

Thermal pyrolysis as a potential method for the management of plastic waste in developing countries

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ABSTRACT Plastic is a cheap and versatile material. The production and manufacture of plastics has risen tremendously to cater the needs of the growing world population, even more in the effort of fighting the COVID-19 pandemic. Lack of proper technology and human irresponsibility contribute to the mismanagement of plastic waste. Hence, the severity of plastic waste pollution is heightening, and the Earth and all living things are suffering the consequences. This review explores thermal pyrolysis as a more effective method to manage plastic waste in developing countries like Malaysia. Thermal pyrolysis is compared to existing plastic waste management methods. Factors influencing the yield and composition of pyrolysis products are also being discussed. These include feedstock type, reactor type, temperature, residence time, pressure, and fluidizing gas type and flow rate. Several topics such as the manipulation of pyrolysis parameters and the use of Appropriate Technology-based reactors, are raised as possible areas for further research.

KEYWORDS: Pyrolysis; plastic waste; waste management; thermal degradation; plastic upcycling

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Review Article

INTRODUCTION

Where there is higher demand for a commodity, there is a rise in the supply of such commodity and vice versa (Gordon, 2022). This law of supply and demand is applicable to the manufacture of plastics around the world. Plastic is a versatile material due to its desirable physical and chemical properties – high flexibility, impermeable to liquid or water resistant, high chemical resistance, and sustainable towards physical elements that cause material degradation. Growth in world population and low-cost production further endorse the manufacture of plastics over other types of material. In 2015, Malaysia manufactured USD 580.1 million worth of plastics. The Grand View Research forecasted the market of plastics to expand by 6.6% annually. Figure 1 shows the plastic market growth by product in Malaysia, within the forecast period from 2014 to 2025, and the revenue measured in USD million (Grand View Research, 2015).

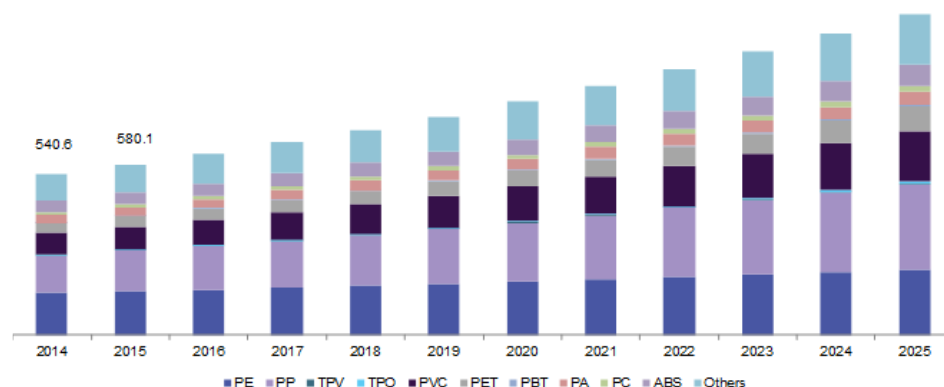


Figure 1. Plastic market growth by product in Malaysia from 2014 to 2025 (Grand View Research, 2015).

The COVID-19 pandemic has raised the manufacture of plastics to a higher level worldwide. This involves the production of personal protective equipment and single-use plastic items such as gloves, containers, bags, face masks and various packaging material, as a preventative measure towards the spread of the virus. This phenomenon did not just occur in developed countries such as China where over 240 tons of single-use medical plastic waste was generated by the hospitals in Wuhan at the peak of COVID-19 (Zuo, 2020), and in Singapore where 1470 tons of plastic waste was generated from takeaway packaging (Bengali, 2020; Elangovan, 2020). This phenomenon also occurred in developing nations such as the Phillipines where 309 tons more medical waste was generated in Manila on a daily basis (Bengali, 2020), and in Bangladesh where approximately 14500 tons of hazardous medical plastic waste was generated after the first month of lockdown (Sultana & QuaziShahreenHaq, 2020).

Plastic waste is a worsening universal issue due to the lack of a proper waste management system. In other words, the existing technology and methods applied for plastic waste disposal are insufficient to handle the amount of plastic waste being generated at a high rate. From a global material balance study on plastics, it is reported that 79% of total plastics are being discarded as waste, whereas 9% of total plastics are being recycled (UNEP, 2018). Most countries resort to getting rid of plastic waste in landfills. At present, 40% of plastic waste in the United States, and 31% of plastic waste in the European Union are being disposed in landfills (Brivio et al., 2018). Being the top-8th country with improper management of plastic waste in 2018 (Figure 2) (Sakthipriya, 2022), Malaysia disposes a huge proportion (approximately 89%) of waste in landfills (Manaf et al., 2009). The total average recyclable material per capita is 0.12 kg/person/day, with roughly 5% of municipal solid waste being recycled in a proper manner which includes the separation of wastes (Agamuthu & Fauziah, 2011). The use of landfills for plastic waste disposal is reaching its limit due to depleting availability of landfill space as a result of urbanisation.

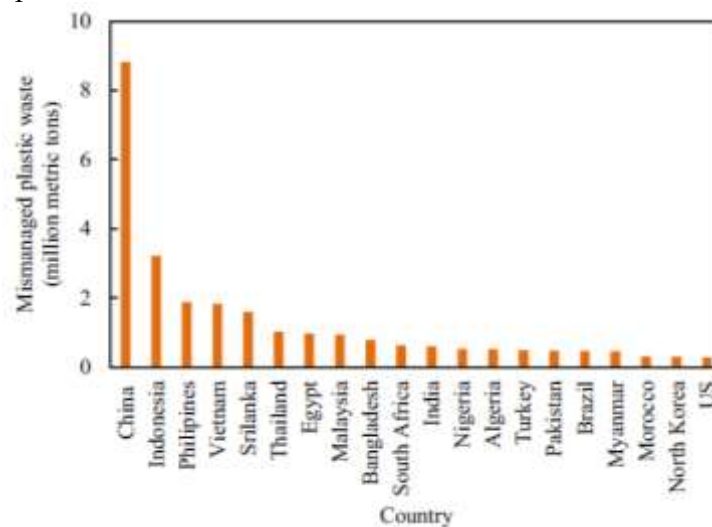


Figure 2. Top 20 countries with improper management of plastic waste in 2018 (Sakthipriya, 2022).

Plastic waste, being non-biodegradable, has a number of negative impacts on living things and the environment. One of the major problems is the breakdown of plastic waste into microplastics as they are exposed to the natural elements. Microplastics will easily release toxic substances which contaminate water sources such as rivers and the ocean. The uptake of microplastics by aquatic plants and animals leads to microplastics incorporation into the food chain, eventually resulting in the accumulation of plastic molecules in higher-level organisms via biological magnification (Rochman et al., 2013; Saad, 2016). Table 1 shows the human ingestion of microplastics via consumption of shellfish. Table 2 classifies the quantity and size range of microplastics collected

from various sites in Malaysia (Fauziah et al., 2021). Inappropriate plastic waste disposal also causes blockages in drainage systems and waterways, leading to flash floods when there is heavy rain, as well as uncontrolled breeding of pests which act as diseases-transmitting agents (Kehinde et al., 2020).

Table 1. Human ingestion of microplastics via consumption of shellfish (Fauziah et al., 2021).

Country	Microplastic ingestion (particles/person/year)	References
Belgium	479	(Cho et al., 2019)
Canada	8407	(Cho et al., 2019)
China	6636	(Cho et al., 2019)
France	145-1139	(Cho et al., 2019)
Italy	11970	(Cho et al., 2019)
South Korea	521	(Cho et al., 2019)
Spain	87	(Cho et al., 2019)
United Kingdom	341	(Cho et al., 2019)
Malaysia	5750	(Hamid et al., 2020)

Table 2. Quantity and size range of microplastics collected from various sites in Malaysia (Fauziah et al., 2021).

Location	Type of beach	Quantity	Microplastic size range	References
Cherating River, Pahang	Residential/fishery/tourism areas	0.0070±0.0033 particles/m ³ (mainstream)	<0.1 mm; 0.1-5.0 mm	(Pariatamby et al., 2020)
Cherating Mangrove, Pahang	Mangrove	0.0051±0.0053 particles/m ³	<0.1 mm; 0.1-5.0 mm	(Pariatamby et al., 2020)
Kuantan Port, Pahang	Fishing	0.14-0.15 pcs/L	1.0-5.0 mm	(Khalik et al., 2018)
Kuala Nerus Port, Terengganu	Fishing	0.13-0.69 pcs/L	1.0-5.0 mm	(Khalik et al., 2018)
Pulau Karah/Bidong/Redang, Terengganu	Recreational	983 particles (average 3.3 particles/L)	Fibre size: 310-1200 µm Fragment size: 12-75 µm	(Amin et al., 2020)
Skudai River, Johor	Fishing/recreational	200±80 particles/kg	0-100 µm; 101-500 µm; 501-1000 µm; 1001-5000 µm	(Sarijan et al., 2018)
Tebrau River, Johor	Fishing/industrial	680±140 particles/kg	0-100 µm; 101-500 µm; 501-1000 µm; 1001-5000 µm	(Sarijan et al., 2018)

This article puts pyrolysis forward as a potential method to improve plastic waste management in Malaysia. Generally, pyrolysis is the decomposition of long-chain polymer molecules into simpler molecules by subjecting the material to high temperature. The process is usually carried out in the absence of oxygen. Plastic waste pyrolysis is less laborious and more flexible in terms of the type and condition of the feedstock. This process will result in plastic waste volume reduction as well as energy recovery. The three main products of plastic pyrolysis are solid char, liquid oil and gas. Gas produced can be reused to generate heat and power. Solid char is useful for enhancing soil quality, or as recycled material for road construction, or as absorbents for wastewater treatment (Sharuddin et al., 2016; Aguado et al., 2008). Liquid oil can be utilised as an alternative fuel in diesel engines. However, waste plastic pyrolysis oil may require upgrading or chemical treatment before it is

suitable for commercial use (Buekens & Yang, 2014). The yield and quality of plastic pyrolysis products can be altered by adjusting the process parameters. Topics such as existing methods of plastic waste management, thermal pyrolysis and its process parameters, and future outlook of thermal pyrolysis will be discussed in the following sections.

EXISTING METHODS OF PLASTIC WASTE MANAGEMENT IN MALAYSIA

Plastic waste management methods commonly implemented in Malaysia include landfilling, incineration and mechanical recycling. Landfilling is widely carried out due to the method being economically affordable. However, with the high rate at which plastic waste is being generated, the space taken up for landfill use is enlarging rapidly and will eventually reach its limit. Another issue is the degradation of plastics in landfills as they are exposed to natural elements, resulting in air, water and soil pollution (Panahi et al., 2019).

Incineration guarantees complete decomposition of plastic waste so that it will not occupy space such as in landfills. Heat is generated during incineration, and this is a form of energy recovery (Ahamed et al., 2020; Al-Salem et al., 2009b; Antelava et al., 2019). Unfortunately, the consequences of incinerating plastic waste include the release of toxic gases and irritants into the atmosphere, which is detrimental to living things and the environment. Among the toxic substances, dioxins expose humans to higher risk of cancer as well as reproductive abnormalities (Demetrious & Crossin, 2019).

Mechanical recycling of plastic waste is considered to be tedious, time and energy-consuming, and laborious. Stringent requirements in terms of physical condition and chemical composition of plastic waste to be recycled need to be fulfilled. Recycling involves separating the plastic waste into individual plastic types, shredding the plastics, cleaning or washing, drying and quenching (Rigamonti et al., 2014). High costs are incurred due to labour work and energy consumption. There is also a limit to the number of times a plastic material can be recycled before it is degraded to an unacceptable quality. As a result, only a small percentage (15 to 20%) of plastic waste managed to be recycled (Al-Salem et al., 2014). Besides that, carbon emissions from the mechanical recycling process contribute to global warming (Ansar et al., 2021; Sati et al., 2011).

The advantages and disadvantages of these existing methods of plastic waste management in Malaysia are summarized in Table 3.

Table 3. Advantages and disadvantages of existing methods of plastic waste management in Malaysia.

Method	Advantages	Disadvantages
Landfilling	Economic disposal method. Straightforward and convenient.	Occupies enlarging area of space. Waste degradation due to natural elements leads to environmental pollution.
Incineration	Waste is decomposed completely. Energy recovery through heat generation.	Release of toxic gases and irritants lead to air pollution. Emission of greenhouse gases contributes to global warming.
Mechanical recycling	Plastic material is used for a different purpose instead of being discarded.	Tedious, labour-intensive, high consumption of time and energy, hence incurring high costs. Carbon emission contributes to global warming.

FACTORS TO CONSIDER FOR THERMAL PYROLYSIS

Type of Feedstock

The chemical properties of the plastic feedstock have a significant influence on the yield and composition of pyrolysis products, especially in terms of moisture content, fixed carbon, volatile matter and ash content, which can be measured using proximate analysis (Kreith & Goswami, 2004). Table 4 shows the proximate analysis of various plastic types. Plastics with high volatile matter produce higher oil yield, whereas plastics with high ash content produce higher char and gas yield (Abnisa & Wan Daud, 2014). Plastics are good materials to be pyrolysed for the production of oil as they generally have very high volatile matter and low ash content. Table 5 is a summary of plastic pyrolysis studies on different types of plastic feedstock.

Table 4: Proximate analysis of various plastic types (Abnisa & Wan Daud, 2014).








Plastic type	Symbol	Moisture content (wt%)	Fixed carbon (wt%)	Volatile matter (wt%)	Ash content (wt%)	Reference
Polyethylene terephthalate (PET)		0.46	7.77	91.75	0.02	(Zannikos et al., 2013)
		0.61	13.17	86.83	0.00	(Heikkinen et al., 2004)
High-density polyethylene (HDPE)		0.00	0.01	99.81	0.18	(Ahmad et al., 2013)
		0.00	0.03	98.57	1.40	(Heikkinen et al., 2004)
Polyvinyl chloride (PVC)		0.80	6.30	93.70	0.00	(Hong et al., 1999)
		0.74	5.19	94.82	0.00	(Heikkinen et al., 2004)
Low-density polyethylene (LDPE)		0.30	0.00	99.70	0.00	(Park et al., 2012)
		-	-	99.60	0.40	(Aboulkas et al., 2010)
Polypropylene (PP)		0.15	1.22	95.08	3.55	(Jung et al., 2010)
		0.18	0.16	97.85	1.99	(Heikkinen et al., 2004)
Polystyrene (PS)		0.25	0.12	99.63	0.00	(Abnisa et al., 2014)
		0.30	0.20	99.50	0.00	(Park et al., 2012)
Polyethylene (PE)		0.10	0.04	98.87	0.99	(Jung et al., 2010)
Acrylonitrile butadiene styrene (ABS)		0.00	1.12	97.88	1.01	(Othman et al., 2008)
Polyamide (PA) / Nylons		0.00	0.69	99.78	0.00	(Othman et al., 2008)
Polybutylene terephthalate (PBT)		0.16	2.88	97.12	0.00	(Heikkinen et al., 2004)

Table 5. Plastic pyrolysis studies summary.

Plastic type	Reactor type	T (°C)	Q (°C/min)	P	t (min)	Product yield (wt%)			Other	Reference
						Gas	Liquid	Solid		
PET	Fixed bed	500	10	-	-	76.90	23.10	0.00	-	(Cepeliogullar & E. Putun, 2000)
	-	500	6	1 atm	-	52.13	39.89	8.98	-	(Fakhrhoseini & Dastanian, 2013)
HDPE	Batch	450	-	-	60	5.80	74.50	19.70	-	(Ahmad et al., 2015)
	Batch	550	5	-	-	16.30	84.70	0.00	-	(Lee et al., 2002)
	Semi-batch	400	7	1 atm	-	16.00	82.00	2.00	Stirring rate: 200 rpm; FCC catalyst 10 wt%	(Miskolczi et al., 2004)
	Semi-batch	450	25	1 atm	-	4.10	91.20	4.70	Stirring rate: 50 rpm; FCC catalyst 20 wt%	(Abbas-Abadi et al., 2013)
	Fluidized bed	500	-	-	60	10.00	85.00	5.00	Silica alumina catalyst	(Luo et al., 2000)
	Fluidized bed	650	-	-	20-25	31.50	68.50	0.00	-	(Marcilla et al., 2009)
	Horizontal steel	350	20	-	30	17.24	80.88	1.88	-	(Mastral et al., 2002)
PVC	Vacuum batch	520	10	2 kPa	-	0.34	12.79	28.13	HCl yield: 58.2 wt%	(Cepeliogullar & E. Putun, 2000)
	Fixed bed	500	10	-	-	87.70	12.30	0.00	-	(Miranda et al., 1999)
LDPE	Batch	430	3	-	-	8.20	75.60	7.50	Wax yield: 8.7 wt%	(Onwudili et al., 2009)
	Batch	550	5	-	-	14.60	93.10	0.00	-	(Uddin et al., 1997)
	Pressurized batch	425	10	0.8-4.3 MPa	60	10.00	89.50	0.50	-	(Fakhrhoseini & Dastanian, 2013)
	Fixed bed	500	10	-	20	5.00	95.00	0.00	-	(Bagri & Williams, 2002)
	Fluidized bed	600	-	1 atm	-	24.20	51.00	0.00	Wax yield: 24.8 wt%	(Marcilla et al., 2009)
	-	500	6	1 atm	-	19.43	80.41	0.16	-	(Williams & Williams, 1999)
PP	Batch	380	3	1 atm	-	6.60	80.10	13.30	-	(Ahmad et al., 2015)
	Batch	740	-	-	-	49.60	48.80	1.60	-	(Sakata et al., 1999)
	Semi-batch	400	7	1 atm	-	13.00	85.00	2.00	Stirring rate: 200 rpm; FCC catalyst 10 wt%	(Lee et al., 2002)
	Semi-batch	450	25	1 atm	-	4.10	92.30	3.60	Stirring rate: 50 rpm; FCC catalyst 10 wt%	(Abbas-Abadi et al., 2014)
	Horizontal steel	300	20	-	30	28.84	69.82	1.34	-	(Fakhrhoseini & Dastanian, 2013)
	-	500	6	1 atm	-	17.76	82.12	0.12	-	(Demirbas, 2004)

Table 5. Plastic pyrolysis studies summary (continue).

Plastic type	Reactor type	T (°C)	Q (°C/min)	P	t (min)	Product yield (wt%)			Other	Reference
						Gas	Liquid	Solid		
PS	Batch	500	-	-	150	3.27	96.73	0.00	Zn catalyst (Catalyst/Polym er: 5 w/w)	(Lee et al., 2002)
	Batch	581	-	-	-	9.90	89.50	0.60	64.9 wt% of liquid is styrene	(Onwudili et al., 2009)
	Pressurized batch	425	10	0.31- 1.6 MPa	60	2.50	97.00	0.50	-	(Adnan et al., 2014)
	Semi-batch	400	7	1 atm	-	6.00	90.00	4.00	Stirring rate: 200 rpm; FCC catalyst (Catalyst/Polym er: 10 w/w)	(Demirbas, 2004)
Mixed	Fluidized bed	730	-	-	-	35.00	48.40	2.20	75% polyolefins (PE, PP), 25% PS, <1% PVC	(Kaminsky et al., 1996)
	Bubbling fluidized bed	650, 728	-	-	3.25 s (650 °C), 2.98 s (728°C)	37.00 (650 °C), 42.00 (728°C)	48.00 (650 °C), 44.00 (728 °C)	15.00 (650 °C), 14.00 (728 °C)	46% LDPE, 30% HDPE, 24% PP	(Demirbas, 2004)

T: Temperature; Q: Heating rate; P: Pressure; t: Residence time
Nitrogen is used as the fluidizing gas for all experiments.

Based on previous pyrolysis experiments mentioned in Table 5, PET is recommended to be used as pyrolysis feedstock when gaseous product is desired. Gas obtained from pyrolysis is usually used as energy to raise the temperature of the reactor. The oil yield of PET pyrolysis is very low. From the pyrolysis of HDPE, the oil obtained has very low sulfur content (0.019%), so it is considered clean to the environment (Kumar & Singh, 2011). The use of PVC as pyrolysis feedstock is discouraged because the process releases hydrogen chloride which is corrosive and toxic, potentially damaging the pyrolysis equipment as well as the environment. Chlorine content in pyrolysis feedstock should not exceed 1 wt% in order to produce high quality oil (Demirbas, 2004). The oil yield of PVC pyrolysis is very low. When oil is desired as the main pyrolysis product, PS is highly recommended to be used as the feedstock because it is easily degradable without the use of any catalyst, and a very high volume of oil is obtained from the process (97 wt%) (Onwudili et al., 2009).

Type of Reactor

A key requirement for the pyrolysis process is to reach high temperatures in the absence of oxygen, and for a short duration. Thus, it is necessary to design the pyrolysis reactor such that it can maintain higher heat transfer and minimise residence time (Musale et al., 2013). Being mindful that liquid oil is the targeted pyrolysis product, lower heat transfer rate and longer residence time will produce higher yield of char and gas.

Batch reactors function as an entirely closed system, whereas semi-batch reactors allow material introduction and elimination as the pyrolysis reaction occurs. The former reactor promotes high conversion rates by increasing the residence time of a material, but shortfalls include complexity in upscaling to meet higher product demands, high labour costs, and low throughput among batches resulting in product instability (Miskolczi et al., 2011). The latter reactor also incurs high labour costs, but it is more time efficient in terms of material incorporation without the need to heat and

cool the reactor from batch to batch (Worstell, 2015). These reactors have simple configuration, incur minimal cost for construction, and provide convenient control of pyrolysis parameters. They are suitable for thermal and catalytic pyrolysis between 300 °C and 800 °C. A semi-batch reactor was claimed to be energetically sustainable as its energy balance analysis was positive (+700 kJ/kg) as discovered by (López et al., 2011).

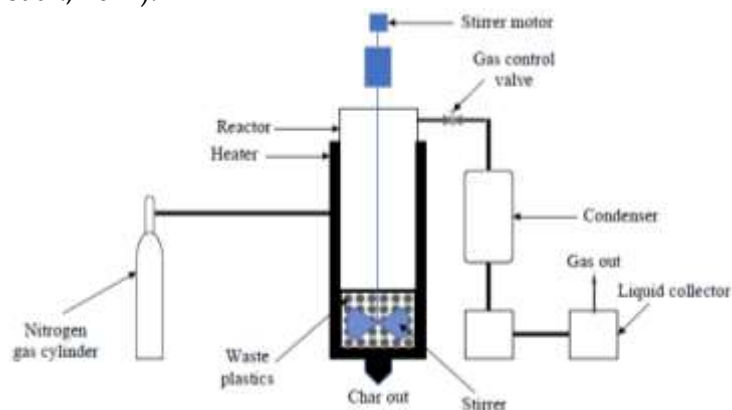


Figure 3. Diagram of a batch reactor (Jahirul et al., 2022).

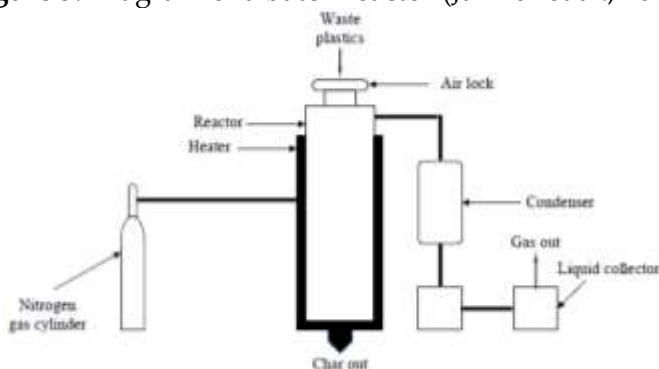


Figure 4. Diagram of a semi-batch reactor (Jahirul et al., 2022).

Fixed bed reactors are preferable when the desired product obtained from pyrolysis is char as oil and syngas are minimally produced in this type of reactors. This reactor has a simple design, and it is easy to construct. The use of feedstock for this reactor is flexible in terms of size. The reason behind char being the main product of pyrolysis using a fixed bed reactor is due to the reactor being capable for lower heating rate and extended residence time. The reactor is unable to sustain a uniform temperature profile. It requires high input of feedstock, and its batch configuration has diminished its cost-effectiveness (Jahirul et al., 2022). Fixed bed reactors were used in secondary pyrolysis (Onu et al., 1999; Vasile et al., 2001). Liquid and gaseous products from primary pyrolysis were quickly channeled into the reactor.

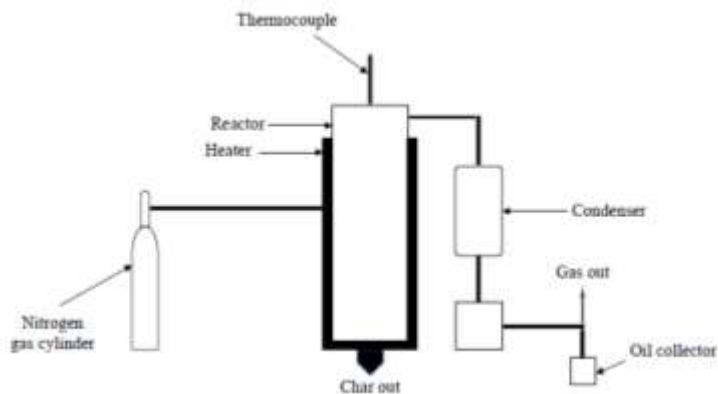


Figure 5. Diagram of a fixed bed reactor (Jahirul et al., 2022).

A fluidized bed reactor is an improved version of the fixed bed reactor such that a continuous feeding mechanism is incorporated for higher efficiency in the production of oil, up to 80 wt% (Mastellone et al., 2002; Yin et al., 2007). It has a solid bed, preferably consisting of sand for increased surface area and heat transfer (Beheshti et al., 2015). Cyclones are utilised to separate char from the pyrolysis products to prevent secondary cracking. A fluidised bed reactor was used to pyrolyse PE-type plastics at temperatures and residence times between 500 °C to 600 °C and 12.4 s to 20.4 s respectively (Zhao et al., 2020). Oil yield decreased (81.2 wt% to 28.5 wt%) and syngas yield increased (8.2 wt% to 56.8 wt%) with the rise in temperature and prolonged residence time. An energy balance analysis was also performed on the fluidised bed reactor (Zhou et al., 2021). The authors found that this reactor is not feasible for large-scale manufacturing operations as the pyrolysis of 1 kg of plastic waste with energy content of 45.8 MJ resulted in products with energy content of 45.5 MJ, at the expense of 5 MJ electricity.

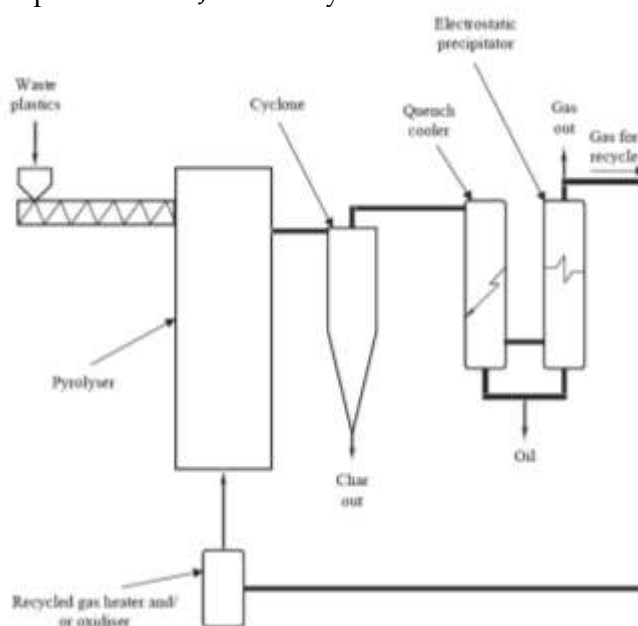


Figure 6. Diagram of a bubbling fluidised bed reactor (Jahirul et al., 2022).

A conical spouted bed reactor is useful for keeping close interaction between phases as well as preventing agglomeration of particles in the bed by increased rate of collision. Fused polymers have enhanced uniform covering due to the cyclic movement of sand particles (Aguado et al., 2005). There is flexibility in the size distribution and density of particles introduced into the reactor (Fogler, 2016). Some issues that may be encountered when using conical spouted bed reactors include catalyst input and entrainment, and pyrolysis products collection (Hafeez et al., 2018). The reactor's design has higher complexity as several pumps are included in the system. Hence, it is harder to construct and incurs higher capital expenditure. A conical spouted bed reactor was used to pyrolyse waste plastic at 450 °C, 500 °C and 600 °C (Arabiourrutia et al., 2012). The pyrolysis products mainly consist of wax. In another experiment at 500 °C and involving the use of HY zeolite catalyst, 68.7% of gasoline fraction was obtained (Elordi et al., 2007).

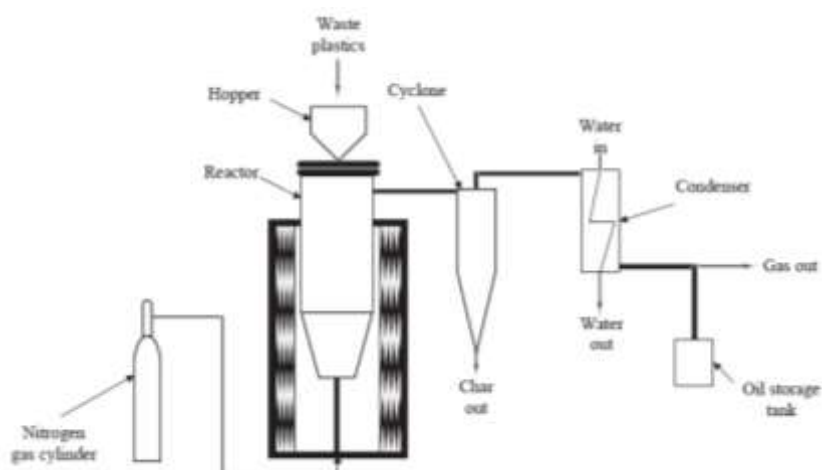


Figure 7. Diagram of a conical spouted bed reactor (Jahirul et al., 2022).

An auger reactor or screw reactor is tubular-shaped and operates in continuous mode. The screw is part of the transportation system for plastic waste to be channeled into the reactor. It also plays a role in heat transmission through the tubular wall of the reactor. The screw is an important component for the mixing of plastic waste and regulating the residence time of feedstock in the reactor. The size of the auger reactor can be minimised so that it is portable. Using the reactor at the site of feedstock availability saves operating expenses as charges on feedstock transportation are avoided (Badger & Fransham, 2006). Faults or lack of precision in the reactor's design will result in the deposition of polymeric materials within the reactor due to inefficient heat transmission and management of temperature (Qureshi et al., 2020). An auger reactor was used to carry out the co-pyrolysis of plastic waste and wood at 450 °C and 525 °C (Bhattacharya et al., 2009). Oil obtained from the process had lower oxygen and water content as well as higher calorific value compared to pyrolysis oil from a batch reactor. In another study, syngas produced from a 1000 kW pyrolysis was put through combustion and generated 4200 kW of power, resulting in 3200 kW available power (Martínez et al., 2013).

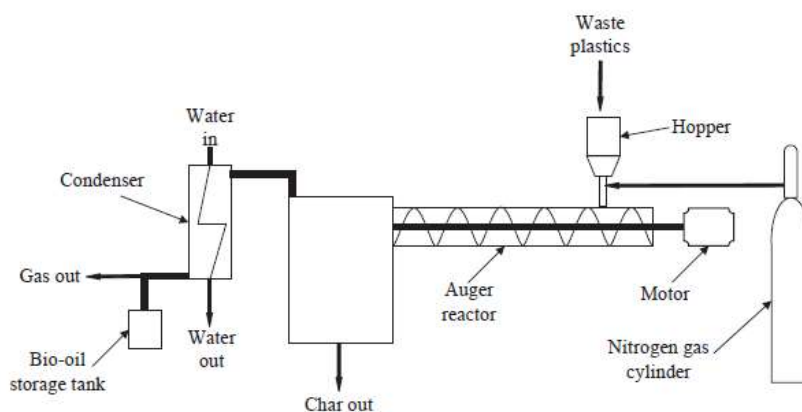


Figure 8. Diagram of an auger reactor (Jahirul et al., 2022).

A microwave reactor requires the mixing of plastic waste with microwave-absorbent material such as carbon, in order to convert microwave radiation energy into thermal energy for higher intensity of pyrolysis (Lam & Chase, 2012). Direct transmission of microwave energy to the feedstock promotes heating without spending lots of time raising the surrounding temperature (Fernandez et al., 2011). Hence, heating rate and processing speed are enhanced, and lower cost is incurred. Variation in the heating efficiency of different types of feedstock due to altered dielectric properties may be an obstacle in the implementation of microwave reactors for pyrolysis (Lam & Chase, 2012). In a pyrolysis study involving the use of carbon and shredded tyres as microwave

absorbers separately, the former resulted in higher oil yield, whereas the latter resulted in higher char yield (Undri et al., 2014). It was also found that gas products with energy content of 6.1 MJ were produced from the microwave pyrolysis of 1 kg of plastic waste, expending 5 MJ of electrical energy, so the energy efficiency was 89.5% (Zhou et al., 2021).

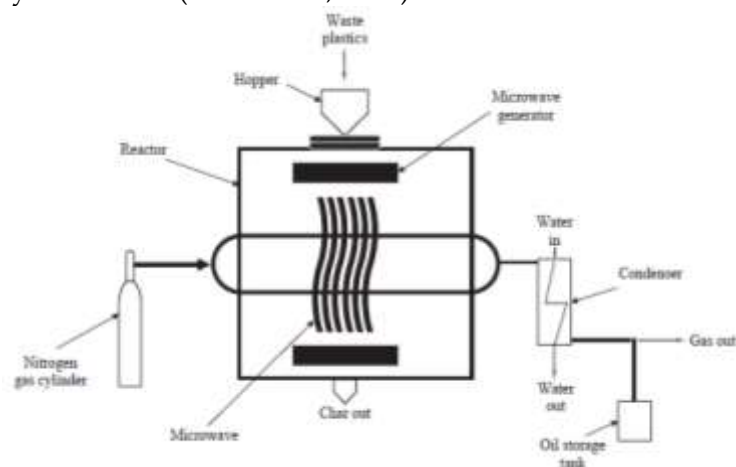


Figure 9. Diagram of a microwave reactor (Jahirul et al., 2022).

Residence Time

Residence time is defined as the average duration a particle is confined in the reactor. It is a key parameter which influences the distribution of pyrolysis products (Mastral et al., 2002). Non-condensable fluid products were increasingly yielded with prolonged residence time (Ludlow-Palafox & Chase, 2001). Longer residence time allows higher conversion of polyolefin polymers into liquid products of high thermal stability (Mastral et al., 2003). Residence time has a more prominent influence on yield and composition of pyrolysis products compared to temperature (McCaffrey et al., 1995), favouring gas production in secondary plastic pyrolysis reactions (Conesa et al., 1994). Prolonged residence time resulted in larger fraction of condensable liquid in the pyrolysis of end-of-life tyres (Al-Salem et al., 2009a) as well as higher conversion rate of PET (Andel et al., 2009).

Mastral et al. (2002) performed the pyrolysis of HDPE using a fluidised bed reactor to study the relationship between residence time and pyrolysis product distribution. Residence time was altered from 0.64 s to 2.6 s, and temperature was kept constant at 640 °C, 685 °C, 730 °C, 780 °C and 850 °C for separate experiments. At 640 °C, the yield percentage of wax varied from 79.7 wt% at 0.8 s to 68.5 wt% at 1.5 s, and that of gas altered between 11.4 wt% at 1 s to 31.5 wt% at 1.5 s. At 780 °C, the yield percentage of gas was 86.4 wt% and that of oil was 9.6 wt% at 1.34 s. The authors suggested that the pyrolysis process was most efficient when carried out between 750 °C to 780 °C for longer duration.

Onwudili et al. (2009) performed the pyrolysis of LDPE and PS separately. At zero residence time, the pyrolysis of LDPE produced 91.1 wt% oil and 8.70 wt% gas at 450 °C, whereas PS was totally thermally degraded into liquid oil with some solid char and gas. After 120 minutes, the yield percentage of oil decreased to 61 wt% and that of gas increased to 28.5 wt% for LDPE pyrolysis. For PS pyrolysis, the yield percentage of char and gas increased to 3.4 wt% and 1 wt% respectively.

Temperature

Temperature is the parameter that moderates the main decomposition behaviour and cracking reaction of plastics. Temperature rise causes stronger vibration and breaking of Van der Waals force between molecules so that carbon chain is broken (López et al., 2011). At higher temperatures, temperature has a more prominent effect on pyrolysis product distribution compared to product concentration, plastic feedstock type and residence time (Westerhout et al., 1998). Plastic pyrolysis at

high temperatures mainly produced gas, whereas solid was mainly produced at temperatures below 700 °C (Scott et al., 1990). The temperature at which plastic degradation begins varies for different plastic types. For instance, HDPE, LDPE, PP and PS begin to degrade at above 325 °C (Chin et al., 2014; Marcilla et al., 2005), 360 °C (Williams & Williams, 1999), below 400 °C (Jung et al., 2010), and approximately 300 °C (Onwudili et al., 2009) respectively. Gas production increases with the rise in temperature, as long-chain molecules break down into smaller organic molecules. There is a tendency for secondary reactions to occur, leading to the conversion of oil and wax into gas. This can be observed in a study conducted by (Singh & Ruj, 2016), whereby pyrolysis products with heavier hydrocarbon content were formed (Adrados et al., 2012).

Karaduman et al. (2001) conducted the pyrolysis of PS using a free-fall reactor under vacuum. Temperature was varied between 700 °C and 875 °C. The maximum yield of liquid oil (32 wt%) was at approximately 750 °C, whereas that of styrene was at 825 °C. Solid yield was reduced while gaseous yield was increased with the rise in temperature.

In the study conducted by Mastral et al. (2002) involving the pyrolysis of HDPE using a fluidised bed reactor, temperature and residence time were altered between 640 °C and 850 °C, and 0.64 s to 2.6 s respectively. Gas yield increased from 64.2 wt% to 79 wt% as temperature increased from 685 °C to 730 °C, achieving a maximum yield of 86.4 wt% at 780 °C, but declined at 850 °C. There was no solid yield above 730 °C.

Pressure

Majority of pyrolysis experiments were conducted at atmospheric pressure. Hence, further research is required to find out the effect of pressure on the composition and yield of products. A study showed that the effect of pressure on the yield of pyrolysis products was more prominent at lower temperatures (Murata et al., 2004). Pyrolysis of HDPE was carried out in a continuous stirred tank reactor with varying pressure from 0.1 MPa to 0.8 MPa. At 410 °C, the production of gas increased from 6 wt% to 13 wt%, whereas at a slightly higher temperature of 440 °C, the gas product yield only increased from 4 wt% to 6 wt% as pressure was increased.

From the same study, it was found that higher pressure produces gases with smaller molecular weight. Pressure is involved in carbon-carbon (C-C) bonds scission in the plastics due to a link between double bond formation and C-C bonds scission. The researchers reported a decrease in the rate of double bond formation as pressure was increased. The C-C bonds scission involved in the thermal degradation of polymers are chain-end scission and random chain scission. Chain-end scission occurs at gas/liquid interface, and its occurrence is affected by pressure while its rate is proportional to the number of molecules. The resulting products of chain-end scission are volatile as a result of reactor contents dissipation. Random chain scission occurs in the liquid phase, and its occurrence is not pressure-dependent. Its rate is proportional to the number of C-C bonds. Random chain scission results in a decrease in the molecular weight of the polymer, and an increase in the product formation rate.

A study was conducted on the continuous pyrolysis of waste tyres using a conical spouted bed reactor pilot plant (Lopez et al., 2010). The reactor was operated between 425 °C to 500 °C, under vacuum at 25 kPa and 50 kPa, as well as at atmospheric pressure. Experiments under vacuum condition resulted in higher diesel fraction yield of liquid product. The carbon blacks resulting from the process had higher surface areas as pore blockage was reduced. The yield of gaseous product was higher and the yield of single ring (C₁₀) aromatic hydrocarbons was lower for experiments under vacuum.

Type and Flow Rate of Fluidising Gas

The fluidising gas functions as a carrier of vapourised products into the condenser. It must be inert so that it will not react with the pyrolysis products to form other by-products. Argon, ethylene, helium, hydrogen, nitrogen and propylene are used as fluidising gas. The composition of pyrolysis products is dependent on the molecular weight of the fluidising gas as shown in Table 6.

Table 6. Product yield and composition from the pyrolysis of PP with various types of carrier gas (Abbas-Abadi et al., 2014).

Gas	W_m	Condensed product yield (%)	Non-condensable product yield (%)	Coke (%)	Olefins (%)	Paraffins (%)	Naphthalenes (%)	Aromatics (%)	Olefins / paraffin ratio
H ₂	2	96.7	3.0	0.3	30.86	46.53	20.54	2.07	0.66
He	4	94.7	3.2	2.1	43.32	33.41	19.29	3.98	1.30
N ₂	28	92.3	4.1	3.6	44.63	32.87	17.23	5.27	1.36
Ethylene	28	93.8	5.1	1.1	41.76	34.76	19.75	3.73	1.20
Propylene	42	87.8	9.7	2.5	42.36	31.85	20.92	4.87	1.33
Ar	37	84.8	9.8	5.4	45.21	25.27	21.93	7.59	1.78
No gas	51.3	33.8	14.9	-	-	-	-	-	-

W_m : Molecular weight; T = 450 °C; Stirring rate = 50 rpm; Catalyst/PP = 0.1

Increasing molecular weight of the carrier gas results in decreasing yield of condensed product or liquid oil. Hydrogen which has the smallest molecular weight (2) produced 96.7 wt% liquid oil, whereas propylene which has a larger molecular weight (42) produced 87.8 wt% liquid oil. When no carrier gas was used, the yield of liquid oil dropped to 33.8 wt% (Abbas-Abadi et al., 2014). Formation of coke is dependent on the reactivity of the carrier gas. Although ethylene and propylene have similar molecular weight (28), higher reactivity of ethylene causes the chemical equilibrium to shift so that it has a higher yield of liquid oil (93.8 wt%) (Abbas-Abadi et al., 2014).

The typical choice of fluidising gas is nitrogen. It is easy and safe to handle, easy to acquire, and comes at an affordable cost (Sharuddin et al., 2016). Elevating the flow rate of fluidising gas enlarges the liquid and gaseous fraction in the products. At lower flow rates, the overall rate of plastic degradation is reduced, and the long duration of contact for the primary product increases coke precursor (BTX) formation with the secondary product (Lin & Yang, 2007).

FUTURE OUTLOOK

Further research needs to be done to establish the relationship between pyrolysis parameters on the yield and composition of pyrolysis products. This can be carried out by performing pyrolysis experiments with varying temperature, heating rate, residence time, pressure, fluidising gas flow rate etc., whilst comparing the results to those obtained in existing studies. Plastic pyrolysis should also be experimented with different reactors and the use of different catalysts. The effects of manipulating the reaction mechanism on the yield and quality of products need to be observed and analysed, implementing characterisation methods where necessary. As plastic feedstock type influences the yield and composition of pyrolysis products, further studies need to be conducted on the pyrolysis of various individual plastic types as well as mixtures of different plastics.

For the benefit of developing countries like Malaysia, research should be done on the application of Appropriate Technology-based plastic pyrolysis. This involves looking into the design and construction of pyrolysis reactors with materials and technology that are available and affordable to the local community, then performing an energy balance analysis to determine the efficiency of the pyrolysis reactor. Pyrolysis can be carried out using waste plastics that are common in the local area, and the yield and composition of products should be assessed. Liquid oil obtained from pyrolysis can be analysed and processed so that it is suitable for use as an alternative to non-renewable sources of fuel.

CONCLUSIONS

Thermal pyrolysis is an improved and effective method for plastic waste management. The existing methods commonly practised in Malaysia to manage plastic waste, such as landfilling, incineration and mechanical recycling, still impose negative effects on the environment. Thermal pyrolysis does not just help to reduce the volume of plastic waste, but it converts plastic waste into useful products such as oil for fuel, and char and gas as alternative sources of energy. Despite complexity of products resulting from the process, thermal pyrolysis has outperformed the existing practices of landfilling, incineration and mechanical recycling, in terms of efficiency and economically. The yield and composition of pyrolysis products are dependent on several factors, namely the choice of plastic feedstock, reactor, temperature, heating rate, pressure and residence time. Exploring the use of catalysts in plastic pyrolysis and implementing Appropriate Technology-based reactors are potential areas of research for the purpose of overcoming the plastic waste issue that is prevalent in developing countries like Malaysia.

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