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# Influence of temperature and reaction time on the conversion of polystyrene waste to pyrolysis liquid oil

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#### ABSTRACT

This paper aims to investigate the effect of temperature and reaction time on the yield and quality of liquid oil produced from a pyrolysis process. Polystyrene (PS) type plastic waste was used as a feedstock in a small pilot scale batch pyrolysis reactor. At 400 °C with a reaction time of 75 min, the gas yield was 8% by mass, the char yield was 16% by mass, while the liquid oil yield was 76% by mass. Raising the temperature to 450 °C increased the gas production to 13% by mass, reduced the char production to 6.2% and increased the liquid oil yield to 80.8% by mass. The optimum temperature and reaction time was found to be 450 °C and 75 min. The liquid oil at optimum conditions had a dynamic viscosity of 1.77 mPa s, kinematic viscosity of 1.92 cSt, a density of  $0.92 \text{ g/cm}^3$ , a pour point of -60 °C, a freezing point of -64 °C, a flash point of 30.2 °C and a high heating value (HHV) of 41.6 MJ/kg this is similar to conventional diesel. The gas chromatography with mass spectrophotometry (GC–MS) analysis showed that liquid oil contains mainly styrene (48%), toluene (26%) and ethyl-benzene (21%) compounds.

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# 1. Introduction

The Kingdom of Saudi Arabia (KSA) was the world's twelfth largest primary energy consumer in 2012 with a total energy consumption of 9 quadrillions British thermal units (Btu) (US-EIA, 2014; Anjum et al., 2016). The current electricity generating capacity of KSA is 55 GW<sub>e</sub>; which is estimated to surpass 120 GW<sub>e</sub> by 2032 (Royal Decree, 2010). The electricity demand in KSA is increasing by 8% per annum, of which 50% is only consumed in the residential sector (Farnoosh et al., 2014). Fossil fuels are the only source of energy in KSA (SEC, 2012; Rehan et al., 2016a). The Government has launched a special program; King Abdullah City of Atomic and Renewable Energy (KACARE) to generate about

http://dx.doi.org/10.1016/j.wasman.2016.09.023 0956-053X/© 2016 Elsevier Ltd. All rights reserved. half of the energy (corresponding to a capacity of  $72 \text{ GW}_{e}$ ) from renewable sources such as solar, nuclear, wind, waste-to-energy (WTE) and geothermal by 2032 (KACARE, 2012; Nizami et al., 2015a; Demirbas et al., 2016a).

KSA is one of the major plastic producer country in the world with annual plastic production of around 6 million metric tons (Nizami et al., 2015b; Khan and Kaneesamkandi, 2013). The average life span of about 40% of the consumed plastic in KSA is less than a month (Siddiqui and Redhwi, 2009). As a result, it is the second largest waste stream (17.4%) of total generated MSW in KSA (Nizami et al., 2015c). Moreover, excessive quantities of plastic waste are produced due to serving of meals in disposable plastics to millions of religious pilgrims and visitors, coming every year to KSA (Nizami et al., 2016). All of the collected MSW (around 15 million tons per year) including plastic waste is untreated and disposed to landfills (Khan and Kaneesamkandi, 2013). The clogging effects and the slow biodegradable nature of plastics with toxic additives and dyes are an added environmental burden through landfills and landfill operation (Miandad et al., 2016a).

Worldwide, there are different plastic waste management techniques such as reducing, reusing, WTE, mechanical and chemical

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Abbreviations: CO, carbon monoxide; HDPE, high density polyethylene; HHV, higher heating value; KACARE, King Abdullah City of Atomic and Renewable Energy; KSA, Kingdom of Saudi Arabia; LDPE, low density polyethylene; MSW, municipal solid waste; NOx, oxides of nitrogen; PE, polyethylene; PP, polypropylene; PS, polystyrene; RDF, refuse derived fuel; SWM, solid waste management; TGA, thermogravimetric analyzer; TIC, total ion chromatogram; WTE, waste-to-energy.

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recycling and landfilling (Sriningsih et al., 2014; Sadef et al., 2015; Miandad et al., 2016b,c). Mechanical recycling methods such as sorting, grinding, washing and extrusion can recycle only 15–20% of all plastic waste (Ashworth et al., 2014). Combustion and landfilling of plastic waste results in air and waterborne pollutants (Ouda et al., 2016; Rahmanian et al., 2015; Eqani et al., 2016). Chemical recycling of plastic waste through hydrolysis, methanolysis, and glycolysis (Sinha et al., 2010) along with WTE technologies such as gasification, pyrolysis, refuse derived fuel (RDF) and plasma arc gasification are seen as preferable and as such are the subject of more scientific attention in recent years (Miandad et al., 2016a,b).

The pyrolysis process converts organic materials including plastic waste into energy (liquid oil) and value-added product (char) (Bartoli et al., 2015; Rathore et al., 2016; Demirbas et al., 2016b). The process can be carried out by using different types of reactor such as tube reactor (Miskolczi et al., 2009), rotary kiln reactor (Li et al., 1999), microwave reactor (Undri et al., 2011; Undri et al., 2013), fixed bed reactor (Ringer et al., 2006), semi batch reactor (Lopez et al., 2011), and batch reactor (Syamsiro et al., 2014). Batch and semi-batch reactors are widely used at laboratory scale due to their easy operation, simple design, and safety point of view (Almeida and Margues, 2016; Chen et al., 2014; Ates et al., 2013). However, for fuel or monomer production at commercial scale, continuous pilot reactors such as fluidized bed and spouted bed reactors are used with continuous plastic feeding (Artetxe et al., 2015; Mo et al., 2014; Jung et al., 2013; Aguado et al., 2003). The factors affecting the yield and quality of produced liquid oil are temperature, reaction time, heating rate, particle size, feedstock composition and moisture content (Rehan et al., 2016b; Tröger et al., 2013; Nizami et al., 2016; Miandad et al., 2016d).

The scientific literature shows that the pyrolysis studies mostly used either pure/ virgin plastic (Borsodi et al., 2011) or processed plastic types as a feedstock (Siddiqui and Redhwi, 2009). For instance, Syamsiro et al. (2014) used industrial manufactured granules of high density polyethylene (HDPE) and polystyrene (PS) as feedstock. Lerici et al. (2015) and Lopez et al. (2011) used pellets of commercial polymers of different plastic such as low density polyethylene (LDPE), HDPE, polypropylene (PP) and PS as feedstock. However the interest in pyrolysis of municipal plastic waste, especially in PS waste has gained significant attention in recent years (Bartoli et al., 2015; Lerici et al., 2015; Adnan and Jan, 2014; Frediani et al., 2014; Mo et al., 2014; Undri et al., 2014a). The focus of these studies was mainly to increase the guantity of produced liquid oil. The most frequent reported analysis of pyrolytic liquid oil involved GC-MS to establish the composition of the produced liquid oil (Kumar and Singh, 2011; Syamsiro et al., 2014; Sarker et al., 2012; Onwudili et al., 2009; Undri et al., 2015). However, the effect of process parameters on the quality of liquid oil characteristics, including viscosity (dynamic and kinematic viscosity), density, high heating value (HHV), flash point, and cold flow properties such as pour point, and freezing point and their comparison with conventional diesel is seldom studied (de Marco et al., 2009; Bartoli et al., 2015, 2016; Lee, 2007; Lee et al., 2015; Lopez et al., 2011), which was the focus of this research. Moreover, the recovery of styrene from PS waste using pyrolysis process and its potential application has been discussed in detail.

In KSA, neither WTE facilities exist to convert any waste into energy (Nizami et al., 2016), nor has the plastic waste been characterized for its potential role as an energy recovery feedstock (Nizami et al., 2015a; Miandad et al., 2016c). The effect of temperature and reaction time on the yield and quality of liquid oil from a pyrolysis process was investigated. Furthermore, the produced liquid oil has been characterized for its chemical composition, dynamic and kinematic viscosities, density, flash point, HHV and cold flow properties. On the basis of these characterization results, the potential of liquid oil for the recovery of styrene, and generation of energy or as a source of transport fuel was discussed in detail. In addition, the potential of char was highlighted for various environmental applications.

# 2. Materials and methods

## 2.1. Feedstock preparation

The plastic waste in the form of disposable plates was collected from different canteens and hotels of Jeddah city and used as a process feedstock. Most of the food items are usually served in these plastic plates, which are primarily PS plastic. The samples were washed and dried in an oven to remove the impurities and moisture content. After washing and drying, the feedstock was shredded into small pieces with an average size of about 5 cm<sup>2</sup>.

# 2.2. Reactor startup

A small pilot scale batch pyrolysis reactor was commissioned and used for the conversion of plastic waste into liquid oil and char (Fig. 1). The reactor has 20 L capacity and is made of stainless steel and covered with a loop of an electric heater, which allows a maximum temperature of 600 °C. A tube type condenser coupled with a water chiller is installed at the end of the reactor. The detailed reactor characteristics are given in Table 1. Organic vapors produced in the heating chamber were condensed into liquid oil. The condensed organic vapors were collected at the bottom of the system, while the uncondensed products in the form of gases coming from same liquid oil pipe were exhausted from the reactor (Fig. 1).

#### 2.3. Experimental setup

In all of the experiments, 1000 g of feedstock was used. The heating chamber of the pyrolysis reactor was heated at a rate of 10 °C per min to achieve the set temperature. The feedstock was converted into organic vapors, which were condensed into liquid oil after passing through the condenser and collected in the collection tank at the bottom. The temperature of the condenser chamber was kept below 10 °C using a LabTech water chiller with coolant flowrate of 30 L/min to achieve the maximum condensation of organic vapors. Reaction time of each experiment was counted from the first drop of liquid oil produced. The residue (char) at the end of each experiment was collected from the heating chamber after allowing the system to cool down to room temperature. After finishing each experiment, a mass balance of pyrolysis products was established through weighing of liquid oil and char quantities by using a standard digital balance and the remaining weight percentage to make up to 100% was all assumed to be gas product.

# 2.4. Analytical methods

The feedstock and process products (liquid oil and char) were characterized by following the standard ASTM and APHA methods (Dezuane, 1997; APHA, 1998). TGA of PS plastic was carried out by a Mettler Toledo TGA (SDTA851) to assess the optimum process temperature and reaction time by following the feedstock's thermal behavior under control conditions. TGA analysis was carried out using 10 µg sample poured into an aluminum oxide crucible, and heated at a rate of 10 °C per min from 25 to 900 °C under nitrogen flow at a constant rate of 50 ml/min. The liquid oil viscosities (kinematic and dynamic), density, pour point, and freezing point

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