11}

Plastics are complex organic compounds primarily derived from hydrocarbon sources within petroleum-based constituents. Their rapid production can be attributed to their unique characteristics. On an annual basis, a staggering volume of approximately 280 million metric tons of plastic is transported globally, inevitably ending in the waste stream. The exponential growth in Municipal Solid Waste (MSW) generation, reaching an astounding 1.3 billion metric tons annually worldwide, is mainly a consequence of both rapid population expansion and urbanization, coupled with heightened expectations of living standards.^{12,13} This rising demand for products made of plastic prompts many waste management challenges, including the

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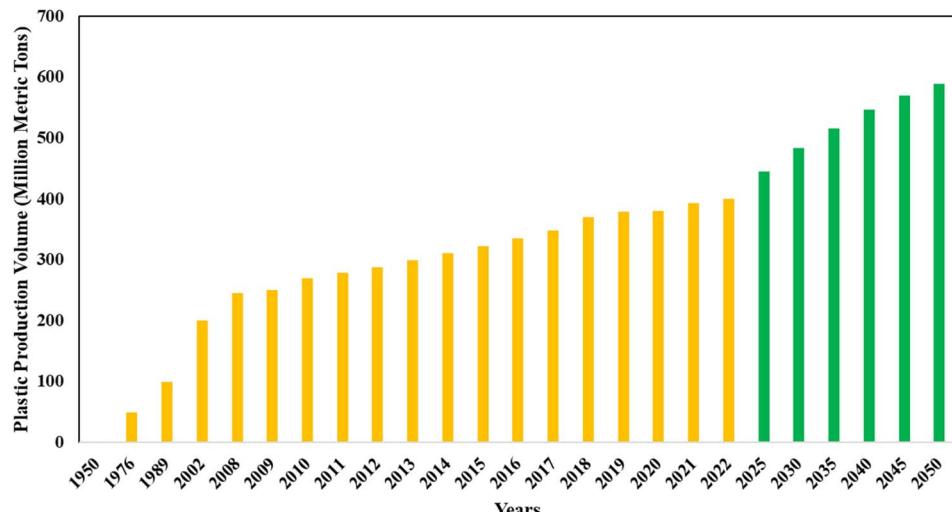


Fig. 1 Worldwide variation of plastic waste production in the past few years and future forecast.^{10,11}

collection, disposal, and transportation of waste plastic to treatment facilities, exerting substantial environmental and socio-economic burdens.¹⁴

By a broad categorization, plastics encompass a variety of types, notably high-density polyethylene (HDPE), low-density polyethylene (LDPE), polystyrene (PS), polypropylene (PP), polyethylene terephthalate (PET), and polyvinyl chloride (PVC). Their distinct characteristics, applications, and roles in the pyrolysis process are elucidated in Table 1.^{15–17} Concurrently, the expanding use of plastics has presented an opportunity to harness waste plastic as a source for fuel production, given its inherent hydrocarbon-based composition. Numerous organizations have developed frameworks for managing plastic waste to mitigate its adverse environmental impact. It is estimated that a staggering 600 billion pieces of plastic are produced annually, with a mere 10% being subjected to recycling, while the remainder contributes to waste generation and environmental issues. The various types of plastics and their applications are depicted in Fig. 2.¹⁸

With the advent of more efficient mechanical processes, the traditional landfill approach for managing plastic waste has become increasingly impractical. Due to its non-soluble properties, plastic continues to pose a persistent threat to the environment. In this context, thermal treatments such as pyrolysis, gasification, and waste-to-energy methods emerge as more sustainable and feasible approaches for plastic waste management. From a chemical standpoint, plastic comprises elements including hydrogen, carbon, nitrogen, chlorine, and various other constituents, rendering it highly durable.¹⁹

The consistent disposal of plastic in landfills results in significant ecological challenges.²⁰ Additionally, the reusability of plastic necessitates source segregation, rendering it a difficult and resource-intensive process,²¹ thereby making plastic reuse both problematic and costly. Furthermore, not all types of plastic can be effectively recycled or reused, as these possibilities are contingent upon numerous factors such as design, colour, texture, chemical composition, and more. Coloured or

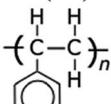
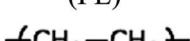
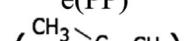
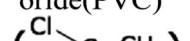
blistered plastics, for instance, are considerably less preferred by consumers. Transparent plastics, however, can be modified through colouring to create new products with greater versatility and appeal to manufacturers.^{21–23} Traditional recycling methods, primarily involving grinding, manage to reuse only a modest fraction, approximately 15–20%, of the total plastic waste generated.^{24,25}

In recent times, thermal and catalytic pyrolysis and plasma gasification, along with plasma gasification, have gained significant attention from researchers as alternative methods for recycling plastic waste.^{12,26} These processes involve subjecting plastic waste to high temperatures for a specific duration without oxygen,²⁷ making pyrolysis a particularly versatile approach.

As a tertiary recycling process, pyrolysis employs high-temperature thermal oxidation to convert natural polymers into liquid oil, heat, and gases.^{16,26,28} Extensive research has been conducted across a range of temperatures, spanning from 300–900 °C; however, the optimal temperature for plastic waste pyrolysis typically falls within the range of 500–550 °C.¹⁶ Moreover, pyrolysis of various types of plastic waste has been explored at varying heating rates, such as 4 °C min⁻¹,²⁹ 20–25 °C min⁻¹, and 10 °C min⁻¹.³⁰ Additionally, different researchers have employed various residence times for the pyrolysis process, with experiments conducted at durations ranging from 40–70 minutes, 120 minutes, and 45 minutes.⁹ Mangesh *et al.*³¹ identified an investigation gap in plastic combustion and developed a clean fuel made from polypropylene that passes environmental standards. The present investigation was carried out by hydroprocessing post-consumer polypropylene pyrolysis oil with nickel–gold metal implanted on a mordenite support as a catalyst at 70 bar hydrogen pressure and 350 °C.

This review paper provides a comprehensive overview of the production of waste plastic pyrolysis oil (PPO). The primary focus is on plastic pyrolysis oil (covered in Section 2), where the advantages of the pyrolysis process are discussed. Within this section, subheadings delve into the types of pyrolysis processes, specifically thermal and catalytic pyrolysis processes.

Table 1 Types of plastic, and their characteristics, application, and role in pyrolysis^{15–17}

Plastic	Aspects	Uses	Pyrolysis feedstock	Composition of pyrolysis oil
Polystyrene (PS) 	Heat flexibility Light weight Strong Maximum durability	Toys Medical materials Electric things Food packing	Heat at low temperatures in contrast to PP and PE types of plastic Give less slimy oil in comparison to PE and PP plastic	Styrene and toluene Benzene and xylene Benzene Naphthalene
Polyethylene (PE) 	HDPE HDPE is a heavy polymer chain Highly crystalline Strong properties polymer	Making toys Oil tanks Milk bottles	Withstand a high-temperature >500 °C as it contains a lengthy chain structure It changes into wax rather than liquid fuel in heating pyrolysis The wax production occurs at the external side of the catalyst	1-Hexene Cyclohexene 1-Octane
Polypropylene (PP) 	LDPE Low tensile strength Low toughness Good water-resistant Good heat resistance Low weight High rigidity High toughness	Trash bags Wrapping foil for packaging Plastic bags Carpets Furniture Storage box Flowerpot Car bumpers Automotive interior Credit cards	Withstand a high-temperature Difficult to break under thermal pyrolysis Produces liquid oil with high aromatic compounds by catalyst pyrolysis	1-Nonene Benzene Toluene Xylene Toluene Xylene Indene
Polyvinyl Chloride (PVC) 	Resistant to fire, versatile plastic	Medical devices Packaging Food foil Boots Window frames	Produce dangerous chlorine gas Catalyst activity is affected by the presence of chlorine and due to this, coke formation increases	Naphthalene Toluene Xylene Ethylbenzene 1-Heptene 1-Octene

Furthermore, Section 2.3 explores the various parameters that influence the pyrolysis process, encompassing the impact of temperature, residence time, feedstock, catalyst application, pyrolysis reactor type, and product yield. Finally, Section 3 discusses the reviewed studies, with a concise summary of the reviewed studies and a concise summary in the conclusion, followed by future recommendations.

2. Plastic pyrolysis process

Pyrolysis emerges as a viable strategy for recovering energy from plastic waste, representing an effective method for transforming waste materials into energy-rich liquid and gaseous products.³² Pyrolysis, or thermal breakdown, uses heat to break down long-chain polymer molecules into smaller parts. Many

experts contend that pyrolysis can yield a substantial quantity of liquid oil, approximately 79% by weight at around 500 °C.^{27,33}

The pyrolysis procedure typically unfolds in four stages: initiation, transition, decomposition, and termination.³⁴ Computational models in computer simulations consider numerous potential reactions during the thermal decomposition of feedstock materials.³⁵ Factors such as temperature, residence time, heating rates, feedstock composition, and the presence of moisture or hazardous substances all play pivotal roles in influencing the outcomes of the pyrolysis process.³⁶

The primary focus of the studies above was to maximize the yield of liquid oils through pyrolysis while establishing the carbon chain composition necessary for producing liquid oil.^{17,37,38} However, details regarding the density, viscosity, high heating value (HHV), flash point, and cold flow properties (e.g.,

Fig. 2 Plastics along with the use.¹⁸

pour point and solidification point) of liquid pyrolysis fuels derived from blends of various types of plastics, as well as their compatibility with conventional diesel fuel properties, have been rarely disclosed.^{15,39,40}

Most experiments utilised a feedstock comprising 1 kg of waste plastic within the pyrolysis reaction chamber and the blend structure. The reaction chamber was maintained at 455 °C, with a heating rate of 15 degrees Celsius per minute. Across all tests, a consistent maintenance period of 70 minutes was employed, as outlined in the initial experimental setup detailed in Table 2. The selection of these parameters, including the temperature and duration, was guided by Thermogravimetric Analysis (TGA) of the specific plastic materials under controlled conditions, alongside safety considerations. The waste pieces of plastic changed into gaseous organic compounds, which then condensed into liquid oil and collected in a condenser at the bottom of the accumulation tank. To optimize the accumulation of organic vapors in the coolant, the cooling cell's temperature was maintained below 10 °C, with a flow rate of 35 mL min⁻¹.⁹

The volatile components and solid debris in the feedstock are the primary factors influencing the yield of liquid oil in the pyrolysis process. Higher levels of volatile matter promote the production of liquid oil, while a significant presence of solid debris reduces the liquid oil yield, leading to increased gas production and heat generation.³³ The analysis revealed that the

volatile matter content for all plastics is substantially higher than that of solid debris, which is relatively low. These characteristics underscore that plastics have the potential to yield a significant amount of liquid oil through the pyrolysis process. Given the compelling results of this analysis of plastics, the subsequent discussion will focus on the process system requirements associated with the pyrolysis process, as these factors have a notable impact on liquid oil production.

In a study by Kumar and Singh,⁴¹ a semi-batch reaction chamber was employed to analyze the thermal pyrolysis of HDPE at temperatures ranging from 400 to 550 °C. It was observed that the highest liquid output (80.05 wt%) and gas product (24.65 wt%) were achieved at a temperature of 550 °C, in contrast to wax, which dominated the product composition at higher temperatures between 500 and 550 °C. The resulting light brown oil from the breakdown of plastic waste contained no valuable residue and exhibited a boiling range of 82 to 352 °C. As depicted in Table 3, blending various oil components, such as coal, kerosene, and diesel, with the HDPE pyrolytic oil allows for attaining conventional fuel properties. The HDPE pyrolytic oil boasted a low sulfur content (0.019%), rendering it environmentally safe for use on Earth.

2.1. Advantages of pyrolysis

The quality of the liquid oil produced is exceptional due to the multiple operations with no modifications to the process.²⁷

Table 2 Effect of different types of waste plastic experimental values⁹

Waste plastic type	Amount taken (kg)	Ratio (%)	Retention time (min)	Temperature (°C)	Heating rate (°C min ⁻¹)
PE	1	100	70	455	10
PP	1	100	70	455	10
PP/PE	1	50/50	70	455	10
PS/PE/PP/PET	1	40/20/20/20	70	455	10

Table 3 Proximate analysis of different types of waste plastics

Types of plastics	Moisture (wt%)	Fixed carbon (wt%)	Volatile (wt%)	Ash content (wt%)	Ref.
Polyethylene terephthalate (PET)	0.46	6.95	92.85	0.03	30
	0.61	13.17	86.83	0.00	22
High-density polyethylene (HDPE)	0.00	0.02	99.75	0.17	23
	0.00	0.03	98.57	1.40	22
Polyvinyl chloride (PVC)	0.80	6.30	93.70	0.00	33
	0.74	5.19	94.82	0.00	22
Low-density polyethylene (LDPE)	0.30	0.00	99.70	0.00	42
	—	—	99.60	0.40	43
Polypropylene (PP)	0.15	1.22	95.08	3.55	44
	0.18	0.16	97.85	1.99	22
Polystyrene (PS)	0.25	0.12	99.63	0.00	45
	0.30	0.20	99.50	0.00	42
Polyethylene (PE)	0.10	0.04	98.87	0.99	44
Nylons	0.00	0.69	99.78	0.00	46
Acrylonitrile butadiene styrene (ABS)	0.00	1.12	97.88	1.01	46

Additionally, the gaseous fuel generated possesses a high calorific value, making it suitable for fulfilling the energy requirements of the pyrolysis plant itself. Pyrolysis is preferred over traditional recycling methods because it offers easier and more flexible handling. Unlike recycling, pyrolysis does not pose a water pollution concern. It is considered a green technology, and the gaseous byproduct of pyrolysis holds a significant calorific value and can be recycled to meet the energy needs of the pyrolysis plant.³³ The resulting liquid oil can be utilized in various applications, including furnaces, boilers, generators, and diesel engines, without requiring any modifications.³²

The pyrolysis process yields various products such as gas, oil/wax, and heat, with their composition and production influenced by factors such as plastic-type, reactor type, and process conditions, particularly reaction temperature and heating rate.⁴⁷⁻⁵¹ Numerous researchers have also explored the impact of catalysts on enhancing the extraction of crude oil from the process.^{47,52-57}

2.2. Types of pyrolysis

2.2.1. Thermal/heating pyrolysis. Thermal pyrolysis of waste plastic, also referred to as non-catalytic pyrolysis, is a heat-driven process that does not require the presence of a catalyst. Table 4 provides an overview of thermal pyrolysis experiments conducted on various plastics.

The thermal degradation of polystyrene (PS) was completed under milder conditions compared to the thermal degradation of high-density polyethylene (HDPE), low-density polyethylene (LDPE), and polypropylene (PP). This difference arises from the fact that polyethylene (HDPE and LDPE) and PP require significantly higher temperatures for decomposition when compared to PS plastic.⁴⁴ Polyethylene (PE) is converted without a catalyst into wax rather than liquid oil.⁴⁵ The liquid oil produced through thermal degradation consists of complex mixtures of heavy oil compounds with long carbon chains. However, due to its lower octane number and solid residues and contaminants such as sulfur, nitrogen, and phosphorus, the quality of the liquid oil obtained was relatively poor.⁴⁴

2.2.2. Reactant/catalytic pyrolysis. The utilization of a catalyst enables the implementation of catalytic pyrolysis. This catalytic approach demonstrates significant potential for converting waste plastic into liquid oil, offering improved product quality at lower temperatures and shorter reaction times than thermal pyrolysis (as illustrated in Table 5). Various catalysts, including HZSM-5,⁴⁵ ZSM-5,⁶⁸ Cu-Al₂O₃, Co-Mo/Z, basic zeolite (NZ), Red Mud,⁶⁹ Al(OH)₃, Ca(OH)₂,⁴⁶ and Fe₂O₃, have been employed to expedite and enhance the catalytic pyrolysis process. In contrast to thermal pyrolysis, many plastics like HDPE, LDPE, PP, and PS yield hydrocarbons (HCs) with lower carbon chain lengths (gaseous range) when subjected to catalytic pyrolysis. Introducing a catalyst tends to increase the production of gaseous products while reducing the yield of liquid products. Nevertheless, the catalytic process achieves conversion at lower temperatures compared to thermal pyrolysis.⁷⁰

2.3. Factors affecting the pyrolysis process

Variables such as temperature,⁷⁰ residence time,⁴⁰ the physical structure of waste plastic pieces,⁷¹ catalyst use,⁷² moisture content²⁹ heating rate⁷³ and molecular composition,⁷⁴ all play an important role in influencing the outcome of the plastic pyrolysis process.

2.3.1. Temperature. Temperature is a significant variable that influences the quality and quantity of pyrolysis yields. Temperature considerably impacts breakdown reactions, which affects the formation of gases and liquids. However, it has little influence on char development.⁷⁵ Lower heating temperatures result in the formation of long-chain hydrocarbons by pyrolysis. In contrast, higher operating temperatures result in the formation of short-chain hydrocarbons *via* the breaking of C-C bonds.

2.3.2. Maintenance time and feedstock configuration. Maintenance time has been found to impact the yield of pyrolysis substantially. Experiment results show that equivalent oil production may be attained with maintenance times varying from 35 to 115 minutes.⁷⁵ Additionally, it was found that the



Table 4 Thermal pyrolysis of different types of plastics and their product yield

Plastic	Thermal temp. [°C]	Time [min]	Oil (wax) [%]	Gas [%]	Char [%]	Ref.
PS	450	75	80.8	13	6.2	34
PS	330	—	80	—	—	58
LDPE	437–486	—	94	—	—	59
PP	378–456	—	86	—	—	59
PP	350	—	82.6	—	—	58
PP	450	30	67.48	8.85	23.67	60
HDPE	—	—	84	13	3	61
HDPE	—	—	—	—	—	62
HDPE	—	—	—	—	—	62
HDPE	430	—	75.5	20	4.5	62
HDPE	450	—	82	18	—	63
HDPE	450	—	80	—	—	58
PP	540	—	61	31	7	64
PP	—	—	—	—	—	65
LDPE	—	—	—	—	—	65
HDPE	—	—	—	—	—	65
LDPE	550	—	93.1	14.6	—	64
HDPE	550	—	84.7	16.3	—	64
LDPE	375	—	68	—	22	66
HDPE	430	150	72.66	—	—	67
LDPE	450	150	73.91	—	—	67
PP	400	150	83.81	—	—	67

aromatic compounds present in the liquid oil remained consistent across different maintenance times at the same temperature. The composition of the feedstock also influences the yield of pyrolysis. Because of their different and more complicated chemical structures, polyethylene (PE) and polypropylene (PP) plastic require greater temperatures for decomposition than polystyrene (PS) plastic.³⁶

2.3.3. Catalyst application. Catalysts play a crucial role in enhancing the quality of pyrolysis products and reducing the process temperature and residence time for overall process optimization. Various catalysts, including Fe_2O_3 , $\text{Ca}(\text{OH})_2$, FCC, selective zeolite, and synthetic zeolite, have been widely employed by numerous researchers in the catalytic pyrolysis process.⁷⁶ Catalysts actively improve the proportion of

Table 5 Catalyst pyrolysis of different types of plastics and their product yields

Plastic	Catalyst	Catalytic oil (%)	Temp. (°C)	Gas (%)	Char (%)	Ref.
PS	Natural zeolite	54	450	12.8	32.8	34
	Synthetic zeolite	50	450	22.6	27.4	
PP	Silica aluminium	59.57	320	—	—	58
LDPE	Zeolite	51	—	—	—	59
PS	Silica aluminium	50	290	—	—	58
PP	Zeolite	58	—	—	—	59
HDPE	Alumina	82	450	15.9	2.1	62
PP	Kaolin	69.75	450	14.01	16.24	60
HDPE	ZSM-5	35	—	63.5	1.5	61
HDPE	Silica aluminium	48.3	350	—	—	58
HDPE	FCC	79.7	—	19.4	0.9	62
HDPE	Silica/NaOH	81	450	19	0	63
HDPE	Mordenite	78.5	450	18.5	3	62
PP	Calcium bentonite	88.5	500	—	—	65
PP	Fe-SBA-15	73–77	540	24–21	2–0.8	64
LDPE	Calcium bentonite	82	500	—	—	65
HDPE	Calcium bentonite	82.5	500	—	—	65
LDPE	HZSM-5	18.3	550	70.7	0.5	64
HDPE	HUSY	41.0	550	39.5	1.9	64
LDPE	KAB/kaolin	84	295	—	<1	66
HDPE	10% dolomite	80.73	430	—	—	67
LDPE	10% dolomite	83.04	450	—	—	67
PP	10% dolomite	85.2	400	—	—	67



decomposition processes, resulting in higher gas output and lower liquid oil yield.⁵⁴ Because some of the bigger carbon chain compounds are physically bound to the catalyst or further broken down into smaller carbon chain compounds, the consistency of the generated liquid oil is improved. The catalytic activity of a catalyst is influenced by parameters such as pore size, pore volume, and acidity.

2.3.4. Pyrolysis reactor and yield. Various parameters play a significant role in enhancing product yield and the efficiency of the pyrolysis process. Factors such as temperature, reactor type, feedstock weight, catalyst selection, type of fluidizing gas, and residence time directly impact liquid oil production in pyrolysis.

In the thermal cracking of plastics, temperature is a paramount operating parameter in the process, as it governs the breaking reactions of carbon chains. Different plastics have distinct degradation temperature ranges based on their molecular structures. For instance, thermal degradation temperatures of common plastics like PET, LDPE, HDPE, PS, and PP range between 250 and 360 °C, while PVC decomposes at a lower temperature of around 230 °C. The specific operational temperature requirements depend strongly on the desired product composition. If the preference is for gaseous products, higher temperatures exceeding 450 °C are recommended, whereas a lower temperature range of 300–500 °C is suitable for obtaining liquid products.^{17,77}

Apart from temperature, selecting an appropriate reaction chamber configuration is crucial for the economically viable conversion of plastic waste into fuel. Each reactor type has unique advantages and limitations, depending on its intended use. Batch or semi-batch reactors have traditionally been used for plastic decomposition without catalysis, as they allow for controlled conditions. However, these reactors may not be suitable for catalytic pyrolysis due to the tendency of coke formation, which can hinder the contact between the catalyst and plastic pieces, thus reducing the catalytic activity. In contrast, fluidized bed reactors, such as conical spouted-bed reactors (CSBRs), are considered suitable for catalytic plastic decomposition as they allow periodic catalyst replenishment and offer excellent mixing to handle large amounts of feedstock and promote bed circulation compared to bubbling fluidized beds.⁷⁸

Nevertheless, certain operational challenges are associated with reactor operation, including complex system arrangements, catalyst handling, and the collection of solid and liquid products, which can affect overall efficiency.⁷⁹

3. Discussion

In summary, feedstock weight and reaction time play significant roles in pyrolysis. Larger feedstock loads can increase the production of gaseous products and affect the distribution of molecular weights in both the liquid and vapor phases. However, this effect is more pronounced at higher temperatures. Incineration is a commonly used waste management method that does not differentiate waste composition, including plastics. Therefore, catalytic pyrolysis of plastic waste

is considered a preferable approach. Additionally, the type and flow rate of the fluidizing gas used during pyrolysis also influence the process.

The fluidizing gas, often referred to as the carrier gas, serves the sole purpose of transporting vaporized products and does not participate in the actual decomposition of the feedstock. Various gases can be used for fluidization, including nitrogen, helium, argon, ethylene, propylene, and hydrogen.⁸⁰ After careful consideration, most experts have concluded that nitrogen is the most suitable fluidizing gas for plastic pyrolysis. It is easier and safer to handle compared to highly reactive gases like hydrogen and propylene, which can be more volatile.

At the lowest fluidizing gas flow rate of 300 ml min⁻¹, Lin and Yen⁸¹ observed a considerable increase in the rate of deterioration. This is because a lower flow rate provides a longer contact time for the feedstock, allowing for the accumulation of coke precursor compounds (BTX) and increasing the secondary cracking reactions, even though the overall cracking rate is relatively mild.⁸² The separation between gas and hydrocarbon products becomes more pronounced at the highest flow rate of 910 ml min⁻¹. This discussion underscores the influence of fluidizing gas flow rate on the final product distribution.

Regarding catalytic degradation, thermal technology employs a catalyst to accelerate the desired reactions and enhance hydrocarbon formation, resulting in pyrolysis liquids with properties similar to conventional fuels like gasoline and diesel.

During the heating of waste plastic, three types of catalysts are commonly used: basic zeolites, fluidized cracking catalysts, and silica-alumina catalysts. The utilization of zeolite catalysts during plastic heating has been found to reduce the impurities in the resulting oil, as demonstrated by Miskolczi *et al.*³⁶ Lee *et al.*⁸³ reported that the solid residue left after catalytic pyrolysis decreased from 4.5% to 0.9% by weight. In contrast to these catalytic applications, more research has been conducted on silica-alumina catalysts, which are non-destructive. The mole ratio of SiO₂/Al₂O₃ determines the catalytic activity of silica-alumina catalysts. The precise acidity characteristics of the catalyst have a significant impact on the outcome of plastic pyrolysis.

Table 6 provides information on the physical properties of pyrolyzed liquid fuel obtained from plastic. The calculated calorific values of pyrolyzed oil from plastic waste exceed 40 MJ kg⁻¹, which makes it a valuable energy source. The calculations indicate that polystyrene (PS) has a lower calorific value compared to low-density polyethylene (LDPE) and high-density polyethylene (HDPE) because PS contains aromatic rings, which have lower energy content compared to other straight-chain hydrocarbons.⁸⁷ On the other hand, PVC and PET have lower calorific values of around 30 MJ kg⁻¹ due to the presence of rings in PET and the negative impact of chlorine compounds in PVC.

Table 7 presents ideal heating conditions to enhance liquid oil production in catalytic and thermal pyrolysis under various scenarios. The pyrolysis of plastics is influenced by factors such as the type of reaction chamber, feedstock mass, heating rate, and residence time. Nitrogen gas is commonly used to create an



Table 6 The pyrolysis oil's fuel properties are derived from plastics

Properties	Units	Types of plastics (typical experimental value)						Commercial standard value (ASTM 1979)	
		PET ⁷⁷	HDPE ²³	PVC ^{77,84}	LDPE ⁸⁵	PP ²³	PS ^{80,86}	Gasoline ⁸²	Diesel ⁸²
Calorific value	MJ kg ⁻¹	28.2	40.5	21.1	39.5	40.8	43.0	42.5	43.0
API gravity @ 60 °F	—	—	27.48	38.98	48.05	33.03	—	55	38
Viscosity	mm ² s ⁻¹	—	5.06	7.05	5.56	5.02	1.8	1.18	1.9–4.1
Density @ 15 °C	g cm ⁻³	0.90	0.90	0.79	0.79	0.85	0.80	0.658	0.907
Ash	wt%	—	0.00	—	0.035	0.00	0.007	—	0.02
Octane number MON (min)	—	86	—	—	88	—	82–86	—	—
Octane number RON (min)	—	96	—	—	98	90–98	90–94	—	—
Pour point	°C	—	-4	—	—	-10	-68	—	7
Flashpoint	°C	—	49	39	40	29	27	43	51
Aniline point	°C	—	56	—	—	39	—	69	78
Diesel index	—	—	30	—	—	35	—	—	39

inert atmosphere in all these processes. However, two types of plastics, PET and PVC, yield lower liquid products, which have led to fewer research studies on these materials.

Pyrolysis of PVC, in particular, results in low liquid oil production and poses environmental hazards due to the release of hydrochloric acid during the process. The pyrolysis oil derived from PVC can degrade the oil's quality and harm the environment.

Studies have shown that the optimal temperature range for increasing liquid oil production in thermal pyrolysis typically falls between 500 and 550 °C. This optimal temperature can be lowered

to 300–400 °C using suitable catalysts, resulting in higher oil yields. While it is possible to increase liquid products by providing extreme conditions during the heating of different plastic types, polystyrene (PS) stands out as a unique material in this regard.⁸⁷

In contrast, polystyrene (PS) is the most favorable plastic for pyrolysis because it yields more liquid oil than other plastics. Furthermore, in thermal pyrolysis, low-density polyethylene (LDPE) yielded the highest liquid oil content at 93.1% by weight, followed by high-density polyethylene (HDPE) at 84.7% by weight, and polypropylene (PP) at 82.12% by weight. However, with the introduction of suitable catalysts, especially fluidized

Table 7 Effect of various parameters on the generation of liquid oil, gas, and solid from the waste of various plastics utilized in the reactor

Plastic-type	Reaction chamber	Procedure parameter				Production (wt%)			
		Temperature (°C)	Pressure (atm)	Heating rate (°C min ⁻¹)	Duration (min)	Oil	Gas	Solid	Ref.
PET	Fixed bed	510	—	12	—	23	77	0	77
PET	—	505	1 atm	6	—	39	53	9	12
HDPE	Horizontal steel	360	—	19	29	81.1	16.9	2	82
HDPE	Semi-batch	400	1 atm	6	—	82	15	3	88
HDPE	Batch	455	—	—	65	74	6	20	89
HDPE	Semi-batch	455	1 atm	28	—	92	3	5	89
HDPE	Fluidized bed	550	—	—	59	90	9	1	87
HDPE	Batch	500	—	6	—	83	17	0	90
HDPE	Fluidized bed	600	—	—	21–26	69.1	30.9	0	91
PVC	Fixed bed	550	—	12	—	13.1	86.9	0	77
PVC	Vacuum batch	550	2.5 kPa	9	—	11	1	29	92
LDPE	Pressurized batch	450	0.8–4.3 MPa	12	59	90	9	1	93
LDPE	Batch	440	—	4	—	76	8.9	8	94
LDPE	Batch	550	1 atm	5	—	79.5	20	0.8	27
LDPE	Fixed bed	520	—	11	19	94	6	0	95
LDPE	Batch	500	—	8	—	87	13	0	90
LDPE	Fluidized bed	580	1 atm	—	—	50	25	0	96
PP	Horizontal steel	350	—	19	29	68	29	1.5	82
PP	Semi-batch	420	1 atm	8	—	85	12	3	88
PP	Semi-batch	425	1 atm	20	—	93	3	4	97
PP	Semi-batch	520	1 atm	5	—	81	18	0.25	27
PP	Batch	720	—	—	—	49	48	3	37
PS	Semi-batch	450	1 atm	6	—	89	5	3.5	88
PS	Pressurized batch	450	0.25–1.7 MPa	11	59	96	3	0.25	93
PS	Batch	550	—	—	149	96.5	3.5	0	98
PS	Batch	579	—	—	—	89	10	1	37



cracking catalysts (FCC), operating at optimal temperatures, the oil yield can be further enhanced to exceed 89% by weight.

Moreover, the potential value of the obtained oil can be estimated based on the total amount of plastic waste available in Saudi Arabia. The Kingdom of Saudi Arabia generates roughly 53 MMT of waste annually, 95% of which is in landfills. From 2020 to the first part of 2021, the Kingdom recycled barely 5% of its total garbage, including plastic, metal, and paper.⁹⁹ Saudi Arabia's total GHG emissions have increased by 225% since 1990, accounting for 1.47% of world emissions.¹⁰⁰

4. Conclusion & future recommendations

Plastic waste can be effectively processed through pyrolysis to produce a valuable alternative fuel source. Pyrolysis of plastic waste results in high-performance oil, offering environmental sustainability and reducing the dependence on fossil fuels while also addressing the issue of plastic waste disposal. Extensive experimental research has been conducted to optimize the pyrolysis process for extracting oil from plastic waste, leading to critical findings summarized below:

- Thermal pyrolysis of plastic waste often yields low-quality liquid oil and requires high heating temperatures and extended maintenance times. To address these challenges, catalytic pyrolysis of plastic waste has been introduced.
- Various catalysts have been found to enhance the efficiency of the pyrolysis process by improving the quality of liquid oil and gas products while reducing the required heating temperature and time. Notable catalysts researchers use include ZSM-5, HZSM-5, FCC, Al₂O₃, Red Mud, and natural zeolite (NZ).
- Natural zeolite is increasingly being utilized as a catalyst in pyrolysis due to its availability and cost-effectiveness.
- Catalyst modifications, such as metal doping (e.g., Co, Ni, Zn, and Mo) on acidic catalysts, have been shown to enhance catalyst activity. Catalysts with larger surface areas and varying acidity levels can influence gas and liquid oil production differently.

Further studies can improve the efficiency of the pyrolysis process for plastic waste, such as exploring the potential of generated liquids and gases with high heating values as alternative energy sources.

- Using the huge surface area of pyrolysis heat for environmental applications such as heavy metal adsorption and pollutant removal from wastewater and air.
- Assessing how heating temperatures, maintenance time, plastic waste composition, and catalyst use affect the pyrolysis process and final product quality.
- Investigating advanced catalyst modifications, including thermal, acidic, and metal doping treatments, to enhance catalytic activity and properties.

Data availability

The authors confirm that the data supporting the findings of this study are available within the article.

Conflicts of interest

The authors declare no conflict of interest.

Nomenclature

ABS	Acrylonitrile butadiene styrene
BTX	Butene toluene xylene
C–C	Carbon–carbon
Co–Mo/Z	Cobalt–molybdenum/zeolite
CSBR	Conical spouted bed reactor
Cu–Al ₂ O ₃	Copper–aluminum trioxide
FCC	Fluidized catalytic cracking
HDPE	High-density polyethylene
HHV	High heating value
HCs	Hydrocarbons
HZSM-5	Hydrogen zeolite Socony mobile-5
LDPE	Low-density polyethylene
MPW	Municipal plastic waste
MSW	Municipal solid waste
NZ	Natural zeolite
PE	Polyethylene
PET	Polyethylene terephthalate
PP	Polypropylene
PS	Polystyrene
PVC	Polyvinyl chloride
SA-1	Silicon aluminium-1
TGA	Thermo-gravimetric analysis
ZSM-5	Zeolite Socony mobile-5

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