



A review on Transforming plastic wastes into fuel

K. Manickavelan^a, S. Ahmed^a, K. Mithun^{a,*}, P. Sathish^a, R. Rajasekaran^b, N. Sellappan^a

^a Department of Engineering, Mechanical Engineering Section, University of Technology and Applied Sciences - Salalah, Salalah - Oman

^b Department of Engineering, Chemical Engineering Section, University of Technology and Applied Sciences - Salalah, Salalah - Oman

Abstract

The application of plastics in various sectors led to its increased production globally and this demand, in turn, caused an overflow of plastic waste in landfills, illegal dumping in the sea, and environmental pollution. To overcome this issue, several alternatives for managing plastic wastes have been developed and among them, reuse, recycling, and energy recovery methods are highly acknowledged methods. Nonetheless, recycling methods come with certain disadvantages like mixing and segregation of wastes, high labour costs associated with segregation and processing, by-product disposal, and its usage. Researchers have shifted their focus to energy recovery systems because of these drawbacks. Extensive research in this area led to the development of converting waste plastics into liquid fuel through the process called pyrolysis. The pyrolysis process can thermally degrade plastics in the absence of oxygen producing oil and monomers. The temperature has the most impact on the pyrolysis process and depending on the types of plastic wastes, the pyrolysis temperature varies between 300 – 800 °C. The oil yield due to the variation in temperature varies between 45 – 95 wt.% and the calorific value of the oil has been observed to be in the range of 9679 – 11428.5 kCal/kg, which is similar to the other commercial fuels. Also, the review indicates that it is possible to extract up to 84% of fuel from 1-kg plastic at 360 °C. As a result, following refining/blending with conventional fuels, pyrolysis oil can be utilised as an alternate source of energy and transportation fuel. Apart from the temperature, the other influencing factors include, the reactor design and its size, pressure, heating rate, residence time and feedstock composition. The pyrolysis process was examined in terms of plastic types and primary process factors that impacted the end result, such as oil, gaseous, and char. Temperatures, reactor types, residence duration, pressure, catalysts, and other critical factors were examined in this work. Furthermore, the study examines technological problems and current advances.

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1. Introduction

Environmental problems and energy demand concerns have increased the global attention on recycling pathways. However, due to low recycling rates and the ever-expanding use of plastics has led to an exponential growth in the plastic waste generation. Thus, necessitating the development of new waste re-

fining technologies [1]. It is estimated that in the Sultanate of Oman alone, the percentage of plastics in the municipal solid waste (MSW) constitutes to be about 21% and by 2025 globally, the MSW is expected to rise by 2600 million tonnes per year. Plastics have high molecular weight ranging from thousands to millions. The excessive molecular size is the main cause for the non-biodegradable properties of plastics, making them persistent in soil environment for a long time. Plastics, fundamentally, are differentiated depending on their composi-

*Corresponding author tel. no: +968-96726334

Email address: mv.kulkarni@sct.edu.om (K. Mithun)

tion, and normally reported based on their proximate analysis. Proximate analysis refers to a method for determining the chemical properties of the plastic compound based on four elements (1) moisture content, (2) fixed carbon, (3) volatile matter, and (4) ash content [2]. Particularly, the ash content and volatile matter influence oil production. High ash content favours gas and char formation and on the other hand high volatile matter favours liquid oil production [3]. It has been observed that high carbon ratio in the plastics favours producing products with high calorific value. The plastics listed in Table 1, have C ratio of 63.94%, 85.6%, 86.88%, 91.57% and 63.94% for High-density polyethylene (HDPE), Low-density polyethylene (LDPE), polypropylene (PP), Polystyrene (PS) and Polyethylene terephthalate (PET), respectively. Depending on the chemical structure, plastics have different thermal decomposition temperatures. Usually for plastics listed in Table 1, the thermal decomposition starts at 350 °C. However, if the desired output is other than liquid, then the operating temperature should be above 500 °C, which helps in producing gas and char. Research indicates that plastics such as PET and PVC produced little liquid yield and some plastics like PVC will never be used in the pyrolysis process as they produce harmful gases with harmful substances as by-products [4].

Table 1: Proximate analysis of various plastic types

Plastic Type	Moisture (wt.%)	Fixed carbon (wt.%)	Volatile matter (wt.%)	Ash content (wt.%)	Reference
HDPE	0.00	0.00	99.92	0.08	[5]
	0.00	0.01	99.81	0.18	[6]
LDPE	0.3	0.00	99.70	0.00	[7]
PP	0.00	0.09	99.9	0.01	[6]
PS	–	0.1	99.9	–	[8]
PET	0.1	11.8	88.1	–	[8]
Waste Plastics	0.41	0.28	96.88	2.43	[9]

As shown in Table 2, plastics such as PET finds its use in household applications, in packaging industry, mineral water bottles, fruit juice containers and cans, etc. PET is also used in other applications such as printing sheets, magnetic tapes, X-ray films, etc. Since, most applications use PET, its pyrolysis has been observed to yield a liquid of 23.1 wt.% and gas of 76.9% [10, 11]. Acidic characteristics have also been observed in the pyrolysis oil that makes it difficult to directly blend with conventional fuels and/or use it directly in IC engines [12]. Another major contributor to the waste plastics generation from Table 2 is HDPE.

HDPE due to its low cost, high strength properties, ease of forming and break resistance properties is used in several applications. Some applications are listed in Table 2. In a work by Ahmad et al. [6] a steel reactor was used to pyrolyze HDPE at temperatures ranging from 300 to 400°C. Nitrogen was employed as the fluidising medium. At 300 °C, 33.05 wt.% of solid residue was obtained and at 350°C, a total of 80.88 wt.% liquid was collected. Kumar and Singh [13] used a semibatch

reactor to conduct a thermal pyrolysis investigation of HDPE at a higher temperature of 400–550°C. They noted that the thermal decomposition of waste HDPE can be enhanced to produce useful products by using appropriate catalysts. Catalysts are observed to increase the chemical reaction and help in distributing hydrocarbons to obtain pyrolysis liquid that has properties nearly similar to conventional fuels such as diesel and petrol. The most typical catalysts that were employed in this process included zeolite, alumina, and zirconium oxide. Also, the impact of different catalysts on pyrolysis of HDPE is being explored by a variety of researchers. However, the details about the use of the catalyst in the pyrolysis process will be discussed in detail in the sections to follow.

Low-density polyethylene (LDPE) plastics due to their excellent water resistance are used in a wide variety of applications. Bagri and Williams [14] and Marcilla et al. [15] used LDPE as a raw material in the pyrolysis processes for obtaining the liquid fuel oil, a fixed-bed reactor at 500°C with a heating rate of 10°C/min and a batch reactor at 550°C with a heating rate of 5°C/min and liquid yields of 95 and 93.1 percent, were reported by them, respectively [11].

The raw materials derived from waste plastics will play a decisive role in the transformation of the petrochemical industry by 2030 and with technological development, one-third of the plastics entering the global market will be manufactured from recycled plastics [16]. However, recycling of plastics waste must meet several obstacles and problems, along with fiscal unfeasibility. There arises a slew of technological hurdles to overcome, when dealing with increasingly difficult to melt plastic items, such as multi-layer materials or polymers that include many toxic compounds, such as brominated flame retardants, raw material availability, raw material selection, pre-treatment, choice of reactor, etc., [17].

However, before discussing the technical challenges, it is important to discuss various plastic recycling methods. Figure 1 lists the four main plastic recycling methods (primary, secondary, tertiary and quaternary).

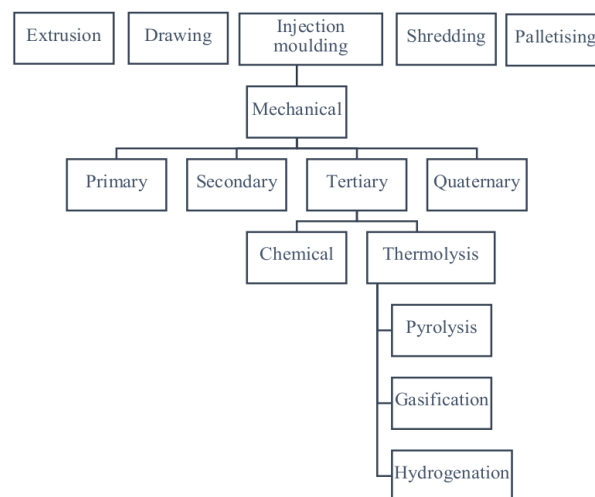


Figure 1: Various approaches for recycling of plastic wastes [19]

Table 2: Municipal Waste Sources, major plastic types from MSWs and pyrolysis products [18]

Source	Types of Solid Waste	Major Plastic Types from MSWs	Pyrolysis Products from waste plastics from MSWs
Residential	Food wastes, paper, cardboard, <i>plastics</i> , textiles, leather, garden wastes, wood, glass, metals, ashes, special wastes (e.g., bulky items, consumer electronics, white goods, batteries, oil, tyres), detergent bottles and household hazardous wastes.	PE, PP, PS, PET, HDPE	Waxes, paraffins, olefins, Benzoic acid, vinyl terephthalate
Industrial and automotive	Housekeeping wastes, packaging products, food wastes, construction hazardous wastes, ashes, <i>plastics & polymers</i> , special wastes.	PUR, PMMA, PA6,	Waxes, paraffins, olefins, Benzene, methane, ethylene, NH ₃ , HCN, Caprolactam
Construction & Demolition	Wood, steel, concrete, dirt, <i>plastic doors</i> , etc.	PUR, PVC	Benzene, methane, ethylene, NH ₃ , HCN, HCl (<300 °C).
Municipal Services	Street sweepings; landscape and tree trimmings; general wastes from parks, beaches, and other recreational areas; Sludge Process, <i>single use plastic bags</i> (manufacturing, etc.)	PE, PP	Waxes, paraffins, olefins.
Agriculture	Spoiled food wastes, agricultural wastes, hazardous wastes (e.g., pesticides), <i>plastics used for storing pesticides</i> , etc	PE, HDPE	Waxes, paraffins, olefins

PE=Polyethylene, PP=Polypropylene, PS=Polystyrene, PA-6=Polyamide 6, PMMA=Polymethyl methacrylate, PET=Polyethylene terephthalate, PUR=Polyurethane resin, PVC=Polyvinyl Chloride, HCl=Hydrochloride

(a) Primary recycling

In this process, the uncontaminated single-use plastic after sorting out or recovered from plastic wastes having properties and characteristics close to virgin materials is recycled [20, 21]. This method needs a better sorting technique as plastics recovered from MSW may not be suitable and useful for recycling [19]. To obtain better materials than the original products, many times clean scarp is added during the recycling process. Often techniques such as injection moulding, blow moulding and other mechanical recycling techniques are used in primary recycling technique [21] and is also one of the simplest methods for recycling plastics. But the process also carries a certain disadvantage like it puts a limit on the number of cycles that waste plastics can be recycled [22].

(b) Secondary recycling

Secondary recycling (SR) refers to the transformation of scrapped thermoplastics into products that are less demanding than compared to the original products. But looking at both primary and secondary techniques, these are well-established techniques and are widely applied in the transformation of plastic wastes into useful products [23]. As

an example for SR, polyolefins are used in the preparation of flooring tiles [19]. SR is also referred to as mechanical recycling [22] and involves cutting, separation of contaminants, and segregation followed by processing, milling, washing, adding pigments and additives for obtaining the granulated form. These are further used for preparing useful products through techniques such as injection moulding, blow moulding, screw extrusion and so on.

(c) Tertiary recycling

In this method, plastics are completely broken down into chemical component materials [24] that help in the production of raw materials used for making plastic components, and thus giving an opportunity for the recyclers to employ this method for recycling giving preference over the primary and secondary techniques [19]. For example, for tertiary recycling, glycolysis of PET into diols and dimethyl terephthalate can then be used to make virgin PET [20]. Tertiary methods can be sub-classified into chemical and thermolysis methods. Thermolysis is further classified into pyrolysis, gasification and hydrogenation as seen from Figure 1. Among these, pyrolysis process is an area where most of the research on recycling plastic wastes has taken

place.

(d) **Quaternary recycling**

In this process, the energy from waste plastics is recovered by burning or firing them. Fuel obtained from scrapped tyres, generally known as Tyre-derived fuel (TDF) is an example of the quaternary recycling method.

2. Technical Challenges

Pyrolysis oil as observed from various literature is made up of various hydrocarbons, many of which are partially oxygenated with the presence of water, ash, and charcoal. The composition of the oil is much influenced by the various process parameters and must overcome the challenges posed by these process parameters. The toxicity of oil and its instability in air possess furthermore challenges for having to be used directly into the engine. Although, the main goal of the pyrolysis of plastic waste oil is to use it in engines directly, but the existing technology does not allow it to do so. The presence of charcoal, water and ash particles needs to be removed before blending it along with conventional fuels and or to replace the existing conventional fuels, raw material availability, viscosity, combustion behaviour, wax formation, the choice of reactors, etc., are other challenges that are discussed below.

2.1. Raw material availability

Even with various approaches, attempts to popularise and make the plastic recycling methods economical have failed in the past due to the non-continuous / non-steady supply of consistent quality raw materials [25]. According to Ragaert et al. [26], the economics of plastic recycling depends on the quantity of the raw material available at any given point in time. Previously, China was the largest importer of plastic wastes, off late it has banned all imports and thus large volume of waste plastics needs to be treated locally [25]. But the ban by China has opened the door of opportunities in waste management sector such as, awareness of reuse and recycling wastes, preserving the ecosystem, employment generation, alternate fuels, alternate materials in construction sector, etc. However, to tap the opportunities, it is necessary to have a steady flow of consistent quality of raw materials, with bans and strict laws by several countries in place supply of raw materials may not be a problem in the future.

2.2. Feedstock selection

The plastic wastes collected from various sources are heterogeneous. The types of polymers used, vary for different applications. The plastic wastes, if segregated at the source of generation could solve most of the problems associated with raw material availability and selection. But for this, awareness among the public is essential.

Polyolefin occupies a major share of plastic items, owing to their chemistry and synergistic reasons, they are considered an ideal choice as a feed for pyrolysis process. Also, most applications use PET and PVC plastics, which contributes largely towards waste plastics generation, yet they are not an ideal choice

for the pyrolysis process. Upon thermal degradation of PET and PVC, the latter has corroded the equipment due to the release of the chlorine containing compounds and renders the oil halogenated. Alternatively, PET tends to decompose into phthalic acids deteriorating the oil quality [25].

2.3. Pre-treatment

Many plastics come with different forms and sizes that make it mandatory to uniformly size them before they are used as a raw material for various other steps. Thus, this step adds an extra cost for the entire process [25].

2.4. Material feeding

One of the most difficult tasks in plastic recycling is the material feeding job, as non-uniform size and shape of waste plastics pose a direct challenge during certain recycling processes. Some recycling methods include screw feeders for processing but plastic wastes when in the form of sheet, wrap around the screw feeders and form a lump/melt of semi solid plastic and make it difficult to continue with the feeding [25].

2.5. Wax formation

One of the principal results of the pyrolysis of plastics, particularly polyolefins, is wax. When wax is the primary result of plastic pyrolysis, the recovery system must be built specifically for waxes. When using standard condensing systems, the wax tends to condense on the condenser walls, making it harder to reclaim the material during the process.

2.6. Choice of reactor

Although there are many types of reactors in use, only four important types of reactors have been reviewed and compared (refer Table 3) in this section.

2.6.1. Fluidized-bed reactor (FB reactor)

In this type of reactor (Figure 2a), due to the presence of solid particles and the fluidisation gas (flowing continuously) on the bed, makes the bed to be in a fluid-like state. The desired reaction occurs when the raw material is fed into the reactor [27]. The FB reactor are known for their ease of operation and less maintenance cost. They are considered the best for continuous operation and provide a degree of freedom when choosing different fluidisation agents and offers excellent heat and mass transfer capabilities. But when the operating conditions are poorly selected possibility of bed defluidization can occur and plastics tend to stick to the surface of the bed particles, thus making the operation a little complicated. Even some times feeding can also be difficult due to particle size restriction [28].

2.6.2. Fluid Catalytic cracking reactor (FCC reactor)

A chemical process (Figure 2b) used to produce gasoline and distillate fuels with the help of catalyst [29]. It is one of the widely used methods in conventional refinery [28]. The catalyst in the solid form is made fluid when the hot vapour and fluid are fed into the FCC. Now, since the catalyst is in the liquid form

it can easily move around between reactor and regenerator vessels in the FCC reactor. Thus, the catalysts and heat are used to break down the larger gas molecules into molecules of petrol, butane, distillates etc., [29]. In this process, during the cracking process, carbon gets deposited on the catalyst and thus will be referred to as catalyst coke. The main disadvantage of carbon deposition is that the ability of the catalyst to crack the oil gets reduced. In the process, flue gas is produced as a cause of regeneration, passes through the environmental control equipment, and finally discharged into the atmosphere.

2.6.3. Continuous Stirred Tank Reactor (CSTR)

In this type of reactor, the product(s) of the reaction concomitantly moves out of the vessel when the reactants, solvents and reagents enter the reactor. Thus making the reactor an important tool in the processing of the chemicals continuously and hence the name CSTR. The advantages of this reactor are effectively mixing, easy accessibility to the interior of the reactor, the cost of reactor construction, and the capability to work under steady-state with uniform properties [30]. Another characteristic feature of CSTR is that the material's composition inside the reactor is the same as the output composition, which is a function of the reaction rate and residence time.

2.6.4. Screw Reactor

Screw reactors contains a tubular reactor and a screw conveyor. This reactor can be used to pyrolyze thermoset plastics, which are otherwise considered as a difficult to treat plastics. The reactor can effectively and efficiently remove chlorine in the case of mixed plastic waste. Also, by varying the screw length and screw speed, it is possible to vary the residence time. Excellent heat transfer and selective zone heating are the added features of screw reactors.

3. What is Pyrolysis?

The thermal degradation of long-chain polymer molecules into smaller and simpler ones is known as pyrolysis. In the absence of oxygen, the technique needs extremely high temperatures for a short duration. The three main products produced by pyrolysis are oil, gas, and char, which are important in industries such as manufacturing and refining.

Many researchers selected pyrolysis because it can create a large volume of liquid oil (up to 80 wt.%) at a modest temperature of roughly 500 °C [4]. Furthermore, pyrolysis is extremely adaptable since process parameters may be tweaked to enhance product yield based on preferences. The liquid oil generated may be utilised in various applications, including furnaces, boilers, turbines, and diesel engines, without any further treatment or upgrade [5]. Biomass pyrolysis oil has received a lot of interest as a more environmentally friendly fuel since it helps lower CO₂ levels in the atmosphere. In contrast to recycling, the process handling is significantly easier and more flexible because it does not require a thorough sorting method, making it less labour intensive [6].

Table 3: Reactor comparison for plastic thermolysis. Modified from [49]

	Reactor type			
	Fixed Bed	Vacuum pyrolysis	CSTR [#]	Screw type
Temperature control	P	S	G	P
Heat transfer	P	S	G	P
Particle size flexibility	S	G	S	S
residence time flexibility	G	G	G	G
process flexibility	P	S	S	S
Thermal mode operation	S	G	S	G
Catalytic mode operation	S	S	na	S
Value of obtained product	G	S	G	S
Scale-up flexibility	P	S	G	S
Economic feasibility	S	S	G	S

Values from various sources; P = Poor; S = Satisfactory; G = Good, na = not available in the literature

Pyrolysis produces a combination of molecules in the form of liquid or wax as the major products, depending on the process circumstances [10]. The liquid or wax that is produced can subsequently be utilised as a feedstock for refining chemicals or fuels [11, 12]. The primary pyrolysis products from various polymers are listed in Table 2. Some resins, such as PS, PA, and PMMA, have high monomer yields, which is of particular importance. However, municipalities collected plastic garbage is frequently a combination of different polymers, resulting in a mixture of these goods.

3.1. Types of Pyrolysis

Pyrolysis is mainly categorised into three types viz., slow, intermediate, and fast as shown in Figure 3. Literature indicate that fast pyrolysis liquid oil obtained can be used in internal combustion engines [11].

Slow pyrolysis includes the gradual heating of waste plastics at over 500°C in the absence of oxygen. Carbonisation is another name for slow pyrolysis. Solid charcoal is a major result of slow pyrolysis [11], where fast pyrolysis involves a great and rapid heating in the absence of air, often in the temperature range of 450 – 650 °C produces products such as char, gas, and organic vapours. In most cases, 60–75 wt.% of the feedstock is converted to oil [31]. Intermediate pyrolysis, also known as

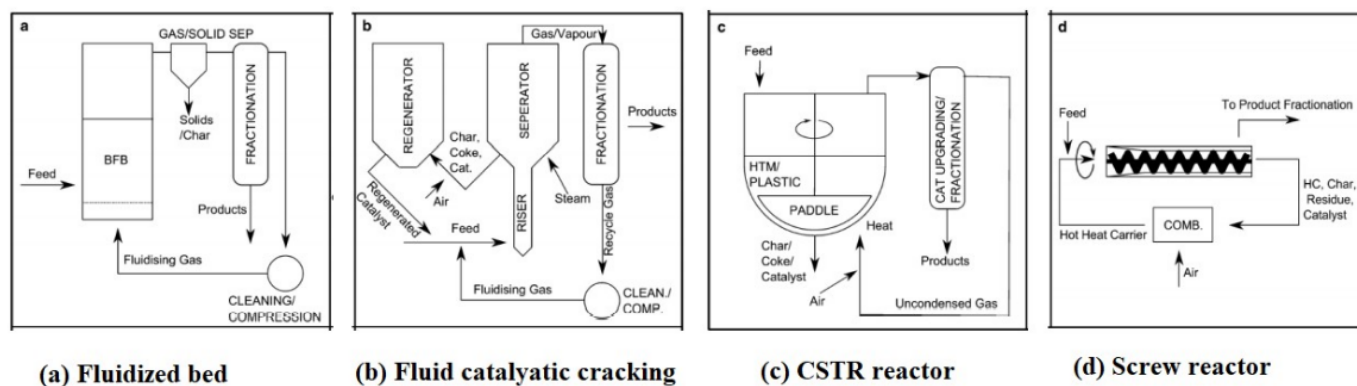


Figure 2: Common reactors for plastic pyrolysis [28]

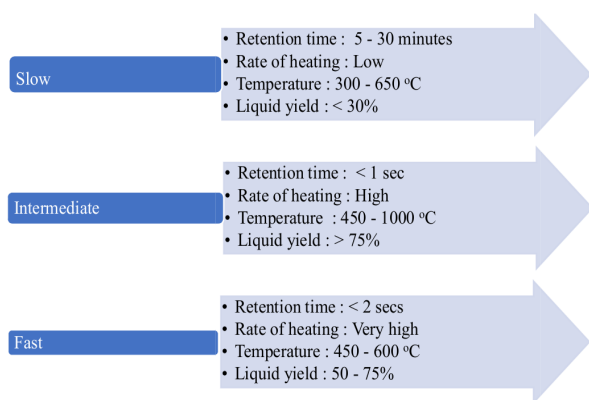


Figure 3: Pyrolysis types and their operating parameters and product yields [11]

flash pyrolysis is a rapid heating process with a short residence time of less than 1 second. Around 75% of the feedstock can be converted into liquid yield using the flash pyrolysis process.

3.2. Process Parameters influence on product yield

In pyrolysis, parameters are crucial for optimising product yield and composition. Temperature, reactor type, pressure, residence time, etc., are factors that impact the liquid oil output during pyrolysis. Table 4 lists the comparison of various parameters with the different reactors. Among the parameters, the temperature controls the cracking reaction; thus, treated as the most important operational parameter in pyrolysis. Depending on the plastic type and its chemical structure, the degradation temperature varies. Usually, the type of product required from pyrolysis is known to be influenced by temperature. For instance, if the char and gaseous product is desired, temperature more than 500 °C is preferred and in case liquid (oil) is desired then the temperature in the range of 300 – 500 °C is preferred for plastics such as PET, PP, PS, etc. [2].

Besides temperature, reactors play an important role in improving the reaction efficiency and producing the desired end product and a few of the important reactors have already been discussed in the previous sections. Pressure and residence time are temperature-dependent factors that influence the pyrolysis

process, especially at lower temperatures. Higher pressure increases the gaseous yield, yet most research is conducted at atmospheric pressure only. The effect of residence time becomes less apparent at higher temperatures. However, at temperature below 450 °C both pressure and residence time factors should be given much importance.

Catalysts are known to and have been tried to enhance the reaction efficiency and improve the hydrocarbon distribution in the pyrolysis process. The use of catalyst helps in obtaining the pyrolysis oil that has characteristics close to regular fuels such as diesel and petrol. The catalyst such as Zeolite was used in the pyrolysis by Miskolezi et al. [32]. It was proved that Zeolite helps in reducing impurities and enhances the efficiency of liquid yield. A study on the use of bentonite clay in the form of pelletized catalyst for the pyrolysis of plastic wastes such as PS, PP, LDPE, and HDPE was taken up by Supattra Budsareechai et al. [33]; observations revealed that the liquid oil produced, had a higher calorific value than compared with the experiments that used catalyst. Maximum production of gas was reported in the case of pyrolysis of PP with an alumina-loaded catalyst by Obali et al. [34]. A pyrolysis comparison study of PP and PS using thermally activated natural zeolite catalyst and acid (HCl) activated natural zeolite catalyst indicated more gas formation using the latter catalyst by Syamsiro et al. [35]. A summary of the effect of process parameters is shown in Table 4.

3.3. Liquid fuel properties of plastic pyrolysis oil

The fuel properties of waste LDPE, HDPE, PP and mixed plastics using the pyrolysis process are summarised in Table 5. The experimental calorific value of waste plastics discussed in Table 4 are close to the commercial standard values as depicted in Table 5.

However, work by Onwudili et al. [40] noted that PS had a lower calorific value than polyolefin plastics because of the presence of an aromatic ring in the chemical structure, which had a lower combustion energy than aliphatic hydrocarbons. Also, Sharuddin et al. [2] in their research review paper noted that, because of the presence of benzoic acid in PET and chlorine compound in PVC, reduced the fuel quality, PET and PVC had the lowest calorific value. The viscosity measurement

Table 4: Effect of process parameters on plastic waste pyrolysis

Process parameters	Findings
Effect of heating rate and operating temperature	Higher heating rates and operating temperature causes breaking of bond and thus helps in the production of smaller molecules [36]. Rise in temperature causes easier conversion by reducing the aliphatic content [37].
Effect of pressure	Coke is formed as a result of condensation of reactive fragments at lower pressure [36]. During thermal degradation of PE plastics, the reaction pressure was seen to have a significant impact on the distribution of degradation products, providing a mechanism to regulate product distribution [38].
Residence time	Usually, residence time increases the conversion. Secondary conversion of primary products happens with longer residence time thereby producing more tar, thermally stable products, and coke [37].
Presence of gases such as N ₂ , Ar, O ₂ or H ₂ .	Presence of gases have an influence over the kinetics, equilibrium, and mechanism. The gases also help in heat generation and product dilution [36, 37].
Catalyst effect	To fast-track the chemical reaction, catalysts are employed. The most widely utilized catalysts in the pyrolysis process are Zeolite, silica (SiO ₂), calcium oxide (CaO), and alumina (Al ₂ O ₃). These catalysts help to shorten the reaction time and enhances the reaction rate [39].

of waste plastics was also made, as it is an important property, and is defined as the fluid resistance to flow [2, 40]. The viscosity values determined at different temperatures can be noted from Table 5.

Except for LDPE and mixed plastics from Table 5 and PS [2], the viscosity of HDPE and PP were close to the viscosity of commercial standard diesel value from Table 6. Pour point refers to the temperature at which a fluid ceases to flow owing to an increase in viscosity and it is also an important quality specification for diesel fuels [41]. Generally, greater aromatic content and lesser wax (paraffin) is observed in fuels with lower PoP [2, 41]. HDPE, mixed plastics, PP from Table 5 and PS [2] have lower PoP than commercial diesel, which has a PoP of 6 °C as shown in Table 5. The values obtained indicate that pyrolysis oil is rich with aromatic content and possesses low calorific value compared to commercial diesel and petrol. One of the important

properties to avoid or prevent fire accidents during storage of fuel is its flash point (FP). The FP is the lowest temperature at which a solvent may ignite a flammable combination in air near the liquid's surface. The lower the flash point of a liquid solvent, the easier it is to ignite it [42]. From Table 5 it is observed that waste plastics possess low FP temperature compared to commercial fuels and it is essential to exercise precaution while handling and storing the pyrolysis oil.

3.4. By-products of the plastic pyrolysis

Along with oil, as discussed previously, the pyrolysis process also produces char and gas as by-products. Researchers have noted that process parameters such as heating rate, the presence of gases such as N₂, Ar, O₂ or H₂, pressure, residence time, and temperature play a greater role in the by-product generation. Table 7 lists the by-products of the pyrolysis process.

Char as a by-product is formed due to (1) slow heating at a low temperature (2) longer residence time. This by-product has certain advantages like being used as an adsorbent in water treatment to remove heavy metals through an upgrading treatment [2], its low sulphur content makes it usable as a fuel as the calorific value of char is about 18.8 MJ/kg, and can be used in laying of roads and building materials [51], char-based sensors and supercapacitors [52, 53, 54, 55]. The pyrolysis of PVC and PET compared to polyolefins and PS produced a large amount of gases. The composition of the gas mainly depends on the type of material used in the pyrolysis process. For instance, plastics such as HDPE, PET, PVC produced gases such as H₂, CH₄, C₄H₁₀, C₂H₆, C₃H₈, etc. Interestingly, PET produced additional gases such as CO₂ and CO, while HCl was produced by PVC. The gases produced using the pyrolysis process also has a good calorific value (PE and PP have a CV of 42 and 50 MJ/kg, respectively) [44]. For maximising the gas production in the pyrolysis process, a longer residence time and higher temperatures are required. But these come with a price, that's lower oil production [56].

4. Recent Developments in plastic waste pyrolysis

Most of the recent works on waste plastic pyrolysis has taken place in the areas related to the use of renewable energy, biorefineries and bimetallic catalysts. The details of which have been discussed below.

Pyrolysis process can be treated as one of the sources of renewable energy, but the process has some drawbacks like it needs an external source of energy to heat the reactors and thus pollution associated with it has also to be taken care of. To deal with these issues, researchers have focussed their attention on the use of solar energy for heating the reactors. Akililu et al. [62] focussed on design and testing a solar-assisted pyrolysis process for the production of liquid fuel from HDPE plastics. The results of the study indicated that 1360 kWh/m² of solar energy was required to produce 14.2 litres of liquid fuel from HDPE waste. Further, they noted that the heating value of the produced liquid fuel was 41.8 MJ/kg. Chaouki Ghenai et al. [63] designed a grid-tied solar PV power system to meet the energy demand

Table 5: Characteristics of pyrolysis oil

Waste plastic Type	Type of Reactor	Characteristics of pyrolysis oil					Reference
		V (cSt)	ρ , g/cc	FP, °C	PoP, °C	CV, kcal/kg	
HDPE	Fixed bed pyrolysis batch reactor	1.980 ^a	0.7477 ^a	14	<-15	9829.35	[43]
		ASTM D445	IP 131/57	ASTM D93	ASTM D97	Bomb Calorimeter 12/58	
	Semi-batch	3.3 ^a	0.8006 ^c	10	18	10,573.71	[5]
		IS:1448 P:25	IS:1448 P:16	IS:1448 P:20	IS:1448 P:10	IS:1448 P:6	
	Pilot scale two stage reactor using batch system	2.319 ^a	0.7991 ^c	<10	24	10234.226	[44]
		ASTM D 445	ASTM D1298	ASTM D93	ASTM D 97	ASTM D240	
Horizontal Steel	5.08 ^a	0.89 ^c	48	-5	9679.732	[2, 6]	
	IP 71/87	IP160/87	IP 34/85	IP 15/67	IP 12/80		
LDPE	Batch reactor	1.24 ^a	0.773 ^c	–	–	–	[45]
		ASTM D445	ASTM D1298	–	–	–	
	Tube reactor	1.117 ^a	–	22	–	11089.87	[46]
Mixed plastic bags (PE, PP)	Self-designed	0.8 ^a	0.735 ^a	29	–	11428.5	[47]
		–	–	–	–	–	
Mixed Plastics	Self-designed	2.8 ^b	0.76 ^a	35	–	10809.27	[48]
		–	–	–	–	–	
	Self-designed	–	0.7365 ^c	22	<-20	11262	[37, 49]
Polyolefin	Self-designed	–	0.68 ^a	29	–	–	[50]
		–	–	–	–	–	
PP	Horizontal Steel	4.09 ^a	0.86 ^c	30	-9	9751.434	[2, 6]
		IP 71/87	IP160/87	IP 34/85	IP 15/67	IP 12/80	

Table 6: Commercial fuel values

Fuel Type	V, cSt	ρ , g/cc	FP, °C	PP, °C	CV, kcal/kg	Reference
Gasoline	1.17	0.780	42	–	10157.74	[43]
Diesel	1.9 – 4.1	0.807	52	6	10277.2	[43]

Viscosity – V; Flash Point – FP; Ploud Point – PoP; Density – ρ ; Calorific Value – CV

^a@ 40°C; ^b @ 25°C; ^c @ 15°C

of the BFK type magnetic rotary stirred pyrolysis reactor. The main objective of their study was to employ some form of renewable energy for the thermal chemical conversion process. A solar powered mobile unit, capable of converting waste plastics into fuel, which is comparable with conventional fuels has been developed by a team of students at IIT – Madras. The best part of this technology is that - being a mobile unit, can be driven directly to the place of waste collection and then process the waste. It is a total decentralised mechanism that needs

no necessity to erect a processing plant and to transfer plastic wastes from the point of collection to the point of processing. The unit is capable of handling plastic bags, packaging material and other plastic items that are not normally collected for recycling by ragpickers can be used as raw materials. The team claims that waste plastic oil can be used as an alternative in generators, boilers, furnaces, pumps and diesel-powered vehicles [64]. Guozhan Jiang et al. [65] performed a process simulation and a techno-economic analysis of pyrolysis of mixed plastic

Table 7: By-products of plastic pyrolysis.

Waste plastic Type	Pyrolysis temperature	Crude oil (wt. %)	Residue (wt. %)	Gas (wt. %)	Wax (wt. %)	References
PE	500	93	0	7	–	[57]
PP		95	0	5	–	
	300	69.82	1.34	28.84	–	[6]
Mixed	370 – 420	90	5	5	–	[58]
HDPE	500	44.32	1.29	25.4	28.99	[5]
	350	80.88	1.88	17.24	–	[6]
	440	74	17	9	–	[59]
Mixed plastic	300-400	60-80	7-10	10-20		[49]
	400 - 500	76.7 ± 1.2	16 ± 1.2	7.3 ± 0.5		[47, 60]
	500	~ 55	~ 5	~ 40	–	[9]
	800	73	23.5	30.4	–	[61]
LDPE	600	51.07	–	19.35	–	[45]
	400	45	–	26	–	[46]
PET	500	23.1	–	76.9	–	[11]

waste (MPW) containing PVC that utilised molten solar salt as the heating medium. They observed that by adding calcium carbonate (CaCO_3) to the salt mixture, a practical way to remove chlorine from PVC was possible. Further, to melt the salt, the electricity generated from the non-condensable pyrolysis gas or concentrated solar power was used. A work on solar energy driven dielectric microwave oven was taken up by Debadyoti Ghosh et al. [66], the work involved use of sodium bentonite clay as a catalyst to endorse the conversion efficiency. HDPE and LDPE wastes were pyrolyzed in the temperature range of 450 °C to 500 °C under sub-atmospheric pressure inside the reactor chamber (vacuum chamber). Due to the vacuum pyrolysis, the harmful gases produced was considered negligible.

Pyrolysis-based biorefineries have a high potential for converting waste into energy and other useful goods, which might aid in the development of circular economies. Miandad et al. [67] worked on pyrolysis-based biorefineries that can convert plastic and biomass waste into energy and has the capability to convert them into valuable products. They used natural zeolite catalysts in a pilot scale reactor fabricated. Plastics such as PS, PE, PP, and PET in mixed ratio was used in the study. Work on co-pyrolysis of mahua seeds (MH) with PS and waste nitrile gloves (WNG) was investigated by Ranjeet Kumar Mishra and Kaustubha Mohanty [68]. The PS and WNG wastes were mixed with MH in varying proportions. The results of blending showed that waste plastics at 20 wt.% yielded a maximum liquid (44.18 ± 1.2 wt.% and 45.89 ± 1.4 wt.% for MH + WNG and MH + PS respectively), which was higher than the thermal pyrolysis of individual MH (39.26 ± 1.2 wt.%). Further, characterization of the obtained co-pyrolytic oil revealed that the oil could be used either directly or blended with the diesel after little up-gradation.

Bimetallic catalysts are regarded as an important type of heterogeneous catalysts with exceptional catalytic characteristics compared to their separate metal components [69]. Because of the existence of two metals, they can develop new and char-

acteristic features. Ganjar Fadillah et al. [70] employed bimetallic catalysts in the pyrolysis of plastic waste to biofuel. Cia et al. [71] employed a carbon-based Fe-Ni bimetallic catalyst for rapid pyrolysis of plastic trash. In the procedure, a fixed bed reactor was employed, and the plastic-to-catalyst ratio was kept at 2:1 at a temperature of 500 °C. The researchers indicated that the Fe-Ni bimetallic catalyst was critical in the oxygen reduction process. Because of the presence of an oxygen-containing functional group on the surface, the catalyst is also capable of avoiding corrosion on its surface. Zhou et al. [72] employed a bimetallic Ni-Fe/ZrO₂ catalyst in their research involving polystyrene waste. The findings demonstrated that bimetallic catalysts increased catalytic activity in waste breakdown.

Also due to the pandemic and post-pandemic stage, the use and disposal of PPEs has increased and to effectively deal with the disposed PPEs which are mainly derived out of plastics, cold plasma technology in pyrolysis system has been adopted. This technology is effective in dealing with infectious medical plastic wastes, along with the high temperature of pyrolysis. The technique involves use of electrons to break the chemical bonds in plastics compared to the conventional pyrolysis. However, the process comes with a disadvantage that it needs an advanced cooling system [73, 74].

5. Conclusion

Pyrolysis process has the capacity to transform most plastic wastes into various valuable products such as liquid oil, wax, and char over other thermal treatment methods. Pyrolysis can be achieved via thermal or catalytic process; use of catalyst helps in attaining higher output of liquid oil for most polymers. The process's long-term viability is unquestionable, given that the amount of plastic waste at any point in the year in each nation is in the millions of tons. Waste management becomes more efficient using the pyrolysis process, which requires less landfill capacity, produces less pollution, and is also more cost-

effective. Furthermore, because of the presence of the pyrolysis process for decomposing plastic into useful energy fuel, the reliance on non-renewable energy sources such as fossil fuels may be minimized, therefore alleviating the growth in energy demand. Among the various plastics, PE and PP plastics have the capacity to yield a greater amount of crude oil when subjected to pyrolysis at 500°C as compared to other plastics. Temperature below 500°C leads to production of more gases and other residues.

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