The Energy and Value-Added Products from Pyrolysis of Waste Plastics

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Abstract Plastic usage in daily life has increased from 5 to 100 million tons per year since the 1950s due to their light-weight, non-corrosive nature, durability and cheap price. Plastic products consist mainly of polyethylene (PE), polystyrene (PS), polypropylene (PP) and polyvinyl chloride (PVC) type plastics. The disposal of plastic waste causes environmental and operational burden to landfills. Conventional mechanical recycling methods such as sorting, grinding, washing and extrusion can recycle only 15–20 % of all plastic waste. The use of open or uncontrolled incineration or combustion of plastic waste has resulted in air and waterborne pollutants. Recently, pyrolysis technology with catalytic reforming is being used to convert plastic waste into liquid oil and char as energy and value-added products. Pyrolysis is one of the tertiary recycling techniques in which plastic polymers are broken down into smaller organic molecules (monomers) in the absence of oxygen at elevated temperatures (>400 °C). Use of catalysts such as aluminum oxides, natural and synthetic zeolites, fly ash, calcium hydroxide, and red mud can improve the yield and quality of liquid oil. The pyrolysis yield depends on a number of parameters such as temperature, heating rate, moisture contents, retention time, type of plastic and particle size. A yield of up to 80 % of liquid oil by weight can be achieved from plastic waste. The produced liquid oil has similar characteristics to conventional diesel; density (0.8 kg/m^3), viscosity (up to 2.96 mm^2/s), cloud point (−18 °C), flash point (30.5 °C) and energy content (41.58 MJ/kg). Char produced from pyrolysis can be activated at standard conditions to be used in wastewater treatment, heavy metals removal, and smoke and odor removal. The produced gases from pyrolysis are

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hydrogen (H_2), carbon monoxide (CO) and carbon dioxide (CO_2) and can be used as energy carriers. This chapter reviews the challenges and, perspectives of pyrolysis technology for production of energy and value-added products from waste plastics.

Keywords Plastic waste · Liquid oil · Energy · Pyrolysis · Char · Hydrogen (H_2)

1 Introduction

1.1 World Energy Demands

The current world population of 7.2 billion is projected to increase by 1 billion in 2025 with an annual growth rate of 1 % (WHO 2014). The developing world is the place, where most of this growth will occur due to rapid growth in urbanization and population. Consequently, the energy demand has increased significantly in developing countries, especially in Asia (Ouda et al. 2013, 2015), that will further increase by 46–58 % with an annual rate of 3.7 % till 2025 (FAO 2010). The present global energy consumption is 524 quadrillion thermal British units (Btu), that will increase upto 820 quadrillion Btu by 2040 (US-EIA 2014). Global electricity demand will increase by 80 % from 2012 to 2040; in which non-OECD countries such as China (33 %), India (15 %), Southeast Asia (9 %) and Middle East (6 %) show highest electricity demand (IEA 2014). About 80 % of the present global energy requirements are fulfilled by thermal power plants including coal, natural gas, oil and nuclear plants, while only 13 % is produced from renewable sources (WEC 2013; Demirbas et al. 2016a).

Energy recovery or waste-to-energy (WTE) from non-food biomass sources such as agricultural and forestary residues and domestic and industrial waste is an eco-friendly approach for renewable energy production (Nizami et al. 2015a, b, c and 2016; Ouda et al. 2016; Rehan et al. 2016; Sadaf et al. 2015; Tahir et al. 2015). Fuel-wood is one of the major sources of bioenergy that produces about 87 % of global bioenergy. About 2 billion people in the world still depend on fuel-wood and charcoal for their daily energy production (UNWWD 2014). Among renewable energy, wind and solar energy are dominant choices, as they produce the least greenhouse gas (GHG) emissions and do not require water for energy production (Evans et al. 2009; IEA 2014). Nevertheless, around 1.3 billion people across the globe are still living without electricity and most of them (95 %) are habitants of sub-Saharan Africa and developing Asia (IEA 2014).

1.2 Energy Consumption in the Kingdom of Saudi Arabia (KSA)

In 2013, KSA was the world's 12th largest primary energy consumer country with a total energy consumption of 9 quadrillions British thermal units (Btu) (US-EIA

2014). The annual electricity demand of KSA has increased at an average rate of 5.8 % from 2006 to 2010 (MEP 2010). Oil fulfils 60 % of this energy demand, while natural gas covers the remaining 40 % energy requirements (KACARE 2012). The KSA's government has planned to double its energy generating capacity from 55 gigawatts (GW) to 120 GW by 2032. For this, the government has launched a special program; King Abdullah City of Atomic and Renewable Energy (KACARE) (Decree 2010). The vision of this initiative is to generate about half of the Saudi electricity capacity from different renewable sources, including solar, nuclear, wind, geothermal and WTE by 2032 (US-EIA 2014; Nizami et al. 2015a).

1.3 Plastic Consumption in the World and KSA

Plastics are composed of petroleum-derivative hydrocarbons, antioxidants, colorants and stabilizers (Hamid et al. 2000; Williams and Williams 1999; Perugini et al. 2005; Siddiqui and Redhwi 2009). The current global plastic consumption is round 154 million tons (Patni et al. 2013). Figure 1 shows the plastic consumption in different parts of the world. Thermoplastic and thermoset are commonly used plastic types. Thermoplastic softens when heating and hardens when cooled while, thermoset become hardened by curing and thus cannot be re-moulded. Thermoplastics

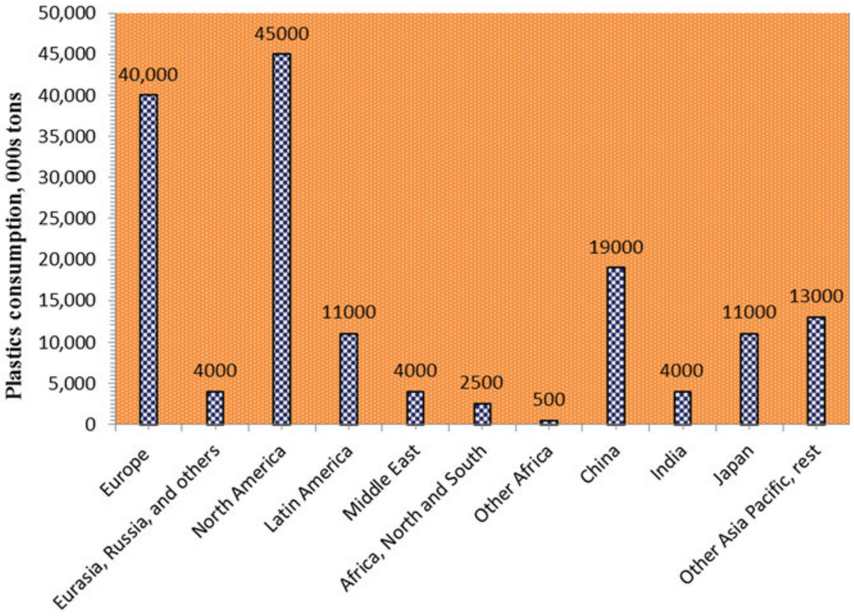

Fig. 1 Plastic consumption in different parts of the world (Patni et al. 2013)

are the most used plastic (around 80 %) in Western Europe (Jude et al. 2009). The plastic products are mostly manufactured from low density polyethylene (LDPE), high density polyethylene (HDPE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC) and polyethylene-terephthalate (PET) (Jude et al. 2009).

Plastic consumption has increased significantly worldwide over the last few decades due to their durability, light weight and low prices (Serrano et al. 2002; Aguado et al. 2008). As a consequence, global plastic waste generation was 280 million tons in 2011 that is expected to increase at an annual rate of 4 % till 2016 (Sriningsih et al. 2014). In the European Union (EU), plastic production remained stable (55–60 million tons per year) since 2000 (Beneroso et al. 2015; Williams 2005). According to Shah et al. (2010), plastic waste production in Western Europe was the same from 1993 to 2003 with a little increase (annual 64–93 kg per capita). In KSA, aroung 15 million tons of MSW is generated every year at an average rate of 1.4 kg per capita per day (Ouda et al. 2015). Plastic waste is the second largest waste stream with 17.4 % of total generated MSW (Siddiqui and Redhwi 2009; Nizami et al. 2015a). Most of the MSW produced in KSA ends up in landfills or dumpsites. Metal and cardboard are the waste materials, whose recycling is being carried out by up to 10–15 % of total produced MSW (Nizami et al. 2015a).

1.4 Potential of Waste Plastic to Energy

Plastic become an environmental problem when used and discarded, as it remains in the environment for longer periods of time due to its non-biodegradable or very slow degradation nature (Achilias et al. 2007). Disposal of plastic waste in landfills causes environmental and operational problems (Khan and Kaneesamkandi 2013). Plastic waste management is carried out using different methods, including reducing, reusing, incineration, energy recovery and mechanical recycling (Sriningsih et al. 2014). Conventional mechanical recycling methods such as sorting, grinding, washing and extrusion can recycle only 15–20 % of all plastic waste (Ashworth et al. 2014). Uncontrolled or open combustion or burning and landfilling of plastic waste cause air, water and soil pollution (Buekens and Huang 1998; Rahmanian et al. 2015; Eqani et al. 2016)). WTE and recycling are two widely used techniques in modern plastic waste management system (Serrano 2007; Lopez et al. 2012).

Pyrolysis, as one of the WTE technologies, is being used to convert plastic waste into energy (liquid oil) and value-added products (char and gases) (Sharma et al. 2014). Pyrolysis is one of the tertiary recycling techniques in which plastic polymers are broken down into smaller organic molecules (monomers) in the absence of oxygen at high temperatures (>400 °C) (Sharma et al. 2014; Chen et al. 2014a, b). Most of the Pyrolysis studies concluded that optimum temperature range for pyrolysis of plastic waste is between 450 and 550 °C (Table 1). Pyrolysis of all types of plastic waste is possible except for PET and PVC, as they cause corrosion and pipeline obstruction problems (Lopez et al. 2012). The produced liquid oil has similar characteristics to conventional diesel (Syamsiro et al. 2014).

Table 1 Pyrolysis reactor types, conditions, feedstock used and comparative results

Reactor type	Experiment conditions			Feedstock	Catalyst used	Obtained results			References
	Temperature (°C)	Residence time (min)	Heating rate (°C/min)			Oil (%)	Char (%)	Syngas (%)	
Semi-batch	500	15–30	20	PP, PS, PET, PE, PVC	–	65.2	–	–	Lopez et al. (2011a)
Semi-batch	440	30	20	Industrial packing waste	ZSM-5	42.6	47.7	9.7	Lopez et al. (2011b)
Semi-batch	350	60	–	LDPE	NZ with Ni, Co, Mo	71.49	–	–	Sriningsih et al. (2014)
Semi-batch	450	–	–	PP	FCC	92.3	3.6	4.1	Abbas-Abadi et al. (2014)
Semi-batch	440	30		Mix Plastic	ZSM-5	80	18	2	Lopez et al. (2011c)
Packed bed	450	–	–	HDPE	HY-Zeolite	70	–	–	Syamsiro et al. (2013)
Packed bed	450	–	–	PS	HY-Zeolite	88	–	–	Syamsiro et al. (2013)
Fluidized bed	500	–	20	HDPE	HZSM-5	67.6	11.4	21	Hernández et al. (2007)
Bench scale	420	300	20	Municipal plastic	FCC	79.08	13.05	7.87	Lee (2009)
Two stage	450	–	–	HDPE	Natural zeolite	58	35	7	Syamsiro et al. (2014)
Fluidized bed	530	–	–	PE	–	92.3	0.1	7.6	Williams (2006)

The aim of this chapter is to review the challenges, and perspectives of pyrolysis technology for producing energy and value-added products from plastic waste.

2 Plastic Waste Disposal

2.1 Recycling of Plastic Waste

Plastic waste has increased with the increase of its consumption worldwide. Conventional techniques for the handling of plastic waste such as combustion or burning and landfilling has resulted in serious environmental problems. The US-EPA reported that in 2000, there was a 50 % increase in plastic waste dumping compared to early 1990s. Increase in plastic waste urged the scientists to look for alternative techniques for sustainable plastic waste management. Therefore, recycling of plastic waste is encouraged and practiced to overcome inherent plastic's problems. As a result, since the last few decades, recycling of plastic waste has increased at a very high rate. There are four different types of plastic recycling as follow;

- Primary recycling
  Primary recycling involves plastic waste recycling into a product that has similar characteristics as the original products. Mostly, PET plastic type recycling fits into this category.
- Secondary recycling
  Secondary recycling involves the recycling of plastic waste into a product that has different characteristics as compared to original products. PS, PE and PP are the main plastic types that fall into this category (Lerici et al. 2015).
- Tertiary recycling
  Tertiary recycling involves processes such as pyrolysis, in which plastic waste is converted into liquid oil at high temperatures. All types of plastic can recycle through tertiary recycling except PET and PVC. The PVC plastic produces hazardous chlorine gas and also corrodes the process apparatus (Lopez et al. 2012).
- Quaternary recycling
  Quaternary recycling involves the process of retrieving energy from the plastic waste through burning under controlled conditions. All types of plastic can be recycled via quaternary recycling.

Primary recycling is used when semi-cleaned plastic waste is available; although its use is very limited. While, secondary plastic recycling is used to recycle plastic waste into products that can be used as substitute for wood, concrete and metal. Mostly, secondary plastic recycling products are used as fences, benches, desks, chairs, etc. Tertiary recycling techniques such as pyrolysis convert plastic into liquid oil, while quaternary recycling burns plastic waste to produce energy. The latter was widely used due to high energy contents of plastic, but due to air pollution its use has limited (Ahmad 2015).

2.2 *Pyrolysis of Plastic Waste*

The pyrolysis process converts plastic waste through thermal decomposition to organic vapours and char and gases in the absence of oxygen. The produced organic vapours, are converted into oil as liquid fuel by a condensation process. It takes about 2–4 h to convert waste into useful energy products (Fonts et al. 2009); however there is a scope of time reduction and process optimization. The inorganic gradient remains unchanged and hence can be reused in plastic industries as a raw material for the manufacturing of new plastic products. Liquid oil is the main product from the pyrolysis process, while char and gases are by-products. About 80 % of plastic can be converted into liquid oil through pyrolysis (Lee 2009).

Dechlorination is used to stop the chlorine generation when pyrolysis of PVC plastic is carried out either at low temperature, as PVC decomposes at 250–320 °C (Lopez et al. 2011a, b) or can be removed via physical or chemical adsorption methods using different adsorbents (Lopez et al. 2012). The produced liquid oil has similar heating value (HHV) as compared to conventional diesel (Table 2), thus can be used as alternative fuel for various energy generating applications. According to Demirbas (2010), HHV value can be derived as per Eq. 1.

$$\mathrm{HHV(MJ/kg)} = 0.335\ \mathrm{C} + 1.423\ \mathrm{H} - 0.154\ \mathrm{O} - 0.145\ \mathrm{N} \tag{1}$$

where C is carbon content (wt%), H is hydrogen content (wt%), O is oxygen content (wt%), and N is nitrogen content (wt%).

Table 2 High heating values (HHV) of produced liquid oil from different feedstock

Feedstock	HHV (MJ/kg)	References
Tires	43.22	Wongkhorsub and Chindaprasert (2013)
Plastic	46.19	
Diesel	45.81	
PE Bag 1	41.45	Syamsiro et al. (2014)
HDPE waste	42.82	Syamsiro et al. (2014)
PE Bag 2	46.67	Syamsiro et al. (2014)
HDPE	45.86	Sharma et al. (2014)
HDPE	45.78	Kumar and Singh (2011)
Mixed plastic	44.40	Kim et al. (2010)
LDPE	38–39	Panda et al. 2010
HDPE	40.17	Kumar et al. (2010)
Mixed waste	40–40.5	Mani et al. (2011)

Pyrolysis is carried out in different types of reactors such as fixed bed (Wang et al. 2006), tube (Miskolczi et al. 2009), rotary kiln (Li et al. 2005) and two-stage reactors (Syamsiro et al. 2014) that have both advantages and disadvantages (Table 3).

2.2.1 Selection of Plastic Types for Pyrolysis

Pyrolysis of different feedstocks has been carried out by a number of researchers including, sewage sludge (Xiong et al. 2013), tires (Antoniou and Zabaniotou 2013), electronic waste (Yang et al. 2013) and plastic waste (Chen et al. 2014a, b). Plastic waste contains different types of plastic such as PS, PP, PE (e.g. LDPE and HDPE), PVC and PET. Pyrolysis has been successfully used to convert all types of plastic waste into liquid oil except PVC and PET (Table 4). Only few studies were carried out on pyrolysis of PVC due to production of hazardous chlorinated gas. Moreover, PE is also not suitable for thermal pyrolysis because of wax formation instead of liquid oil (Lee 2012). PS plastic decomposes at low temperature in comparison to PE and PP (Lee and Shin 2007).

2.2.2 Factors Affecting the Pyrolysis Process

There are different factors affecting the pyrolysis process such as temperature, retention time, feedstock composition, moisture content, heating rate and particle size of the feedstock. Temperature is the most influential and widely studied factor by scientists (Li et al. 1999; Yoshioka et al. 2004; Ji et al. 2006), as it affects thermal cracking and secondary reaction of the pyrolysis process. López et al. (2010) reported that solid residue (char) produced at different temperature remains the same, however the yield of liquid and gases changes. The liquid yield decreases and gas yield increases with temperature increase. Moreover, the increase in temperature affected the quality of the produced liquid oil.

At lower temperatures, long chain hydrocarbons are produced, while increase in temperature results in shorter carbon chains due to cracking of C–C bonds (Hernández et al. 2007; Lopez et al. 2009). Similarly, at higher temperature (around 600 °C), aromatic compounds are produced, while at lower temperature (around 460–500 °C) aromatic compounds with unsaturated hydrocarbons are produced (Lopez et al. 2011a). However, some scientists argue that aromatics are produced by secondary reactions due to increase in temperature (Kaminsk et al. 1999; Li et al. 1999, 2005).

Polyaromatic hydrocarbon (PAH) are also produced at high temperature that leads to increase in percentage composition of aromatic (Sánchez et al. 2009). At 600 °C, >C13 fraction decreases, while at the same temperature C10–C13 fraction increases which showing that higher temperature favours formation of short carbon chain compounds (Marcilla et al. 2009; Jung et al. 2010). However, at high temperature (500–600 °C), styrene production decreases. It shows that styrene is

Table 3 Advantages and disadvantages of pyrolysis reactors

Reactor Type	Advantages	Disadvantages	References
Fixed bed	• Used to identify the governing parameters that effect the pyrolysis products	• Low heating rate (HR) and low heat transfer coefficient • Temperature is not uniform when high mass is used as feedstock • Decomposition of feedstock at different temperature	Wang et al. (2006)
Rotary kiln	• Good for heating up the feedstock • Good mixing of waste (feedstock) during the pyrolysis process due to slow rotation of reactor • Residence time for feedstock is 1 h • Extensive pre-treatment for feedstock is not required • Maintenance of the reactor is simple	• Used for slow pyrolysis process at slow HR • Less information for heat transfer coefficient for heterogeneous MSW	Li et al. (2002, 2005), Chen et al. (2014a, b)
Fluidised-bed	• Heating rate is high • Feedstock blending is good • Used to find out the effect of temperature and residence time on the products of pyrolysis • Low thermal conductivity • High viscosity • Widely used for MPW	• Application at industrial scale for MSW is not common • Separation method for coke from bed-material is a challenge • Separation of bed material, recirculation and external heating and MSW pre-treatment increase cost of process which decreases its value economically	Al-Salem et al. (2010), Arena and Mastellone (2006), Mastral et al. (2002, 2003), Dai et al. (2001a, b), Chen et al. (2014a, b)
Tubular	• Consist of various tubes with fixed wall • Heated externally • Simple and safe • Coke and gas can be obtained from reactor Continuously • Suitable to use for both thermal and catalytic pyrolysis processes	• Required extensive pretreatment for MSW • Small channel for the passage of feedstock • Erosion of the reactor due to presence of sand and other solid contaminants present in the feedstock • Heat transfer co-efficient is not well defined	Aguado et al. (2002), Walendziewski (2002), Marculescu et al. (2007)

(continued)

Table 3 (continued)

Reactor Type	Advantages	Disadvantages	References
	• Thermoselect process, Compact power process and CNRS thermo-chemical convertor are the types of tubular reactor		
Multi stage	• Consist of two stages and three stages • Have the potential to control at different conditions • Provide solution to run pyrolysis technology independently • Produce HCl gas can be separated from volatile value products at different stages		Ohmukai et al. (2008), Zhao et al. (2011)
Plasma	• Convert waste into synthetic gas • High heat transfer which increase reactor temperature rapidly • Control process temperature, high process rate, low reaction volume • Produced syngas has optimum composition • Produced products are harmless to human health and environment	• Required high energy to run the process as temperature required is 1000 °C • Only applied for hazardous waste • Economically not favorable for MSW	Wang and Huang (2008), Huang and Tang (2007), George (1994)
Microwave	• Used for homogenous waste • Rapid increase of reactor temperature • Easy to control • Can be run at desire temperature • Lower and higher temperature for reaction vessels and for reaction mixture respectively	• Very fine feedstock particles are required to get rapid heating rate • To reduce secondary cracking solid-laden vapors has to be removed rapidly from reactor	Baghurst and Mingos (1992), Yin (2002)

Table 4 Suitability of plastic for pyrolysis

Resin	Suitability for pyrolysis	Temperature required	References
Polystyrene (PS)	Good and gives better fuel properties	Low temperature is required as compared to PP and PE	Lee and Shin (2007)
Polyethylene (PE)	Good, but mostly is converted into wax, if catalyst is not used	Required Temperature is high >500 °C	Miskolczi et al. (2009), Lee (2012)
Polypropylene (PP)	Good	Requires high temperature	Miskolczi et al. (2009)
PVC	Not suitable, Produce hazardous chlorinated gas, Dechlorination via low temperature (250–320 °C) or physical or chemical adsorption is required		Lopez et al. (2011a, 2012)
PET	Not suitable, and contains Heteroatom's		Thorat et al. (2013)

produced at low temperature, while at higher temperature it decomposes into other chemicals like toluene and ethyl-benzene (Lopez et al. 2009; Lee and Shin 2007). Demirbas (2004) reported that decrease in styrene yield at high temperature is due to secondary reactions. Pyrolysis of PP and PE require high temperature (>450 °C), as they produce high carbon chain fractions in the liquid due to presence of long carbon chain compounds (López et al. 2010).

Retention time also affects the pyrolysis process, however its impact is lower than temperature. According to Lopez et al. (2009), at shorter retention times, aromatic hydrocarbons are produced, especially when feedstock consist of PS plastic. About 60 % of aromatic hydrocarbons are produced from the pyrolysis of mixed plastic waste containing PS, PP and PE at 350 °C (Lee and Shin 2007). Moreover, the effect of retention time on the carbon chain fraction is less, as similar carbon chain compounds are produced at each temperature with different retention times. However at higher temperature, an increase in the >C13 fraction is observed. According to Lopez et al. (2009), this may be due to high retention time in reactors, as plastic and its derivatives decompose and generate high carbon chain compounds in comparison to light carbon chain compounds that are formed at low retention time.

López et al. (2010) studied catalytic pyrolysis of various feedstock including film, paper and char by using ZSM-5 zeolite catalyst. They reported that even at low temperature (440 °C), more than 90 % by weight decomposition is occurred when feedstock consist of 65 % PE. However, paper-rich samples produced less organic liquid (25.5 wt%) and gases (29.4 wt%), while glass-rich samples produced more char (12.9 wt%) in comparison to both paper and film-rich samples. High char production may be due to the reaction of the glass-rich samples with ZSM-5 zeolite catalyst.

The type of plastic also affects the quantity and quality of produced liquid oil from the pyrolysis process. According to Siddiqui and Redhwi (2009), PS plastic produces less viscous liquid oil due to shorter carbon chain compounds in comparison to PE and PP that produce long carbon chain compounds. Therefore, liquid oil produced from PE and PP has high viscosity (Syamsiro et al. 2014). During the winter season or areas where temperature is very low, high viscous oil affects the oil fluidity, resulting in poor atomization and poor engine performance (Kim et al. 2009; Oasmaa and Czernik 1999).

The effect of moisture contents in feedstock is limited. However its presence in paper, pulp and bamboo feedstocks leads to decrease in H_2 production and increase in tar concentration (Chen et al. 2014a, b). Luo et al. (2010) examined MSW pyrolysis with different feedstock and particle size range (0–5, 5–10 and 10–20 mm). They found that with smaller particle size, the gas fractions increase in comparison to liquid and char fractions. Moreover, there are some other factors that affect pyrolysis process such as flash and fast pyrolysis, which increase liquid oil yield production (Sharma et al. 2014). Furthermore, continuous stirring of feedstock inside the reactor decreases the overall process retention time (Abbas-Abadi et al. 2014), while insulation of the reactor saves energy (Chen et al. 2014a, b). Hernández et al. (2007) used sand to increase the temperature of the reactor in order to reduce the parasitic energy demand of the process.

2.3 *Effect of Catalyst on Pyrolysis*

Catalysts are used to improve the quality of produced liquid oil and overall performance of pyrolysis process. Different types of catalyst are used including, Red Mud (López et al. 2010), FCC (Lee 2009), Ca $(OH)_2$ (Sarker et al. 2011), and Fe_2O_3 (Sarkar et al. 2011). Saw dust was also used to improve the quality of the produced oil from the pyrolysis of rubber waste (Wang et al. 2014). Moreover, different types of natural and synthetic zeolite catalysts have also been used including, ZSM-5 zeolite (Lopez et al. 2010), HZSM-5 zeolite (Hernández et al. 2007) and natural zeolite (Syamsiro et al. 2014). Modifications in natural zeolite catalysts using different processes were also carried out such as zinc-modified zeolite via wet impregnation (Ciobanu et al. 2008), ZSM-5 modified with boron via impregnation (Zhou et al. 2014) and natural zeolite catalyst modified with Ni, Ni-Mo, Co and Co-Mo metals (Sriningsih et al. 2014).

Use of a catalyst has different effects on the pyrolysis process, however one of the main effects is to increase the quality of produced liquid oil (Wang and Wang 2011). The lighter fraction, especially gasoline is increased by the use of catalyst. According to Lopez et al. (2011a), catalysts also decrease energy consumption of the pyrolysis process. According to Miskolczi et al. (2009), the use of ZSM-5 catalyst decreased the impurities in liquid oil as well as nitrogen and sulphur contents.

The effect of catalyst varies with the type of plastic waste. By using ZSM-5 zeolite catalyst, it was found that plastic waste containing mostly PE type plastic achieve higher yields of liquid oil. The maximum liquid oil yield was obtained at 440 °C from PE plastic; however the same result was also achieved at 500 °C without using a catalyst. This means that the catalyst decreases the temperature requirement of the pyrolysis process (Lopez et al. 2011a).

In another study by Lee (2012), pyrolysis of PE plastic type without catalyst resulted in wax formation. The use of a catalyst with this wax produced liquid oil with a high H/C ratio and hydrocarbons. The textural properties of a catalyst plays a vital role in liquid oil's purifying characteristic. The ZSM-5 catalyst has a high micropore area and volume that means this catalyst has high internal porosity. While, red mud has low porosity and most of the macro and meso pores are located on the external surface of the catalyst. Moreover, red mud is less acidic than ZSM-5 catalyst and thus has less effect on product yield in comparison to the ZSM-5 catalyst (Lopez et el. 2011b).

Modification in zeolite catalyst has been under consideration for the last few decades. By making zeolite composites with zinc, adsorption capacity has increased due to narrower pores of zeolites. Modified zeolites catalysts have an average particle size of few microns, thus internal surface area can represent more than 99 % of the total surface area. Almost all active sites are located inside the pores increasing its adsorption capacity and thus enhancing catalyst purifying ability (Ciobanu et al. 2008).

3 Energy and Value-Added Products of Plastic Waste Pyrolysis

3.1 Liquid Oil as an Energy Source

Liquid oil is the main product of the pyrolysis process. According to Lopez et al. (2010) and Williams (2006), 1 kg of plastic can produce around 72–84 % by weight liquid oil. Theoretically, 1.047 MJ/kg energy is required to convert PE plastic into liquid oil by pyrolysis. The produced liquid oil has an energy value of around 43 MJ/kg that is much higher than the energy consumed by the process (Gao 2010). Pyrolysis of PE plastic converts feedstock into wax instead of liquid oil, however use of catalyst can convert PE into liquid oil (Lee 2009). According to Achilias et al. (2007), pyrolysis of PE and PP is difficult to carry out without catalyst. Moreover by using the ZSM-5 catalyst, a maximum yield from PE is obtained at low temperature (440 °C) in comparison to high temperature (500 °C) without using a catalyst (Lopez et al. 2011a). Use of catalysts not only reduce the process time, but also remove the impurities from produced liquid oil. According to Miskolczi et al. (2009), use of catalysts decrease sulphur content in produced liquid oil.

The produced liquid oil from different feedstock has different physical and chemical properties such as viscosity, density, cold flow properties and HHV. Viscosity and density are the main properties of liquid oil with regards to its operational use (Table 5). Liquid oil from plastic pyrolysis has viscosity of 1–2.96 mm^2/s. PS plastic liquid oil has a lower viscosity compared to PE and PP, as it produces

Table 5 Density and viscosity of pyrolysis liquid fuel

Feedstock	Density g/cm^3 (15 °C)	Viscosity mm^2/s (40 °C)	Reference
PE Bag 1	0.8544	1.739	Syamsiro et al. (2014)
HDPE waste	0.7991	2.319	
PE Bag 2	0.824	1.838	
LDPE	0.7787	1.89	Panda et al. (2010)
HDPE	0.790	2.1	Kumar et al. (2010)
Waste plastic	0.8355	2.52	Mani et al. (2011)

short carbon chain compounds (Williams and Williams 1999; Siddiqui and Redhwi 2009). While, PE and PP plastic types produce high viscous oils due to presence of long carbon chain compounds (Syamsiro et al. 2014; Panda and Singh 2013).

Density of the produced liquid oil also varies from 0.77 to 0.91 g/cm^3. However, the values for density are similar to the conventional diesel (0.815–0.870 g/cm^3) (Syamsiro et al. 2014). Therefore, pyrolytic liquid oil can be used as an energy source. Moreover, cold flow properties of produced liquid oil are below its freezing point. These properties are critical for the use of any petroleum product. Cold flow properties include cloud point (where crystals begin to appear) and pour point (below this temperature liquid does not flow) (Isioma et al. 2013; Gardy et al. 2014). Low cold flow properties show that the produced liquid oil has the potential to be used as an alternative fuel oil in those areas where temperature is extremely low. Moreover, liquid oil produced from pyrolysis of plastic waste has the same properties as conventional diesel (Table 6).

3.2 *Char as by-Product*

Char is an unburnt feedstock left in the pyrolysis reactor. It is produced in very low quantities, for example, 1.1–3 % char by weight is produced from 1 kg of feedstock (Lopez et al. 2011a; Williams 2006). Lopez et al. (2010) reported that increase in temperature decreases the quantity of produced char. Elemental and proximate analysis show that char contains volatile matter, fixed carbon, ash, etc. (Table 7).

Table 6 Comparison of pyrolysis liquid oil with conventional diesel

Parameters	Units	Pyrolytic liquid fuel	Conventional diesel	Reference
Viscosity	mm^2/s	1.89	1–4.11	Wongkhorsub and Chindaprasert (2013)
Density	g/cm^3	0.854	0.815–0.870	Syamsiro et al. (2014)
Kinematic viscosity	cSt	1.77	2.0–5.0	Syamsiro et al. (2014)
Pour point	°C	−18	Max 18	Syamsiro et al. (2014)
HHV	MJ/kg	41.58	46.67	Syamsiro et al. (2014)

Table 7 Elemental and proximate analysis of char (wt%)

Feedstock	Pyrolysis Temp (°C)	Moisture content	Volatile matter	Fixed carbon	Ash	C	H	N	Cl	HHV (MJ/kg)	Ref
PS	450	0.91	37.44	57.28	4.37	91.14	4.09	0.09	–	36.29	Syamsiro et al. (2013)
HDPE	450	3.09	19.14	57.99	19.78	65.88	2.01	1.50	–	23.04	Syamsiro et al. (2013)
Mix plastic	440	0.7	–	–	–	23.0	2.2		0.4	9.4	Lopez et al. 2012
Packaging waste	440	–	–	–	–	60.9	10.2	0.2	0.2	41.5	Lopez et al. (2010)
PE bag	450	1.12	35.29	14.13	49.47	–	–	–	–	19.80	Syamsiro et al. (2014)
HDPE	450	1.74	44.47	25.88	27.33	–	–	–	–	26.35	Syamsiro et al. (2014)

Temp Temperature; *Ref* Reference

According to Jamradloedluk and Lertsatitthanakorn (2014), char produced from HDPE plastic type has volatile matter (51.40 %), fixed carbon (46.03 %), moisture content (2.41 %), and a small amount of ash. Moreover, char produced from HDPE and PS has HHVs of 23.04 and 36.29 MJ/kg respectively (Syamsiro et al. 2013). High heating value of char shows its potential to be used as a source of energy. Jamradloedluk and Lertsatitthanakorn (2014) crushed the HDPE char into powder and produced briquettes and used 1 kg for water heating (from room temperature to boiling temperature) within 13 min. Produced char has potential to be used in other environmental applications such as adsorption of heavy metals from municipal and industrial wastewaters and toxic gases (Heras et al. 2014). According to Lopez et al. (2009), thermal activation of char at 900 °C for 3 h increased its BET surface area and pore volume upto 55 and 44 %, respectively. Moreover, it decreased the pore size upto 5 %. Steam activation of char produced from waste tires decreased the sulphur content of char, thus making it a more environmental friendly product.

3.3 Gases

Gases are produced as by-products of pyrolysis of different feedstock. By using the mass balance formula, it was estimated that 1 kg of feedstock can produce 13–26.9 % gases by weight from the pyrolysis process (Lopez et al. 2011a; Williams 2006). The yield of produced gases is highly affected by the process temperature. Lopez et al. (2009) reported that an increase in temperature will increase the yield of gases and decrease the yield of liquid oil. The major gases are H_2, CO and CO_2. In addition, PVC feedstock produces HCl gas that is hazardous gas and causes apparatus corrosion (Chen et al. 2014a, b; Lopez et al. 2012). The BET surface area of catalysts also affects the yield of gas production. Higher BET areas provide more contact for feedstock with the catalyst, resulting in higher gas yield (Syamsiro et al. 2014).

4 Conclusion and Future Perspective

The tremendous increase in plastic consumption worldwide for a wide range of products is causing serious waste disposal and environmental issues. This increases the importance of plastic recycling and treatment technologies to deal with such problematic waste in an environmental friendly manner. Pyrolysis is a promising technology used to convert waste plastic into liquid oil and other valuable by-products such as char and gases under controlled conditions and is considered to be a relatively more environmental friendly technology than uncontrolled incineration. The pyrolysis products yield depend on a number of process parameters such as temperature, heating rate, moisture contents, retention time, type of plastic and particle size. A yield of up to 80 % of liquid oil by weight can be achieved from plastic waste. The produced liquid oil has similar characteristics to the conventional diesel including, density (0.8 kg/m^3), viscosity (up to 2.96 mm^2/s), cloud point (−18 °C), flash point (30.5 °C) and energy content (41.58 MJ/kg), and can be used as an energy source. Char produced from the pyrolysis can be activated at standard conditions to be used in wastewater treatment, heavy metals removal, and smoke and odor removal. The produced gases from pyrolysis are H_2, CO and CO_2 and can be used as energy carriers. High temperature and retention time are the main limitations of pyrolysis of plastic waste, which need to be optimized to make the process more economically and environmentally favorable.

A number of catalysts have been used in pyrolysis process resulting in improved liquid oil yield and quality, however exploration and utilization of cheaper catalysts such as natural zeolites requires more intense research. Moreover, catalysts modification require further attention to improve their performance to optimize the overall pyrolysis process. Since this book chapter focused on the case study of KSA, it is important to mention that intensive research and development work is still required to understand the full scope and potential of pyrolysis of plastics, in terms of technical, economic and environmental issues using life cycle assessment (LCA) tools in relation to local social and environmental conditions, and for adapting this technology as a WTE technology in KSA (Shahzad et al. 2015; Rathore et al. 2016; Demirbas et al. 2016b; Lai et al. 2016; Nizami and Ismail 2013).

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