Energy Conversion and Management 115 (2016) 308–326

Contents lists available at ScienceDirect

Energy Conversion and Management

journal homepage: www.elsevier.com/locate/enconman

Review

# A review on pyrolysis of plastic wastes

Shafferina Dayana Anuar Sharuddin, Faisal Abnisa *, Wan Mohd Ashri Wan Daud, Mohamed Kheireddine Aroua

*Department of Chemical Engineering, Faculty of Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia*

ARTICLE INFO

*Article history:*
Received 14 December 2015
Accepted 12 February 2016

*Keywords:*
Plastic wastes
Pyrolysis
Liquid product
Fuel
Energy recovery

ABSTRACT

The global plastic production increased over years due to the vast applications of plastics in many sectors. The continuous demand of plastics caused the plastic wastes accumulation in the landfill consumed a lot of spaces that contributed to the environmental problem. The rising in plastics demand led to the depletion of petroleum as part of non-renewable fossil fuel since plastics were the petroleum-based material. Some alternatives that have been developed to manage plastic wastes were recycling and energy recovery method. However, there were some drawbacks of the recycling method as it required high labor cost for the separation process and caused water contamination that reduced the process sustainability. Due to these drawbacks, the researchers have diverted their attentions to the energy recovery method to compensate the high energy demand. Through extensive research and technology development, the plastic waste conversion to energy was developed. As petroleum was the main source of plastic manufacturing, the recovery of plastic to liquid oil through pyrolysis process had a great potential since the oil produced had high calorific value comparable with the commercial fuel. This paper reviewed the pyrolysis process for each type of plastics and the main process parameters that influenced the final end product such as oil, gaseous and char. The key parameters that were reviewed in this paper included temperatures, type of reactors, residence time, pressure, catalysts, type of fluidizing gas and its flow rate. In addition, several viewpoints to optimize the liquid oil production for each plastic were also discussed in this paper.

© 2016 Elsevier Ltd. All rights reserved.

**Contents**

1. Introduction . . . 309
2. Pyrolysis of plastics . . . 309
   2.1. Polyethylene terephthalate (PET) . . . 310
   2.2. High-density polyethylene (HDPE) . . . 310
   2.3. Polyvinyl chloride (PVC) . . . 311
   2.4. Low-density polyethylene (LDPE) . . . 311
   2.5. Polypropylene (PP) . . . 311
   2.6. Polystyrene (PS) . . . 312
   2.7. Mixed plastics . . . 312
3. Process parameters condition . . . 312
   3.1. Temperature . . . 313
   3.2. Type of reactors . . . 313
      3.2.1. Batch and semi-batch reactor . . . 313
      3.2.2. Fixed and fluidized bed reactor . . . 314
      3.2.3. Conical spouted bed reactor (CSBR) . . . 315
      3.2.4. Microwave-assisted technology . . . 316
   3.3. Pressure and residence time . . . 317
   3.4. Catalysts . . . 317

* Corresponding author. Tel.: +60 162709281; fax: +60 379675319.
*E-mail addresses:* dayanareen@gmail.com (S.D. Anuar Sharuddin), faisal.abnisa@gmail.com (F. Abnisa), ashri@um.edu.my (W.M.A. Wan Daud), mk_aroua@um.edu.my (M.K. Aroua).

http://dx.doi.org/10.1016/j.enconman.2016.02.037
0196-8904/© 2016 Elsevier Ltd. All rights reserved.

3.4.1. Catalyst importance in pyrolysis of plastics . . . 317
3.4.2. Type of catalysts . . . 317
3.5. Type and rate of fluidizing gas . . . 320
4. Characteristics of plastic pyrolysis oil . . . 320
4.1. Physical properties . . . 320
4.2. Chemical properties . . . 321
5. By-products of the plastic pyrolysis . . . 322
5.1. Char . . . 322
5.2. Gas . . . 323
6. Discussion on plastic pyrolysis scenarios . . . 323
7. Conclusion . . . 324
Acknowledgement . . . 324
References . . . 324

## 1. Introduction

Plastic plays a vital role in enhancing the standard lives of human being for more than 50 years. It is a key of innovation of many products in various sectors such as construction, healthcare, electronic, automotive, packaging and others. The demand of commodity plastics has been increased due to the rapid growth of the world population. The global production of plastic has reached about 299 million tons in 2013 and has increased by 4% over 2012 [1]. The continuous rising of plastic demand led to the growing in waste accumulation every year. It was reported that 33 million tons of plastic waste are generated in the US based on 2013 statistic [2]. As in Europe, 25 million tons of plastic ended up in waste stream during the year of 2012 [1]. Based on the statistic established in Europe, about 38% of the plastic waste still went to the landfill, 26% were recycled while 36% were utilized for energy recovery [1]. This shows that the percentage of plastic waste ended up in the landfill still very high that it occupied a huge space. Plastics may take up to billions of years to degrade naturally. They degrade gradually since the molecular bonds containing hydrogen, carbon and few other elements such as nitrogen, chlorine and others that make plastic very durable. The continuous disposal of plastic in the landfill would definitely cause serious environmental problem.

In order to reduce plastic disposal to the landfill, recycling method is considered as another alternative to manage plastic waste. Back to the statistic mentioned above, the percentage of recycling still at the lowest. Recycling plastic has proven difficult and it can be costly because of the constraints on water contamination and inadequate separation prior to recycle that is labor intensive [3]. Separation is needed since plastics are made of different resin compound, transparency and color. Normally, pigmented or dyed plastics have lower market value. Clearly transparent plastics are often desirable by the manufacturers since they can be dyed to transform into new products, thus have greater flexibility [4]. With the stringent requirement to get high value product, recycling plastic becomes quite challenging nowadays.

Although plastic recycling able to reduce some amount of plastic waste, the more reliable and sustainable method has been established. Since high demand of plastics have been received each year, the reduction of fossil fuel such as coal, gas and especially petroleum that made up plastic itself has gained great interest of many researchers to discover and develop potential energy resources due to the rising in energy demand. Some of the new energy resources that have been explored include solar energy, wind power, geothermal and hydropower technology. Recently, the energy conversion from waste has been an intelligent way to fully utilize the waste to meet the increased energy demand. The conversion of plastics to valuable energy is possible as they are derived from petrochemical source, essentially having high calorific value. Hence, pyrolysis is one of the routes to waste minimization that has been gaining interest recently.

Pyrolysis is the process of thermally degrading long chain polymer molecules into smaller, less complex molecules through heat and pressure. The process requires intense heat with shorter duration and in absence of oxygen. The three major products that are produced during pyrolysis are oil, gas and char which are valuable for industries especially production and refineries. Pyrolysis was chosen by many researchers since the process able to produce high amount of liquid oil up to 80 wt% at moderate temperature around 500 °C [5]. In addition, pyrolysis is also very flexible since the process parameters can be manipulated to optimize the product yield based on preferences. The liquid oil produced can be used in multiple applications such as furnaces, boilers, turbines and diesel engines without the needs of upgrading or treatment [6]. Unlike recycling, pyrolysis does not cause water contamination and is considered as green technology when even the pyrolysis by-product which is gaseous has substantial calorific value that it can be reused to compensate the overall energy requirement of the pyrolysis plant [7]. The process handling is also much easier and flexible than the common recycling method since it does not need an intense sorting process, thus less labor intensive.

Many research papers have been published regarding the potential of various types of plastics in pyrolysis processes for liquid production. It should be noted that the product yield and quality heavily depends on the set up parameters. Therefore, this review focused on different type of plastic pyrolysis that has been explored together with the main affecting parameters in plastic pyrolysis process that need an attention in order to maximize liquid oil production and enhance the oil quality. The main parameters include temperature, type of reactors, residence time, pressure, different catalysts usage and type of fluidizing gas with its flow rate. Additionally, some relevant discussion regarding the optimization of liquid oil yield was also presented in this paper.

## 2. Pyrolysis of plastics

Fundamentally, different types of plastics have different compositions that normally reported in terms of their proximate analysis. Proximate analysis can be defined as a technique to measure the chemical properties of the plastic compound based on four particular elements which are moisture content, fixed carbon, volatile matter and ash content [8]. Volatile matter and ash content are the major factors that influence the liquid oil yield in pyrolysis process. High volatile matter favored the liquid oil production while high ash content decreased the amount of liquid oil, consequently increased the gaseous yield and char formation [7]. Table 1 summarized the proximate analysis of different plastics. Based on Table 1, it was observed that the volatile matter for all plastics is

**Table 1**
Proximate analysis of plastics [7].

| Type of plastics | Plastics type marks | Moisture (wt%) | Fixed carbon (wt%) | Volatile (wt%) | Ash (wt%) | Ref. |
|---|---|---|---|---|---|---|
| Polyethylene terephthalate (PET) | 1 PET | 0.46 | 7.77 | 91.75 | 0.02 | [9] |
| | | 0.61 | 13.17 | 86.83 | 0.00 | [10] |
| High-density polyethylene | 2 HDPE | 0.00 | 0.01 | 99.81 | 0.18 | [11] |
| | | 0.00 | 0.03 | 98.57 | 1.40 | [10] |
| Polyvinyl chloride (PVC) | 3 V | 0.80 | 6.30 | 93.70 | 0.00 | [12] |
| | | 0.74 | 5.19 | 94.82 | 0.00 | [10] |
| Low-density polyethylene | 4 LDPE | 0.30 | 0.00 | 99.70 | 0.00 | [13] |
| | | – | – | 99.60 | 0.40 | [14] |
| Polypropylene | 5 PP | 0.15 | 1.22 | 95.08 | 3.55 | [15] |
| | | 0.18 | 0.16 | 97.85 | 1.99 | [10] |
| Polystyrene | 6 PS | 0.25 | 0.12 | 99.63 | 0.00 | [16] |
| | | 0.30 | 0.20 | 99.50 | 0.00 | [13] |
| Polyethylene (PE) | 7 OTHER | 0.10 | 0.04 | 98.87 | 0.99 | [15] |
| Acrylonitrile butadiene styrene (ABS) | | 0.00 | 1.12 | 97.88 | 1.01 | [17] |
| Polyamide (PA) or Nylons | | 0.00 | 0.69 | 99.78 | 0.00 | [17] |
| Polybutylene terephthalate (PBT) | | 0.16 | 2.88 | 97.12 | 0.00 | [10] |

very high while the ash content is considered low. These characteristics indicate that plastics have high potential to produce large amount of liquid oil through pyrolysis process. Since the results of plastics proximate analysis are very convincing, the following discussion would focus more on the process parameters involved during the pyrolysis process that would have major influence in the liquid production.

### 2.1. Polyethylene terephthalate (PET)

PET has become the great choice for plastic packaging for various food products, mainly beverages such as mineral water, soft drink bottle and fruit juice containers. This is due to its intrinsic properties that are very suitable for large-capacity, lightweight and pressure-resistant containers. Other applications of PET include electrical insulation, printing sheets, magnetic tapes, X-ray and other photographic film [18]. The extensive applications of PET would cause an accumulation of PET waste in the landfill. Recycling PET waste was the current practice of handling accumulated plastic waste. However, the bulkiness of the containers causes high frequency of collections and therefore, increases the transport costs. To ease the recycling process, the PET waste needs to be sorted into different grades and colors that make its recovery inefficient and uneconomical. Hence, other alternative for PET recovery such as pyrolysis process has been explored and the product yield was analyzed by several researchers.

Cepeliogullar and Putun [19] have explored the potential of PET in pyrolysis process to produce liquid oil using fixed-bed reactor at 500 °C. The heating rate was 10 °C/min and nitrogen gas was used as the sweeping gas in this experiment. It was observed that the liquid oil yield was lesser than the gaseous product. The liquid oil obtained was 23.1 wt% while the gaseous product was 76.9 wt % with no solid residue left. The low liquid yield could be explained through the proximate analysis based on Table 1, showing the relatively low volatile content of PET around 86.83% in comparison with other plastics in which the volatile contents were all above 90%. Unfortunately, almost half of the oil composition contained benzoic acid which was around 49.93% based on the gas chromatography–mass spectroscopy (GC–MS) analysis. The acidic characteristic in pyrolysis oil was unfavorable due to its corrosiveness that deteriorated the fuel quality [19]. Besides that, benzoic acid was a general sublime that could clog piping and heat exchanger, thus need a serious attention if running in industrial scale [20,21].

On the other hand, Fakhrhoseini and Dastanian [5] found slightly higher liquid oil yield at the same operating temperature and heating rate. The liquid yield obtained was 39.89 wt%, gaseous was 52.13 wt% and solid residue was 8.98 wt%. Therefore, it can be concluded that the liquid oil production from the PET pyrolysis obtained in the ranges of 23–40 wt% while gaseous yield in the ranges of 52–77 wt%. Based on these results, PET might be the most suitable plastic to be used in pyrolysis if gaseous product became a preference, for instance to provide energy supply to heat up the reactor at the desired temperature.

### 2.2. High-density polyethylene (HDPE)

HDPE is characterized as a long linear polymer chain with high degree of crystallinity and low branching which leads to high strength properties. Due to its high strength properties, HDPE is widely used in manufacturing of milk bottles, detergent bottles, oil containers, toys and more. The various applications contribute about 17.6% in plastic waste category which is the third largest plastic type found in municipal solid waste (MSW) [22]. HDPE wastes have a great potential to be used in pyrolysis process since it can produce high liquid yield depends on the set up parameters. Many studies have been conducted on HDPE pyrolysis at different operating parameters to investigate the product yield obtained.

Ahmad et al. [23] explored the pyrolysis study of HDPE using micro steel reactor. The pyrolysis temperatures were within 300–400 °C at heating rate of 5–10 °C/min. Nitrogen gas was used as the fluidizing medium. From the experiment, they found that the highest total conversion happened to be at 350 °C with liquid

was the dominant product yield (80.88 wt%). The solid residue was very high at 300 °C (33.05 wt%) but the amount was reducing to 0.54 wt% at the highest temperature of 400 °C.

On the other hand, Kumar and Singh [24] have done the thermal pyrolysis study of HDPE using semi-batch reactor at higher temperature range of 400–550 °C. It was observed that the highest liquid yield (79.08 wt%) and gaseous product (24.75 wt%) obtained at temperature of 550 °C while wax started to dominate in product fraction at higher temperature of 500–550 °C. The dark brownish oil obtained from the pyrolysis had no visible residue and the boiling point was from 82 to 352 °C. This suggested the mixture of different oil component such as gasoline, kerosene and diesel in the oil that matched the properties of conventional fuel as shown in Table 2. Besides, the sulfur content in the HDPE pyrolytic oil was very low (0.019%) that made it cleaner to the environment.

Besides that, Marcilla et al. [26] have also studied the HDPE pyrolysis at 550 °C using batch reactor. The liquid oil yield was 84.7 wt% and gaseous product around 16.3 wt%. This results proven that higher liquid oil could be obtained at higher temperature but there was also a limitation that should be noted. Too high temperature would reduce the liquid oil yield and increased the gaseous product since the process had passed the maximum thermal degradation point. Mastral et al. [27] conducted the HDPE pyrolysis in a fluidized bed reactor at 650 °C and they found that the liquid oil production was around 68.5 wt% and 31.5 wt% gaseous product. This shows that the liquid was cracked to gaseous when further heated up at a very high temperature above 550 °C.

### 2.3. Polyvinyl chloride (PVC)

Unlike other thermoplastics such as polyethylene (PE), polystyrene (PS) and polypropylene (PP) which can be softened by heating and solely derived from oil, PVC is exceptional since it is manufactured from the mixture of 57% chlorine (derived from industrial grade salt) and 43% carbon (derived from hydrocarbon feedstock such as ethylene from oil or natural gas) [28]. The chlorine property makes PVC an excellent fire resistance, thus very suitable for electrical insulation. The compatibility PVC to be mixed with many additives makes it a versatile plastic. Regular applications of PVC include wire and cable insulation, window frames, boots, food foil, medical devices, blood bags, automotive interiors, packaging, credit cards, synthetic leather, etc. Even though it has wide applications, the research done on the PVC pyrolysis found in the literature was very less due to the dangerous substance that it tend to release when heated at high temperature.

Miranda et al. [29] conducted the pyrolysis of PVC in a batch reactor at temperature range of 225–520 °C and heating rate of 10 °C/min. The experiment was done under vacuum and total pressure of 2 kPa was applied. Liquid oil obtained was not that high and varied from 0.45 wt% to 12.79 wt% as the temperature increased. Tar accumulation was even higher than the liquid oil obtained and the amount kept increasing up to 19.6 wt%. Hydrogen chloride (HCl) was found to be the main product obtained from the experiment with the highest yield of 58.2 wt%. HCl tend to be corrosive and toxic when heated moderately that caused damage to the process equipment. This was one of the main reasons that led to the shutdown of the pyrolysis pilot plant in Ebenhausen, Germany [29].

Therefore, it can be concluded that PVC was not preferable for pyrolysis since the yield of liquid oil was very minimum. Furthermore, PVC waste accumulated in MSW was very minimal, about less than 3% in plastic waste category which was very limited [22]. Additionally, the release of harmful product such as HCl and the presence of chlorinated compound such as chlorobenzene in the pyrolysis liquid could be toxic to the environment. To overcome this, a dechlorination process of PVC was required to reduce the chlorine content in liquid oil. This process could be achieved through several methods such as stepwise pyrolysis, catalytic pyrolysis and pyrolysis with adsorbents added to the PVC sample [30]. Hence, the pyrolysis of PVC required an additional cost when an extra dechlorination step was needed which was one of the disadvantages to the industry.

**Table 2**
Comparison of HDPE pyrolytic oil and conventional fuel properties.

| Type of oil | HDPE pyrolytic oil properties [24] | | Conventional fuel properties [25] | |
|---|---|---|---|---|
| | Boiling point (°C) | Cv (MJ/kg) | Boiling point (°C) | Cv (MJ/kg) |
| Gasoline | 82–352 | 42.9 | 40–200 | 43.4–46.5 |
| Kerosene | | | 150–300 | 43.0–46.2 |
| Diesel | | | 150–390 | 42.8–45.8 |

### 2.4. Low-density polyethylene (LDPE)

In contrast to HDPE, LDPE has more branching that results in weaker intermolecular force, thus lower tensile strength and hardness. However, LDPE has better ductility than HDPE since the side branching causes the structure to be less crystalline and easy to be molded. It has an excellent resistance to water, thus widely applied as plastic bags, wrapping foils for packaging, trash bags and much more. All these items are commonly used in our daily lives and therefore, LDPE waste has been accumulated day by day that it is known as the second largest plastic waste in MSW after PP [22]. As one way to recover energy and reduce waste, pyrolysis of LDPE to oil product has received much attention by researchers nowadays.

Bagri and Williams [31] have investigated the LDPE pyrolysis in fixed-bed reactor at 500 °C with heating rate of 10 °C/min. The experiment was done for duration of 20 min and nitrogen was used as fluidizing gas. It was observed that high liquid yield of 95 wt% was obtained with low gas yield and negligible char. High liquid oil yield of 93.1 wt% has also been obtained by Marcilla et al. [26] when the experiment was carried out in a batch reactor at 550 °C, but this time with lower heating rate of 5 °C/min.

There are also some researchers who studied the LDPE pyrolysis at lower operating temperature less than 500 °C. From the research conducted by Uddin et al. [32] using batch reactor at 430 °C, the liquid yield obtained was around 75.6 wt%. Aguado et al. [33] have obtained a closer yield with Uddin et al. [32] which was 74.7 wt% when using the same type of reactor at 450 °C. However, the liquid oil yield could be increased when pressure was applied in the reactor during the process, even though at lower temperature. This was proven by Onwudili et al. [34] who used pressurized batch reactor (0.8–4.3 MPa) in LDPE pyrolysis at 425 °C. From the experiment, they have obtained 89.5% liquid oil, 10 wt% gaseous and 0.5 wt% char. This indicates that pressure may have an influence on the composition of pyrolysis product that would be discussed afterward in this paper.

### 2.5. Polypropylene (PP)

PP is a saturated polymer with linear hydrocarbon chain that has a good chemical and heat resistance. Unlike HDPE, PP does not melt at temperature below than 160 °C. It has a lower density than HDPE but has higher hardness and rigidity that makes it preferable in plastic industry. PP contributes about 24.3% in plastic wastes category which are the largest amount of plastics found in

MSW [22]. The diverse applications include flowerpot, office folders, car bumpers, pails, carpets, furniture, storage boxes and more. The high demand of PP in daily life causes the amount of PP wastes to increase each year and therefore, pyrolysis of PP is one of the methods that can be used for energy recovery. Several researchers have investigated the pyrolysis of PP at various parameters to measure the liquid oil yield and properties.

In a study conducted by Ahmad et al. [23] on PP pyrolysis within 250–400 °C using micro steel reactor, they summarized that the highest liquid oil was achieved at temperature of 300 °C around 69.82 wt% with total conversion of 98.66%. The increase in temperature to 400 °C only reduced the total product conversion to 94.3% and increased solid residue from 1.34 to 5.7 wt%. This indicates that coke formation started to dominate at higher temperature. However, Sakata et al. [35] have explored the PP pyrolysis at higher temperature of 380 °C. They found higher liquid yield of 80.1 wt%, 6.6 wt% gaseous and 13.3 wt% solid residue left. On the other hand, Fakhrhoseini and Dastanian [5] obtained higher liquid yield about 82.12 wt% when performed PP pyrolysis at 500 °C. Nevertheless, further increase in temperature more than 500 °C only reduced the liquid yield collected. This was proven by Demirbas [36] who carried out the PP pyrolysis at extreme temperature of 740 °C in a batch reactor which resulted in 48.8 wt% liquid yield, 49.6 wt% gaseous and 1.6 wt% char.

### 2.6. Polystyrene (PS)

PS is made of styrene monomers obtained from the liquid petrochemical. The structure consists of a long hydrocarbon chain with phenyl group attached to every other carbon atom. PS is naturally colorless but it can be colored by colorants. It is heat resilience and it offers reasonable durability, strength and lightness that make this polymer desirable to be used in variety of sectors such as in food packaging, electronics, construction, medical, appliances and toys. The wide range of applications signifies the large waste amount of PS in MSW accumulated each year. Unfortunately, PS is not included in the roadside recycling program in which the recycling bins only included glasses, papers, cans, and certain plastics. Even though there is a plastic category, normally people will not throw the foam food packaging into plastics recycle bin and they often go to the general bin. Thus, PS is generally not separated and not economically to collect for recycling due to its low density polystyrene foam. Hence, the only way the PS waste can be fully utilized is through pyrolysis process in which it can be turned into more valuable oil product rather than to end up in the landfills forever.

Onwudili et al. [34] have investigated the pyrolysis of PS in a batch pressurized autoclave reactor at 300–500 °C for one hour duration. The heating rate used was 10 °C/min and the experimental pressure given was 0.31 MPa up to 1.6 MPa. From the experiment, they found that the PS pyrolysis produced a very high liquid oil yield around 97.0 wt% at optimum temperature of 425 °C. The maximum amount of gas produced was only 2.5 wt%.

The high yield of liquid oil product was also supported by Liu et al. [37]. The difference was during this time, the pyrolysis of PS was conducted using fluidized bed reactor at temperature of 450–700 °C. The highest liquid oil obtained was 98.7 wt% at 600 °C. Nevertheless, the amount of liquid oil produced was also considered high at lower temperature of 450 °C which was around 97.6 wt% and it differed by only 1.1 wt%. In the case when energy saving was the priority, lower temperature was preferable as it could reduce the energy cost incurred. Based on the study done by Demirbas [36], the liquid oil reduced to 89.5 wt% when the PS pyrolysis was running at 581 °C in a batch reactor. Therefore, the PS pyrolysis was not recommended to run at temperature more than 500 °C to optimize the liquid oil production.

### 2.7. Mixed plastics

As previously mentioned, pyrolysis process has an added advantage over the recycling process since it does not need an intense sorting process. In recycling process, most plastics are not compatible with each other to be processed together during recycling. For instance, a slight amount of PVC contaminant present in PET recycle stream will degrade the whole PET resin by becoming yellowish and brittle that requires reprocessing [38]. This shows that recycling process is very sensitive to contaminants that it requires all plastics to be sorted based on type of resins, colors and transparency. However, pyrolysis process seems to be more sustainable since liquid oil still can be produced from the mixed plastics in the feedstock. This has been encountered by several researchers who conducted studies of mixed plastics pyrolysis.

Kaminsky et al. [39] studied the pyrolysis of mixed plastic wastes collected from German households which was composed approximately 75% of polyolefins (PE, PP) and 25% PS. There was indeed a small amount of PVC content remained in the material after the separation step about less than 1 wt% and this was shown by the presence of the chlorine content in the product yield. The experiment was conducted in a fluidized bed reactor at 730 °C which finally produced 48.4 wt% liquid oil. The amount of liquid oil obtained was very similar to the study conducted by Demirbas [36] in pyrolysis of polyolefins (PP, PE) and PS mixture collected from landfill which was approximately 46.6 wt%. The gaseous and solid yields were reported to be 35 wt% and 2.2 wt% respectively. In terms of the oil composition, it contained 4 ppm chlorine resulted from the remaining PVC left in the material. However, it did not deteriorate the oil quality since the minimum chlorine limit in petrochemical processing was less than 10 ppm. Furthermore, the rest of the chlorine content was found to be the largest in solid residue. Therefore, the author concluded that the chlorine content in the feedstock could not be more than 1 wt% to ensure high quality oil was produced.

The potential of polyolefins mixed plastics in pyrolysis was also explored by Donaj et al. [40]. The mixed plastics were composed of 75 wt% LDPE, 30 wt% HDPE and 24 wt% PP. The experiment was operated at high temperatures of 650 °C and 730 °C in a bubbling fluidized bed reactor. The results showed that the liquid obtained was higher at lower temperature of 650 °C which was around 48 wt%. However, this oil fraction consisted of 52% heavy fraction such as heavy oil, wax and carbon black. In contrast, it was up to 70% light fraction of liquid contained in the pyrolysis oil (44 wt%) running at 730 °C. This means that the higher the temperature, the lighter the hydrocarbon liquid or gaseous produced. Therefore, it should be noted that there was a tremendous change in the product distribution when the temperature was further increased.

In comparison to the single plastic pyrolysis, it can be seen that the pyrolysis of mixed plastics produced lower liquid yield less than 50 wt%. Nevertheless, the quality of oil produced was comparable to the single plastic pyrolysis in terms of the oil composition that made it ideally suited for further processing in petrochemical refineries.

## 3. Process parameters condition

Parameters play major role in optimizing the product yield and composition in any processes. In plastic pyrolysis, the key process parameters may influence the production of final end products such as liquid oil, gaseous and char. Those important parameters may be summarized as temperature, type of reactors, pressure, residence time, catalysts, type of fluidizing gas and its rate. The desired product can be achieved by controlling the parameters at

different settings. In-depth discussions of the operating parameters are reviewed in the following subsections.

### 3.1. Temperature

Temperature is one of the most significant operating parameters in pyrolysis since it controls the cracking reaction of the polymer chain. Molecules are attracted together by Van der Waals force and this prevents the molecules from collapsed. When temperature in the system increases, the vibration of molecules inside the system will be greater and molecules tend to evaporate away from the surface of the object. This happens when the energy induced by Van der Waals force along the polymer chains is greater than the enthalpy of the C–C bond in the chain, resulted in the broken of carbon chain [41].

The thermal degradation behavior of the plastics can be measured using thermogravimetry analyzer. The analyzer produces two types of graphs which are thermogravimetry analysis (TG) curve and derivative thermogravimetry analysis (DTG) curve. The TG curve measures the weight change of substance as function of temperature and time [24]. On the other hand, the DTG curve gives the information on the degradation step occurred during the process which is indicated by the number of peaks [24]. In the PET pyrolysis study conducted by Cepeliogullar and Putun [19], they observed that the main PET degradation started at 400 °C with a very small weight change occurred when the temperature was in the range of 200–400 °C. The maximum weight loss of the substance happened at temperature of 427.7 °C. No significant changes were observed at temperature more than 470 °C. Therefore, the authors concluded that the thermal degradation of PET happened at temperature range of 350–520 °C.

As for the HDPE, Chin et al. [42] reported the thermal degradation started at 378–404 °C and was almost completed at 517–539 °C based on the thermogravimetry analysis (TG) at different heating rates in the range of 10–50 °C/min. Higher heating rates speeds up the weight loss, thus increases the rate of reaction. In another thermal behavior study carried out by Marcilla et al. [43], they found that the maximum degradation rate of HDPE occurred at 467 °C. This important temperature needs to put into consideration when running the pyrolysis experiment to ensure the most optimum liquid yield.

On the other hand, PVC may have different thermal behavior than others when the major weight loss occurred at two different temperature ranges as reported by Cepeliogullar and Putun [19]. The first temperature range was between 260 and 385 °C in which maximum weight loss of 62.25% from the initial weight occurred. The second temperature range happened to be between 385 and 520 °C where about 21.74% weight loss from the original weight. As the temperature was raised up till 800 °C, the weight loss of the substance became insignificant (1.62%). Thus, it was concluded that the degradation temperature of PVC was in the range of 220–520 °C [19].

In LDPE pyrolysis, Marcilla et al. [44] observed that small amount of liquid oil formation started at temperature of 360–385 °C. The maximum liquid yield was collected at 469–494 °C. Onwudili et al. [34] observed that the oil conversion of LDPE started at 410 °C. A brown waxy material formed at temperature below than 410 °C indicated the incomplete conversion of oil. They concluded that the most optimum temperature to obtain the highest liquid was at 425 °C for LDPE. In another study done by Marcilla et al. [26], they concluded that the most optimum temperature to obtain high liquid oil was at 550 °C. Further increase in temperature to 600 °C only reduced the liquid yield obtained [45]. Hence, it can be summarized that the LDPE thermal degradation occurred at temperature range of 360–550 °C.

PP had lower thermal degradation temperature if compared to HDPE. According to Jung et al. [15] who studied the effect of temperature on HDPE and PP pyrolysis in a fluidized bed reactor, they found that the main decomposition of HDPE and PP happened within the range of 400–500 °C based on derivative thermogravimetry analysis (DTG) curves. However, it was observed that the weight loss of PP fraction started to occur at lower temperature below 400 °C in comparison to the HDPE fraction. Marcilla et al. [43] discovered that the maximum degradation temperature for PP was 447 °C while HDPE was 467 °C where the major weight loss happened. Theoretically, PP degraded faster than HDPE since half of the carbon in PP chain is tertiary carbon, consequently ease the formation of tertiary carbocation during the degradation [15].

Among all plastics, PS degraded at the lowest temperature during pyrolysis process. Onwudili et al. [34] have investigated the PS pyrolysis in a batch reactor. From their studies, they found that no reaction seems to take place at 300 °C. However, they found that PS degraded completely into highly viscous dark-colored oil at lower temperature of 350 °C. The highest liquid oil was achieved at 425 °C. The increase of temperature to 581 °C only reduced the liquid oil production and increased gaseous product [36]. Thus, it is worth noting that the thermal degradation temperature of PS would be in the range of 350–500 °C approximately.

Therefore, it was proven that the temperature has the greatest impact on reaction rate that may influence product composition of liquid, gaseous and char for all plastics from the previous discussion. The operating temperature required relies strongly on the product preference. If gaseous or char product was preferred, higher temperature more than 500 °C was suggested. If liquid was preferred instead, lower temperature in the range of 300–500 °C was recommended and this condition is applicable for all plastics.

### 3.2. Type of reactors

The type of reactors has an important impact in the mixing of the plastics and catalysts, residence time, heat transfer and efficiency of the reaction towards achieving the final desired product. Most plastic pyrolysis in the lab scale were performed in batch, semi-batch or continuous-flow reactors such as fluidized bed, fixed-bed reactor and conical spouted bed reactor (CSBR). The advantages and downsides of each reactor would be discussed in the following subsections.

#### 3.2.1. Batch and semi-batch reactor

Batch reactor is basically a closed system with no inflow or outflow of reactants or products while the reaction is being carried out. High conversion in batch reactor can be achieved by leaving the reactant in the reactor for an extended time which is one of its advantages. However, the disadvantages of batch reactor are the variability of product from batch to batch, high labor costs per batch and the difficulty of large scale production [46].

In contrast, a semi-batch reactor allows reactant addition and product removal at the same time. The flexibility of adding reactants over time is an added advantage of the semi-batch reactor in terms of reaction selectivity. The disadvantage of semi-batch reactor is similar with the batch reactor in terms of labor cost, thus it is more suitable for small scale production.

Some researchers preferred to use batch reactors or semi-batch reactors in plastic pyrolysis laboratory scale experiment due to the simplest design and ability to control the operating parameters easily [47–56]. Pyrolysis in batch reactor or semi-batch reactor normally performed at temperature range of 300–800 °C for both thermal and catalytic pyrolysis. Some researchers added catalysts to the plastics to improve hydrocarbon yield and for product upgrading. In catalytic pyrolysis, the catalyst was mixed together

with the plastic sample inside the batch reactor. The drawback of this process would be a high tendency of coke formation on the surface of the catalyst which reduced the catalyst efficiency over time and caused high residue in the process. Besides that, it was also a challenge to separate the residue from the catalyst at the end of the experiment.

Sakata et al. [35] used batch reactor to study the pyrolysis of PP and HDPE at 380 °C and 430 °C accordingly using various catalysts and also without catalyst. The authors found that the liquid oil obtained from catalytic pyrolysis was even lower than the thermal pyrolysis for some catalysts. The liquid yield from PP in thermal pyrolysis was 80.1 wt% and from HDPE was 69.3 wt%. With the usage of several catalysts such as silica–alumina (SA-1) and HZSM-5, the liquid yield for both PP and HDPE reduced to 47–78 wt% and 49.8–67.8 wt% respectively. However, the usage of certain catalysts such as silica–alumina (SA-2) and mesoporous silica catalysts (FSM) improved the liquid yield for both plastics slightly than the thermal pyrolysis with a very small increase of around 1.0–7.0 wt%. Therefore, different catalysts might have different reactivity to the plastic type. However, it has to be noted that the tendency of the coke formation on the catalyst surface also might be one of the reasons that degraded the effectiveness of the catalyst used in batch reactor over time.

Nevertheless, the direct contact of the catalyst with the plastics in some cases may also improve the liquid yield. Abbas-Abadi et al. [57] conducted the PP pyrolysis in semi-batch reactor using FCC catalyst at 450 °C. From the experiment, they found that very high liquid yield of 92.3 wt% was obtained. Some of the batch and semi-batch reactors were also equipped with stirrer that running at different speed depends on the required setting as illustrated in Fig. 1. Seo et al. [58] studied the pyrolysis of HDPE using batch reactor equipped with stirrer at 450 °C. The stirrer speed was 200 RPM. Higher liquid oil was obtained than Sakata et al. [35] in thermal pyrolysis which was around 84.0 wt%. Besides that, the amount of liquid product obtained through catalytic pyrolysis using similar catalyst of silica–alumina was also higher than Sakata et al. [35] which was 78 wt% while Sakata el al. [35] obtained 74.3 wt%. Therefore, it was clearly seen that the stirrer in the batch reactor helped to enhance the liquid oil yield by improving the mixing for the catalysts and plastics inside the reactor. More studies of semi-batch reactors with stirrer were also done by Abbas-Abadi et al. [59] and Kyong et al. [60,61].

Therefore, from the literature study, it was concluded that the batch or semi-batch reactors are the best reactors to be used in thermal pyrolysis to obtain high liquid yield since the parameters can be easily controlled. However, these reactors were not suggested for catalytic pyrolysis in consideration of the potential coke formation on the catalyst outer surface that would disturb the overall product yield. In addition, batch operation was not suitable for large scale production since it required high operating cost for feedstock recharging and thus, it was more appropriate for laboratory experiment.

### 3.2.2. Fixed and fluidized bed reactor

In fixed-bed reactor, the catalyst is usually in palletized form and packed in a static bed as shown in Fig. 2. It is easy to design but there are some constraints such as the irregular particle size and shape of plastics as feedstock that would cause problem during feeding process. Besides, the available surface area of the catalyst to be accessed by the reaction is also limited. However, there were several researches chose to use fixed-bed reactor for the plastic pyrolysis [19,31,63–66]. In certain conditions, the fixed-bed reactors are merely used as the secondary pyrolysis reactor because the product from primary pyrolysis can be easily fed into the fixed-bed reactor which generally consists of liquid and gaseous phase [46]. Onu et al. [67] and Vasile et al. [68] used two-step process on the study of various plastic pyrolysis. However, there are very few studies being done in two-step process as it is not cost effective and the results obtained are quite comparable with a single-step process.

On the other hand, fluidized bed reactor solves some of the problems occur in fixed-bed reactor. In contrast to fixed-bed reactor, the catalyst in fluidized bed reactor sits on a distributer plate as illustrated in Fig. 3 where the fluidizing gas passes through it and the particles are carried in a fluid state. Therefore, there is better access to the catalyst since the catalyst is well-mixed with

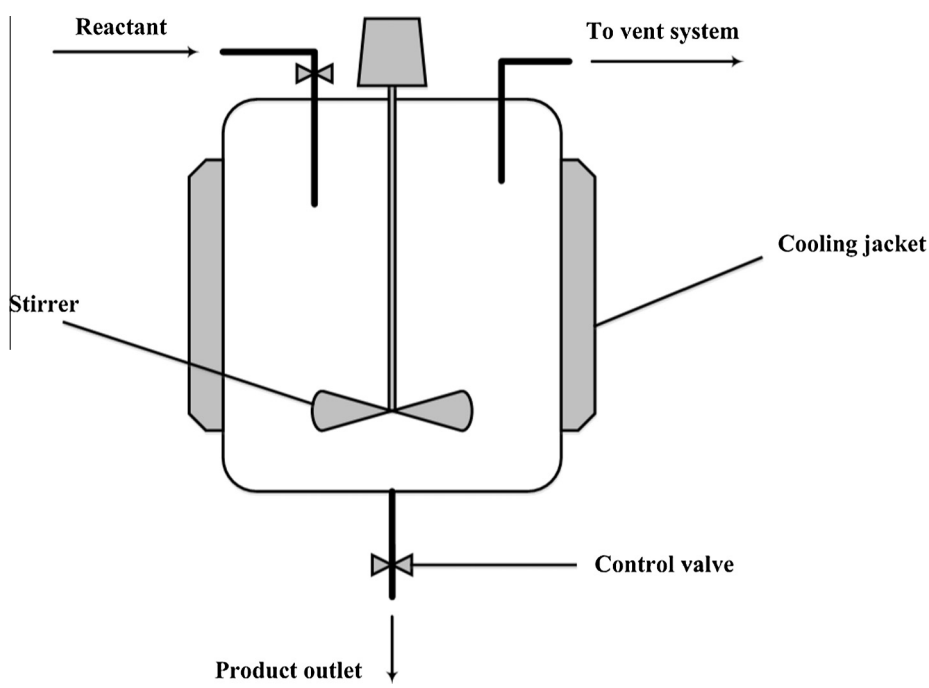


**Fig. 1.** Illustration of batch reactor with stirrer equipment [62].

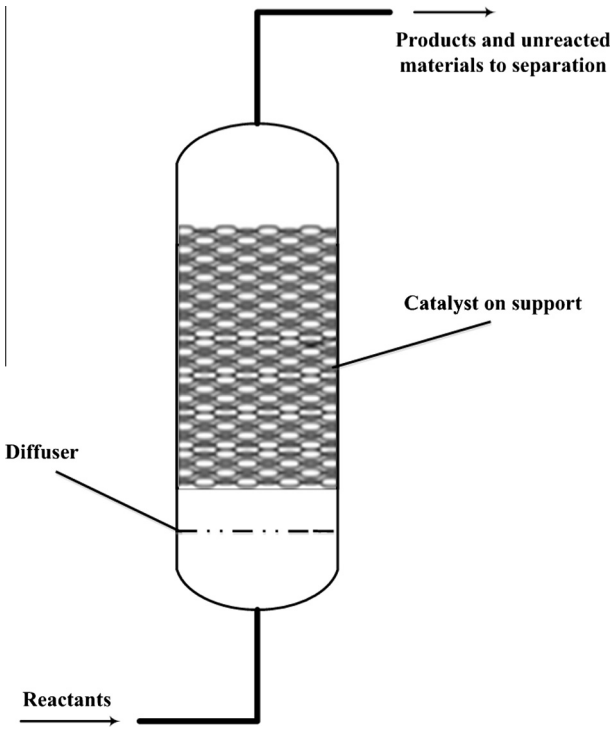


**Fig. 2.** Diagram of fixed-bed reactor [62].

the fluid and thus provides larger surface area for the reaction to occur [69]. This reduces the variability of the process conditions with good heat transfer. Besides, it is also more flexible than the batch reactor since frequent feedstock charging can be avoided and the process does not need to resume often. Hence, as for conventional design scale, fluidized bed reactor would be the best reactor to be used in the pilot plant due to the lower operating cost.

Many researches preferred to use fluidized bed reactor in catalytic cracking of plastics over fixed bed reactor [27,37,45,70–76]. Jung et al. [15] chose to use fluidized bed reactor for PP and PE pyrolysis because it provides almost a constant temperature with high mass and heat transfer, giving shorter residence time in the reactor and consequently more uniform spectrum of products. The plastic pyrolysis in fluidized bed reactors were carried out normally at temperature as low as 290–850 °C for both thermal and catalytic process. The comparison between HDPE and PP in catalytic degradation in fluidized bed reactor was studied by Luo et al. [77] using silica–alumina catalyst. The author reported that the liquid produced by PP was 87 wt% while HDPE produced lower at 85 wt% liquid composition at 500 °C. This result was expected since HDPE had higher strength properties than PP.

Therefore, fluidized bed reactor is concluded to be the best reactor to perform catalytic plastic pyrolysis since the catalyst can be reused many times without the need of discharging, considering catalyst is a very expensive substance in the industry. Besides, it is more flexible than the batch reactor since frequent feedstock charging can be avoided for continuous process and the process does not need to resume often. Hence, fluidized bed reactor would be the most suitable reactor for large scale operation in terms of economic point of view.

### *3.2.3. Conical spouted bed reactor (CSBR)*

Conical spouted bed reactor (CSBR) provides good mixing with the ability to handle large particle size distribution, larger particles and difference in particle densities [46]. There were some researchers used CSBR for their catalytic cracking of plastic experiments [78–83]. Olazar et al. [81] claimed that CSBR had lower attrition and low bed segregation than the bubbling fluidized bed. It also had high heat transfer between phases and minor defluidization problem when handling sticky solids. However, a variety of technical challenges during operation of this reactor have been encountered such as catalyst feeding, catalyst entrainment and product (solid and liquid) collection that make it less favorable [46]. Additionally, its complicated design that requires many pumps to be

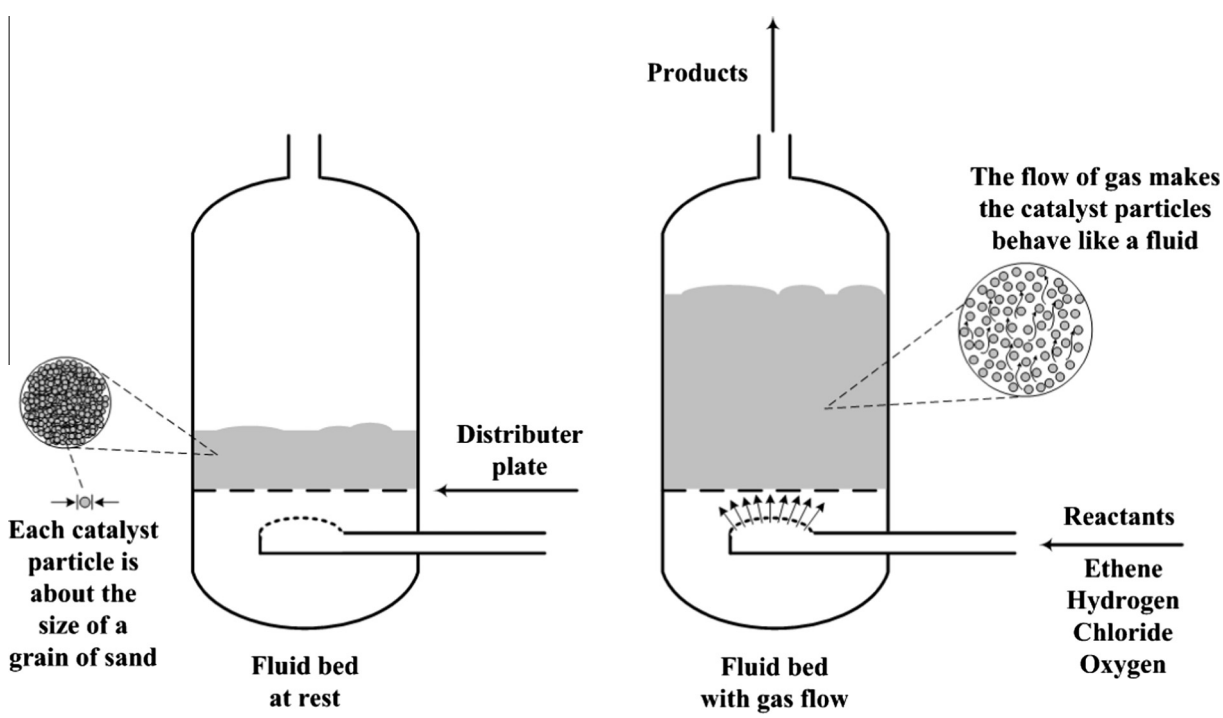


**Fig. 3.** Diagram of fluidized bed reactor [62].

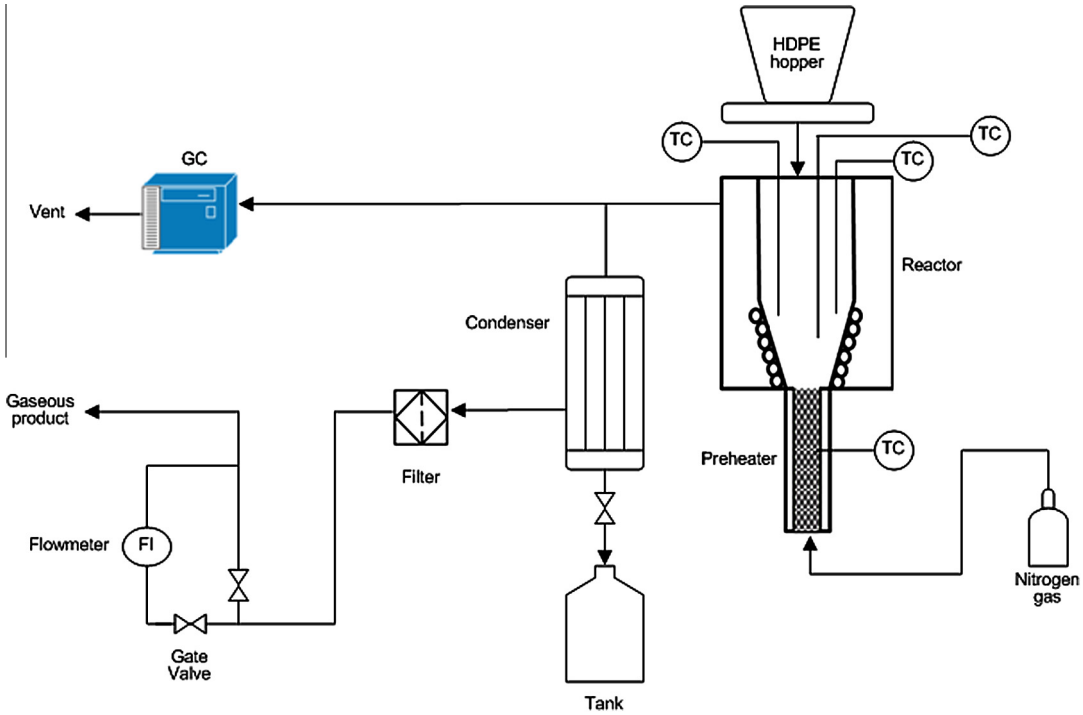


**Fig. 4.** Diagram of CSBR in HDPE pyrolysis using zeolite catalyst [84].

used in the system makes it unfavorable due to the high operating cost involved.

Elordi et al. [84] used CSBR to conduct HDPE pyrolysis with HY zeolite catalyst at 500 °C that resulted in 68.7 wt% gasoline fraction (C5–C10) and the process was illustrated in Fig. 4. The gasoline had an octane number of RON 96.5 which was closed with the standard gasoline quality. On the other hand, Arabiourrutia et al. [82] explored the waxes yield and characterization from HDPE, LDPE and PP pyrolysis at 450–600 °C using the CSBR. According to them, CSBR had the versatility of handling sticky solid that was hard to handle in fluidized bed reactor. The spouted bed design was particularly suitable for low temperature pyrolysis to obtain wax. The authors observed that the amount of waxes yield decreased with the temperature. At higher temperature, more waxes are cracked into liquid or gaseous product. HDPE and LDPE waxes production were very similar around 80 wt% while PP produced higher waxes at lower temperature about 92 wt%.

### 3.2.4. Microwave-assisted technology

The recent interest in microwave technology offers a new technique for waste recovery via pyrolysis process. In this process, a highly microwave-absorbent material such as particulate carbon is mixed with the waste materials. The microwave absorbent absorbs microwave energy to create adequate thermal energy in order to achieve the temperatures required for extensive pyrolysis to occur [85]. Microwave radiation offers several advantages over the conventional pyrolysis method such as rapid heating, increased production speed and lower production costs. Unlike conventional methods, microwave energy is supplied directly to the material through the molecular interaction with the electromagnetic field, thus no time is wasted to heat up the surrounding area [86]. Despite the advantages of microwave heating, there is also a major limitation which preventing this technology from being widely explored in industrial scale such as the absence of sufficient data to quantify the dielectric properties of the treated waste stream. The efficiency of microwave heating depends heavily on the dielectric properties of the material. For instance, plastics have low dielectric constant and the mixture with carbon as the microwave absorber during pyrolysis may improve the energy absorbed to be converted into heat in shorter time [85]. Therefore, the heating efficiency may differ for each material and it has been a great challenge to the industries.

The microwave heating was explored by Undri et al. [87] in pyrolysis process of polyolefin wastes (HDPE and PP) using two types of microwave absorbers which were carbon and tires. Different microwave power was used ranging from 1.2 to 6.0 kW. From the results obtained, the highest liquid yield for HDPE was 83.9 wt % while PP was 74.7 wt%. It was observed that both experiments were using carbon as the microwave absorber with microwave power ranging from 3 to 6 kW. High power reduced the residence time of the polymers in the oven, thus more polymers were converted into liquid rather than non-condensable gases. Using tires as the microwave absorber increased the solid residue amount up to 33 wt%, in which accountable only to other substances in tire that could not be pyrolyzed. In comparison with using carbon as the microwave absorber, the solid residue accumulated was as low as 0.4 wt% due to cocking process. Carbon material was a good microwave absorbent that has high capacity to absorb and convert microwave energy into heat. Therefore, emphasis needs to be given on the microwave power and absorber type in order to maximize the liquid yield in microwave-induced pyrolysis process.

In other study, Ludlow-Palafox and Chase [88] have conducted a microwave-induced pyrolysis on two different materials: HDPE pallets and toothpaste packaging which was in combination of aluminum and polyethylene laminates. Carbon was used as the microwave absorber with 5 kW microwave power. This experiment was quite different from others since a quartz vessel reactor with 180 cm in diameter, equipped with 6 RPM impeller was placed inside the microwave. The product yield resulted from HDPE pyrolysis was recorded at temperature of 500–600 °C. Liquid oil collected was around 79–81 wt%, gaseous 19–21 wt% and 0 wt% of solid residue formed. For the aluminum and polyethylene laminates, no specific amount of product was reported. However, the authors mentioned that there was no significant difference in the

product yield produced from the laminates and the HDPE pellets at the same operating temperatures. Only the average molecular weight was slightly higher but the molecular weight distribution for both cases were similar. In fact, the aluminum did not influence the product yield since it was easily separated by sieving and be seen as a shiny clean surface. During the experiment, they observed a compound known as titanium dioxide which appeared as white powder adhered to the reactor side wall. Titanium oxide clearly presented in the painted surface of the toothpaste tube. This shows that this substance had no influence in the pyrolysis product since it was separated from the organic content of the laminate during pyrolysis. In conclusion, a real waste such as the toothpaste packaging was successfully pyrolyzed through microwave-induced pyrolysis method.

Several parameters that influenced the microwave heating performance in plastic pyrolysis such as the effect of nitrogen flow rate, different absorber type and microwave rotation design were also explored by Khaghanikavkani [89]. The in-depth reviews of microwave heating in pyrolysis have also been done by Fernandez et al. [86], Lam and Chase [85] and Undri et al. [90].

### 3.3. Pressure and residence time

The effect of pressure to the HDPE pyrolysis product was studied by Murata et al. [91] in a continuous stirred tank reactor at elevated temperature of 0.1–0.8 MPa. Based on the studies, they discovered that the gaseous product increased tremendously from around 6 wt% to 13 wt% at 410 °C but only a small increase from 4 wt% to 6 wt% at 440 °C as the pressure went up from 0.1 to 0.8 MPa. This shows that pressure had high influence to the gaseous product at higher temperature. Pressure also affected the carbon number distribution of the liquid product by shifting to the lower molecular weight side when it was high. Besides, pressure also had a significant effect on the rate of double bond formation. As reported by Murata et al. [91], the rate of double bond formation decreased when pressure increased and this suggested that pressure directly affected the scission rate of C–C links in polymer. They also discovered that pressure had greater impact on residence time at lower temperature. However, as the temperature increased more than 430 °C, the effect of pressure to the residence time became less apparent.

Residence time can be defined as average amount of time that the particle spends in the reactor and it may influence product distribution [27]. Longer residence time increases the conversion of primary product, thus more thermal stable product is yielded such as light molecular weight hydrocarbons and non-condensable gas [88]. Nevertheless, there is a temperature limitation in the process that may influence the product distribution where until that instant, the residence time has not much effect on the product distribution. Mastral et al. [92] studied the effect of residence time and temperature on product distribution of HDPE thermal cracking in fluidized bed reactor. It was found that higher liquid yield obtained at longer residence time (2.57 s) when the temperature was not more than 685 °C. However, the residence time had less influence on the liquid and gaseous yield at higher temperature above 685 °C.

Therefore, it was concluded that pressure and residence time are both temperature dependence factors that may have potential influence on product distribution of the plastic pyrolysis at lower temperature. Higher pressure increased the gaseous product yield and affected the molecular weight distribution for both liquid and gaseous products but only apparent at high temperatures. Based on the literature review, most researchers conducted their plastic pyrolysis studies at atmospheric pressure and focused more on the temperature factor. The residence time was not brought up to attention while carrying out the experiment since the effect would become less apparent at higher temperatures. Moreover, in terms of economic viewpoint, additional units such as compressor and pressure transmitter need to be added into the overall system, thus increase the operation cost if the factor of pressure is considered. However, it should be noted that these two factors should be put under consideration based on the product distribution preference especially when running at temperature below 450 °C.

### 3.4. Catalysts

#### 3.4.1. Catalyst importance in pyrolysis of plastics

Catalyst speeds up chemical reaction but remains unchanged towards the end of the process. Catalysts are widely used in industries and researches to optimize product distribution and increase the product selectivity. Hence, catalytic degradation is particularly interesting to obtain product of great commercial interest such as automotive fuel (diesel and gasoline) and C2–C4 olefins, which have a huge demand in petrochemical industry [80]. When catalyst is used, the activation energy of the process is lowered down, thus speeds up the rate of reaction. Therefore, catalyst reduces the optimum temperature required and this is very crucial since the pyrolysis process requires high energy (highly endothermic) that hinders its commercial application. The usage of catalyst may help in saving energy as heat is one of the most expensive costs in industry. Besides that, catalyst was also used by many researchers for product upgrading to improve the hydrocarbon distribution in order to obtain pyrolysis liquid that had similar properties to the conventional fuel such as gasoline and diesel.

#### 3.4.2. Type of catalysts

There are two types of catalyst which are *homogeneous* (only one phase involve) and *heterogeneous* (involves more than one phase). Homogeneous catalyst used for polyolefin pyrolysis has mostly been classical Lewis acid such as $AlCl_3$ [93,94]. However, the most common type of catalyst used is heterogeneous since the fluid product mixture can be easily separated from the solid catalyst. Hence, heterogeneous catalyst is economically preferable because various catalysts are quite costly and their reuse is demanded. Heterogeneous catalyst can be classified as nanocrystalline zeolites, conventional acid solid, mesostructured catalyst, metal supported on carbon and basic oxides [95]. Some examples of nanocrystalline zeolites are HZSM-5, HUSY, Hβ and HMOR which are extensively used in the researches of plastic pyrolysis. Besides, the non-zeolites catalysts such as silica–alumina, MCM-41 and silicalite have also received much attention in current researches. Hence, the three types of catalysts that are widely used in plastic pyrolysis which are zeolites, FCC and silica–alumina catalysts would be discussed in the next subsections.

*3.4.2.1. Zeolite catalyst.* Zeolites are described as crystalline aluminosilicate sieves having open pores and ion exchange capabilities [96,97]. The structure is formed by three-dimensional framework where oxygen atoms link the tetrahedral sides. It is built by different ratio of $SiO_2/Al_2O_3$ depends on its type. The ratio of $SiO_2/Al_2O_3$ determines the zeolite reactivity which affects the final end product of pyrolysis.

Artetxe et al. [79] proven that the ratio of $SiO_2/Al_2O_3$ of the HZSM-5 zeolite highly affected the product fraction yield in HDPE pyrolysis. Low ratio of $SiO_2/Al_2O_3$ indicated the high acidity of the zeolite. The highest acidic catalyst ($SiO_2/Al_2O_3 = 30$) was more active in cracking waxes, thus producing higher light olefins and lower heavy fraction of C12–C20 compared than the lowest acidic catalyst ($SiO_2/Al_2O_3 = 280$). The reduction of $SiO_2/Al_2O_3$ ratio from 280 to 30 improved the yield of light olefins from 35.5 to 58.0 wt % and decreased the yield of C12–C20 from 28.0 to 5.3 wt%.

**Table 3**
Comparison of fuel properties of gasoline fraction obtained using three type of HZSM-5 with different ratio of $SiO_2/Al_2O_3$ [79].

| $SiO_2/Al_2O_3$ | Octane number | Olefins (vol%) | Aromatics (vol%) | Benzene (vol%) |
|---|---|---|---|---|
| 30 | 94.1 | 33.1 | 43.3 | 4.2 |
| 80 | 86.7 | 61.2 | 13.5 | 1.3 |
| 280 | 85.9 | 68.9 | 6.9 | 0.46 |
| Required | 95 | <18 | <35 | <1 |

Besides, the reduction of $SiO_2/Al_2O_3$ ratio in zeolite also raises the yield of light alkanes and aromatics. Table 3 compares the fuel properties of gasoline fraction obtained with three type of HZSM-5 zeolite which having different ratio of $SiO_2/Al_2O_3$. As depicted, the highest acidity catalyst with the lowest ratio of $SiO_2/Al_2O_3$ led to a higher octane number with high content of aromatics and benzene, but lower concentration of olefins. Even though the octane number was lower and the olefins, aromatics and benzene standard exceeded the specification established by European Union (EU), the absence of sulfur in the gasoline composition made it possible to be blended with refinery stream to achieve the standard outlined by EU.

Besides HZSM-5, some more examples of zeolite catalyst are HUSY and HMOR which are widely used in plastic catalytic pyrolysis. Garfoth et al. [70] investigated the efficiency of different zeolite catalysts to the HDPE pyrolysis which were HZSM-5, HUSY and HMOR with polymer to catalyst ratio of 40 wt%. In their studies, it was found that HZSM-5 had higher catalytic activity than HUSY and HMOR, referring to the very less residue left by HZSM-5 around 4.53 wt% while HUSY and HMOR were leaving about 7.07 wt% and 8.93 wt% residues behind respectively. This shows that HZSM-5 able to maximize the total product conversion in plastic pyrolysis over other zeolites.

In terms of product selectivity, different zeolites may have different product preferences. Marcilla et al. [98] studied the HZSM-5 and HUSY performance on HDPE and LDPE at constant temperature of 550 °C and 10 wt% polymer to catalyst ratio in a batch reactor. Higher liquid oil was recovered when using HUSY catalyst (HDPE = 41.0 wt%, LDPE = 61.6 wt%) compared with HZSM-5 catalyst (HDPE = 17.3 wt%, LDPE = 18.3 wt%) Oppositely, higher gaseous product obtained when using HZSM-5 catalyst (HDPE = 72.6 wt%, LDPE = 70.7 wt%). This proves that different catalysts have different product selectivity. The same trend of product selectivity was also reported by Lin and Yen [71] on PP pyrolysis using the HZSM-5 and HUSY zeolites.

Seo et al. [58] also investigated the effect of HZSM-5 in HDPE pyrolysis with catalyst to polymer ratio of 20 wt% at 450 °C. They observed that HZSM-5 produced very less liquid yield around 35 wt% but higher gaseous product of 63.5 wt%. Hernández et al. [99] obtained even lesser liquid yield around 4.4 wt% and 86.1 wt % gaseous product when running the HDPE pyrolysis at 500 °C with same catalyst to polymer ratio as Seo et al. [58]. Lin and Yen [71] also obtained very small amount of liquid product in PP pyrolysis at 360 °C with catalyst to polymer ratio of 40 wt% using HZSM-5 and HUSY zeolite catalysts. The liquid yield obtained was only 2.31 wt% and 3.75 wt% respectively. Nevertheless, HZSM-5 had higher resistance to coking than HUSY catalyst when the product stream such as isobutane and isopentanes remained unaffected throughout the process while the olefins (butane and pentene) increased [71,100,101].

Besides that, the usage of zeolite catalyst in pyrolysis of real municipal plastic waste may also help to reduce the impurities in the oil produced and this was proven in the study conducted by Miskolczi et al. [102]. In this study, the source of waste HDPE and PP were collected from agriculture and packaging sectors. Both plastics were washed and shredded before pyrolysis. From the properties analysis, both plastics contained sulfur (HDPE = 238 mg/kg, PP = 35 mg/kg). However, more impurities such as nitrogen, phosphorus and calcium (963 mg/kg, 47 mg/kg, and 103 mg/kg) additionally found in the HDPE waste obtained from the agriculture. The impurities were most probably come from the fertilizer which contained ammonium nitrate and superphosphate which could be accumulated on the HDPE waste that failed to be removed by washing procedure. The catalytic pyrolysis was done at 520 °C in the presence of 5 wt% HZSM-5 catalyst. After the pyrolysis was done, the used catalyst structure was analyzed by SEM and EDAX. Results showed that trace of sulfur, nitrogen and phosphorus were attached on the catalyst surface besides of the silica–alumina structure of HZSM-5 zeolite (silica, aluminum, oxygen, magnesium, potassium, sodium and calcium). This indicates the elements of impurities came from the waste plastic. Nevertheless, the impurities attached on the catalyst surface did not affect the product properties because the properties were rather affected by the grain diameter or catalyst pore structures. In fact, the catalyst obtained from the waste plastic pyrolysis could be re-used since the pore diameter was found to be similar with the fresh catalyst [102]. In term of liquid oil properties, the usage of catalyst helped to reduce the impurities content in the oil. This was clearly shown in the results when the sulfur content in HDPE waste pyrolysis reduced tremendously from 75 mg/kg to 37 mg/kg with the usage of HZSM-5 catalyst. The same reduction trend was also observed for nitrogen and phosphorus content. No calcium content was found in the gasoline and light oil fraction, while it could be only found in the heavy oil fraction.

Besides direct cracking of plastics, some researchers have also analyzed the zeolite catalyst performance in two-step reaction process involving thermal and catalytic reactors sequentially [68,103]. Aguado et al. [33] have explored the catalytic conversion of LDPE in two-step reaction process consisted of batch and fixed bed reactor. The thermal cracking of plastic would take place in the batch reactor and in the meanwhile, the vapors generated were carried over to the fixed-bed reactor where the 10 wt% HZSM-5 catalyst was placed. The pyrolysis was conducted within 425–475 °C. From the results, it was observed that the catalytic reforming over zeolite catalyst led to a significant increase of the gas fraction. The gaseous product had risen to 74.3 wt% at the highest temperature whereas only 21.9 wt% of liquid hydrocarbons was collected. Therefore, the trend of result observed was very similar to the direct catalytic cracking which produced high gaseous product over the usage of HZSM-5 catalyst.

As a final conclusion, it is worth noting that the usage of zeolite catalyst in plastic pyrolysis only maximized the production of volatile hydrocarbon. As for higher efficiency and longer cycle time usage, HZSM was recommended since the deactivation rate of the catalyst was extremely low and thus, more efficient for regeneration.

*3.4.2.2. FCC catalyst (fluid catalytic cracking).* FCC catalyst is made of zeolite crystals and non-zeolite acid matrix known as silica–alumina with the binder [97,104–106]. The main component of FCC catalyst for over 40 years is Zeolite-Y due to its high product selectivity and thermal stability [107]. FCC catalyst is normally used in the petroleum refining industry to crack heavy oil fractions from crude petroleum into lighter and more desirable gasoline and liquid petroleum gas (LPG) fractions [107].

FCC catalyst that has been used is often known as 'spent FCC catalyst' and usually can be obtained from commercial FCC process in petroleum refineries. It comes with different level of contamination yet still valuable and can be reused in the pyrolysis process. Kyong et al. [60] investigated the effect of spent FCC catalyst on the pyrolysis of HDPE, LDPE, PP and PS in stirred semi-batch reac-

tor at 400 °C. 20 g of catalyst was added into 200 g of reactants and heated up at rate of 7 °C/min. As a result, all plastics produced more than 80 wt% liquid oil with PS being the highest (around 90 wt% liquid yield). The liquid yields based on the plastic types were arranged in this order: PS > PP > PE (HDPE, LDPE). The gaseous product yield had a reverse order with that of liquid in this following order: PE > PP > PS. This shows that PS was less cracked to the gaseous product since PS contained benzene ring that created more stable structure. Overall, it is concluded that spent FCC catalyst still has high catalytic performance with the liquid yield obtained above 80 wt% for all plastic samples. Additionally, it is more cost effective since it is a 'reused' catalyst.

The effectiveness of spent FCC catalyst over thermal pyrolysis of HDPE without catalyst was further explored by Kyong et al. [108] using exactly the same parameters as Kyong et al. [60] but this time with higher temperature of 430 °C. From the experiment, it was found that the liquid oil yield was increased slightly from 75.5 to 79.7 wt% while the gaseous product reduced slightly from 20.0 to 19.4 wt% when the catalyst was used. However, the amount of solid residue left reduced drastically from 4.5 to 0.9 wt% with presence of the catalyst. Moreover, the catalytic pyrolysis also lowers down the reaction temperature of HDPE when the initial liquid formation was observed at about 350 °C. In the non-catalyzed pyrolysis, the initial liquid only formed after 30 min at 430 °C. This implies that the usage of spent FCC catalyst in thermal pyrolysis increased the rate of reaction besides improving the overall product conversion.

Apart from that, the limitation of the polymer ratio to the catalyst also needs to be considered in order to maximize the pyrolysis product conversion. Different ratio of HDPE to FCC catalyst was investigated by Abbas-Abadi et al. [57] from the range of 10 to 60 wt% at constant temperature of 450 °C using the semi-batch stirred reactor. From the study, it was found that the best optimum ratio for higher conversion to liquid yield was at 20 wt% catalyst/polymer ratio. The liquid product obtained was very high at 91.2 wt% with gaseous and coke around 4.1 wt% and 4.7 wt% respectively. As the catalyst/polymer ratio was increased more than 20 wt%, more coke and gas were produced, thus liquid production was minimized. This shows that there was a certain constraint of the catalyst/polymer ratio to enhance the product conversion especially liquid oil yield and reduced coke formation on the catalyst.

Besides that, different condition of FCC may also influence the product distribution of plastic pyrolysis. For instance, steaming FCC catalyst would change the catalyst structure and composition. This was proven by Olazar et al. [81] who conducted a study on fresh, mild and severe steaming of FCC catalyst. The mild steaming was carried out at 760 °C for 5 h and the severe steaming at 816 °C for 8 h. The result showed that the catalytic performance of FCC has improved by steaming. Severe steaming of FCC increased the production of diesel fraction (comprised of C10+ hydrocarbon) and reduced the gaseous fraction (comprised of C1–C4 hydrocarbon). On the other hand, the fresh FCC catalyst produced less diesel fraction while very high gaseous product. The product yield was summarized in Table 4.

The effectiveness of FCC catalyst to the different types of plastics was studied by Kyong et al. [60] at 400 °C with the catalyst/polymer ratio of 10 wt%. They observed that the liquid yield produced were in the range of 80–90 wt% for HDPE, LDPE, PP and PS. This result shows that FCC able to maximize the liquid oil yield in pyrolysis process for most plastic types. Abbas-Abadi et al. [57] also obtained very high liquid oil yield about 92.3 wt% in PP pyrolysis at 450 °C with 10 wt% catalyst/polymer ratio.

In conclusion, the usage of FCC catalyst in plastic pyrolysis was encouraged to maximize the liquid oil production. Additionally, the usage of 'spent FCC catalyst' was an added advantage in terms of economical view. However, it should be noted that catalyst/polymer ratio cannot be more than 20 wt% to avoid the domination of coke and gaseous product.

*3.4.2.3. Silica–alumina catalyst.* Silica–alumina catalyst is an amorphous acid catalyst that contains Bronsted acid sites with an ionizable hydrogen atom and Lewis acid site, an electron accepting sites. The acid concentration of silica alumina catalyst is determined by the mole ratio of $SiO_2/Al_2O_3$. Unlike zeolite, the acid strength of silica–alumina is determined oppositely in which the high ratio of $SiO_2/Al_2O_3$ indicates the high strength of acidity. For instance, SA-1 ($SiO_2/Al_2O_3 = 4.99$) has higher acidity than SA-2 ($SiO_2/Al_2O_3 = 0.27$) and both of them are the commercial silica–alumina available in the market [109].

Different strength of acidity in catalyst has great influence in the final end product of plastic pyrolysis. Sakata et al. [109] explored the effect of catalysts acidity (SA-1, SA-2, ZSM-5) on the product distribution of HDPE pyrolysis. The experiment was performed at 430 °C in a semi-batch reactor where 1 g of catalyst was mixed with 10 g of HDPE. The acidity of the catalysts are tested using NH3 temperature programmed desorption (TPD) and were in this following order: SA-1 > ZSM-5 > SA-2. As a result, it was observed that SA-2 catalyst with lower acidity produced higher amount of liquid oil (74.3 wt%), followed by SA-1 (67.8 wt %) and ZSM-5 (49.8 wt%). ZSM-5 possessed strong acid sites, thus produced more gaseous products than the other two acid catalysts but very less liquid yield. Uddin et al. [32] have also studied the effect of SA-2 to HDPE and LDPE at the same temperature and catalyst/polymer ratio. The results that they obtained for liquid oil yield were not far with the one obtained by Sakata et al. [109]. HDPE and LDPE pyrolysis each produced 77.4 wt% and 80.2 wt% respectively when SA-2 catalyst was used. HDPE structure was stronger than LDPE due to its linear chain, thus the lower amount of liquid yield obtained was expected.

Besides HDPE and LDPE, Sakata et al. [35] have investigated the effectiveness of silica–alumina catalyst on PP at 380 °C, but this time with different catalyst contact mode: liquid phase and vapor phase. As for the liquid phase, the catalyst was mixed together with the PP pallets and loaded into the batch reactor. Oppositely for vapor phase, the catalyst was placed on the stainless steel net suspended 10 cm from bottom of the reactor. From their study, they found that the catalyst in liquid mode produced higher liquid product (68.8 wt%) since the wax residue decomposed into lighter hydrocarbon over silica–alumina catalyst. On the other hand, higher gaseous product (35 wt%) found from the catalyst in vapor phase since the hydrocarbon further decomposed into gaseous product over silica–alumina catalyst. Therefore, catalyst mode was also an important factor that needs an attention since it influenced the final product distribution in plastic pyrolysis.

**Table 4**
Product distribution of FCC in fresh and steaming state [81].

| Type of FCC catalyst | C1–C4 (gaseous) (wt%) | C5–C9 (medium gasoline) (wt%) | C10+ (diesel) (wt%) |
|---|---|---|---|
| Fresh FCC | 52 | 35 | 15 |
| Mild steaming | 25 | 38 | 40 |
| Severe steaming | 5 | 20 | 70 |

Besides catalyst contact mode, the reactivity of catalyst can also be optimized under certain range of temperatures. Luo et al. [77] performed the HDPE and PP pyrolysis using silica–alumina catalyst at higher temperature of 500 °C in fluidized bed reactor. The liquid oil obtained for HDPE was about 85.0 wt% while PP was around 90 wt% which was higher than the studies conducted by Sakata et al. [35] and Uddin et al. [32]. This shows that temperature also plays an important role in maximizing the catalyst performance in order to increase the liquid oil production in plastic pyrolysis process.

As a final conclusion, the best catalyst to optimize liquid oil production in plastic pyrolysis would be FCC catalyst. FCC catalyst able to produce high liquid yield above 90 wt% for HDPE and PP pyrolysis while the highest product yield by silica–alumina for HDPE and PP was within the range of 85–87 wt% [57,59,77]. This shows that these two catalysts were comparable in terms of the liquid oil production but FCC had better catalytic performance. Besides that, the 'spent FCC catalyst' can also be used instead of fresh FCC that made it more economically attractive.

### 3.5. Type and rate of fluidizing gas

Fluidizing gas is an inert gas (also known as carrier gas) which only engaged in transportation of vaporized products without taking part in the pyrolysis. There are many type of fluidizing gas that can be used for the plastic pyrolysis such as nitrogen, helium, argon, ethylene, propylene and hydrogen. Each type of fluidizing gas has different reactivity based on its molecular weight. Abbas-Abadi et al. [57] reported that the molecular size of the carrier gas helped in determining the product composition and also dependent on the temperature. Table 5 shows that the molecular weight of the carrier gas did affect the product distribution of catalytic PP pyrolysis. The lighter gas able to produced high amount of condensed product which was liquid oil. As depicted in Table 5, $H_2$ produced the highest liquid yield of 96.7 wt% while without any carrier gas, only 33.8 wt% liquid was yielded. This proves the importance of carrier gas in enhancing the product yield in pyrolysis process. Besides that, it was also observed that the reactivity of the carrier gas influenced the coke formation. $H_2$ coke yield was very minimal which was about 0.3 wt%, followed by ethylene, helium and propylene. Ethylene and nitrogen were having the same molecular weight. However, ethylene seems to produce higher amount of liquid yield and lower coke formation than nitrogen. This is because ethylene is more reactive than nitrogen that it could shift the equilibrium to produce more liquid yield [57]. Nevertheless, of all those gases, nitrogen was commonly used by most researchers as fluidizing gas in plastic pyrolysis since it was easier and safer to handle than the high reactivity gas like hydrogen and propylene due to their flammability hazard. Besides, even though helium able to produce high liquid yield after hydrogen, it was rarely used since the availability was limited and more expensive than nitrogen.

Besides type of fluidizing gas, the fluidizing flow rate also may influence the final product distribution. Lin and Yen [71] investigated the effect of different fluidizing gas rate on product distribution of PP pyrolysis over HUSY catalyst at 360 °C. They found that the rate of degradation dropped instantly at the lowest fluidizing flow rate of 300 ml/min. The contact time for primary product is high at lower flow rate, causing the formation of coke precursor (BTX) to increase with the secondary product obtained even though the overall degradation rate is slower [110]. This was indicated by the high residue left when lower fludizing flow rate was applied. The gasoline and hydrocarbon gases fraction were also maximized at the highest fluidizing flow rate of 900 ml/min. Hence, the type and rate of fluidizing gas are also very important in plastic pyrolysis as they clearly influence product distribution as discussed above.

## 4. Characteristics of plastic pyrolysis oil

### 4.1. Physical properties

Table 6 summarized the fuel properties of the liquid oil produced in pyrolysis process. The experimental calorific value of HDPE, PP and LDPE are all above 40 MJ/kg and were considered high for energy utilization. According to Ahmad et al. [23], the calculated calorific value for both HDPE and PP were above 45 MJ/kg, and thus very closer to the commercial fuel grade criteria of gasoline and diesel. The calorific value of PS was commonly lower than the polyolefin plastic due to the existence of the aromatic ring in the chemical structure which had lesser combustion energy than the aliphatic hydrocarbon [34]. Overall, PET and PVC had the lowest calorific value below 30 MJ/kg due to the presence of benzoic acid in PET and chlorine compound in PVC that deteriorated the fuel quality. Benzoic acid also consisted of aromatic ring that explained the low calorific value in PET.

API gravity was the method used for measuring the density of the petroleum relative to water which was established by the American Petroleum Institute (API) and was also known as specific gravity [116]. The API gravity of HDPE and PP were 27.48 and 33.03 respectively while the densities were 0.89 and 0.86 g/cm$^3$ accordingly [23]. The API gravity of PVC was very close to the diesel API gravity value which was 38.98. On the other hand, the API gravity of LDPE was approaching the gasoline standard value which was 47.75. Therefore, all of these values were comparable to the commercial diesel fuel except LDPE which was comparable to the standard gasoline. In terms of density, all values seem comparable with the commercial standard value of both gasoline and diesel.

**Table 5**
The effect of carrier gas on the product yield and the condensed product composition [57].

| Carrier gas | Molecular weight | Condensed product yield (%) | Non-condensable product yield (%) | Coke yield (%) | Olefins (%) | Paraffins (%) | Naphthenes (%) | Aromatics (%) | Olefins/paraffin ratio |
|---|---|---|---|---|---|---|---|---|---|
| $H_2$ | 2 | 96.7 | 3 | 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 | 1.3 |
| $N_2$ | 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 | 1.2 |
| 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 carrier gas | 51.3 | 33.8 | 14.9 | n.d.[a] | n.d. | n.d. | n.d. | n.d. | n.d. |

*T*: 450 °C, stirrer rate: 50 r min$^{-1}$, catalyst/PP = 0.1.
[a] Not determined.

**Table 6**
Fuel properties of plastic pyrolysis oil.

| Physical properties | Type of plastics (experimental typical value) | | | | | | Commercial standard value (ASTM 1979) | |
|---|---|---|---|---|---|---|---|---|
| | PET [19,111] | HDPE [23] | PVC [19,112] | LDPE [113] | PP [23] | PS [114,115] | Gasoline [23] | Diesel [23] |
| Calorific value (MJ/kg) | 28.2 | 40.5 | 21.1 | 39.5 | 40.8 | 43.0 | 42.5 | 43.0 |
| API gravity @ 60 °F | n.a | 27.48 | 38.98 | 47.75 | 33.03 | n.a | 55 | 38 |
| Viscosity ($mm^2/s$) | n.a | 5.08[a] | 6.36[b] | 5.56[c] | 4.09[a] | 1.4[d] | 1.17 | 1.9–4.1 |
| Density @ 15 °C ($g/cm^3$) | 0.90 | 0.89 | 0.84 | 0.78 | 0.86 | 0.85 | 0.780 | 0.807 |
| Ash (wt%) | n.a | 0.00 | n.a | 0.02 | 0.00 | 0.006 | – | 0.01 |
| Octane number MON (min) | n.a | 85.3 | n.a | n.a | 87.6 | n.a | 81–85 | – |
| Octane number RON (min) | n.a | 95.3 | n.a | n.a | 97.8 | 90–98 | 91–95 | – |
| Pour point (°C) | n.a | −5 | n.a | n.a | −9 | −67 | – | 6 |
| Flash point (°C) | n.a | 48 | 40 | 41 | 30 | 26.1 | 42 | 52 |
| Aniline point (°C) | n.a | 45 | n.a | n.a | 40 | n.a | 71 | 77.5 |
| Diesel index | n.a | 31.05 | n.a | n.a | 34.35 | n.a | – | 40 |

n.a., not available in the literature.
[a] Viscosity at 40 °C.
[b] Viscosity at 30 °C.
[c] Viscosity at 25 °C.
[d] Viscosity at 50 °C.

The viscosity on the other hand was defined as a measurement of the fluid resistance to flow. Viscosity is very crucial in petroleum industry since it determines how easy the oil can flow from the reservoir to the well during extraction process and also plays a crucial role in fuel injection process [23,116]. In Table 6, the viscosity values were determined at different temperatures as denoted at the bottom of the table. Based on Table 6, it depicted the value of kinematic viscosity of all plastics were very close with the viscosity of diesel except for PS which the viscosity value was closer to the gasoline viscosity. In terms of ash content, HDPE and PP had negligible ash content and these indicated that the HDPE and PP pyrolysis oil was free from any metal contamination. The ash content in PS was also lower than the standard diesel which was less than 0.01 wt%. LDPE had slightly higher ash content of 0.02 wt% but the value was still tolerable since the difference was very minimal.

Besides that, the research octane number (RON) and motor octane number (MON) which was important to characterize the anti-knock quality for the gasoline range (C6–C10) was also determined. The high octane number indicates the better anti-knock quality that the fuel possesses. Knock is usually caused by the rapid combustion of gasoline in an engine that produces an explosive noise and degrades the engine performance over time [117]. Therefore, the anti-knock quality is very important to avoid engine damage. The MON and RON value for HDPE pyrolysis oil was 85.3 and 95.3 respectively. PP pyrolysis oil had higher MON and RON value which were 87.6 and 97.8 accordingly. The RON value for PS also matched the range of standard gasoline value which was in the range of 90–98. This suggests that the octane number of HDPE, PP and PS were comparable with commercial gasoline (MON = 81–85, RON = 91–95).

Pour point is known as the temperature at which the fluid stops to flow [118]. Generally, the increase in viscosity may cause the fluid losses its flow characteristic. Liquid fuel that has lower pour point has lesser paraffin content but greater aromatic content [119]. HDPE, PP and PS pyrolysis oil had lower pour point around −5, −9 °C and −67 °C respectively than the commercial diesel which having the pour point of 6 °C. This indicates that the pyrolysis oil obtained from plastic pyrolysis were rich with aromatic content. This relates to the lower calorific value of HDPE, PP and PS pyrolysis oil in comparison with the commercial gasoline and diesel.

One of the important properties in fuel handling to prevent fire hazard during storage was the flash point. Flash point of the liquid is defined as the lowest temperature at which the liquid may vaporize and form a mixture in the air that ignites when an external flame is applied [120]. The flash point of HDPE, PVC and LDPE pyrolysis oil were very close to the commercial gasoline. This indicates that the flash point of those three plastics was comparable to the light petroleum distillate fuel. The flash point of PP and PS were lower than both commercial gasoline and diesel. This shows that PP and PS pyrolysis oil easier vaporized and thus need an extra precaution when handling.

Aniline point is a temperature at which the aniline compound ($C_6H_5NH_2$) forms a single phase with the liquid oil [121]. Lower aniline point indicates the higher existence of aromatic compound. Oppositely, the higher aniline point indicates the higher amount of paraffin compound in the oil. Olefin has the aniline point in between those aromatic and paraffin value [121]. Referring to Table 6, the aniline point of HDPE and PP pyrolysis oil were 45 °C and 40 °C respectively which were much lower than the commercial gasoline and diesel. Gasoline and diesel were both having aniline point of 71 °C and 77.5 °C. This once again proves that the pyrolysis oil obtained from HDPE and PP was rich with aromatic compounds.

Diesel index evaluates the ignition quality of the diesel fuel in which the higher diesel index of the fuel indicates the higher quality of the fuel [122–124]. The diesel index of the HDPE pyrolysis oil was 31.05 while PP was 34.35. Even though the diesel index was not meeting the ASTM 1979 standard, the mixing of additives to fuel oil can improve the ignition quality of the diesel fuel and has shown growing acceptance nowadays [125]. Therefore, Ahmad et al. [23] concluded that liquid product produced by HDPE and PP met the commercial fuel grade and suggested to be a blend of gasoline and diesel hydrocarbon range.

### 4.2. Chemical properties

Table 7 shows the main chemical compound from the plastic pyrolysis. The liquid oil composition was usually characterized using the FTIR and GC–MS equipment for detailed analysis. In PET pyrolysis, Cepeliogullar and Putun [19] reported that almost half of the liquid oil around 49.93% contained benzoic acid compound. The corrosiveness of the acid made it unfavorable to be used in thermochemical conversion system. As the reaction proceeded during pyrolysis, PET tended to lose more aliphatic compound than the aromatic compound and this resulted in higher liquid yield than PVC. According to Cepeliogullar and Putun [19],

**Table 7**
Main oil composition from the pyrolysis of plastics.

| PET [19] | HDPE [15] | PVC [19] | LDPE [45] | PP[15] | PS [34] |
|---|---|---|---|---|---|
| 1-Propanone | 1-Methylcyclopentene | Azulene | Benzene | 2-Methyl-1-Pentene | Benzene |
| Benzoic acid | 3-Methylcyclopentene | Naphthalene, 1-methyl- | Toluene | 3-Methylcyclopentene | Toluene |
| Biphenyl | 1-Hexene | Biphenyl | Xylene | 1-Heptene | Ethylbenzene |
| Diphenylmethane | Cyclohexene | Naphthalene, 1-ethyl- | Dimethylbenzene | 1-Octene | Xylene |
| 4-Ethylbenzoic acid | 1-Heptene | Naphthalene, 1-(2-propenyl)- | Trimethylbenzene | C4–C13 hydrocarbon | Styrene |
| 4-Vinylbenzoic acid | 1-Octene | Naphthalene, 2,7-dimethyl- | Indane | Over C14 hydrocarbon | Cumene |
| Fluorene | 1-Nonene | Naphthalene, 1,6-dimethyl- | Indene | Benzene | Propylbenzene |
| Benzophenone | 1-Decene | Naphthalene, 1,7-dimethyl- | Methylindenes | Toluene | 2-Ethyltoluene |
| 4-Acetylbenzoic acid | 1-Undecene | Naphthalene, 1,4-dimethyl- | Naphthalene | Xylene | Naphthalene |
| Anthracene | 1-Tridecene | Naphthalene, 1,6,7-trimethyl- | Methylnaphthalenes | Ethybenzene | Diphenylmethane |
| Biphenyl-4-carboxylic acid | C4–C13 hydrocarbon | 9H-Fluorene | Ethylnaphthalene | Indene | Anthracene |
| 1-Butanone | Over C14 hydrocarbon | Naphthalene, 1-(2-propenyl)- | Dimethylnaphthalene | Biphenyl | 1,2-Diphenylethane |
| m-Terphenyl | Benzene | Phenanthrene, 1-methyl | Acenaphthylene | | 2,2-Diphenylpropane |
| | Toluene | Fluoranthene, 2-methyl- | Acenaphthene | | 1,3-Diphenylpropane |
| | Xylene | 1H-Indene, 2,3-dihydro-5-methyl- | Trimethylnaphthalenes | | Phenylnaphthalene |
| | | Naphthalene, 2-phenyl- | Fluorene | | Diphenylbenzene |
| | | | Tetramethylnaphthalene | | Triphenylbenzene |

PET pyrolysis yielded 23.1 wt% liquid oil while PVC only produced 12.3 wt% liquid oil. This shows that the liquid yield of PET almost doubled the PVC. The low liquid yield in PVC indicated the high production of gaseous product during the pyrolysis. The structure of PVC that comprised of the halogen ($Cl^-$) with high electronegativity explained the situation. High temperature during the pyrolysis would cause the dehydrochlorination process to occur, consequently increased the gaseous product and reduced the liquid oil yield [126]. The release of hydrochloric acid and chlorine compound during the PVC pyrolysis indicated that the liquid oil was not suitable to be used as fuel since it depreciated the fuel quality. Based on Table 7, it was clearly seen that most of the PVC compound was decomposed to naphthalene and its derivative around 33.55% [19].

In PP and HDPE pyrolysis oil, Jung et al. [15] observed that the liquid oil contained primarily aliphatic, monoaromatic and polyaromatic compounds. As for the PP fraction, the increase in the temperature reduced the aliphatic concentration in the oil to 2.9 wt% at 746 °C. In contrast, high aliphatic concentration was found in HDPE pyrolysis oil around 20 wt% at 728 °C. This indicates the complexity of the HDPE structure to degrade during thermal degradation process. Besides that, the BTX aromatics in PP pyrolysis oil (53 wt%) were found higher than in the HDPE fraction (32 wt %) at the same temperature as mentioned previously. The most abundant compound comprised in the BTX aromatics was the benzene. The concentration of benzene and toluene increased with the temperature except xylene compound which did not have a significant difference with the temperature. In terms of hydrocarbon product distribution, paraffins were the main product observed (66.55%) for PP derived liquid compared than HDPE (59.70%). Hence, PP pyrolytic oil was more value added than the HDPE derived liquid since paraffins released extra energy for combustion than other hydrocarbon groups such as olefins and naphthenes.

As for the LDPE derived liquid oil, Williams and Williams [45] reported that the aliphatic compound which consisted of alkanes, alkenes and alkadienes was the main composition found. As the temperature increased, the aliphatic concentration was in decreasing trend. However, the aromatic compound showed an opposite trend in which the aromatic concentration increased with the temperature. Among the aromatic compound, benzene and toluene concentration showed a dramatic increase as the temperature increased except xylene and this observation matched the trend observed in PP and HDPE pyrolysis as reported by Jung et al. [15]. However, it should be noted that the chemical concentration depends strongly on the pyrolysis operating temperature. According to Williams and Williams [45], the oil contained no aromatic and polyaromatic hydrocarbon at temperature of 500–550 °C. Nevertheless, a significant increase in the single ring aromatic compound and polycyclic aromatic compound (PAH) happened when the temperature increased to 700 °C that comprised around 25% of the liquid oil composition.

For PS pyrolysis oil, Onwudili et al. [34] reported that the benzene, toluene and ethyl benzene were three main components in the PS oil product that increased with the temperature. On the other hand, styrene monomer kept decreasing with the temperature and this suggest that the styrene radical formed during the degradation process of PS was very reactive. Liu et al. [37] also reported the same observation. The styrene and monoaromatics were among the major components in the liquid oil product that they covered around 80 wt% in the liquid fraction. These components were categorized in the low boiling point fraction of less or equal to 200 °C [37].

## 5. By-products of the plastic pyrolysis

Pyrolysis of plastics also produces char and gas as by-products. The proportion of by-product in pyrolysis strongly depends on several parameters such as temperature, heating rate, pressure and residence time. Some information about the by-products generated is discussed below.

### 5.1. Char

Generally, slow heating rate at very low temperature and long residence time maximizes the char formation in pyrolysis process. Even though the char formation in fast pyrolysis process is commonly low, it is worth noting the properties and usage of the char to fully maximize the potential of plastic pyrolysis. Jamradloedluk and Lertsatitthanakorn [127] analyzed the char properties obtained from the pyrolysis of HDPE plastic waste. From the proximate analysis, volatile matter and fixed carbon were found to be the main components of the char (>97 wt%) while moisture and ash were the minorities. These components were closely related to the proximate analysis of the raw plastic as tabulated in Table 1, showing that most plastics were composed from almost 99 wt% of volatile matter. The calorific value of the char was about 18.84 MJ/kg. Furthermore, the low sulfur content made it suitable to be used as fuel, for instance in combustion with coal or other wastes.

Besides that, the char formation was found to be increased with the temperature and this trend was observed by Jung et al. [15] in pyrolysis of PE and PP wastes. The char formation was increased

from 2 wt% to 4 wt% in PP pyrolysis and from 0.7 wt% to 2 wt% in PE pyrolysis as the temperature was raised from 668 °C to 746 °C. Unfortunately, the char obtained from both plastics consisted mainly of inorganic matters up to 98.9 wt% which originated from the inorganic substance in the feed fraction. In this case, the high inorganic matters caused the application of char as fuel to be difficult. However, it still has potential to be used as road surfacing and as a building material [15].

Nevertheless, char can also be used as an adsorbent in water treatment to remove heavy metal through an upgrading treatment. A multistep upgrading of chars was studied by Bernando [128] in a co-pyrolysis of PE, PP and PS plastic wastes, pine biomass and used tires. The adsorption properties of the upgraded chars were examined and the result indicated that the chars were mainly mesoporous and macroporous material with adsorption capacities for methylene blue dye in the range of 3.59–22.2 mg/g. This indicates that the upgraded chars should have good adsorption properties towards bulky molecules. Therefore, the upgrading treatments performed on the chars allowed carbonaceous residue from pyrolysis to be reused as precursors for adsorbents to be obtained. Other potential applications of pyrolysis char include using as feedstock in production of activated carbon and as solid fuel for boilers [86].

### 5.2. Gas

According to Prabir [129], high temperature and long residence time were the best condition to maximize gas production in pyrolysis process. However, these conditions are opposite with the parameters to maximize oil production. Generally, gas production in pyrolysis process of polyolefins and PS plastics were quite low in the range of 5–20 wt% and it is strongly depends on the temperature and type of plastics used in pyrolysis. The effect of temperature and plastic types were further studied by Onwudili et al. [34] in a pyrolysis of LDPE, PS and their mixture. At 350 °C, it was discovered that the gas product from the mixture was more than the pyrolysis of individual plastic. The gas continued to increase to 8.6 wt% at 425° where at this point, the gas product was higher than pyrolysis of PS alone but lower than LDPE. At the same temperature, pyrolysis of PS produced some amount of char but not any significant gas product. However, the pyrolysis of LDPE did produce more gas but no char at this temperature. Hence, the authors noted that the amount of gas produced from the mixture was significantly contributed by the LDPE component, whereas char formation related closely to PS. At 450 °C, the gas production increased continuously to 12.8 wt% for the plastic mixture.

On the other hand, the pyrolysis of PET and PVC plastics produced large amount of gases in comparison to other polyolefin plastics and PS. Cepeliogullar and Putun [19] discovered that the amount of gas produced in pyrolysis of PET (76.9 wt%) and PVC (87.7 wt%) waste plastics were much higher than the liquid yield at 500 °C. The same trend was observed by Fakhrhoseini and Dastanian [5] in the pyrolysis of PET at the same temperature when 52.13 wt% of gas product collected from the process. This indicates that PET and PVC decomposed mainly to gas product at this temperature. PET used very less energy content to convert into other chemical structures and this mechanism caused more gas production in the pyrolysis process. Conversely, a dehydrochlorination step might occur during the pyrolysis of PVC that caused a high amount of gas to be released rather than the liquid product.

The gas composition depends on the composition of feedstock material. Williams and Williams [130] studied the pyrolysis of HDPE, LDPE, PP, PS, PET and PVC individually and they found that the main gas components produced during pyrolysis of each plastic were hydrogen, methane, ethane, ethene, propane, propene, butane and butene. However, PET produced additional gas components of carbon dioxide and carbon monoxide while hydrogen chloride was also produced by PVC. The gas produced in pyrolysis process also has significant calorific value. Jung et al. [15] reported that the gas produced from the pyrolysis of PE and PP alone had high calorific value between 42 and 50 MJ/kg. Thus, the pyrolysis gas had high potential to be used as heating source in pyrolysis industrial plant. Additionally, the ethene and propene can be used as chemical feedstock for the production of polyolefins if separated from other gas components. The pyrolysis gas can also be used in gas turbines to generate electricity and direct firing in boilers without the need for flue gas treatment [86].

## 6. Discussion on plastic pyrolysis scenarios

This review showed that many researches have been done to study the potential of plastic pyrolysis process in order to produce valuable products such as liquid oil and the results were convincing. This technique offers several advantages such as enhancing the waste management system, reducing the reliability to fossil fuels, increasing energy sources and also prevents the contamination to the environment. The technique can be executed at different parameters that resulted in different liquid oil yield and quality. Besides that, this technique offers great versatility and better economic feasibility in terms of the process handling and the variability of the product obtained.

As mentioned in the paragraph above, various parameters could influence the liquid oil yield and the most critical factor was the temperature. Different plastics may have different degradation temperature depends on their chemical structures. Therefore, the effective temperatures for the liquid optimization in pyrolysis also varied for each plastic and it also strongly dependent on other process parameters. Such parameters include the type of catalyst used, the ratio of catalyst/polymer and also type of reactors operated.

Table 8 summarized the optimum temperature required to optimize liquid oil yield in thermal and catalytic pyrolysis at different conditions. Other affected parameters include the type of reactors, pressure, heating rate and pyrolysis duration for each type of plastics. All experiments carried out were using nitrogen gas as the fluidizing medium. Based on Table 8, PET and PVC are two plastics that produced very low yield of liquid oil in comparison with other plastic types, which made these plastics infrequently explored by researchers. It also should be noted that not all plastic types are recommended for pyrolysis. PVC was not preferred in pyrolysis since it produced the major product of harmful hydrochloric acid and very low yield of liquid oil. Additionally, the pyrolysis oil also contained chlorinated compound that would degrade the oil quality and also toxic to the environment.

As summarized in Table 8, it can be concluded that the most effective temperature to optimize the liquid oil yield in plastic pyrolysis would be in the range of 500–550 °C for thermal pyrolysis. However, with the usage of catalyst in the pyrolysis, the optimum temperature could be lowered down to 450 °C and higher liquid yield was obtained. In most plastics, the usage of catalyst in the process might improve the liquid oil yield, but PS was exceptional. This is because PS degraded very easily without the needs of any catalysts to speed up the reaction and yet 97 wt% of oil was produced [34]. Therefore, PS was the best plastic for pyrolysis since it produced the highest amount of liquid oil production among all the plastics. As for the polyolefin plastic type, LDPE produced the highest liquid oil yield (93.1 wt%), followed by HDPE (84.7 wt%) and PP (82.12 wt%) in thermal pyrolysis. However, with addition of catalyst such as FCC and at the right operating temperature, the liquid yield could be further maximized to above 90 wt%.

**Table 8**
Summary of studies on plastic pyrolysis.

| Reference* | Type of plastic | Reactor | Process parameters | | | | Yield | | | Others |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Temperature (°C) | Pressure | Heating rate (°C/min) | Duration (min) | Oil (wt%) | Gas (wt%) | Solid (wt%) | |
| [19] | PET | Fixed bed | 500 | – | 10 | – | 23.1 | 76.9 | 0 | |
| [5] | PET | – | 500 | 1 atm | 6 | – | 38.89 | 52.13 | 8.98 | |
| [23] | HDPE | Horizontal steel | 350 | – | 20 | 30 | 80.88 | 17.24 | 1.88 | |
| [60] | HDPE | Semi-batch | 400 | 1 atm | 7 | – | 82 | 16 | 2 | Stirring rate 200 RPM, FCC catalyst 10 wt% |
| [48] | HDPE | Batch | 450 | – | – | 60 | 74.5 | 5.8 | 19.7 | |
| [59] | HDPE | Semi-batch | 450 | 1 atm | 25 | – | 91.2 | 4.1 | 4.7 | Stirring rate 50 RPM, FCC catalyst 20 wt% |
| [77] | HDPE | Fluidized bed | 500 | – | – | 60 | 85 | 10 | 5 | Silica alumina catalyst |
| [26] | HDPE | Batch | 550 | – | 5 | – | 84.7 | 16.3 | 0 | |
| [27] | HDPE | Fluidized bed | 650 | – | – | 20–25 | 68.5 | 31.5 | 0 | |
| [19] | PVC | Fixed bed | 500 | – | 10 | – | 12.3 | 87.7 | 0 | |
| [29] | PVC | Vacuum batch | 520 | 2 kPa | 10 | – | 12.79 | 0.34 | 28.13 | Also yield HCl = 58.2 wt% |
| [34] | LDPE | Pressurized batch | 425 | 0.8–4.3 MPa | 10 | 60 | 89.5 | 10 | 0.5 | |
| [32] | LDPE | Batch | 430 | – | 3 | – | 75.6 | 8.2 | 7.5 | Also yield wax = 8.7 wt% |
| [5] | LDPE | – | 500 | 1 atm | 6 | – | 80.41 | 19.43 | 0.16 | |
| [31] | LDPE | Fixed bed | 500 | – | 10 | 20 | 95 | 5 | 0 | |
| [26] | LDPE | Batch | 550 | – | 5 | – | 93.1 | 14.6 | 0 | |
| [45] | LDPE | Fluidized bed | 600 | 1 atm | – | – | 51.0 | 24.2 | 0 | Also yield wax = 24.8 wt% |
| [23] | PP | Horizontal steel | 300 | – | 20 | 30 | 69.82 | 28.84 | 1.34 | |
| [35] | PP | Batch | 380 | 1 atm | 3 | – | 80.1 | 6.6 | 13.3 | |
| [60] | PP | Semi-batch | 400 | 1 atm | 7 | – | 85 | 13 | 2 | Stirring rate 200 RPM, used FCC catalyst 10 wt% |
| [57] | PP | Semi-batch | 450 | 1 atm | 25 | – | 92.3 | 4.1 | 3.6 | Stirring rate 50 RPM, used FCC catalyst 10 wt% |
| [5] | PP | – | 500 | 1 atm | 6 | – | 82.12 | 17.76 | 0.12 | |
| [36] | PP | Batch | 740 | – | – | – | 48.8 | 49.6 | 1.6 | |
| [60] | PS | Semi-batch | 400 | 1 atm | 7 | – | 90 | 6 | 4 | Stirring rate 200 RPM, used FCC catalyst, cat/poly = 10 w/w |
| [34] | PS | Pressurized batch | 425 | 0.31–1.6 MPa | 10 | 60 | 97 | 2.50 | 0.5 | |
| [49] | PS | Batch | 500 | – | – | 150 | 96.73 | 3.27 | 0 | Used Zn catalyst, cat/poly = 5 w/w |
| [36] | PS | Batch | 581 | – | – | – | 89.5 | 9.9 | 0.6 | 64.9 wt% of liquid comprised of styrene |

* All experiments used nitrogen gas as fluidizing medium.

## 7. Conclusion

This review has provided concise summary of plastic pyrolysis for each type and a discussion of the main affecting parameters to optimize liquid oil yield. Based on the studies on literatures, pyrolysis process was chosen by most researchers because of its potential to convert the most energy from plastic waste to valuable liquid oil, gaseous and char. Therefore, it is the best alternative for plastic waste conversion and also economical in terms of operation. The flexibility that it provides in terms of product preference could be achieved by adjusting the parameters accordingly. The pyrolysis could be done in both thermal and catalytic process. However, the catalytic process provided lower operating temperature with greater yield of liquid oil for most plastics with the right catalyst selection. The sustainability of the process is unquestionable since the amount of plastic wastes available in every country is reaching millions of tons. With the pyrolysis method, the waste management becomes more efficient, less capacity of landfill needed, less pollution and also cost effective. Moreover, with the existence of pyrolysis method to decompose plastic into valuable energy fuel, the dependence on fossil fuel as the non-renewable energy can be reduced and this solves the rise in energy demand.

## Acknowledgement

The authors would like to thank the University of Malaya for fully funding the work described in this publication through the PPP project number PG066-2015B. A special thanks is also extended to the Universiti Teknologi Mara (UiTM) and Ministry of Higher Education (MOHE) for providing financial support under the Young Lecturer's Scheme (TPM).

## References

[1] Association of Plastic Manufacturers Europe. An analysis of European plastics production, demand and waste data. Belgium: European Association of Plastics Recycling and Recovery Organisations; 2015. p. 1–32.
[2] U.S. Environmental Protection Agency. Common wastes and materials. US; 2014.
[3] Kukreja R. Advantages and disadvantages of recycling. Conserve Energy Future; 2009.
[4] Masanet E, Auer R, Tsuda D, Barillot T, Baynes A. An assessment and prioritization of "design for recycling" guidelines for plastic components. In: Electronics and the environment, IEEE international symposium; 2002. p. 5–10.
[5] Fakhrhoseini SM, Dastanian M. Predicting pyrolysis products of PE, PP, and PET using NRTL activity coefficient model. Hindawi Publishing Corporation; 2013. p. 1–5.
[6] Bridgwater AV. Review of fast pyrolysis of biomass and product upgrading. Biomass Bioenergy 2012;38:68–94.
[7] Abnisa F, Wan Daud WMA. A review on co-pyrolysis of biomass: an optional technique to obtain a high-grade pyrolysis oil. Energy Convers Manage 2014;87:71–85.
[8] Kreith F. The CRC handbook of mechanical engineering. 2nd ed. CRC Press, Inc; 1998.
[9] Zannikos F, Kalligeros S, Anastopoulos G, Lois E. Converting biomass and waste plastic to solid fuel briquettes. J Renew Energy 2013;2013:9.
[10] Heikkinen JM, Hordijk JC, de Jong W, Spliethoff H. Thermogravimetry as a tool to classify waste components to be used for energy generation. J Anal Appl Pyrol 2004;71:883–900.
[11] Ahmad I, Ismail Khan M, Ishaq M, Khan H, Gul K, Ahmad W. Catalytic efficiency of some novel nanostructured heterogeneous solid catalysts in pyrolysis of HDPE. Polym Degrad Stab 2013;98:2512–9.
[12] Hong S-J, Oh SC, Lee H-P, Kim HT, Yoo K-O. A study on the pyrolysis characteristics of poly(vinyl chloride). J Korean Inst Chem Eng 1999;37:515–21.
[13] Park SS, Seo DK, Lee SH, Yu T-U, Hwang J. Study on pyrolysis characteristics of refuse plastic fuel using lab-scale tube furnace and thermogravimetric analysis reactor. J Anal Appl Pyrol 2012;97:29–38.
[14] Aboulkas A, El harfi K, El Bouadili A. Thermal degradation behaviors of polyethylene and polypropylene. Part I: pyrolysis kinetics and mechanisms. Energy Convers Manage 2010;51:1363–9.

[15] Jung S-H, Cho M-H, Kang B-S, Kim J-S. Pyrolysis of a fraction of waste polypropylene and polyethylene for the recovery of BTX aromatics using a fluidized bed reactor. Fuel Process Technol 2010;91:277–84.
[16] Abnisa F, Daud WMAW, Sahu JN. Pyrolysis of mixtures of palm shell and polystyrene: an optional method to produce a high-grade of pyrolysis oil. Environ Prog Sustain Energy 2014;33:1026–33.
[17] Othman N, Basri NEA, Yunus MNM, Sidek LM. Determination of physical and chemical characteristics of electronic plastic waste (Ep-Waste) resin using proximate and ultimate analysis method. In: International conference on construction and building technology; 2008. p. 169–80.
[18] Çepelioğullar Ö, Pütün AE. Thermal and kinetic behaviors of biomass and plastic wastes in co-pyrolysis. Energy Convers Manage 2013;75:263–70.
[19] Cepeliogullar O, Putun AE. Utilization of two different types of plastic wastes from daily and industrial life. In: Ozdemir C, Sahinkaya S, Kalipci E, Oden MK, editors. ICOEST Cappadocia 2013. Turkey: ICOEST Cappadocia; 2013. p. 1–13.
[20] Wan Ho M. Waste plastics into fuel oil? UK: Institute of Science in Society; 2015.
[21] Shioya M, Kawanishi T, Shiratori N, Wakao H, Sugiyama E, Ibe H, et al. Development of waste plastics liquefaction technology, feedstock recycling in Japan. In: Muller-Hagedorn M, Bockhorn H, editors. Feedstock recycling of plastics, Germany; 2005. p. 19–42.
[22] Michael PA. Plastic waste total in MSW. Society of the Plastic Industry; 2010.
[23] Ahmad I, Khan MI, Khan H, Ishaq M, Tariq R, Gul K, et al. Pyrolysis study of polypropylene and polyethylene into premium oil products. Int J Green Energy 2014;12:663–71.
[24] Kumar S, Singh RK. Recovery of hydrocarbon liquid from waste high density polyethylene by thermal pyrolysis. Braz J Chem Eng 2011;28:659–67.
[25] Boundy B, Diegel SW, Wright L, Davis SC. Biomass energy data book. 4th ed. US: Oak Ridge National Laboratory; 2011.
[26] Marcilla A, Beltrán MI, Navarro R. Thermal and catalytic pyrolysis of polyethylene over HZSM5 and HUSY zeolites in a batch reactor under dynamic conditions. Appl Catal B Environ 2009;86:78–86.
[27] Mastral FJ, Esperanza E, Garcia P, Juste M. Pyrolysis of high-density polyethylene in a fluidized bed reactor. Influence of the temperature and residence time. J Anal Appl Pyrol 2001;63:1–15.
[28] British Plastics Federation. Polyvinyl chloride (PVC). London; 2015.
[29] Miranda R, Jin Y, Roy C, Vasile C. Vacuum pyrolysis of PVC kinetic study. Polym Degrad Stab 1998;64:127–44.
[30] López A, de Marco I, Caballero BM, Laresgoiti MF, Adrados A. Dechlorination of fuels in pyrolysis of PVC containing plastic wastes. Fuel Process Technol 2011;92:253–60.
[31] Bagri R, Williams PT. Catalytic pyrolysis of polyethylene. J Anal Appl Pyrol 2001;63:29–41.
[32] Uddin MA, Koizumi K, Murata K, Sakata Y. Thermal and catalytic degradation of structurally different types of polyethylene into fuel oil. Polym Degrad Stab 1996;56:37–44.
[33] Aguado J, Serrano DP, San Miguel G, Castro MC, Madrid S. Feedstock recycling of polyethylene in a two-step thermo-catalytic reaction system. J Anal Appl Pyrol 2007;79:415–23.
[34] Onwudili JA, Insura N, Williams PT. Composition of products from the pyrolysis of polyethylene and polystyrene in a closed batch reactor: effects of temperature and residence time. J Anal Appl Pyrol 2009;86:293–303.
[35] Sakata Y, Uddin MA, Muto A. Degradation of polyethylene and polypropylene into fuel oil by using solid acid and non-solid acid catalysts. J Anal Appl Pyrol 1999;51:135–55.
[36] Demirbas A. Pyrolysis of municipal plastic wastes for recovery of gasoline-range hydrocarbons. J Anal Appl Pyrol 2004;72:97–102.
[37] Liu Y, Qian J, Wang J. Pyrolysis of polystyrene waste in a fluidized-bed reactor to obtain styrene monomer and gasoline fraction. Fuel Process Technol 1999;63:45–55.
[38] Hopewell J, Dvorak R, Kosior E. Plastics recycling: challenges and opportunities. Philos Trans R Soc London B Biol Sci 2009:2115–26.
[39] Kaminsky W, Schlesselmann B, Simon CM. Thermal degradation of mixed plastic waste to aromatics and gas. Polym Degrad Stab 1996;53:189–97.
[40] Donaj PJ, Kaminsky W, Buzeto F, Yang W. Pyrolysis of polyolefins for increasing the yield of monomers' recovery. Waste Manage 2012;32:840–6.
[41] Sobko AA. Generalized Van der Waals-Berthelot equation of state. Dokl Phys 2008;53:416–9.
[42] Chin BLF, Yusup S, Al Shoaibi A, Kannan P, Srinivasakannan C, Sulaiman SA. Kinetic studies of co-pyrolysis of rubber seed shell with high density polyethylene. Energy Convers Manage 2014;87:746–53.
[43] Marcilla A, García-Quesada JC, Sánchez S, Ruiz R. Study of the catalytic pyrolysis behaviour of polyethylene–polypropylene mixtures. J Anal Appl Pyrol 2005;74:387–92.
[44] Marcilla A, Beltrán MI, Navarro R. Evolution of products during the degradation of polyethylene in a batch reactor. J Anal Appl Pyrol 2009;86:14–21.
[45] Williams PT, Williams EA. Fluidised bed pyrolysis of low density polyethylene to produce petrochemical feedstock. J Anal Appl Pyrol 1998;51:107–26.
[46] Fogler HS. Elements of chemical reaction engineering. 4th ed. New Jersey: Pearson Education Inc.; 2010.
[47] Jan MR, Shah J, Gulab H. Catalytic degradation of waste high-density polyethylene into fuel products using $BaCO_3$ as a catalyst. Fuel Process Technol 2010;91:1428–37.
[48] Miskolczi N, Bartha L, Deák G, Jóver B, Kalló D. Thermal and thermo-catalytic degradation of high-density polyethylene waste. J Anal Appl Pyrol 2004;72:235–42.
[49] Adnan, Shah J, Jan MR. Thermo-catalytic pyrolysis of polystyrene in the presence of zinc bulk catalysts. J Taiwan Inst Chem Eng 2014;45:2494–500.
[50] García RA, Serrano DP, Otero D. Catalytic cracking of HDPE over hybrid zeolitic–mesoporous materials. J Anal Appl Pyrol 2005;74:379–86.
[51] Kim SS, Kim S. Pyrolysis characteristics of polystyrene and polypropylene in a stirred batch reactor. Chem Eng J 2004;98:53–60.
[52] Cardona SC, Corma A. Tertiary recycling of polypropylene by catalytic cracking in a semibatch stirred reactor: use of spent equilibrium FCC commercial catalyst. Appl Catal B Environ 2000;25:151–62.
[53] Adrados A, De Marco I, Caballero B, López A, Laresgoiti M, Torres A. Pyrolysis of plastic packaging waste: a comparison of plastic residuals from material recovery facilities with simulated plastic waste. Waste Manage 2012;32:826–32.
[54] Uemura Y, Azeura M, Ohzuno Y, Hatate Y. Flash-pyrolyzed product distribution of major plastics in a batch reactor. J Chem Eng Jpn 2001;34:1293–9.
[55] Lee K-H, Shin D-H. Characteristics of liquid product from the pyrolysis of waste plastic mixture at low and high temperatures: influence of lapse time of reaction. Waste Manage 2007;27:168–76.
[56] Shah J, Jan MR, Mabood F, Jabeen F. Catalytic pyrolysis of LDPE leads to valuable resource recovery and reduction of waste problems. Energy Convers Manage 2010;51:2791–801.
[57] Abbas-Abadi MS, Haghighi MN, Yeganeh H, McDonald AG. Evaluation of pyrolysis process parameters on polypropylene degradation products. J Anal Appl Pyrol 2014;109:272–7.
[58] Seo Y-H, Lee K-H, Shin D-H. Investigation of catalytic degradation of high-density polyethylene by hydrocarbon group type analysis. J Anal Appl Pyrol 2003;70:383–98.
[59] Abbas-Abadi MS, Haghighi MN, Yeganeh H. Evaluation of pyrolysis product of virgin high density polyethylene degradation using different process parameters in a stirred reactor. Fuel Process Technol 2013;109:90–5.
[60] Kyong HL, Nam SN, Dae HS, Seo Y. Comparison of plastic types for catalytic degradation of waste plastics into liquid product with spent FCC catalyst. Polym Degrad Stab 2002;78:539–44.
[61] Lee KH. Composition of aromatic products in the catalytic degradation of the mixture of waste polystyrene and high-density polyethylene using spent FCC catalyst. Polym Degrad Stab 2008;93:1284–9.
[62] The University of York. Chemical reactors. The Essential Chemical Industry [online]. UK: The University of York; 2013.
[63] Saad JM, Nahil MA, Williams PT. Influence of process conditions on syngas production from the thermal processing of waste high density polyethylene. J Anal Appl Pyrol 2015;113:35–40.
[64] Renzini MS, Lerici LC, Sedran U, Pierella LB. Stability of ZSM-11 and BETA zeolites during the catalytic cracking of low-density polyethylene. J Anal Appl Pyrol 2011;92:450–5.
[65] Choi SJ, Park Y-K, Jeong K-E, Kim T-W, Chae H-J, Park SH, et al. Catalytic degradation of polyethylene over SBA-16. Korean J Chem Eng 2010;27:1446–51.
[66] Ballice L. A kinetic approach to the temperature-programmed pyrolysis of low-and high-density polyethylene in a fixed bed reactor: determination of kinetic parameters for the evolution of n-paraffins and 1-olefins. Fuel 2001;80:1923–35.
[67] Onu P, Vasile C, Ciocilteu S, Iojoiu E, Darie H. Thermal and catalytic decomposition of polyethylene and polypropylene. J Anal Appl Pyrol 1998;49:145–53.
[68] Vasile C, Pakdel H, Mihai B, Onu P, Darie H, Ciocalteu S. Thermal and catalytic decomposition of mixed plastics. J Anal Appl Pyrol 2000;57:287–303.
[69] Kaminsky W, Kim J-S. Pyrolysis of mixed plastics into aromatics. J Anal Appl Pyrol 1999;51:127–34.
[70] Garfoth AA, Lin YH, Sharratt PN, Dwyer J. Production of hydrocarbons by catalytic degradation of high density polyethylene in a laboratory fluidized-bed reactor. Appl Catal A Gen 1998;169:331–42.
[71] Lin YH, Yen HY. Fluidised bed pyrolysis of polypropylene over cracking catalysts for producing hydrocarbons. Polym Degrad Stab 2005;89:101–8.
[72] Marcilla A, Hernández MdR, García ÁN. Study of the polymer–catalyst contact effectivity and the heating rate influence on the HDPE pyrolysis. J Anal Appl Pyrol 2007;79:424–32.
[73] Lin YH, Yang MH, Yeh TF, Ger MD. Catalytic degradation of high density polyethylene over mesoporous and microporous catalysts in a fluidised-bed reactor. Polym Degrad Stab 2004;86:121–8.
[74] Mastral JF, Berrueco C, Gea M, Ceamanos J. Catalytic degradation of high density polyethylene over nanocrystalline HZSM-5 zeolite. Polym Degrad Stab 2006;91:3330–8.
[75] Sharratt P, Lin Y-H, Garforth A, Dwyer J. Investigation of the catalytic pyrolysis of high-density polyethylene over a HZSM-5 catalyst in a laboratory fluidized-bed reactor. Ind Eng Chem Res 1997;36:5118–24.
[76] Yan R, Liang DT, Tsen L. Case studies—problem solving in fluidized bed waste fuel incineration. Energy Convers Manage 2005;46:1165–78.
[77] Luo G, Suto T, Yasu S, Kato K. Catalytic degradation of high density polyethylene and polypropylene into liquid fuel in a powder-particle fluidized bed. Polym Degrad Stab 2000;70:97–102.

[78] Elordi G, Olazar M, Castaño P, Artetxe M, Bilbao J. Polyethylene cracking on a spent FCC catalyst in a conical spouted bed. Ind Eng Chem Res 2012;51:14008–17.
[79] Artetxe M, Lopez G, Amutio M, Elordi G, Bilbao J, Olazar M. Cracking of high density polyethylene pyrolysis waxes on HZSM-5 catalysts of different acidity. Ind Eng Chem Res 2013;52:10637–45.
[80] Elordi G, Olazar M, Lopez G, Amutio M, Artetxe M, Aguado R, et al. Catalytic pyrolysis of HDPE in continuous mode over zeolite catalysts in a conical spouted bed reactor. J Anal Appl Pyrol 2009;85:345–51.
[81] Olazar M, Lopez G, Amutio M, Elordi G, Aguado R, Bilbao J. Influence of FCC catalyst steaming on HDPE pyrolysis product distribution. J Anal Appl Pyrol 2009;85:359–65.
[82] Arabiourrutia M, Elordi G, Lopez G, Borsella E, Bilbao J, Olazar M. Characterization of the waxes obtained by the pyrolysis of polyolefin plastics in a conical spouted bed reactor. J Anal Appl Pyrol 2012;94:230–7.
[83] Aguado R, Olazar M, Gaisán B, Prieto R, Bilbao J. Kinetic study of polyolefin pyrolysis in a conical spouted bed reactor. Ind Eng Chem Res 2002;41:4559–66.
[84] Elordi G, Olazar M, Aguado R, Lopez G, Arabiourrutia M, Bilbao J. Catalytic pyrolysis of high density polyethylene in a conical spouted bed reactor. J Anal Appl Pyrol 2007;79:450–5.
[85] Lam SS, Chase HA. A review on waste to energy processes using microwave pyrolysis. Energies 2012;5:4209–32.
[86] Fernandez Y, Arenillas A, Menandez JA. Microwave heating applied to pyrolysis. Advances in induction and microwave heating of mineral and organic materials. Spain: InTech; 2011.
[87] Undri A, Rosi L, Frediani M, Frediani P. Efficient disposal of waste polyolefins through microwave assisted pyrolysis. Fuel 2014;116:662–71.
[88] Ludlow-Palafox C, Chase HA. Microwave-induced pyrolysis of plastic waste. Ind Eng Chem Res 2001;40:4749–56.
[89] Khaghanikavkani E. Microwave pyrolysis of plastic. J Chem Eng Process Technol 2013;04.
[90] Undri A, Rosi L, Frediani M, Frediani P. Microwave pyrolysis of polymeric materials. In: Chandra Usha, editor. Microwave heating. InTech; 2011.
[91] Murata K, Sato K, Sakata Y. Effect of pressure on thermal degradation of polyethylene. J Anal Appl Pyrol 2004;71:569–89.
[92] Mastral FJ, Esperanza E, Berrueco C, Juste M, Ceamanos J. Fluidized bed thermal degradation products of HDPE in an inert atmosphere and in air–nitrogen mixtures. J Anal Appl Pyrol 2003;70:1–17.
[93] Ivanova SR. Selective catalytic degradation of polyolefins. Prog Polym Sci 1990;15:193–215.
[94] Stelmachowski M. Thermal conversion of waste polyolefins to the mixture of hydrocarbons in the reactor with molten metal bed. Energy Convers Manage 2010;51:2016–24.
[95] Aguado J, Serrano DP, Escola JM. Catalytic upgrading of plastic wastes in feedstock recycling and pyrolysis of plastic wastes, Spain; 2006.
[96] International Zeolite Association; 2005.
[97] Degnan Jr TF. Applications of zeolites in petroleum refining. Top Catal 2000;13:349–56.
[98] Marcilla A, Beltran MI, Navarro I. Thermal and catalytic pyrolysis of polyethylene over HZSM-5 and HUSY zeolites in a batch reactor under dynamic conditions. Appl Catal B Environ 2008;86:78–86.
[99] Hernández MdR, Gómez A, García ÁN, Agulló J, Marcilla A. Effect of the temperature in the nature and extension of the primary and secondary reactions in the thermal and HZSM-5 catalytic pyrolysis of HDPE. Appl Catal A Gen 2007;317:183–94.
[100] Uemichi Y, Hattori M, Itoh T, Nakamura J, Sugioka M. Deactivation behaviors of zeolite and silica–alumina catalysts in the degradation of polyethylene. Ind Eng Chem Res 1998;37:867–72.
[101] Obeid F, Zeaiter J, Al-Muhtaseb AaH, Bouhadir K. Thermo-catalytic pyrolysis of waste polyethylene bottles in a packed bed reactor with different bed materials and catalysts. Energy Convers Manage 2014;85:1–6.
[102] Miskolczi N, Angyal A, Bartha L, Valkai I. Fuels by pyrolysis of waste plastics from agricultural and packaging sectors in a pilot scale reactor. Fuel Process Technol 2009;90:1032–40.
[103] Syamsiro M, Saptoadi H, Norsujianto T, Noviasri P, Cheng S, Alimuddin Z, et al. Fuel oil production from municipal plastic wastes in sequential pyrolysis and catalytic reforming reactors. Energy Proc 2014;47:180–8.
[104] Magee JS, Mitchell MM. Fluid catalytic cracking: science and technology. Elsevier; 1993.
[105] Humphries A, Wilcox J. Zeolite components and matrix composition determine FCC catalyst performance. Oil Gas J 1989;87.
[106] Rajagopalan K, Habib Jr E. Understand FCC matrix technology. Hydrocarb Process 1992;71.
[107] Marcilly CR. Where and how shape selectivity of molecular sieves operates in refining and petrochemistry catalytic processes. Top Catal 2000;13:357–66.
[108] Kyong HL, Sang GJ, Kwang HK, Nam SN, Dae HS, Park J, et al. Thermal and catalytic degradation of waste high density polyethylene (HDPE) using spent FCC catalyst. Korean J Chem Eng 2003;20:693–7.
[109] Sakata Y, Uddin MA, Muto A, Kanada Y, Koizumi K, Murata K. Catalytic degradation of polyethylene into fuel oil over mesoporous silica (KFS-16) catalyst. J Anal Appl Pyrol 1997;43:15–25.
[110] Lin YH, Yang MH. Catalytic pyrolysis of polyolefin waste into valuable hydrocarbons over reused catalyst from refinery FCC units. Appl Catal A Gen 2007;328:132–9.
[111] Sarker M, Kabir A, Rashid MM, Molla M, Din Mohammad ASM. Waste polyethylene terephthalate (PETE-1) conversion into liquid fuel. J Fundam Renew Energy Appl 2011;1:1–5.
[112] Manickaraja E, Tamilkolundu S. Catalytic degradation of waste PVC into liquid fuel using $BaCO_3$ as catalyst and its blending properties with diesel fuel. Discover 2014;23:74–8.
[113] Desai SB, Galage CK. Production and analysis of pyrolysis oil from waste plastic in Kolhapur city. Int J Eng Res Gen Sci 2015;3:590–5.
[114] Pinto F, Costa P, Gulyurtlu I, Cabrita I. Pyrolysis of plastic wastes. 1. Effect of plastic waste composition on product yield. J Anal Appl Pyrol 1998;51:39–55.
[115] Blazso M. Composition of liquid fuels derived from the pyrolysis of plastics. In: Scheirs J, Kaminsky W, editors. Feedstock recycling and pyrolysis of waste plastics: converting waste plastics into diesel and other fuels. Hungary: John Wiley & Sons; 2006. p. 315–42.
[116] Meyer RF, Attanasi ED. Heavy oil and natural bitumen-strategic petroleum resources. US: U.S. Geological Survey; 2003. p. 1–6.
[117] Kalghatgi GT. Fuel anti-knock quality – Part 1. Engine studies. Chester, UK: Shell Global Solutions; 2001.
[118] Bozbas K. Biodiesel as an alternative motor fuel: production and policies in the European Union. Renew Sustain Energy Rev 2008;12:542–52.
[119] Schlumberger. Pour point. Oilfield glossary; 2015.
[120] Horng JL, Chia LT, Jim SL. A model for predicting the flash point of ternary flammable solutions of liquid. Combust Flame 2004;138:308–19.
[121] Schlumberger. Aniline point test. Oilfield glossary; 2015.
[122] Cookson DJ, Latten JL, Shaw IM, Smith BE. Property-composition relationships for diesel and kerosene fuels. Fuel 1984;64:509–19.
[123] Becker A, Fischer H. A suggested index of diesel fuel performance. SAE technical paper; 1934.
[124] Kumar S, Prakash R, Murugan S, Singh RK. Performance and emission analysis of blends of waste plastic oil obtained by catalytic pyrolysis of waste HDPE with diesel in a CI engine. Energy Convers Manage 2013;74:323–31.
[125] Nino EF, Nino TG. Fuels and combustion. Manila: Rex Bookstore, Inc.; 1997.
[126] Kim S. Pyrolysis of PVC waste pipe. Waste Manage 2001;21:609–16.
[127] Jamradloedluk J, Lertsatitthanakorn C. Characterization and utilization of char derived from fast pyrolysis of plastic wastes. Proc Eng 2014;69:1437–42.
[128] Bernando M. Physico-chemical characterization of chars produced in the co-pyrolysis of wastes and possible routes of valorisation. Portugal: Chemical Engineering. Universidade Nova de Lisboa; 2011. p. 27–36.
[129] Prabir B. Biomass gasification and pyrolysis. Practical design and theory. USA: Elsevier Inc.; 2010.
[130] Williams PT, Williams EA. Interaction of plastics in mixed-plastics pyrolysis. Energy Fuel 1998;13:188–96.