Pyrolysis process to produce fuel from different types of plastic – a review

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Abstract: Fast exhaustion of oil resources and increase in energy demand have focused the researchers to find alternate ways to produce high quality oils that could replace fossil fuels. The idea of waste to energy recovery is one of the promising techniques for managing the waste plastic. Waste plastics are attractive for energy conversion because of their high heat of combustion and bulk availability. Exponential rate of increase in plastic production happens in every year due to the wide range of plastic appliances in domestic as well as industrial purposes. The drastic increase in the plastics production naturally lead to large amount of plastic waste that endangers the environment because of their disposal problems. The conversion of plastic to high quality liquid oil through pyrolysis process is highly advisable as the oil produced has high calorific value than that of commercial fuel. This paper describes commonly used verities of plastics and potential of pyrolysis process to produce fuel using them.

Key words: Plastic waste, Pyrolysis, Fuel production, Energy recovery

1. Introduction
Plastics are organic compounds having long chained hydrocarbon synthesized from petroleum products. Because of its own special features plastic had acquired wide popularity in short time. Plastic production and consumption rate increased exponentially due to its low cost, non-degradable nature, easy availability and management, wide range of usage and application. According to the estimate given by APME (Association of Plastic Manufacturers Europe), the global production of plastic has crossed 280 million tons in 2011 and it is increasing exponentially [1]. The increasing demand of plastic products also increases the accumulation of plastic waste that endangers the environment because of their disposal problems [2]. The rising plastics demand also led to the exhaustion of non-renewable crude oil as plastics are petroleum-based material. To minimize the adverse environmental impacts of plastic waste, many organizations are implemented with plastic waste management systems, for control/reduction of plastic waste formation.

Various methods of waste plastic treatment can be categorized as follows [3, 4]:
1) Plastic scrap can be re-introduced in the heating cycle of plastic processing line itself to increase production (primary method);

2) Mechanical recycling (secondary methods): mechanical (physical) treatment to re-extrude, process and convert plastic solid waste to new plastic products blended with virgin polymers to reduce the overall production cost;

3) Chemical (tertiary) methods: chemical alteration in the polymer structure of plastic material can be performed through chemical or thermo-chemical means to utilize it as a monomer feedstock in industrial recycling loops and;

4) Energy recovery: which entails recovery of steam, heat and electricity from waste plastic through combustion.

2. Plastic for fuel production

Recycling of plastic is difficult and costly because of the restrictions on contamination of water and labor intensive segregation of different plastics before recycle which is labor intensive [5]. Segregation of different plastic materials are essential since they are made of different resin compound for difference in transparency and color. Dyed or pigmented plastics have a lower market value too [6]. Segregation of different plastic materials are essential since they are made of different resin compound for difference in transparency and color. Dyed or pigmented plastics have a lower market value too [6]. Clearly transparent plastics can be easily dyed to transform into new products, have greater flexibility and are mostly desirable by the manufacturers [6, 7]. Recycling plastic is energy intensive too. As there is an alarming depletion of energy sources, means of energy recovery from plastic waste is a good option. Pyrolysis is a suitable method for energy recovery from plastic waste and is one of the finest techniques for the conversion of mass to energy with liquid and gaseous products with high energy values [8]. Figure 1 represents the processes involved in the pyrolysis of plastic.

![Flow chart of plastic pyrolysis process](image)

**Figure 1.** Flow chart of plastic pyrolysis process

Pyrolysis or thermal cracking involves thermal degradation of long chain polymer molecules into less complex smaller molecules. The process takes place in the absence of oxygen at increased pressure and temperature for a short duration. Pyrolysis process is proposed by many researchers since the process is able to produce large quantity of liquid oil up to 80 wt% at temperatures around 500°C [9]. The process parameters can be altered to generate products based on personal preferences. Hence pyrolysis is often referred as a flexible process. The liquid oil produced is of high quality as it can be used in multiple applications without any upgradation or treatment [8]. The gaseous fuel produced as the byproduct of pyrolysis, can be reused to compensate the energy requirement of the pyrolysis plant.
as the gaseous fuel produced is of high calorific value [12]. Pyrolysis is mostly employed over common recycling processes since handling is much easier and flexible. Moreover, pyrolysis does not require intense sorting process and hence it is less labor intensive process.

Many published research papers are available on the potential of pyrolysis processes on various types of plastics for liquid fuel production. The present review comprehends the properties and use of various categories of plastics and description of pyrolysis process for fuel production for each category.

3. Thermal pyrolysis process
The commonly used plastics can be classified into six different types of plastics such as Polyethylene terephthalate (PET), High-density polyethylene (HDPE), Polyvinyl chloride (PVC), Low-density polyethylene (LDPE), Polypropylene (PP) and Polystyrene (PS). The pyrolysis process results of each of these are described in the following sections.

3.1. Polyethylene terephthalate
PET plastics are mainly used for packaging of food products, fruit juice containers, mineral water bottles, soft drink bottles etc. PET plastics have other applications in the production of electrical insulation, printing sheets, magnetic tapes, X-ray and other photographic films [11]. The extensive applications of PET plastics contribute huge amount of plastic waste that endangers the environment because of their disposal problems. Recycling PET waste is the current method for reducing PET plastic waste. Large use of containers causes fast accumulation of PET plastics which requires high frequency of collections and hence, increases the transport costs. Cepeliogullar and Putun [10] have conducted the pyrolysis of PET to produce liquid oil using fixed-bed reactor at 500°C. In the experiment, the rate of heating was 10°C/min. Nitrogen gas was used as the sweeping gas. The gaseous product obtained was 76.9 wt % and the liquid oil obtained was 23.1 wt%. The pyrolysis oil had acidic characteristic which is unfavorable to use in I.C. engines directly due to its corrosiveness that deteriorates the fuel quality [13]. Benzoic acid was a general sublime but needed a serious attention if running in industrial scale [20, 21]. Another liquid oil with slightly higher yield at the same operating temperature and heating rate was found by Fakhrhoseini and Dastanian [15]. The liquid yield was found to be 39.89 wt%, gaseous was 52.13 wt% while solid residue was 8.98 wt%. PET pyrolysis resulted in the generation of liquid oil in the ranges of 23 – 40 wt% while gaseous was in the ranges of 52 – 77 wt%. The polymer structure of PET is shown in Figure 1, together with its most likely thermal cleavage mechanisms.

![Image](image_url)

**Figure 2.** Chemical reaction involved in pyrolysis [35].
3.2. High-density polyethylene

HDPE is a long linear polymer chain having high strength properties. The features contributing to the strength are high degree of crystallinity and low branching. There are wide range of applications for HDPE. It is typically used for the production of milk bottles, detergent bottles, oil containers, toys and many more. It is the third largest plastic type found in MSW (Municipal Solid Waste) [14, 16].

Ahmad et al. [17] conducted the pyrolysis of HDPE using a steel reactor at a temperature range of 300–400°C. The fluidizing medium used was nitrogen. 80.88 wt% of liquid was obtained and the total conversion was happened to be at 350°C. 33.05 wt% solid residue was obtained at 300°C which found to be large. Thermal pyrolysis study of HDPE was conducted by Kumar and Singh using a semi-batch reactor at higher temperature of 400 – 550°C. The highest liquid yield and gaseous product (79.08 wt% and 24.75 wt% respectively) was obtained at a temperature of 550°C. Also a dark brownish oil was obtained. Beltrán et al. [20] have also conduct pyrolysis of HDPE plastics at 550°C. The liquid oil yield obtained was 84.7 wt% and gaseous product was found to be 16.3 wt%. This results show that higher liquid oil yield is possible from HDPE at higher temperature. However, too high temperature would reduce the liquid oil yield and would increase the gaseous product yield as the process may go beyond the maximum thermal degradation point of HDPE. This result was proved by the experiment on HDPE pyrolysis in a fluidized bed reactor at 650°C by Mastral et al [21]. The experiments provided a liquid oil production of around 68.5 wt% and 31.5 wt% of gaseous product. So it can be concluded that at high temperature above 550°C, the liquid was cracked to gaseous state.

3.3. Polyvinyl chloride

PVC is exceptional from other thermoplastics such as polyethylene, polystyrene and polypropylene and it is manufactured from the mixture of chlorine (57%) and carbon (43%) [22]. Due to the chlorine content, PVC have high fire resistance, and is suitable for electrical insulation. The works done on the PVC pyrolysis are very less due to the hydrogen chloride (HCl) fumes that is released when heated at high temperature. Jin et al. [23] conduct pyrolysis of PVC in a batch reactor at temperature range of 220 – 520°C and with a heating rate of 10°C/min. Liquid oil obtained was of range 0.45 wt% to 12.79 wt%. 58.2 wt% of HCl was also obtained from the experiment.

3.4. Low-density polyethylene

LDPE has lower tensile strength and hardness. This is because of the weaker intermolecular force of LDPE. In comparison with HDPE, LDPE has more branching. LDPE waste is the second largest plastic waste in MSW after PP [24]. Bagri and Williams [25] conducted LDPE pyrolysis in fixed-bed reactor at a temperature of 500°C. The experiment was conducted for a duration of 20 min and nitrogen gas was used as fluidizing medium. The liquid yield obtained was 95 wt% with low gas yield and negligible amount of char. 93.1 wt% of liquid oil was obtained when the same experiment was conducted in a batch reactor at a temperature of 550°C by Marcilla et al. [24]. From the research conducted by Koizumi et al. [26], 75.6 wt% of liquid oil was obtained in a batch reactor at 400°C. Aguado et al. [27] have obtained 74.7 wt% of liquid oil when using the same type of reactor at a temperature of 450°C. Onwudili et al. [28] conducted pyrolysis of LDPE at a temperature of 425°C in a pressurized batch reactor (0.8 – 4.3 MPa). The liquid oil yield obtained was 89.5%, gas obtained was 10 wt% and char was 0.5 wt%.

3.5. Polypropylene

PP have high chemical as well as heat resistance properties. It is a saturated polymer having linear hydrocarbon chain. It does not melt below than 160°C. PP has high hardness and rigidity which makes it preferable for plastic industry. Unlike HDPE, PP has a lower density. It is the largest contributor of plastics in MSW [22]. The diversified applications of PP include making of flowerpot, office folders, car bumpers, buckets, carpets, various furniture, storage boxes etc. Many researchers have studied the process of pyrolysis of PP by altering the parameters to optimize the liquid oil yield. One experiment conducted by Ahmad et al. [17] on PP pyrolysis was done at 250 – 400°C temperature. From the experiments it was found that 69.82 wt% of liquid oil was achieved at temperature of 300°C. Pyrolysis
of PP was conducted by Sakata et al. [29] on PP at temperature of 380°C and was obtained a liquid yield of 80.1 wt%, gas yield of 6.6 wt% and obtained a 13.3 wt% solid residue. Fakhrhoseini and Dastanian [15] conducted PP pyrolysis at 500°C and obtained 82.12 wt% of liquid yield. The liquid yield was reduced when the temperature is more than 500°C. Demirbas [30] conducted pyrolysis of PP at 740°C in a batch reactor and 48.8 wt% liquid, 49.6 wt% gas and 1.6 wt% char yield were obtained. This experiment inferred a reduction in liquid yield with increasing temperature.

3.6. Polystyrene
PS is synthesized from the liquid petrochemical and is the polymer of styrene monomers. It has compounds of long hydrocarbon chain with phenyl group attached to every carbon atom. It is a colorless compound, but can be colored with suitable colorants. Due to its reasonable durability, strength and lightness, PS is used in variety of applications including in food packaging, electronics, construction, medical, appliances, toys and many more. As the range of applications is higher, large waste accumulation is there. PS cannot be included in the roadside recycling program as the recycling bins only include glasses, papers, cans, and other light plastics. People won’t throw the foam food packaging into plastics recycle bin but will be put into the general bin. So recycling is challenging in the case of PS. The only way for the recovery of PS waste is pyrolysis process which converted it into high quality liquid oil. Pyrolysis of PS have been studied by many researchers. Of them Onwudili et al. [28] have conducted pyrolysis process in a pressurized autoclave reactor. The experimental duration was one hour and was conducted at a temperature of 300°C-500°C. The heating rate used was 10°C and the pressure applied was in the range of 0.31MPa-1.6MPa. From the experiment, the oil yield obtained was around 97.0 wt% at a temperature of 425°C. Maximum gas production was only 2.5 wt%. Liu et al. [31] also obtained high yield of liquid oil in their experiments. They used fluidized bed reactor at temperature of 450 – 700°C. 98.7 wt% of liquid oil was obtained at a temperature of 600°C. The liquid oil production was also high at lower temperatures of about 450°C. However, the experiments done by Demirbas [30] on PS resulted a decreased liquid oil production. The production was 89.5 wt% at 581°C in a batch reactor.

3.7. Mixed plastics
Unlike recycling, pyrolysis does not require a keen sorting of different plastics. It is one of the most meritorious point of pyrolysis of plastics. Most plastics are not compatible with each other and hence cannot be processed together during recycling. For example, a slight presence of PVC in PET recycle stream will degrade the whole PET resin by becoming yellowish and brittle [32]. Schlesselmann et al. [33] investigated the pyrolysis of mixed plastic wastes by collecting German households which consist 75% of polyolefin (mixture of PE and PP) and 25% PS.

Similar liquid oil production was found in another study conducted by Demirbas [30]. The experiment was conducted on the polyolefin and PS mixture collected from landfill which was approximately 46.6 wt% of total plastic waste. The respective yields of gas and solid were reported as 35 wt% and 2.2 wt%. The composition of oil showed the presence of about 4 ppm chlorine. Donaj et al. [34] conducted a study on pyrolysis of polyolefin mixed plastics. The mixed plastics consist 75 wt% LDPE, 30 wt% HDPE and 24 wt% PP. The experiments were conducted at temperatures of 650°C and 730°C in a fluidized bed reactor. In this experiment the liquid obtained was more at lower temperature of 650°C which was quantified around 48 wt%.

4. Conclusions
This review provides a concise summary of different types of plastics and the potential of pyrolysis for fuel production. The summary of pyrolysis results of the various category plastics can be consolidated as in Table 1.
# Table 1. Summary of studies on plastic pyrolysis

| Reference | Types of plastic | Reactor | Process Parameters | Products |
|-----------|------------------|---------|--------------------|----------|
|           |                  |         | Temperature | Pressure | Duration (min) | Oil (wt%) | Gas (wt%) | Solid (wt%) |
| [11]      | PET              | Fixed bed | 500        | –         | –            | 23.1      | 76.9       | 0          |
| [15]      | PET              | –        | 500        | 1 atm     | –            | 38.89     | 52.13      | 8.98       |
| [14]      | HDPE             | Horizontal steel | 350    | –         | 30           | 80.88     | 17.24      | 1.88       |
| [16]      | HDPE             | Semi-batch | 400      | 1 atm     | –            | 82        | 16         | 2          |
| [17]      | HDPE             | Batch    | 450        | –         | 60           | 74.5      | 5.8        | 19.7       |
| [20]      | HDPE             | Fluidized bed | 500      | –         | 60           | 85        | 10         | 5          |
| [21]      | HDPE             | Batch    | 550        | –         | –            | 84.7      | 16.3       | 0          |
| [19]      | HDPE             | Fluidized bed | 650      | –         | 20–25        | 68.5      | 31.5       | 0          |
| [22]      | PVC              | Fixed bed | 500        | –         | –            | 12.3      | 87.7       | 0          |
| [24]      | PVC              | Vacuum batch | 520      | 2 kPa     | –            | 12.79     | 0.34       | 28.13      |
| [25]      | LDPE             | Pressurized batch | 425      | 0.8–4.3 MPa | 60          | 89.5      | 10         | 0.5        |
| [31]      | LDPE             | –        | 500        | 1 atm     | –            | 80.41     | 19.43      | 0.16       |
| [28]      | LDPE             | Fixed bed | 500        | –         | 20           | 95        | 5          | 0          |
| [26]      | LDPE             | Batch    | 550        | –         | –            | 93.1      | 14.6       | 0          |
| [29]      | LDPE             | Fluidized bed | 600      | 1 atm     | –            | 51.0      | 24.2       | 0          |
| [22]      | PP               | Horizontal steel | 300      | –         | 30           | 69.82     | 28.84      | 1.34       |
| [17]      | PP               | Batch    | 380        | 1 atm     | –            | 80.1      | 6.6        | 13.3       |
| [31]      | PS               | Semi-batch | 400      | 1 atm     | –            | 90        | 6          | 4          |

Based on the studies, pyrolysis process is approved as a potential method to generate energy from plastic waste. It resulted in the production of valuable liquid oil, gaseous fuel and char instead of waste accumulation in landfills and hence contribute heavily to environmental pollution. For mini-scale batch pyrolysis process, liquid fuel is preferable both in the view of fuel handing and its storage. The plastic category PS found to give maximum liquid yield whereas PET category, the least. Pyrolysis process is not advisable for PVC category as it produce HCl fumes which is highly toxic. But pyrolysis is a reliable and sustainable method to find a solution for the problem of plastic waste accumulation in the country which is increasing tremendously day by day. Waste management can be effectively done by the process of pyrolysis of plastic wastes. The process is economical and cost effective too. Moreover, the proper use of the advantages of the pyrolysis process can reduce the dependence over the conventional energy sources like fossil fuels. Thus the rise in the energy demand can be reduced.

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