

## Effect of plastic waste types on pyrolysis liquid oil



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### ARTICLE INFO

#### Article history:

Received 29 June 2016

Received in revised form

26 August 2016

Accepted 19 September 2016

Available online 10 October 2016

#### Keywords:

Plastic waste

Pyrolysis

Polystyrene (PS)

Polyethylene (PE)

Polypropylene (PP)

Liquid oil

### ABSTRACT

This paper aims to examine the effect of different plastic waste types such as polystyrene (PS), polyethylene (PE), polypropylene (PP) and polyethylene terephthalate (PET) on the yield and quality of produced liquid oil from the pyrolysis process. A small pilot scale pyrolysis reactor was commissioned for this purpose, and operated at optimum temperature and retention time of 450 °C and 75 min respectively. PS plastic waste showed maximum production of liquid oil (80.8%) along with least production of gases (13%) and char (6.2%) in comparison to other plastic types. Liquid oils from all plastic types contained mostly aromatic compounds with some alkanes and alkenes. Liquid oil from PS pyrolysis contained styrene (48.3%), ethylbenzene (21.2%) and toluene (25.6%). Pyrolysis liquid oils found to have ranges of dynamic viscosity (1.77–1.90 mPa s), kinematic viscosity (1.92–2.09 cSt), density (0.91–0.92 g/cm<sup>3</sup>), pour point (−11(−60 °C)), freezing point (−15(−65 °C)), flash point (28.1–30.2 °C) and high heating value (HHV) (41.4–41.8 MJ/kg) similar to conventional diesel, thus have potential as an alternative energy source for electricity generation. Upgrading of liquid oil using different post-treatment methods such as distillation, refining and blending with conventional diesel is required to make it suitable as a transport fuel due to presence of high aromatic compounds. The recovery of aromatic compounds especially styrene from pyrolysis oil can be a potential source of precursor chemical in industries for polymerization of styrene monomers.

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## 1. Introduction

The consumption of plastic is increasing worldwide at an alarming rate of 4% per year due to its durability, light weight and low cost (Miandad et al., 2016a). In 2011, the total plastic waste production in the world was around 280 million tons (Sriningsih et al., 2014). Plastic waste is now one of the major components of municipal solid waste (MSW). It is a mixture of various plastic products, mainly made from low density polyethylene (LDPE), high density polyethylene (HDPE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC) and polyethylene-terephthalate (PET) plastics (Table 1). PE and PS are the most available plastic types among municipal plastic waste (MPW) (Onwudili et al., 2009).

Plastic waste is managed by different techniques including, reducing, reusing, recycling, waste-to-energy (WTE) and disposal at landfill sites (Ouda et al., 2016; Sadeef et al., 2016). Conventional

mechanical recycling techniques such as sorting, grinding, washing and extrusion can recycle only 15–20% of all plastic waste types (Nizami et al., 2015a). Beyond this level, the plastic becomes contaminated with materials like soil, dirt, aluminium foils, food wastes and paper labels (Nizami et al., 2015b). The uncontrolled incineration and open burning of plastic waste have caused air and waterborne pollutants (Miandad et al., 2016b; Rahmanian et al., 2015; Eqani et al., 2016; Munir et al., 2016). Therefore in recent years, various plastic-to-fuel (PTF) or WTE technologies such as gasification, pyrolysis, refuse derived fuel (RDF) and plasma arc gasification along with chemical recycling methods such as hydrolysis, methanolysis, glycolysis have gained significant attention for the management of MPW (Nizami et al., 2015a).

The pyrolysis of MPW is a promising WTE or PTF technology for the sustainable management of plastic waste along with production of liquid oil as a source of energy and char and gases as value-added products (Rehan et al., 2016a). The process involves thermal cracking of complex organic molecules or large chain hydrocarbons at elevated temperature (300–600 °C) into smaller molecules or short chain hydrocarbons (Sharma et al., 2014). The process is

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### List of acronyms and abbreviations

|                 |  |     |                            |
|-----------------|--|-----|----------------------------|
| CO <sub>2</sub> | Carbon Dioxide   | MPW | Municipal Plastic Waste    |
| CO              | Carbon Monoxide  | MSW | Municipal Solid Waste      |
| FT-IR           | Fourier Transform Infrared Spectroscopy                | NOx | Oxides of Nitrogen         |
| GC-MS           | Gas Chromatography Coupled with Mass Spectrophotometry | PE  | Polyethylene               |
| HC's            | Hydrocarbons   | PET | Polyethylene Terephthalate |
| HDPE            | High Density Polyethylene                              | PP  | Polypropylene              |
| HHV             | High Heating Value                                     | PS  | Polystyrene                |
| KACARE          | King Abdullah City of Atomic and Renewable             | PTF | Plastic-to-Fuel            |
| KSA             | Kingdom of Saudi Arabia                                | PWM | Plastic Waste Management   |
| LCA             | Life Cycle Assessment                                  | PVC | Polyvinyl Chloride         |
| LDPE            | Low Density Polyethylene                               | RDF | Refuse Derived Fuel        |
|                 |  | TGA | Thermogravimetric Analyzer |
|                 |  | TIC | Total Ion Chromatogram     |
|                 |  | WTE | Waste-to-Energy            |

completed in four steps, including initiation, transfer, decomposition and termination (Faravelli et al., 2001). Computer simulation models consider hundreds of possible reactions happening during thermal cracking of feedstock (Zhang et al., 2015). Therefore, the pyrolysis process depends on series of factors such as temperature, residence time, heating rates, feedstock composition and presence of moisture or toxic elements (Miskolczi et al., 2009).

The scientific literature shows that in most of the pyrolysis studies, resin/virgin plastic or processed plastics were used as a feedstock, mostly in small scale reactors (Syamsiro et al., 2014; Adnan and Jan, 2014; Sriningsih et al., 2014; Miandad et al., 2016a; Ciliz et al., 2004). While, the interest in pyrolysis of real MPW has gained significant attention in recent years (Lee, 2012; Chen et al., 2014; Zeaiter, 2014). The focus of these studies were to increase the quantity of pyrolysis liquid oils along with establishing the carbon chain composition of the produced liquid oil (Sharuddin et al., 2016; Ates et al., 2013; Demirbas et al., 2016). However, the quality of pyrolysis liquid oils, from mixtures of different plastic types, in terms of their properties such as density, viscosity, high heating value (HHV), flash point, and cold flow properties (i.e. pour point and freezing point) along with their comparison with conventional diesel properties is seldom reported (Lee et al., 2015; López et al., 2011; Miandad et al., 2016a). Moreover, the recovery of aromatic compounds such as styrene, ethylbenzene and toluene from pyrolysis liquid oils produced from MPW and their potential applications' studies have been limited (Bozkurt et al., 2016; Shah and Jan 2014; Sarker and Rashid, 2013; Miandad et al., 2016b; Siddiqui and Redhwi, 2009), which was the focus of this study.

The Kingdom of Saudi Arabia (KSA) is one of the major plastic producers in the world with annual plastic generating capacity of around 6 million metric tons (Anjum et al., 2016). The average life span of about 40% of the consumed plastic is less than a month (Siddiqui and Redhwi, 2009). As a result, it is the second largest waste stream (upto 17.4%) of MSW in KSA (Nizami et al., 2016). Moreover, excessive quantities of plastic waste are generated every year due to serving of meals in disposable plastics to millions of pilgrims in the holiest cities of Makkah and Madinah (Nizami et al., 2015c; Nizami et al., 2016; Miandad et al., 2016c).

In KSA, neither WTE facilities exist to convert plastic waste into energy, nor have the plastic waste types been characterized for their potential role as an energy recovery feedstock (Nizami et al., 2016). Therefore, this study aims to examine the effect of different plastic waste types such as PS, PE, PP and PET on the yield and quality of produced liquid oil. A small pilot scale pyrolysis reactor was commissioned for this purpose with total capacity of

20 L. The plastic waste types were used as a feedstock, individually as well as in mixtures. The potential application of liquid oil in generating energy or as a source of transport fuel and for recovery of aromatic compounds especially styrene was evaluated in detail. Moreover, the potential usage of char in various environmental applications was also highlighted.

## 2. Materials and methods

### 2.1. Feedstock preparation and reactor startup

The collected feedstock samples for the present study were consist of disposable plates, grocery bags, and juices or drinking cups that were mainly made of PS, PE, PP and PET plastic types respectively. These plastic types were selected as they are the major components of MPW found in KSA. The collected samples were used individually and in mixture of a 50/50%, 50/25/25%, and 40/20/20% ratios. Feedstock was crushed to small pieces (around 2 cm<sup>2</sup>) to get the homogeneous mixture.

A small pilot scale pyrolysis reactor was commissioned and used for the conversion of plastic waste into liquid oil and char (Fig. 1). The reactor was made of stainless steel and covered with a loop of an electric heater that allows to achieve a maximum temperature of 600 °C. The height of the reactor was 360 mm with 310 mm diameter and a capacity of 20 L (Table 2). A tube type condenser with a length of 860 mm coupled with a water chiller was installed at the end of catalytic reactor. Organic vapors produced within the heating chamber at high temperature were condensed into liquid oil in the condenser. Water circulating chiller with a coolant was used to decrease the temperature of condenser for the maximum condensation of organic vapors into liquid oil in the condenser. The condensed organic vapors (liquid oil) were collected from the oil collector assembly at the bottom of the system. While the uncondensed products (gases) coming from same liquid oil pipe were exhausted outside (Fig. 1).

### 2.2. Experimental setup and scheme

In all of the experiments, 1 kg of feedstock for each plastic type was used in the pyrolysis reactor individually and in mixture form. The reactor was heated from room temperature to 450 °C using a heating rate of 10 °C/min. A retention time of 75 min was used for all experiments (Table 3). These optimum conditions of 450 °C and 75 min for pyrolysis process were determined by Thermogravimetric analysis (TGA) of the used plastic types under controlled conditions together with safety considerations of using

**Table 1**

Plastic types and their characteristics, applications and role in pyrolysis (Miandad et al., 2016a, b; Chen et al., 2014; Sharuddin et al., 2016).

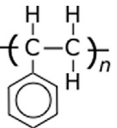
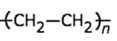
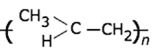
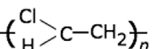
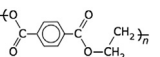
| Plastic types   | Characteristics  | Applications   | As pyrolysis feedstock  | Pyrolysis oil composition  |
|---|--|--|---|--|
| Polystyrene (PS)<br>                   | <ul style="list-style-type: none"> <li>Heat resilience</li> <li>Lightness</li> <li>High strength</li> <li>Reasonable durability</li> </ul>   | <ul style="list-style-type: none"> <li>Toys</li> <li>Medical stuff</li> <li>Electronics</li> <li>Food packaging</li> <li>Construction stuff</li> </ul>   | <ul style="list-style-type: none"> <li>Requires low temperature in comparison to PP and PE plastic types</li> <li>Produces less viscous oil in comparison to PE and PP plastic types</li> </ul>   | <ul style="list-style-type: none"> <li>Styrene</li> <li>Toluene</li> <li>Ethylbenzene</li> <li>Benzene</li> <li>Xylene</li> <li>Cumene</li> <li>Benzene</li> <li>Naphthalene</li> <li>Anthracene</li> <li>Di and triphenylbenzene</li> </ul>   |
| Polyethylene (PE)<br>                  | <p>HDPE</p> <ul style="list-style-type: none"> <li>It is a long polymer chain</li> <li>Highly crystalline</li> <li>High strength properties polymer</li> </ul> <p>LDPE</p> <ul style="list-style-type: none"> <li>Less tensile strength</li> <li>Less hardness</li> <li>Excellent water resistant</li> <li>Desirable polymer for various applications</li> </ul> | <p>HDPE</p> <ul style="list-style-type: none"> <li>Toys</li> <li>Oil containers</li> <li>Detergents bottles</li> <li>Milk bottles</li> </ul> <p>LDPE</p> <ul style="list-style-type: none"> <li>Trash bags</li> <li>Wrapping foil for packaging</li> <li>Plastic bags</li> </ul>   | <ul style="list-style-type: none"> <li>Requires high temperature &gt; 500 °C due to its long chain structure</li> <li>It converts into wax instead of liquid fuel in thermal pyrolysis</li> <li>Wax formation is occurred on external site of catalyst while further cracking of wax into gases and liquid occurred in internal site of catalyst</li> </ul> | <ul style="list-style-type: none"> <li>1- and 3-methylcyclopentene</li> <li>1-hexene</li> <li>Cyclohexene,</li> <li>1-octene</li> <li>1-nonene</li> <li>1-decene</li> <li>Benzene</li> <li>Toluene</li> <li>Xylene</li> <li>Benzene</li> <li>Toluene</li> <li>Xylene</li> <li>Di and trimethylbenzene Indane</li> <li>Indene</li> <li>Aphthalene</li> <li>Fluorene</li> <li>Acenaphthene</li> <li>Benzene</li> <li>Toluene</li> <li>Xylene</li> <li>Ethylbenzene</li> <li>Indene</li> <li>Biphenyl</li> <li>1-heptene</li> <li>1-octene</li> <li>2-methyl-1-pentene</li> <li>Azulene</li> <li>Biphenyl</li> <li>Phenanthrene</li> <li>9H-fluorene</li> <li>Naphthalene and its monomers</li> </ul> |
| Polypropylene (PP)<br>                 | <ul style="list-style-type: none"> <li>Good heat and chemical resistance</li> <li>Low density</li> <li>High rigidity</li> <li>High hardness</li> </ul>   | <ul style="list-style-type: none"> <li>Pail</li> <li>Carpets</li> <li>Furniture</li> <li>Storage box</li> <li>Office folder</li> <li>Flower pot</li> <li>Car bumpers</li> </ul>  | <ul style="list-style-type: none"> <li>Requires high temperature</li> <li>Difficult to degrade under thermal pyrolysis</li> <li>Produces liquid yield with high aromatic compounds under catalytic pyrolysis</li> </ul>   | <ul style="list-style-type: none"> <li>Benzene</li> <li>Toluene</li> <li>Xylene</li> <li>Ethylbenzene</li> <li>Indene</li> <li>Biphenyl</li> <li>1-heptene</li> <li>1-octene</li> <li>2-methyl-1-pentene</li> <li>Azulene</li> <li>Biphenyl</li> <li>Phenanthrene</li> <li>9H-fluorene</li> <li>Naphthalene and its monomers</li> </ul>  |
| Polyvinyl Chloride (PVC)<br>         | <ul style="list-style-type: none"> <li>Resistant to fire</li> <li>ersatile plastic</li> </ul>  | <ul style="list-style-type: none"> <li>Automotive interior</li> <li>Credit cards</li> <li>Medical devices</li> <li>Packaging</li> <li>Electrical insulation</li> <li>Food foil</li> <li>Boots</li> <li>Window frames</li> <li>Food packaging</li> <li>Electrical insulation</li> <li>Magnetic tapes</li> <li>X-ray</li> <li>Printing sheet</li> <li>Photographic film</li> </ul> | <ul style="list-style-type: none"> <li>Produce hazardous chlorine gas</li> <li>Dechlorination via low temperature (250–320 °C) or physical or chemical adsorption</li> <li>Presence of chlorine and deposition of coke affect the catalytic activity of catalyst</li> </ul>   | <ul style="list-style-type: none"> <li>1-Propanone</li> <li>Benzoic acid</li> <li>Biphenyl</li> <li>Fluorene</li> <li>Diphenylmethane</li> <li>Anthracene</li> <li>Benzophenone</li> <li>1-butanone</li> </ul>   |
| Polyethylene Terephthalate (PET)<br> | <ul style="list-style-type: none"> <li>Lightweight</li> <li>Pressure resistance</li> <li>Larger capacity</li> <li>Versatile polymer</li> </ul>   | <ul style="list-style-type: none"> <li>It contains heteroatom's</li> </ul>   |   |  |



Fig. 1. Small pilot scale Batch Pyrolyzer Reactor (Miandad et al., 2016d).

Table 2

Reactor parameters.

| Reactor components             | Features   |
|--------------------------------|------------|
| Height of Heating tank         | 360 mm     |
| Diameter of Heating tank       | 310 $\phi$ |
| Height of Catalyst Tank        | 200 mm     |
| Diameter of Catalyst Tank      | 165 $\phi$ |
| Reactor capacity for feedstock | 20 L       |
| Catalyst tank Capacity         | 1 L        |
| Length of Condenser            | 860 mm     |
| Diameter of Condenser          | 147 $\phi$ |
| Maximum Temperature            | 600 °C     |

Table 3

Experimental scheme.

| Feedstock types | Quantity (kg) | Ratio (%)   | Retention time (min) | Temperature (°C) | Heating rate (°C/min) |
|-----------------|---------------|-------------|----------------------|------------------|-----------------------|
| PS              | 1             | 100         | 75                   | 450              | 10                    |
| PE              | 1             | 100         | 75                   | 450              | 10                    |
| PP              | 1             | 100         | 75                   | 450              | 10                    |
| PS/PP           | 1             | 50/50       | 75                   | 450              | 10                    |
| PS/PE           | 1             | 50/50       | 75                   | 450              | 10                    |
| PP/PE           | 1             | 50/50       | 75                   | 450              | 10                    |
| PS/PE/PP        | 1             | 50/25/25    | 75                   | 450              | 10                    |
| PS/PE/PP/PET    | 1             | 40/20/20/20 | 75                   | 450              | 10                    |

temperatures well below the maximum achievable temperature of the pyrolysis process. The feedstock was converted into organic vapors that were condensed into liquid oil after passing through the condenser and collected in the collection tank at the bottom (Fig. 1). The temperature of the condenser chamber was kept below 10 °C to achieve the maximum condensation of organic vapors at a coolant flow rate of 30 l/min. The unburnt feedstock (char) was collected from heating chamber at the end of each experiment after allowing the system to cool down at room temperature. At the end of each experiment, a mass balance of pyrolysis products was established through weighing of liquid oil, wax/char quantities and the remaining weight percentage to make up to 100% was all assumed to be gases.

### 2.3. Analytical methods

TGA (Mettler Toledo TGA/SDTA851, US) was used to study the thermal degradation trends of all plastic types. The TGA analysis was carried out by heating 10  $\mu$ g of plastic samples at the rate of 10 °C/min from 25 to 900 °C under nitrogen flow at constant rate of 50 ml/min. The pyrolysis liquid oils were further characterized by various analytical equipments including fourier transform infrared spectroscopy (FT-IR), and gas chromatography coupled with mass spectrophotometry (GC-MS), for chemical composition, discovery hybrid rheometer for viscosities, density meter (DMA 35) for densities, AWD-12 pour point tester for pour and freezing points, automatic pensky-martens closed tester for flash point and bomb calorimeter for HHV by following the standard ASTM methods (APHA, 1998).

The chemical structure and functional groups present in the feedstock and liquid oils from all plastic types were studied by FT-IR, Perkin Elmer's, UK. A minimum of 32 scans were performed at an average signal of IR with a resolution of 4  $\text{cm}^{-1}$  in the ranges of 500–4000  $\text{cm}^{-1}$ . The chemical compositions of pyrolysis liquid oils were also analyzed by GC-MS (Hawlett-Packard HP 7890, US) with a 5975 quadrupole detector. The GC has a capillary column with 30 m length and 0.25 mm diameter that was coated with 0.25  $\mu$ m thick film of 5% phenyl-methypolysiloxane (HP-5). Initial temperature for the oven was set to 50 °C for a time interval of 2 min and then increased to 290 °C at 5 °C per min with an isothermal held for 10 min. Splitless injection was applied at 290 °C. The ion source and transfer line temperatures were 230 °C and 300 °C respectively. The data was attained in the full-scan mode between  $m/z$  33–533, and a solvent interval of 3 min was used. Chromatographic peaks were recognized by means of NIST08s mass spectral data library based on their retention times using standard compounds. The percentages of the peaks were calculated from total ion chromatogram (TIC) peak area.

The characteristics of pyrolysis liquid oils were characterised using appropriate procedures based on standard ASTM methods. The AWD-12 pour point tester was used for analysis of the pour and freezing points. The temperature range used was –10 °C for one tank (left side tank) and –65 °C for the other tank (right side tank). The sampling tube was filled with sample up to the mark. The sampling tube was first put in the left side tank till the temperature

reduces to 0 °C and then transferred to the tank on the right side. The sample tube was taken out periodically from the tank after every 2 °C decrease in temperature to observe the flow by holding the tube horizontally for 4 s. This procedure was continued until the pour point and freezing point were reached. A portable density meter (DMA 35 from Anton Paar) was used for the measurement of densities of the pyrolysis liquid oils. The density meter was first calibrated with distilled water and then rinsed with acetone and allowed to dry between each sample, before taking the next measurements.

The dynamic viscosities of the liquid oils were determined by using a discovery hybrid rheometer (HR1 from TA instruments) with a 40 mm parallel plates geometry. A small amount of the liquid oil sample was placed on the bottom horizontal plate. The upper 40 mm plate was lowered at a controlled rate so that the sample was sandwiched between the two plates. The temperature and the shear rate range of the rheometer was set to 40 °C and between 1 and 500 1/s respectively. The rheometer was first calibrated using viscosity standard liquid followed by actual liquid viscosity measurements. The flash point of the liquid oil was assessed by (Automatic Pensky-Martens Closed Tester, Koehler, US) based on ASTM D 93 method. The energy contents of the pyrolysis liquid oils were determined by bomb calorimeter (Parr 6200 Calorimeter, US) in the form of HHV based on standard ASTM D 240. Three replicates were carried out for the liquid oil analysis and the averaged values and ranges were used for better comparison with the literature data and conventional diesel properties.

### 3. Results and discussion

#### 3.1. Effect of plastic waste types on pyrolysis liquid oil yield

The effect of plastic types on pyrolysis product yields, especially on the liquid oils is shown in Fig. 2. All types of plastic waste were degraded into liquid oil at the optimum pyrolysis temperature of 450 °C except for PE. Pyrolysis of PE converted the feedstock into wax instead of liquid oil. Lee (2012) reported the same observation that thermal pyrolysis of PE converts the feedstock into wax instead of liquid oil due to its long carbon chain structure. PS plastic waste

showed maximum conversion of feedstock into liquid oil (80.8%) along with least gases (13%) and char (6.2%) in comparison to other plastic waste types (Fig. 2). Ciliz et al. (2004) also reported similar results that PS produced maximum fraction of liquid oil in comparison to PE and PP plastic types. According to Siddiqui and Redhwi (2009), this maximum degradation of PS was due to its simple structure in comparison to other plastic types. Moreover, PS thermal degradation process includes mainly four steps that are initiation, transfer, decomposition and termination (Faravelli et al., 2001). Thermal pyrolysis of PP produced relatively less amounts of liquid oil (42%) and char (3.5%) along with high yield of gases (54.6%). Kiran et al. (2000) also reported the large amounts of gases produced from PP plastic type along with low liquid oil yield. However, according to Koo and Kim (1993), the slow pyrolysis of PP waste increased the liquid oil yield as compared to gases yield. In the present study, the large amount of gases production can be attributed to the fast pyrolysis, since the experiments were carried out at high heating rate of 10 °C/min (Fig. 2).

Pyrolysis of mixed plastic was also carried out with different ratios (Table 3). The results showed that addition of PS with PP further reduced the liquid oil yield down to 25% from their individual yields of 80.8 and 42% respectively. Similarly, mixing of PS with PE reduced the liquid yield in comparison to individual PS pyrolysis. However in comparison to individual PE that produced wax with only 13% liquid oil, there was an increase in liquid yield (54%) when PS was mixed with PE at ratio of 50/50%. Ciliz et al. (2004) and Wu et al. (2014) explained such conversion of PE into liquid oil instead of wax after mixing with PS that it is due to production of free radicals from PS plastic. The GC-MS results of produced liquid oil from mixing of PS with PE also showed the presence of some aliphatic and olefins compounds that is the characteristics of PE liquid oil. The mixing of PP with PE increased the gases (51.2%) and char (24.8%) yields with a decrease in liquid oil yield (24%). Ciliz et al. (2004) also reported the similar trend of high gases yield from the pyrolysis of PE with PP. Furthermore addition of PS and PP with PE at a ratio of 50/25/25% has slightly increased the liquid oil yield (49%) along with gases (47.1%) and char (3.9%). However, no wax was produced from this mixture as compared to only PE pyrolysis (Fig. 2). Moreover mixing of PS with

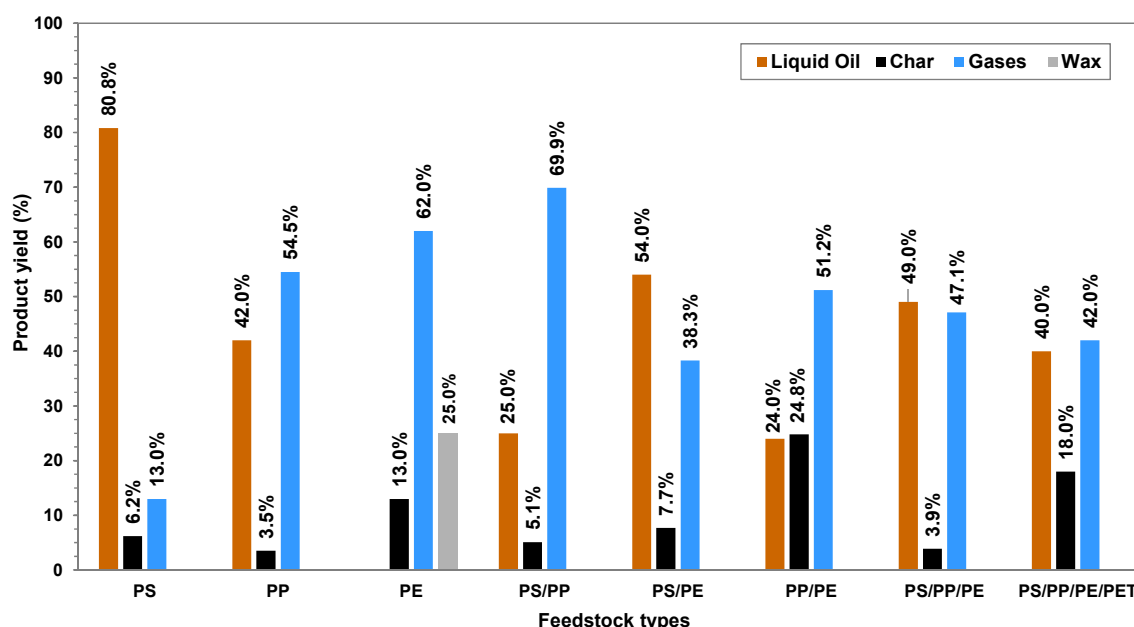


Fig. 2. Effect of plastic waste types on pyrolysis yield.



PET, PP and PE at a ratio of 40/20/20/20% decreased the liquid yields down to 40%, while gases (42%) and char (18%) yields were increased. Moreover, addition of PET increased the production of halogenated compounds in the produced liquid oil (Fig. 2).

TGA was carried out for each type of plastic waste individually to find out its optimum temperature for thermal degradation under control conditions (Fig. 3). The thermal degradation of PP started at around 240 °C, reaching to 50% degradation at around 350 °C and up to 95% degradation at around 425 °C, given  $\pm 5\%$  margin. Similarly the PS showed one step thermal degradation trend, starting at around 330 °C, reaching to 50% degradation at around 430 °C and up to 95% degradation at around 470 °C, given  $\pm 5\%$  margin. However PE showed two step degradation; first starting from around 270 °C up to 365 °C achieving only 12% degradation and then the second step was started at around 385 °C, reaching to 50% degradation at around 430 °C and up to 95% degradation at around 510 °C, given  $\pm 5\%$  margin. It was interesting to note that 50% degradation for both PE and PS was achieved at around 430 °C, however the degradation temperature range (270–510 °C) of PE was almost double than the temperature range of PS (330–470 °C). This difference in PE degradation trend in terms of its wider degradation temperature range and two-step degradation could possibly be attributed to the presence of some impurities and added additives together with its relatively complex structure. Ciliz et al. (2004) and Kim et al. (2002) also carried out TGA experiments using different plastic types and reported similar results for thermal degradation trends. Wu et al. (2014) reported that PE was required higher temperature than PS and PVC for complete thermal degradation even under control conditions. In summary, the TGA results showed that the thermal degradation of more than 50% for all studied plastic types can easily be achieved below 450 °C under controlled conditions (Fig. 3).

### 3.2. Effect of plastic waste types on liquid oil quality

The GC-MS results showed that different kinds of compounds were produced from pyrolysis of each plastic type individually and in mixture (Fig. 4). Although, liquid oil yield from PP pyrolysis was less than PS, but its composition was complex as compared to PS and its mixtures with PE and PP (Fig. 4). Ciliz et al. (2004) also reported the same results with explanation that PP's structural composition was more complicated in comparison to PE and PS plastic types. Liquid oil from PP pyrolysis contained alpha-methylstyrene (4.9%), ethylbenzene (7.3%), benzene (7.8%), propenylbenzene (23.4%), xylene (7.8%), naphthalene (5.3%), methyl-naphthalene (8.4%), phenylnaphthalene (3.3%), and phenanthrene

(7.6%). Therefore, the major compounds in liquid oil from PP pyrolysis were mono and poly-aromatic compounds with some naphthalene. Propenylbenzene, a mono-aromatic compound was also found in maximum composition (23.4%) in comparison to other plastic types (Fig. 4). Moreover, single aromatic ring compounds like xylene, dimethylbenzene and methylstyrene found in PP's liquid oil were also observed by Klemchuk (1997) and Kaminsky (1992). Furthermore, Ciliz et al. (2004) reported the production of toluene, xylene, ethylbenzene, methylstyrene, propenylbenzene aromatic compounds with naphthalene as major compounds from PP pyrolysis, which were similar to present study's GC-MS results as shown in Fig. 4. The GC-MS results for all samples were reconstructed as bar charts in excel for clear and easy cross comparison analysis. However, a typical GC-MS chromatogram of produced liquid oil from pyrolysis of PS/PE plastic, as a representative sample, at ratio of 50/50% together with all the identified compounds with their % area and retention times is also shown in Fig. 5.

The pyrolysis of PS mainly produced styrene (48.3%) with ethylbenzene (21.2%), and toluene (25.6%). Onwudili et al. (2009) reported that there was no direct production of toluene and ethylbenzene from the plastic waste pyrolysis; however they were produced by the reaction of styrene itself. Shah and Jan (2014) and Ramli and Abu Bakar, 2011 reported that increase in temperature increased the production of styrene, but according to Demirbas (2004) increase in temperature after 500 °C decreased the production of styrene. Onwudili et al. (2009) and Demirbas (2004) explained this phenomenon of decrease in styrene production from 500 to 600 °C that it was due to decomposition of styrene at higher temperature and conversion into toluene and ethylbenzene. Lee et al. (2002) reported that liquid oil from catalytic pyrolysis of PS consisted of more than 99% of aromatic compounds with small quantities of n-paraffin (0.02%), iso-paraffin (0.1%), olefins (0.03%) and naphthenes (0.1%). Similarly according to Ramli and Abu Bakar (2011), the liquid oil from thermal and catalytic pyrolysis contained 80% and 85–90% aromatic hydrocarbons respectively. The high ratio of aromatic compounds found in the pyrolysis liquid oil from pyrolysis of PS was due to the high stability of these compounds, which inhibited their further cracking or hydrogenation into paraffin and olefins (Kim et al., 2002).

Liquid oil from mixed plastic pyrolysis also showed the presence of mainly aromatic compounds (Fig. 4). The pyrolysis of PS with PP with a ratio of 50/50% produced mostly same compounds, as were produced from only PS pyrolysis. The produced compounds in liquid oil were styrene (24.5%), methylstyrene (52.0%), benzene (10.6%), ethylbenzene (6.6%), and propylbenzene (6.3%). Sarker and Rashid (2013) also reported that liquid oil produced from pyrolysis of PS with PP produced the aromatic compounds due to presence of benzene group compounds in PS plastic. Siddiqui and Redhwi (2009) observed that when PS pyrolysis was carried out with other plastic types, it produces mainly styrene and styrene oligomers. However liquid oil produced from pyrolysis of PS with PE plastic contained a complex oil composition. The produced liquid oil has major compounds of toluene (14.4%), ethylbenzene (13.6%), annulene (49.4%) and benzene, (1-methylethenyl) (7.9%). The presence of annulene and naphthalene compounds in liquid oil showed the thermal degradation of PE when mixed with PS. Siddiqui and Redhwi (2009) also observed the production of these polycyclic aromatic hydrocarbons besides styrene and styrene oligomers from the pyrolysis of PS with PE.

PP pyrolysis with PE at a ratio of 50/50% produced 1,2-benzenedicarboxylic acid (51.1%), phenol (13.3%), azulene (10.3%), phenanthrene (6.9%), 1-docosanol, acetate (4.2%), naphthalene, and 2-ethenyl (3.2%). Mixing of PP with PE also increased the production of high aliphatic compounds (Fig. 4). Ciliz et al. (2004) also observed

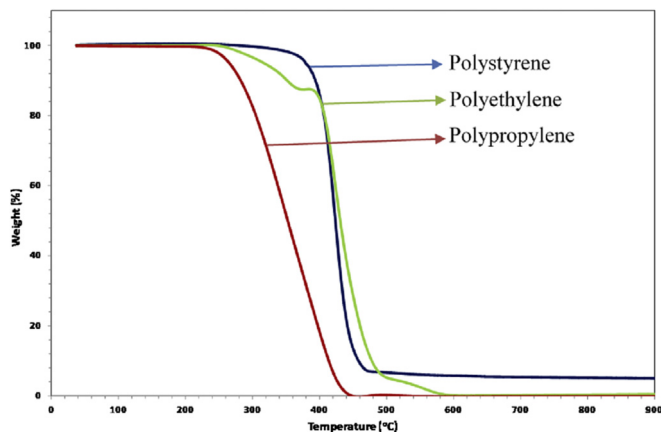


Fig. 3. Thermogravimetric analysis (TGA) of PS, PE and PP plastic types.

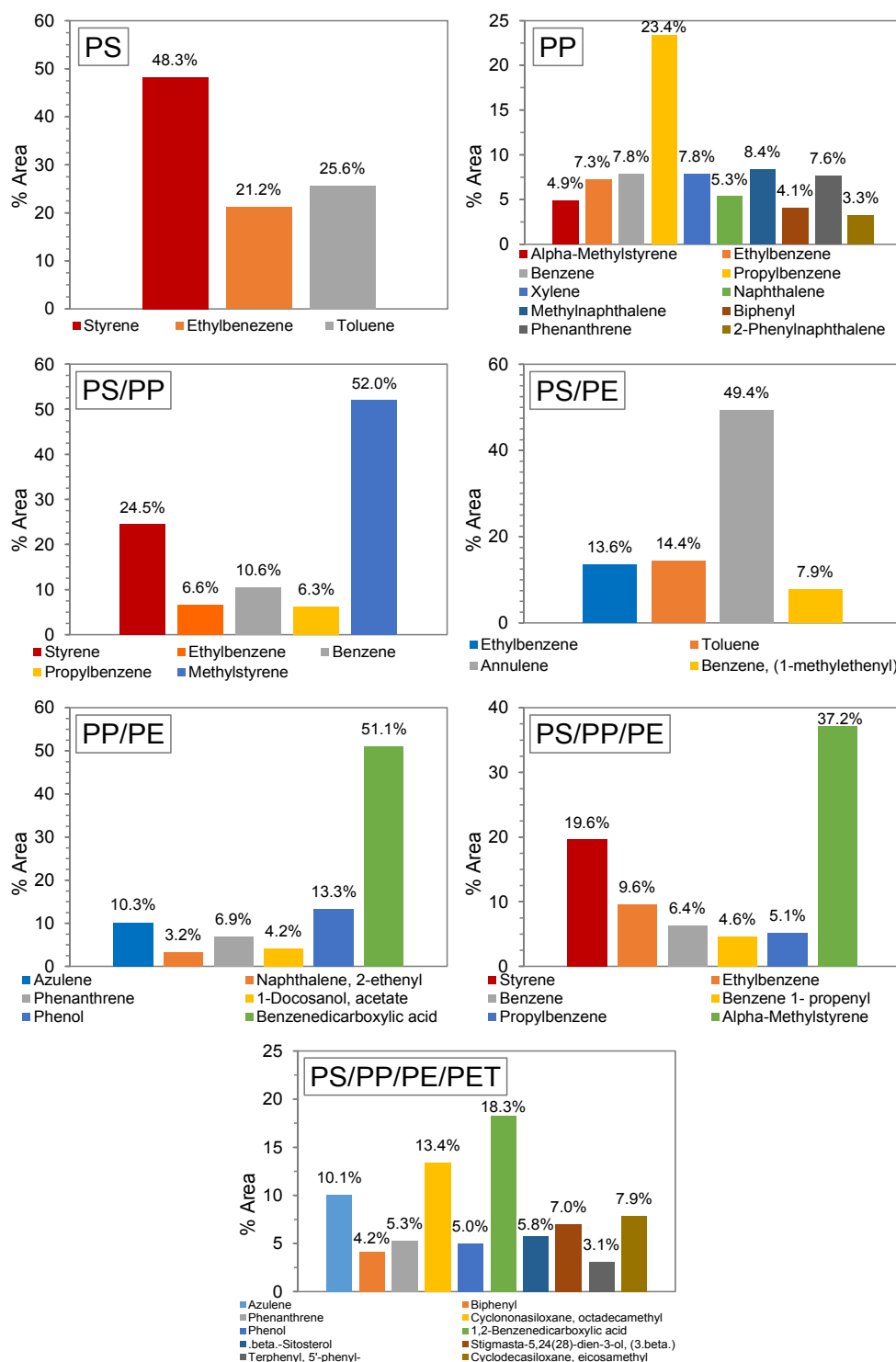
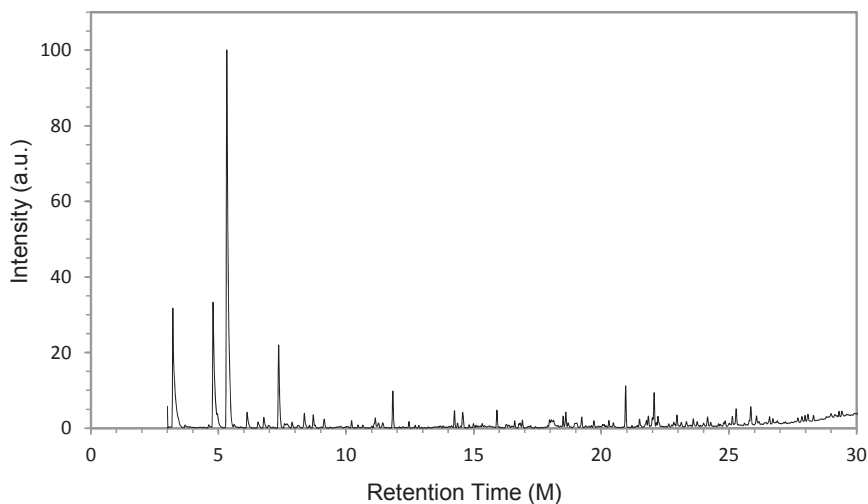


Fig. 4. GC-MS results of liquid oils from pyrolysis of different types of plastic waste.

a maximum production of aliphatic compounds from the pyrolysis of PE with PP at the ratio of 50/50%. In addition, pyrolysis of PP with PE produced liquid oil with alkanes, alkenes, and alkadienes (Fig. 4). The pyrolysis of PS with PE and PP at a ratio of 50/25/25% produced methylstyrene (37.2%), styrene (19.6%), ethylbenzene (9.6%), benzene (6.4%), benzene 1-propenyl (4.6%) and propylbenzene (5.1%) (Fig. 4). Similar compounds in liquid oil of PS pyrolysis with PE and PP were reported by Ciliz et al. (2004) and Sarker and Rashid (2013).

However, according to Kiran et al. (2000), there was a decrease in the production of mono-aromatic and naphthalene compounds when PE was mixed with PS plastic. When PS was mixed with PP, PE and PET at a ratio of 40/20/20/20%, the produced liquid oil has a very complex composition. The produced compounds were benzenedicarboxylic acid (18.3%), cyclononasiloxane, octadecamethyl (13.4%), cyclodecasiloxane, eicosamethyl (7.9%), stigmasta (7.0%), beta-Sitosterol (5.8%), phenanthrene (5.3%), phenol (5.0%), biphenyl



| Peak No | Retention Time | Name                               | Compound formula                | Molecular Weight | Area % |
|---------|----------------|------------------------------------|---------------------------------|------------------|--------|
| 1       | 3.212          | Toluene                            | C <sub>7</sub> H <sub>8</sub>   | 92               | 14.43  |
| 2       | 4.787          | Ethylbenzene                       | C <sub>8</sub> H <sub>10</sub>  | 106              | 13.61  |
| 3       | 5.326          | Annulene                           | C <sub>8</sub> H <sub>8</sub>   | 104              | 49.35  |
| 4       | 7.356          | Benzene, (1-methylethenyl)         | C <sub>10</sub> H <sub>12</sub> | 132              | 7.88   |
| 5       | 8.363          | Benzene, 1-propenyl-               | C <sub>9</sub> H <sub>10</sub>  | 118              | 1.04   |
| 6       | 11.831         | Azulene                            | C <sub>10</sub> H <sub>8</sub>  | 128              | 2.64   |
| 7       | 14.244         | Naphthalene, 2-methyl              | C <sub>11</sub> H <sub>10</sub> | 142              | 1.12   |
| 8       | 14.567         | 1-Methylnaphthalene                | C <sub>11</sub> H <sub>10</sub> | 142              | 1.3    |
| 9       | 15.91          | Naphthalene, 2-ethenyl-            | C <sub>12</sub> H <sub>10</sub> | 154              | 1.13   |
| 10      | 18.607         | Bibenzyl                           | C <sub>14</sub> H <sub>14</sub> | 182              | 1.03   |
| 11      | 20.952         | Propane, 1,3-diphenyl              | C <sub>15</sub> H <sub>16</sub> | 196              | 2.83   |
| 12      | 22.067         | N-Methylene-1,2-diphenylethanamine | C <sub>15</sub> H <sub>17</sub> | 211              | 1.86   |
| 13      | 22.961         | Benzene, (4-methyl-1-decenyl)      | C <sub>12</sub> H <sub>24</sub> | 168              | 0.71   |
| 14      | 25.28          | 2-Phenylnaphthalene                | C <sub>16</sub> H <sub>12</sub> | 204              | 1.07   |

Fig. 5. A typical GC-MS chromatogram (PS/PE) together with all the identified compounds with their % area and retention times.

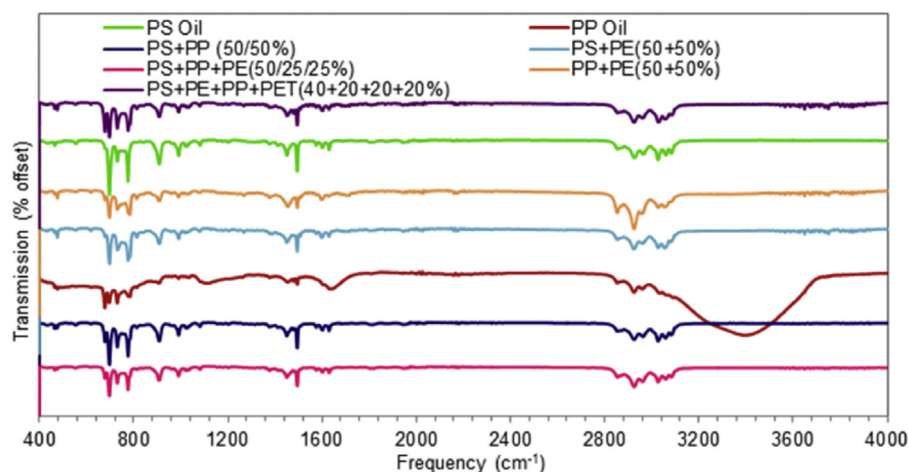
(4.2%), and terphenyl, 5'-phenyl- (3.1%). Rashid and Sarker (2013) also reported the similar results that pyrolysis of PET with PS produced a complex composition liquid oil having aliphatic and aromatic compounds.

The identification of all functional groups present in used plastic waste types such as PS, PE, and PP and liquid oils from their individual and in mixture forms were studied by using FT-IR spectra (Figs. 6 and 7). Overall, PE raw structure has C=C and C=H bond appeared as a double bond that break down to single bond after polymerization. However PP have methyl group while, PS have styrene group. Therefore, the mixing of these three different polymers produced various types of products with different characteristics. This analysis identified the chemical bonds in a molecule by producing an infrared absorption spectrum, leading to identification of functional groups in feedstock and liquid oils. Many clear peaks were generated, ranging from 674 to 3353 cm<sup>-1</sup> for feedstock and liquid oils. FT-IR analysis of plastic feedstock showed that PS and PE consisted of mostly aromatic compounds with some alkanes and alkenes (Fig. 7). However, PP consisted of alkanes, alkenes and aldehydes along with aromatic, and hence liquid oil from PP pyrolysis showed very complex compound composition (Fig. 7).

Liquid oil from PS pyrolysis individually and in mixture with PP,

PE and PET showed the same results (Fig. 6). However liquid oil from PP pyrolysis showed little different results; at start it produced alkanes and alkenes, and in the middle showed strong production of aromatics and at the end produced a strong peak (3353.3 cm<sup>-1</sup>) of amines group. Similar results for PP's pyrolysis liquid oil were reported by Tekin et al. (2012) and Panda and Singh (2013). FT-IR spectrum of PS pyrolysis showed that aromatics were produced at the start, and then strong peaks of aromatics compounds were produced in the middle and small peak of alkanes, and alkenes were produced at the end (Fig. 6). Sarker and Rashid (2013) also reported the similar FT-IR results for PS, HDPE and PP's pyrolysis individually and in mixture form. Wu et al. (2014) reported that liquid oil from PS and PE pyrolysis produced mostly the aromatic compounds with small amounts of alkanes and alkenes compounds. Several other researchers also reported the similar results for FT-IR spectrum of liquid oil from PS and PE pyrolysis (Siddiqui and Redhwi, 2009; Lee et al., 2002; Kim et al., 2002; Sarker and Rashid, 2013; Bozkurt et al., 2016). In addition liquid oil produced from PP with PE showed strong peak or aromatic and alkanes (Fig. 6). The production of alkanes was from PP plastic. However, strong peak was found at 2916.4 cm<sup>-1</sup> that showed the presence of aliphatic compounds due to presence of PE. Bozkurt et al. (2016) reported that during the co-pyrolysis of PE with shale increases





| Peaks  | PS | PP | PS/PP | PS/PE | PE/PP | PS/PP/PE | PS/PP/PE/PET | Bond                  | Functional Group |
|--------|----|----|-------|-------|-------|----------|--------------|-----------------------|------------------|
| 674.6  | X  | ✓  | X     | X     | X     | X        | ✓            | -C≡C-H: C-H bend      | Alkynes          |
| 694.7  | X  | ✓  | X     | ✓     | ✓     | X        | ✓            | C-H "oop"             | Aromatics        |
| 725.1  | X  | ✓  | X     | X     | X     | X        | X            | C-H rock              | Alkanes          |
| 775    | ✓  | X  | ✓     | ✓     | ✓     | ✓        | ✓            | C-H "oop"             | Aromatics        |
| 854.3  | X  | ✓  | X     | X     | X     | X        | X            | C-H "oop"             | Aromatics        |
| 895.8  | X  | X  | X     | ✓     | X     | X        | ✓            | N-H wag               | 1°, 2° amines    |
| 907    | ✓  | X  | ✓     | ✓     | ✓     | ✓        | ✓            | =C-H bend             | Alkenes          |
| 988    | ✓  | ✓  | ✓     | X     | X     | ✓        | X            | O-H bend              | Carboxylic acids |
| 1430.6 | X  | X  | X     | X     | ✓     | ✓        | X            | C-C stretch (in-ring) | Aromatics        |
| 1447.3 | ✓  | ✓  | ✓     | X     | ✓     | ✓        | X            | C-C stretch (in-ring) | Aromatics        |
| 1493   | ✓  | ✓  | ✓     | ✓     | X     | ✓        | ✓            | C-C stretch (in-ring) | Aromatics        |
| 1595.8 | X  | X  | ✓     | X     | X     | ✓        | X            | C-C stretch (in-ring) | Aromatics        |
| 1600   | ✓  | ✓  | ✓     | X     | X     | ✓        | X            | C-C stretch (in-ring) | Aromatics        |
| 2897.1 | X  | X  | X     | ✓     | X     | ✓        | ✓            | C-H stretch           | Alkanes          |
| 2919   | ✓  | X  | ✓     | X     | ✓     | ✓        | X            | C-H stretch           | Alkanes          |
| 3022.4 | ✓  | X  | ✓     | ✓     | X     | ✓        | ✓            | =C-H stretch          | Alkenes          |
| 3353.2 | X  | ✓  | X     | X     | X     | X        | X            | N-H stretch           | 1°, 2° amines    |

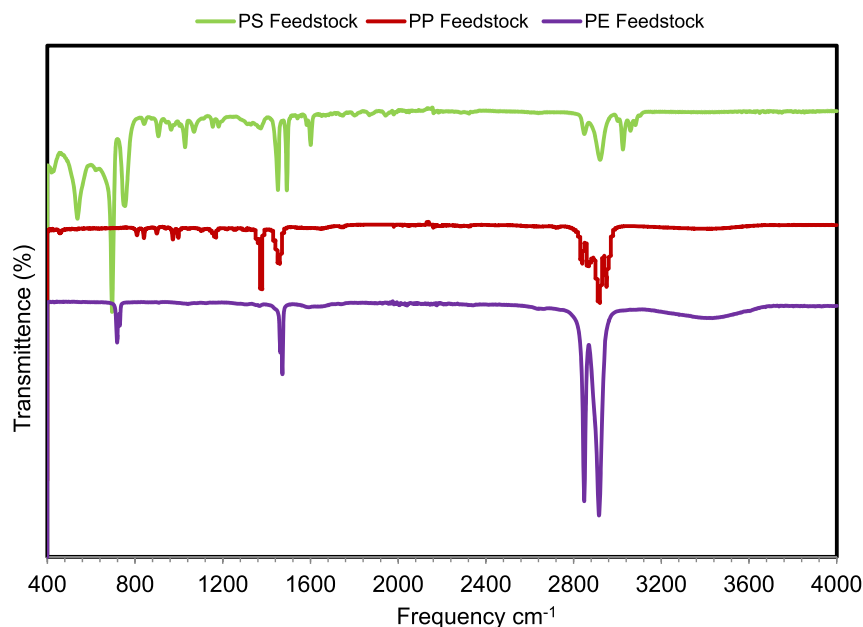
Fig. 6. FT-IR of liquid oils from pyrolysis of different types of plastic waste.

the production of aliphatic compounds because in co-pyrolysis PE act as hydrogenation medium. Moreover Siddiqui and Redhwi (2009) concluded that liquid oil produced from PS with HDPE, LDPE and PP gave the same spectra, where alkanes and alkanes peaks were derived from PE plastic and PS produced mostly aromatics peaks.

The characteristics of pyrolysis liquid oils were further analyzed and compared with conventional diesel (Table 4). The fuel properties such as viscosity, density, pour point, freezing point, flash point and HHV are important to be assessed for analyzing the quality of fuel. Overall, the values of these properties of pyrolysis liquid oils were found to be within comparable range to the conventional diesel. The dynamic viscosity range of pyrolysis liquid oils in this study was found to be 1.77–1.90 mPa s, which is within the range of 1–4.11 mPa s for conventional diesel reported by Wongkhorsub and Chindaprasert (2013). The kinematic viscosity of fuel is another very important characteristics as it dictates the spray

pattern and atomization of injected fuel in a combustion chamber. The higher viscosities of fuel results in poor atomization, leading to poor engine start-up and performance. Furthermore, higher viscous fuels have reduced flow ability, especially during winters, which adversely affects the fuel injector function and causes problems in engine start up and running (Miandad et al., 2016a,b). The kinematic viscosities of pyrolysis liquid oils found in this study were in the range of 1.92–2.09 cSt (Table 4), which is lower than the standard range of 2.0–5.0 cSt for conventional diesel (Syamsiro et al., 2014). Moreover, the kinematic viscosity values found are also comparable with kinematic viscosity of 1.74 cSt for pyrolysis oil from polyethylene (PE) bag, 2.32 cSt from HDPE and 2.18 cSt for PP plastic as reported by Panda and Singh (2013) and Syamsiro et al. (2014).

The density is another important characteristic of any fuel. The density of pyrolysis liquid oils were found to be in the range of 0.91–0.92 g/cm<sup>3</sup>, which is slightly higher but in close comparable



| Peaks                  | PS | PP | PE | Bond                  | Functional group |
|------------------------|----|----|----|-----------------------|------------------|
| 532.27                 | ✓  | X  | X  | C-Br stretch          | Alkyl halides    |
| 708, 716, 745          | ✓  | X  | ✓  | C-H "oop"             | Aromatics        |
| 1028                   | ✓  | X  | X  | =C-H bend             | Alkenes          |
| 1370                   | X  | ✓  | X  | C-H rock              | Alkanes          |
| 1449.75, 1471, 1491.21 | ✓  | ✓  | ✓  | C-C stretch (in-ring) | Aromatics        |
| 1599.21                | ✓  | X  | X  | C-C stretch (in-ring) | Aromatics        |
| 2830.50                | X  | ✓  | X  | H-C=O: C-H stretch    | Aldehydes        |
| 2912, 2950, 3021.96    | ✓  | ✓  | ✓  | C-H stretch           | Alkanes          |

Fig. 7. FT-IR of different types of plastic feedstock.

**Table 4**

Comparison of characteristics of pyrolysis liquid oil with conventional diesel.

| Parameters                  | Units             | This study results | Conventional diesel | Reference                           |
|-----------------------------|-------------------|--------------------|---------------------|-------------------------------------|
| Dynamic Viscosity           | mPa.s             | 1.77–1.90          | 1–4.11              | Wongkhorsub and Chindaprasert, 2013 |
| Kinematic Viscosity @ 40 °C | cSt               | 1.92–2.09          | 2.0–5.0             | Syamsiro et al., 2014               |
| Density @15 °C              | g/cm <sup>3</sup> | 0.91–0.92          | 0.815–0.870         | Syamsiro et al., 2014               |
| Pour Point                  | °C                | (-11)–(-60)        | Max 18              | Syamsiro et al., 2014               |
| Freezing Point              | °C                | (-15)–(-64)        | –                   |                                     |
| Flash Point                 | °C                | 28.1–30.2          | Min 55–60           | Syamsiro et al., 2014               |
| HHV                         | MJ/kg             | 41.4–41.8          | 43.06               | Kamal and Zainuri, 2015             |

range of 0.815–0.870 g/cm<sup>3</sup> for diesel (Syamsiro et al., 2014) (Table 4). The flash point of pyrolysis oils were found in the range of 28.1–30.2 °C, which is lower than the range of 55–60 °C for diesel. This is probably due to high aromatic contents and volatility of pyrolysis liquid oils. The quality of any fuel is also determined by its cold flow properties that dictate the lowest temperature at which the fuel injected system works on its full potential. These properties include cloud point, temperature where wax crystals start to form in liquid, causing cloudiness and pour point, lowest temperature where fuel becomes semi solid, and loses its flow characteristics (Gardy et al., 2014). The pour and freezing points of the pyrolysis liquid oils were found to be quite low, (–11 °C) – (–60 °C) and (–15 °C) – (–65 °C) respectively (Table 4). This is particularly very beneficial, for operational point of view, in areas where very low temperatures occur during winter. Furthermore, any fuel having high pour point will result in formation of wax that if left for longer

can cause blockage in fuel system and thus create problems in engine startup and its performance (Robert, 2011).

HHV is an important characteristic of any petroleum product, especially when considered for energy production. High HHV means high energy contents that result in achieving the required target energy with less amount of fuel (Saptoadi and Pratama, 2015). The HHV range found in this study was 41.4–41.8 MJ/kg (Table 4), which is very close to the HHV of 43.06 MJ/kg for conventional diesel (Kamal and Zainuri, 2015). López et al. (2011) reported that liquid oil from pyrolysis of packaging plastic waste at 440 °C had HHV of 41.5 MJ/kg. Moreover, liquid oil from PE bag and mixed plastic pyrolysis had HHV of 41.5 and 40.5 MJ/kg respectively (Syamsiro et al., 2014; Mani et al., 2011). HHV of the pyrolysis liquid oils showed their potential as an alternative fuel to conventional diesel. According to Saptoadi and Pratama (2015), pyrolysis liquid oil can be potentially utilized as an energy source after mixing with

kerosene oil.

#### 4. Potential applications of liquid oil and char

Liquid oils from pyrolysis of different plastic waste types contained a large number of carbon chains with different fractions that showed their potential utilization as an energy source. Liquid oil utilization as transport fuel requires further upgrading and blending with conventional diesel to improve its quality, as it contains a high percentage of aromatic hydrocarbons, as can be seen from Figs. 4 and 5. The use of pyrolysis liquid oil as transport fuel has been successfully tested after blending with conventional diesel at different ratios (Demirbas, 2004; Gardy et al., 2014; Islam et al., 2010). Lee et al. (2015) blended 20 and 40% of pyrolysis liquid oil with conventional diesel and concluded that at 20%, a successful engine running was achieved, but there was a decrease of output of 13% and 17% at 2450 rpm and 3500 rpm respectively. Moreover mixing of pyrolysis liquid oil with conventional diesel decreased the physical properties of fuel that resulted in an increase in ignition time and hence reduced the produced torque (Lee et al., 2015).

Nileshkumar et al. (2015) blended pyrolysis liquid oils with conventional diesel with the ratio of 10, 20, 30, 40 and 50% and concluded that at 20% fuel consumption was same as conventional diesel. Moreover, the mechanical efficiency was increased with the increase of pyrolysis oil (Miandad et al., 2016a). However, increase in pyrolysis liquid oil ratio also increased the exhaust emissions of HC's, CO, and NOx with low CO<sub>2</sub> (Frigo et al., 2014; Mukherjee and Thamocharan, 2014). The use of pyrolysis liquid oil in a diesel engine is also a promising way to generate electricity (Lee et al., 2015; Rehan et al., 2016a). In addition, the produced liquid oil showed the presence of high aromatic compounds such as styrene, ethylbenzene, and toluene along with others styrene monomers (Figs. 4 and 5). The recovery of these aromatic compounds from produced liquid oils can be a potential source of precursor chemicals in industries for polymerization of plastic monomers (Miandad et al., 2016a,b; Shah and Jan 2014; Sarker and Rashid, 2013). According to Nikodinovic-Runic et al. (2011), a biocompatible and biodegradable plastic can be produced from pyrolysis oil of PS plastic waste.

Char is a by-product of pyrolysis process that has various potential applications (Miandad et al., 2016a,b). Jindaporn and Lertsatitthanakorn (2014) reported that char from the pyrolysis of HDPE had a calorific value of around 18.84 MJ/kg. While char produced from PS plastic wastes had HHV of 36.29 MJ/kg (Syamsiro et al., 2014), thus can be used as a potential energy source. Moreover, different researchers carried out activation of char from pyrolysis of plastic waste and tires using steam activation (López et al., 2011), hydrogen peroxide activation (Heras et al., 2014) and thermal activation (Jindaporn and Lertsatitthanakorn, 2014). All these studies reported that activation of char increased its BET surface

area that enhanced its ability to be used as an adsorbent material for heavy metals, odor and toxic gases removal from wastewater and exhaust emissions. Bernardo (2011) upgraded the produced char from co-pyrolysis of various types of plastics wastes such as PS, PP, and PE with biomass and waste tires. The activated char was used for the adsorption of dyes from wastewater that showed significant removal of methylene blue dye (3.59–22.2 mg/g). Therefore, the produced char from different types of plastics waste can be used as a source of feedstock for activated carbon or energy for boilers as well (Fernández et al., 2011).

##### 4.1. Upgrading of liquid oil

Liquid oil from plastic waste pyrolysis contains some impurities such as sulfur, chlorine, solid residue, moisture, and acids. Presence of these impurities not only decreases the quality of liquid oil but also limits its commercial applications. Therefore, liquid oil requires post-treatment including, upgradation with removal of char particles, and acids removal, and neutralization to improve liquid oil with stable pH and low corrosivity (Table 5). The upgrading procedure of pyrolysis liquid oil depends on its targeted application. There are two reported ways for liquid oil upgrading, including refining and blending with conventional diesel to make it suitable for various commercial applications. After upgrading the liquid oil into gasoline range hydrocarbons and removal of impurities, it can be used in modified diesel engines as transport fuel and for the generation of heat and electricity (Table 6). However according to Frederick et al. (2013) and Demirbas et al. (2016), further research is needed to explore new methods of liquid oil purification and upgradation.

##### 4.2. Future work

The conversion of plastic waste into liquid oil and other valuable products using pyrolysis process is getting significant attention both as waste management and an alternative energy generation technology. The catalytic pyrolysis has advantages over thermal pyrolysis such as it requires lower energy and time for conversion and produces higher quality liquid oil. Pilot scale and commercial scale pyrolysis plants are operating worldwide utilizing plastic waste from MSW, tires, and hospital waste (Chen et al., 2014). For example, plant in Iceland is operating with a capacity of 45 tons per day (Malkow, 2004), Japan with a capacity of 140 tons per day (Kawai, 2009), Germany with a capacity of 6 tons per hour (Malkow, 2004) and China with a capacity of 200 kg per hour (Li et al., 2007).

Despite the operation and recent advancements in pyrolysis technology, several issues and scope for further process optimization still remain. For example, the current study investigated how different types of plastic wastes, used as single type or combination

**Table 5**

Purification and upgrading of pyrolysis liquid oils (Rehan et al., 2016b; Miandad et al., 2016a; Demirbas, 2004).

| Problems                               | Process               | Methods   | Products                            |
|--|-----------------------|---|-------------------------------------|
| Acid contamination                     | Amine treating        | Absorption treatment                            | Liquid HCs and gases free from acid |
| Contaminants                           | Desalting             | Dehydration via absorption                      | Crude oil (desalted)                |
| Sulfur and water                       | Sweetening and drying | Treatment via absorption/thermal                | Dry and sweet HCs                   |
| Lubes and middle distillate            | Furfural extraction   | Absorption via solvent extraction               | Lube oil and diesel of high quality |
| Sulfur contaminants                    | Hydrode-sulfurization | Catalytic treatment                             | Olefins (desulfurized)              |
| Saturated HCs impurities               | Hydrotreating         | Catalytic hydrogenation                         | Lube, distillate, cracker feed      |
| Color, viscosity index                 | Phenol extraction     | Absorption/thermal solvent extraction           | Lube oil of high quality            |
| Asphalt                                | Solvent deasphalting  | Absorption treatment                            | Asphalt, heavy lube oil             |
| Wax (lube stocks)                      | Solvent dewaxing      | Cool/filter treatment                           | Dewaxed lube base stock             |
| Oils (unsaturated)                     | Solvent extraction    | Absorption/precipitation via solvent extraction | Gasoline with high octane           |
| Conversion mercaptan, H <sub>2</sub> S | Sweetening            | Catalytic treatment                             | Gasoline/distillate of high quality |

**Table 6**

Fractions in crude oil and their potential applications (Chem1, 2009; Demirbas et al., 2016; Doc Brown, 2016).

| Name of fraction            | % In crude oil | C Atoms                          | Approximate boiling point (°C) | Potential application   |
|-----------------------------|----------------|----------------------------------|--------------------------------|---|
| LPG, Fuel gas, Refinery gas | 1–2            | C <sub>1</sub> –C <sub>4</sub>   | <25                            | <ul style="list-style-type: none"> <li>• Bottled gas</li> <li>• Feedstock (organic chemicals)</li> <li>• High pressure cylinder</li> <li>• Car fuel</li> </ul>  |
| Gasoline                    | 20–40          | C <sub>5</sub> –C <sub>8</sub>   | 25–75                          | <ul style="list-style-type: none"> <li>• Solvent used for cracking</li> <li>• Aircraft fuel</li> <li>• Domestic heating fuel (Stoves)</li> <li>• Fuel for large vehicle</li> <li>• Fuel for railway</li> <li>• Central heating fuel</li> <li>• Engines Lubricant</li> <li>• Machine lubricant</li> <li>• Heating fuel</li> <li>• Ships fuel</li> <li>• Candles</li> <li>• Lubricants</li> <li>• Road toping</li> <li>• Roofing</li> </ul> |
| Naphtha                     | 10–15          | C <sub>6</sub> –C <sub>10</sub>  | 75–190                         |   |
| Kerosene (Paraffin)         |                | C <sub>10</sub> –C <sub>16</sub> | 190–250                        |   |
| Diesel oil                  | 15–20          | C <sub>14</sub> –C <sub>20</sub> | 250–350                        |   |
| Lubricating oil             |                | C <sub>18</sub> –C <sub>25</sub> | 300–400                        |   |
| Fuel oil                    |                | C <sub>20</sub> –C <sub>27</sub> | 350–450                        |   |
| Wax and greases             |                | C <sub>25</sub> –C <sub>30</sub> | 400–500                        |   |
| Bitumen                     | 40–50          | Over C <sub>35</sub>             | Above 500                      |   |

of mixtures, affected the yield and quality of pyrolysis liquid oil in a small pilot scale pyrolysis reactor. Other important parameters are also under investigation such as utilization of a number of synthetic and natural catalysts in order to improve the yield and quality of liquid oil and to achieve the overall cost minimization and process optimization (Aguado et al., 2006). Moreover, use of catalyst increases the yield of process and inhibits the production of undesirable products that increase the quality of liquid oil as well (Aguado et al., 2006). However, synthetic catalysts are very expensive which make this process economically less favorable. To overcome this issue, reuse of catalyst, use of natural minerals as catalysts, and use of catalysts in reduced quantities were suggested by different researchers (Lin et al., 2010). In addition, some researchers used spent FCC to reduce the cost of catalyst. Nevertheless, reuse of catalyst is challenging and not very efficient due to the deposition of coke that decreases its life cycle and overall functionality with time (López et al., 2011).

Improving the pyrolysis liquid oil quality should be studied further by post-treatment methods such as filtration, chemical treatment, by blending it with diesel and other fuels and distillation and refining to remove heavy hydrocarbons and any impurities. These detailed findings from a pilot scale process can be very important and critical in decision making process for installing commercial scale pyrolysis technology in developing countries as a way forward for both sustainable waste management and alternative energy generation. Nevertheless, life cycle assessments (LCA) of feedstock, products and process are also very important to fully understand the economic, technical and environmental aspects of pyrolysis technology before its installation at commercial scale. Wang et al. (2015) did LCA of pyrolysis plant and concluded that pyrolysis of MSW showed less impact of environment as compared to its disposal to landfill and other treatment processes. In addition focus should be given to the value-added products of pyrolysis process such as char and gases. Char activation and its evaluation for various environmental application should be given due consideration.

## 5. Conclusions

Thermal pyrolysis is an effective way to convert different types of plastic waste into liquid oil and char. All the plastic waste types used in present study were converted into liquid oil at 450 °C and 75 min retention time, except PE that was converted into wax due to its long carbon chain structure. However, mixing of PS and PP

with PE (50/25/25%), converted PE plastic into liquid oil due to the production of free radicals from PS. The GC-MS results showed that liquid oils from different types of plastic waste consisted of mostly aromatic compounds with minor alkanes and alkenes. Liquid oil from PS pyrolysis contained styrene (48.3%), toluene (25.6%), and ethylbenzene (21.2%). PP plastic produced very complex liquid oil that also consisted of mainly aromatic compounds such as propylbenzene (23.4%), ethylbenzene (7.3%), benzene (7.8%), alpha-methylstyrene (4.9%), xylene (7.8%), naphthalene (5.3%), methyl-naphthalene (8.4%), biphenyl (4.1%), phenanthrene (7.6%) and 2-phenylnaphthalene (3.3%). While mixing of PS with PP at the ratio of 50/50% produced liquid oil containing methylstyrene (52.0%), styrene (24.5%), ethylbenzene (6.6%), benzene (10.6%), and propylbenzene (6.3%). However, when PS was mixed with PE and PP at the ratio of 50/25/25%, the produced liquid oil contained alpha-methylstyrene (37.2%), styrene (19.6%), ethylbenzene (9.6%), benzene (6.4%), and benzene1-propenyl (5.1%). Pyrolysis liquid oils found to have ranges of dynamic viscosity of 1.77–1.90 mPa s, kinematic viscosity of 1.92–2.09 cSt, density of 0.91–0.92 g/cm<sup>3</sup>, pour point of –11 to –60 °C, freezing point of –15 to –65 °C, flash point of 28.1–30.2 °C and HHV of 41.4–41.8 MJ/kg; similar to conventional diesel, thus have potential to be used as alternative energy source for electricity generation. However, presence of high aromatic compounds in liquid oil made it unsuitable as a transport fuel until it is upgraded using different post-treatment methods such as distillation, refining or blending with conventional diesel. Overall the study concluded that pyrolysis can be an effective recycling technique for the KSA's plastic waste with dual benefits of plastic waste management and energy production.

## Acknowledgment

Dr. Abdul-Sattar Nizami and Dr. Mohammad Rehan are very grateful to the Ministry of Education, Kingdom of Saudi Arabia for providing funds to complete this work under the Project Grant no of 1/S/1433.

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