



Plastic waste to liquid oil through catalytic pyrolysis using natural and synthetic zeolite catalysts



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ABSTRACT

This study aims to examine the catalytic pyrolysis of various plastic wastes in the presence of natural and synthetic zeolite catalysts. A small pilot scale reactor was commissioned to carry out the catalytic pyrolysis of polystyrene (PS), polypropylene (PP), polyethylene (PE) and their mixtures in different ratios at 450 °C and 75 min. PS plastic waste resulted in the highest liquid oil yield of 54% using natural zeolite and 50% using synthetic zeolite catalysts. Mixing of PS with other plastic wastes lowered the liquid oil yield whereas all mixtures of PP and PE resulted in higher liquid oil yield than the individual plastic feedstocks using both catalysts. The GC–MS analysis revealed that the pyrolysis liquid oils from all samples mainly consisted of aromatic hydrocarbons with a few aliphatic hydrocarbon compounds. The types and amounts of different compounds present in liquid oils vary with some common compounds such as styrene, ethylbenzene, benzene, azulene, naphthalene, and toluene. The FT-IR data also confirmed that liquid oil contained mostly aromatic compounds with some alkanes, alkenes and small amounts of phenol group. The produced liquid oils have high heating values (HHV) of 40.2–45 MJ/kg, which are similar to conventional diesel. The liquid oil has potential to be used as an alternative source of energy or fuel production.

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1. Introduction

In the Kingdom of Saudi Arabia (KSA) and Gulf countries, the rapid growth in population and industrial sector have increased the demand for energy, food, and water (Khan et al., 2017). The fulfilling of energy requirements with the depletion of natural resources has resulted in significant greenhouse gas (GHG) emissions and anthropogenic climate change (Sadef et al., 2016a,b). The gap between the economic growth and environmental sustainability was increasing, until recently with the new governmental policy of Vision 2030 (Vision 2030, 2016). The policy has outlined the need for sustainable technologies, policies and initiatives to mitigate the GHG emissions and produce renewable energy from indigenous sources such as wind, solar, geothermal and waste (Vision 2030, 2016).

Plastic waste is the second largest waste stream (up to 20%) after organic waste in the KSA and other Gulf countries. The KSA is the world's 6th largest plastic producer country (Khan and Kaneesamkandi, 2013). Plastic products have a very short life-

span and mostly end up in the landfills or disposal sites (Anjum et al., 2016). Plastic waste has detrimental environmental and operational problems at landfills due to slow degradation rates and the presence of toxic dyes and additives (Demirbas et al., 2015). Plastic waste causes fire outbreak and releases air and water borne pollutants or act as a habitat for disease-causing vectors, rodents, and flies (Rehan et al., 2017). There are well-established routes to manage plastic waste, including mechanical and chemical recycling, and energy recovery technologies (Breyer et al., 2017). In these routes, pyrolysis has gained significant attention as an emerging waste to energy technology due to its economic and environmental benefits (Miandad et al., 2016a).

The absence of oxygen in pyrolysis process resists the formation of dioxins (Singh and Ruj, 2016). In economic terms, pyrolysis has an advantage over other technologies like incineration and plasma arc gasification with a lower annual capital cost (US \$17–25/t) and net operational cost (US \$2–3/t) along with production of liquid fuel and value-added products (Ouda et al., 2016). The process is completed at a temperature ranging from 400 °C to 900 °C (Nizami et al., 2015a) and liquid oil is the primary product with char and gases as by-products (Miandad et al., 2016b). The quality and yield of the liquid oil vary with the composition of feedstock,

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reactor types and the process parameters such as temperature and retention time (Rehan et al., 2016a). The pyrolysis of plastic waste can be carried out either in the presence of a catalyst (catalytic pyrolysis) or absence of a catalyst (thermal or non-catalytic pyrolysis). The pyrolysis process consists of four main steps, initiation, transfer, decomposition and termination (Nizami et al., 2015b).

In catalytic pyrolysis, the catalyst enhances the targeted reactions, reduces the reaction times and temperature, improves the liquid oil quality and increases the overall process efficiency (Serrano et al., 2012). The surface area, acidity, and pore size and volume are the key features of any catalyst that affect the pyrolysis process (Nizami et al., 2016a). Various catalysts have been used in pyrolysis of plastic waste, including FCC, silica–alumina, MCM-41 and zeolite such as Y-zeolite, HZSM, and ZSM-5 (Miandad et al., 2016a). Miskolczi et al. (2006) reported that FCC microporous catalyst increases the liquid oil yield, whereas ZSM-5 increases the gases yield due to its mesoporous structure. Ratnasari et al. (2016) indicated that microporous catalysts limit the entrance of higher hydrocarbons into the catalyst and improve the quality of liquid oil. A catalyst having high acidity decreases the liquid oil yield but increases the yield of gases (Miandad et al., 2016c). A detailed comparison of catalytic pyrolysis, using natural zeolite without any modification and synthetic zeolite catalysts, in examining the quality of liquid oil is rarely reported (Miandad et al., 2017a,b), which was the focus of this study.

In KSA, neither waste to energy facilities exist to convert any waste into energy (Nizami et al., 2017a), nor have the plastic waste and natural zeolite been characterized for their potential role in catalytic pyrolysis (Miandad et al., 2016c). The authors have previously examined and discussed the catalytic features of natural zeolite in detail using XRD, SEM, FT-IR and BET surface area analysis (Nizami et al., 2016b) and also carried out non-catalytic pyrolysis of different types of plastic waste to examine the effect of feedstock composition on the yield of pyrolysis products and liquid oil composition (Miandad et al., 2017a). These studies concluded that natural zeolite has good potential as a catalyst in the pyrolysis process to convert the plastic waste into liquid oil. This study aims to examine the catalytic pyrolysis of various types of plastic wastes such as polystyrene (PS), polyethylene (PE), polypropylene (PP) and polyethylene terephthalate (PET) in the presence of indigenous Saudi Arabian natural zeolite catalyst in comparison to synthetic commercial zeolite catalyst.

2. Materials and methods

2.1. Feedstock preparation and reactor start-up

The feedstock consisted of disposable plates, grocery bags, disposable juices cups and drinking water bottles, which are mainly composed of PS, PE, PP and PET plastics respectively. All these types of plastic waste are the primary sources of plastic waste produced in KSA. The collected feedstock was crushed into smaller pieces (2 cm²) to get a homogenous mixture for the reactor. After

crushing the collected samples, catalytic pyrolysis was carried out for individual feedstock and their combination with the ratios of 50/50%, 50/25/25% and 40/20/20/20% (Table 1). In each experiment, 1 kg of feedstock was used. Two types of catalysts were used i.e. natural zeolite and synthetic zeolite. Synthetic zeolite was purchased from Zeolyst International, USA and used as received without any further modification (Zeolyst, 2015). Natural zeolite was collected from the Harrat-Shama, an area located in the northwest of Jeddah city, KSA (Nizami et al., 2016b). The sample was collected purely for research purposes, so it was collected without any explicit permission from the governmental or any other official agency. It is confirmed that the area did not contain any endangered or protected species. The collected sample was initially crushed, in a locally manufactured stone crusher present in Saudi geological laboratory at King Abdulaziz University Jeddah KSA, into 3–5 mm size. An automatic mortar grinder (Fritsch Pulverisette-2, Denmark) was further used to reduce the particle size down to 15–35 µm after continuous 2 h crushing. The milled sample was used in the pyrolysis reactor as it is without any further surface modification or activation.

The prepared sample of feedstock was put into the heating reactor/chamber for pyrolysis (Fig. 1). In each experiment, the feedstock was heated to 450 °C with the heating rate of 10 °C per min and retention time of 75 min (Miandad et al., 2016b). At the end of each experiment, the obtained yield was calculated by measuring the fractions of liquid, gases and char on a weight basis. The obtained liquid oil was further characterized to determine the effect of feedstock composition in the presence of natural and synthetic zeolite catalysts. In order to determine the optimum condition (450 °C and 75 min) for pyrolysis, TGA of all feedstocks was carried out under controlled conditions. In TGA, 10 µg of each

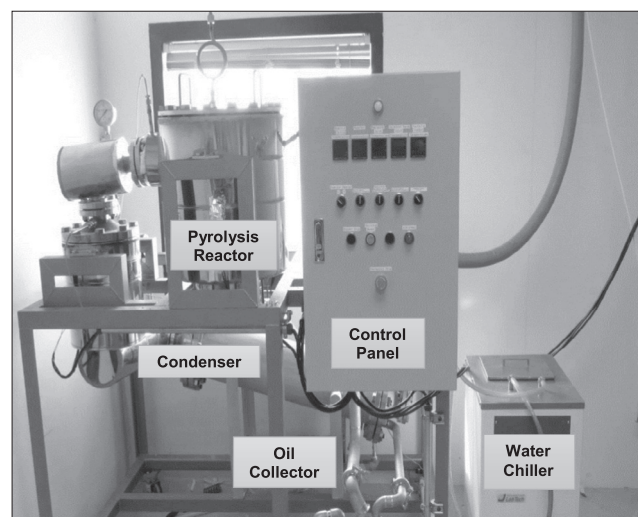


Fig. 1. Small pilot-scale pyrolysis reactor.

Table 1

Experimental scheme of catalytic pyrolysis, each experiment with natural and synthetic zeolite catalysts separately.

Feedstock types	Feedstock quantity (kg)	Feedstock ratio (%)	Catalyst quantity (kg)	Retention time (min)	Reaction temperature (°C)	Heating rate (°C/min)
PS	1	100	0.1	75	450	10
PE	1	100	0.1	75	450	10
PP	1	100	0.1	75	450	10
PS/PE	1	50/50	0.1	75	450	10
PS/PP	1	50/50	0.1	75	450	10
PP/PE	1	50/50	0.1	75	450	10
PS/PP/PE	1	50/25/25	0.1	75	450	10
PS/PP/PE/PET	1	40/20/20/20	0.1	75	450	10

feedstock was taken as per instrument requirement and heated from 25 °C to 900 °C with the heating rate of 10 °C and a constant nitrogen flow rate of 50 ml per min. The authors have previously carried out a detailed study to find out the effect of reaction time and temperature on the products of the pyrolysis process using PS plastic waste (Miandad et al., 2017a).

2.2. Experimental setup

A small pilot scale reactor was commissioned and used to perform the catalytic pyrolysis of various types of plastic waste individually and in combinations. The reactor can be used for both thermal and catalytic pyrolysis (Fig. 1). For catalytic pyrolysis, the catalyst was mixed with the feedstock to examine its catalytic effect on the quantity and quality of products, in particular on the liquid oil (Lopez et al., 2011). At the end of each experiment, the residue was weighed, and the amount of char was calculated by deducting the weight of catalyst used from total residue weight. The remaining was considered as produced char. The reactor is a closed system, and all experiments were carried out in an oxygen-free environment. The reactor has 20 L feedstock holding capacity, and its temperature can be raised to 600 °C with the desired heating rate (Table 2). The plastic feedstock was converted into organic monomers in the pyrolytic chamber, and later these monomers were condensed into liquid oil in the condenser. The optimum condensation of organic vapors was achieved when the temperature of the condenser was maintained below 10 °C using classic coolant (ACDelco®, Australia). The condensed liquid oil was collected from the oil collection assembly and was subjected to further characterization for its composition and potential applications. The details of all experimental runs and their conditions is shown in Table 1.

2.3. Analytical methods

Liquid oils produced by the catalytic pyrolysis of various plastic wastes were characterised by using different instruments, including gas chromatography coupled with mass spectrophotometry (GC–MS), Fourier transform infrared spectroscopy (FT-IR), TGA (Mettler Toledo TGA/SDTA851, USA) and Bomb Calorimeter following the standard ASTM methods (APHA, 1998). The presence of functional groups in the produced liquid oils from all plastic waste types was examined by FT-IR (Perkin Elmer's, UK). FT-IR analysis was carried out in the ranges of 500–4000 cm⁻¹ and minimum of 32 scans were performed on the average signal of IR with a resolution of 4 cm⁻¹. The chemical composition of produced liquid oil was examined by using GC–MS (Hewlett-Packard HP 7890, USA) with a 5975 quadrupole detector. The GC had a capillary column with 30 m length and 0.25 mm diameter, which was coated with 0.25 µm thick film of 5% phenyl-methylpolysiloxane (HP-5). The initial temperature of the oven was set to 50 °C for a time interval of 2 min and then increased up to 290 °C at 5 °C per min with an

isothermal held for 10 min. The 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 and 533, and a solvent interval of 3 min was used. Chromatographic peaks were recognized using NIST08s mass spectral data library based on their retention times using standard compounds (NIST08, 2017). The percentages of the peaks were estimated from the total ion chromatogram (TIC) peak area. Bomb Calorimeter (Parr 6200 Calorimeter, US) was used to assess the high heating value (HHV) of produced liquid oils by following the ASTM D 240 method (Miandad et al., 2016b). The percentage value of produced gases was estimated by the difference of weights of liquid oil and char (Miandad et al., 2016b).

3. Results and discussion

3.1. Characterization of natural zeolite

The Saudi Arabian natural zeolite showed crystalline structure (Nizami et al., 2016b). The identification of Si-O-Al and Si-O-Si peaks along with some other peaks of Al-O and Si-O were identified using the FT-IR analysis. The peaks were identified between the wavelengths of 3500–4000 cm⁻¹ that may show the existence of OH vibration group (Nizami et al., 2016b). The SEM images indicated that natural zeolite has a particle size range of around 50–200 nm with irregular shapes. The morphology of any catalyst may change because of milling from micro to nano size (Rehan et al., 2017). EDX analysis showed the presence of O (52.09%), Na (2.17%), Al (4.12%), Si (37.95%), K (2.57%), Fe (0.74%) and S (0.35%). Natural zeolite had Si/Al ratio of 9.2, BET surface area of 3.21 m²/g, a pore volume of 0.012 cc/g and pore size of 8.34 Å (Nizami et al., 2016b). The TGA analysis showed the high stability of natural zeolite even at high temperature of up to 900 °C (Miandad et al., 2017a). The aforementioned features showed that natural zeolite has potential to be used for catalytic pyrolysis of plastic wastes (Rehan et al., 2017). The chemical name of the synthetic zeolite catalyst was Zeolite type SDUSY, hydrogen form, aluminium oxide and it had a specific gravity of greater than 1 with negligible solubility in water. Synthetic zeolite had BET surface area of 900 m²/g, while the SiO₂/Al₂O₃ ratio of 5.1 with unit cell size is 24.65 Å. The trade name of synthetic zeolite catalyst was ZEO-LYSTTM CBV 780 CY (1.6) Zeolite SDUSY Extrudate (Zeolyst, 2015).

3.2. TGA analysis of plastic wastes feedstock

TGA analysis was carried out for all plastic waste feedstocks, PS, PE, PP, and PET, in the absence of a catalyst to examine the optimum conditions for thermal decomposition under controlled conditions (Fig. 2). The thermal degradation of PP feedstock started

Table 2
The parameters of pyrolysis reactor (Miandad et al., 2016b).

Reactor components	Features
Height of heating tank	360 mm
Diameter of heating tank	310 mm
Height of catalyst tank	200 mm
Diameter of catalyst tank	165 mm
Reactor capacity for feedstock	20 L
Catalyst tank capacity	1 L
Length of condenser	860 mm
Diameter of condenser	147 mm
Maximum temperature	600 °C

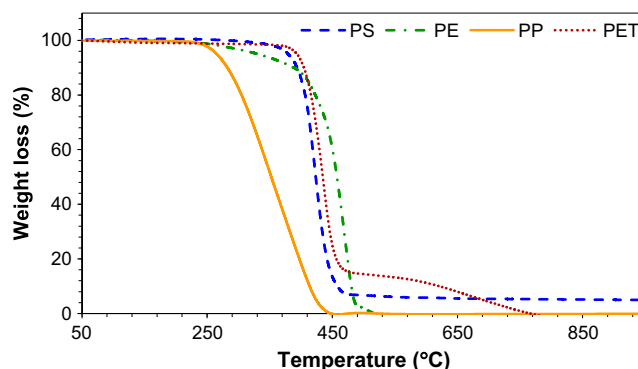


Fig. 2. TGA analysis of feedstocks.

at the lowest temperature of around 240 °C, showing a single step decomposition, and achieved the maximum decomposition (95%) at around 425 °C. According to Jung et al. (2010), PP half carbon chain consists of tertiary carbons which favor carbocation process during the thermal degradation, which may lead to its degradation at a lower temperature. The PS feedstock also showed a single stage decomposition that started at 330 °C, while its 50% decomposition occurred within the further 100 °C increase in temperature and reached maximum decomposition of 95% at the temperature of around 470 °C (Fig. 2). PS degradation follows both end-chain and random chain scission mechanisms which enhance its degradation process (Lee et al., 2012).

PE showed two-stage degradation where the first stage started at around 270 °C and achieved almost 12% degradation when the temperature reached up to 400 °C. The second thermal degradation of PE started at the temperature of around 400 °C, where 50% of degradation was achieved at 450 °C, and maximum decomposition (95%) at around 480 °C (Fig. 2). According to Wu et al. (2014), PE feedstock requires high temperature to degrade as compared to polyvinyl chloride (PVC) and PS feedstocks even under controlled conditions. PE consists of long chain and follows the random chain scission mechanism during its thermal degradation, which requires relatively higher temperature (Lee et al., 2012). The PET initial decomposition started at around 350 °C, achieving up to 85% degradation at 480 °C. The PET second degradation stage started after 480 °C and achieved maximum degradation at 650 °C. Dimitrov et al. (2013) carried out TGA of pure PET feedstock with its products and reported that pure PET showed single step degradation while PET products showed two-stage degradation due to the presence of volatile impurities in the feedstock. Chandrasekaran et al. (2015) also reported that differences in TGA curves of various plastic feedstocks are due to their structures and the consequent degradation mechanisms. TGA analysis of all the feedstocks showed that maximum degradation occurred in between the range of 420 °C to 490 °C (Fig. 2). Lopez et al. (2011) reported that use of a catalyst might decrease the reaction temperature and retention time. All catalytic pyrolysis experiments in this study were carried out at 450 °C with 75 min retention time in line with these findings and process safety considerations.

3.3. Effect of natural and synthetic zeolite catalysts on the pyrolysis products yield

The effect of catalysts on the pyrolysis products yield at 450 °C, and 75 min, specifically on the liquid oil was examined by using natural and synthetic zeolite catalysts (Fig. 3 and Table 3). PS plastic waste produced the highest amounts of liquid oil as compared to all other types of plastic wastes studied (Fig. 3). The catalytic pyrolysis of PS with natural zeolite resulted in higher liquid oil (54%) yield along with char (33.2%) and gases (12.8%) yields as compared to synthetic zeolite pyrolysis yields of liquid oil (50%), char (27.2%) and gases (22.8%) (Table 3). Lee et al. (2001) reported higher liquid oil yield from the catalytic pyrolysis of PS with natural zeolite than synthetic zeolite (HZSM-5), correlating it with low BET surface area, acidity and microporous structure of natural zeolite. Seo et al. (2003) also reported that mesoporous synthetic catalyst with high BET surface and acidity produced lower liquid oil yield. Rehan et al. (2017) also carried out thermal and catalytic pyrolysis of PS and reported that maximum liquid oil yield (80.8%) was obtained from thermal pyrolysis followed by catalytic pyrolysis (54%) with natural zeolite and then synthetic zeolite (50%) catalysts.

The catalytic pyrolysis with both natural and synthetic zeolite catalysts produced very low amounts i.e. 14% and 26%, of liquid oil, whereas the gases yields of 75.4% and 61.3% were very high (Fig. 3). Obali et al. (2012) also reported maximum production of

gases by catalytic pyrolysis of PP with alumina loaded mesoporous catalysts. Kim et al. (2002) explained that catalysts like natural zeolite with low BET surface area, microporous structure, and low acidity support the initial degradation of PP that may increase the production of gases, as observed in this study (Table 3).

The liquid oil yield of 16% from the catalytic pyrolysis of PE with both catalysts (natural zeolite and synthetic zeolite) was also low. The catalytic pyrolysis with natural zeolite showed a high yield of char (49.8%) along with a lower yield of gases (34.2%), while with synthetic zeolite there was an increase in the gases yield (71.4%) and reduction in the char (12.7%) yield (Fig. 3). The higher yield of gases with synthetic zeolite could be attributed to its higher catalytic efficiency because of its higher BET surface area and acidity as compared to natural zeolite catalyst (Miandad et al., 2017a). These observations are in line with the work of Batool et al. (2016), which also reported the maximum yield of gases from catalytic pyrolysis of PE with synthetic catalyst (ZSM-5). Zeaiter (2014) reported 97% of gases yield from PE catalytic pyrolysis with highly acidic synthetic zeolite catalyst (Hbeta). Mesoporous catalysts with high acidity and BET surface area favor higher gases yields, while microporous catalysts with low BET surface area and acidity promote higher liquid oil and char yields (Lopez et al., 2011).

The catalytic pyrolysis of mixed plastic wastes in different ratios was conducted with both natural and synthetic zeolite catalysts separately (Table 1). Mixing of PS with other plastic wastes showed reduced liquid oil yields as compared to single PS feedstock in all the cases, except for slightly higher oil yields obtained in PS/PE/PP and PS/PE/PP/PET samples with synthetic zeolite catalyst. All the mixtures of PP and PE produced higher liquid oil yields than the single PP or PE feedstocks. (Fig. 3). According to Xue et al. (2017) pyrolysis of PE with other plastic show synergetic effect during degradation process, while production and transfer of hydrogen from PE enhanced the degradation process. In mixed plastic wastes, the highest liquid oil yield of 60% was obtained from PS/PE/PP sample with synthetic zeolite, and the lowest yield of 18% was from PP/PE sample with natural zeolite catalysts. The highest gases (69.2%) and char (25.5%) yields were from PP/PE and PS/PE with natural zeolite catalyst.

3.4. Effect of natural and synthetic zeolite catalysts on liquid oil composition

The produced liquid oils by catalytic pyrolysis of different plastic wastes at 450 °C and 75 min in the presence of natural and synthetic zeolite catalysts showed different compounds (Figs. 4 and 5; Table 3). The liquid oil produced by catalytic pyrolysis of PS with both catalysts mostly contained aromatic compounds. The percentage of each compound differed significantly, e.g. ethylbenzene had the highest amount of 60.8% with natural zeolite catalyst but only 10% with synthetic zeolite catalyst. The other common compounds in large quantities were styrene 7.6% and 15.8%, and alpha-methylstyrene 10.7% and 38.3% with natural and synthetic zeolites catalysts respectively. All other compounds with their amounts are given in Table 3. Aguado et al. (2003), Artetxe et al. (2015) and Bartoli et al. (2015) have carried out the catalytic pyrolysis of PS with various types of catalysts and reported that styrene, benzene, alpha-methylstyrene, and indene are the primary compounds found in the produced liquid oil, which is in agreement with the current study. Onwudili et al. (2009) reported that production of toluene and ethylbenzene might occur due to further degradation of styrene itself. The high temperature and retention time also favor the production of alpha-methylstyrene, toluene, and ethylbenzene with a decrease in the styrene production (Artetxe et al., 2015). Ukei et al. (2000) and Shah and Jan (2014) reported that high temperature might lead to hydrogenation of

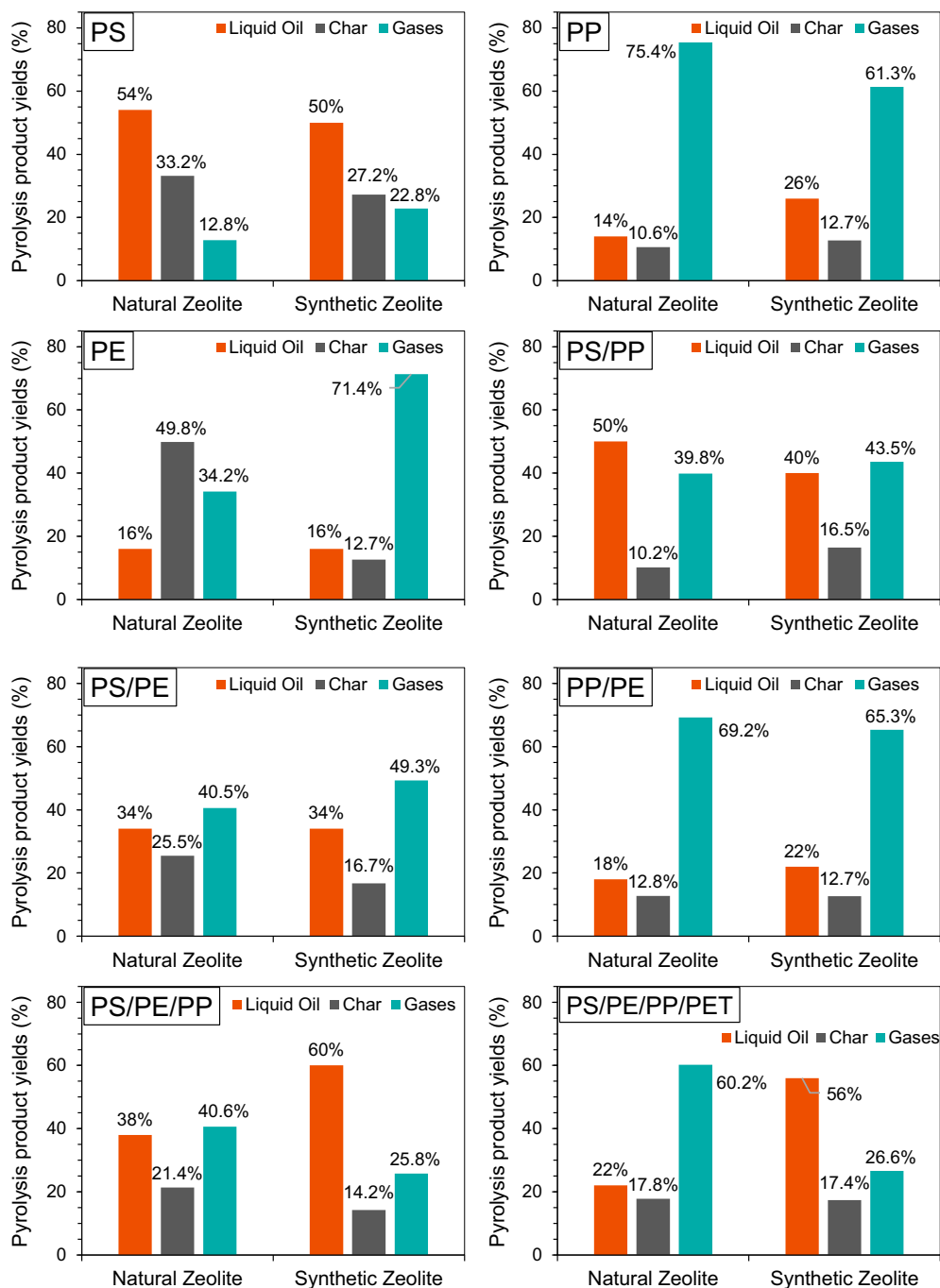


Fig. 3. Pyrolysis products yields by using natural and synthetic zeolites catalysts.

styrene due to the secondary reactions that may decrease styrene and increase its derivate compounds.

The catalytic pyrolysis of PP plastic waste with natural and synthetic zeolite catalysts produced a complex liquid oil composition as compared to other plastic feedstocks, confirmed by GC–MS analysis (Table 3). The compound types and amounts differed in liquid oils from both catalysts. The highest amount of o-xylene (8.8%) was found with natural zeolite catalyst and cyclononasiloxane, octadecamethyl- (22.8%) with synthetic zeolite catalyst. Other compounds and their amounts are given in Table 3. Abbas-Abadi et al. (2014) carried out catalytic pyrolysis of PP with FCC catalyst and reported the production of aliphatic, paraffin, aromatic and naphthenes compounds. The use of acid catalyst increased the production of naphthalene and poly-aromatic compounds that may be

produced through aromatization, oligomerization, and deoxygenation occurring on the active acidic sites of the catalyst. Dawood and Miura (2002) reported that conversion of PP plastic into aromatic and olefins is increased with the use of modified HY-zeolite catalyst. The use of catalysts with Brønsted acid sites increased the cracking process of polymers that may lead to the production of shorter chain hydrocarbons (Ramli et al., 2011).

The GC–MS analysis of liquid oil produced by the catalytic pyrolysis of PE with natural and synthetic zeolite catalysts showed relatively fewer types of compounds, but mainly aromatics hydrocarbons. The common compounds found in both samples were ethylbenzene and naphthalene. During the catalytic pyrolysis there are two possible mechanisms for the degradation of PE; carbenium ion mechanism due to the attack of a proton or hybrid ion

Table 3

Products yield and liquid oil composition produced from catalytic pyrolysis with natural and synthetic zeolite catalysts.

Plastic Type	Pyrolysis type	Pyrolysis products (%)			Liquid oil composition (%)
		Liquid	Gases	Char	
PS	Natural zeolite	54	12.8	33.2	<ul style="list-style-type: none"> Ethylbenzene (60.8) Benzene (3.8) Styrene (7.6) alpha-Methylstyrene (10.7) Indene (3.3) Azulene (4.8)
	Synthetic zeolite	50	22.8	27.2	<ul style="list-style-type: none"> Ethylbenzene (10) Styrene (15.8) Benzene (16.3) Propenylbenzene (4.2) Propylbenzene (3.5) Isopropylbenzene (8) alpha-Methylstyrene (38.3)
PP	Natural zeolite	14	75.4	10.6	<ul style="list-style-type: none"> Ethylbenzene (7.1) o-Xylene (8.8) alpha-Methylstyrene (3.9) Benzene, 1-propenyl (7.1) 1H-Indene (6.2) Benzene, 1,3-diethenyl (9) Benzene 1-methyl-2-cyclopropen (4) Naphthalene, 1-methyl (6.2)
	Synthetic zeolite	26	61.3	12.7	<ul style="list-style-type: none"> Azulene (7.6) Benzoic acid, 2,6-bis[(trimethylsilyl)oxy] (3.6) Phenanthrene (4.4) Cyclononasiloxane, octadecamethyl-(22.8) Cyclooctasiloxane, hexadecamethyl-(4.1) Phenol, 2,2'-methylenebis[6-(1,1-dimethylethyl)-4-methyl-(3.8) 1,2-Benzenedicarboxylic acid, mono(2-ethylhexyl) ester (19.7) Tetracosamethyl-cyclododecasiloxane (28.9)
PE	Natural zeolite	16	34.2	49.8	<ul style="list-style-type: none"> Ethylbenzene (4.2) Styrene (10.2) Naphthalene (3.4)
	Synthetic zeolite	16	71.4	12.7	<ul style="list-style-type: none"> Toluene (15.3) Ethylbenzene (10.4) 1,3,5,7-Cyclooctatetraene (46.5) Benzene, (1-methylethenyl)-(6.8) Azulene (5.2) Naphthalene, 1-methyl-(3.3)
PS/PP	Natural zeolite	50	39.8	10.2	<ul style="list-style-type: none"> Styrene (24.5) Benzene, (1-methylethyl) (10.6) Tetracyclo (6.6) Benzene, propyl- n-Propylbenzene (6.3) alpha-Methylstyrene (52)
	Synthetic zeolite	40	43.5	16.5	<ul style="list-style-type: none"> Azulene (7.3) Phenanthrene (5.5) Cyclooctasiloxane, hexadecamethyl-(7.7) Cyclononasiloxane, octadecamethyl-(19) 1,2-Benzenedicarboxylic acid (16.5) Tetracosamethyl-cyclododecasiloxane (26.7)
PS/PE	Natural zeolite	34	40.5	25.5	<ul style="list-style-type: none"> Azulene (11) Naphthalene, 2-ethenyl-(5) Benzene, 1,1'-(1,3-propanediyl)bis-(3.5) Phenanthrene (11.7) Anthracene, 9-ethenyl-(4.4) Naphthalene, 2-phenyl-(8) Phenol, 2,2'-methylenebis[6-(1,1-dimethylethyl)-4-methyl-(7.1) 1,2-Benzenedicarboxylic acid, mono(2-ethylhexyl) ester (3.3) Azulene (12.1) Naphthalene, 2-methyl-(3.2) Phenanthrene (5.3) 1,2-Benzenedicarboxylic acid, mono(2-ethylhexyl) ester (3.9) Tetracosamethyl-cyclododecasiloxane (50) 13-Docosamide, (Z)-(5) Hexacontane (10.1)
	Synthetic zeolite	34	49.3	16.7	
PP/PE	Natural zeolite	18	69.2	12.8	<ul style="list-style-type: none"> Azulene (16.9) Naphthalene, 2-methyl-(5.5) Naphthalene, 1-methyl-(4) Biphenyl 1,1'-Biphenyl (5.3)

(continued on next page)

Table 3 (continued)

Plastic Type	Pyrolysis type	Pyrolysis products (%)			Liquid oil composition (%)
		Liquid	Gases	Char	
PS/PP/PE	Synthetic zeolite	22	65.3	12.7	<ul style="list-style-type: none"> • Acenaphthene (4.7) • Phenanthrene (9.9) • Acetic acid n-octadecyl ester (3.1) • Phenol, 2,2'-methylenebis[6-(1,1-dimethylethyl)-4-methyl (12.2) • 1,2-Benzenedicarboxylic acid, mono(2-ethylhexyl) ester (35.9)
					<ul style="list-style-type: none"> • Phenanthrene (3.7) • Phenol, 2,2'-methylenebis[6-(1,1-dimethylethyl)-4-methyl-(5.4) • 1,2-Benzenedicarboxylic acid, mono(2-ethylhexyl) ester (51.3) • Cyclononasiloxane, octadecamethyl-(9.1) • Tetracosamethyl-cyclododecasiloxane (20.3)
	Natural zeolite	38	40.6	21.4	<ul style="list-style-type: none"> • Ethylbenzene (10.6) • Styrene (6.6) • alpha-Methylstyrene (8.3) • Naphthalene 2-methyl (5) • Biphenyl (4.5)
					<ul style="list-style-type: none"> • Benzene, 1,1'-(1,3-propanediyl)bis-(4) • 1,2-Benzenedicarboxylic acid, mono(2-ethylhexyl) ester (25) • Cyclononasiloxane, octadecamethyl-(32.8) • Cyclododecasiloxane, eicosamethyl-(3.7) • Cyclooctasiloxane, hexadecamethyl-(4.6) • Tetracosamethyl-cyclododecasiloxane (18.4)
PS/PP/PE/PET	Natural zeolite	22	60.2	17.8	<ul style="list-style-type: none"> • Azulene (10.7) • Naphthalene, 2-methyl-(4.3) • Biphenyl (4.4) • Phenanthrene (9) • Naphthalene, 2-phenyl-(3.3) • Phenol, 2,2'-methylenebis[6-(1,1-dimethylethyl)-4-methyl-(5.5) • 1,2-Benzenedicarboxylic acid, mono(2-ethylhexyl) ester (52)
	Synthetic zeolite	56	26.6	17.4	<ul style="list-style-type: none"> • Azulene (11.2) • Naphthalene, 2-methyl-(6.3) • Biphenyl (4.9) • Phenanthrene (9.3) • Naphthalene, 2-phenyl-(3.3) • Phenol, 2,2'-methylenebis[6-(1,1-dimethylethyl)-4-methyl-(5.8) • 1,2-Benzenedicarboxylic acid, mono(2-ethylhexyl) ester (47)

abstraction through Lewis acid sites (Rizzarelli et al., 2016). According to De Stefanis et al. (2013), the catalytic degradation of PE involves the carbenium ion mechanism by proton addition (Brønsted acid sites) to C—C bonds or hybrid ion abstraction by Lewis acid sites to the PE molecules. Once the degradation is started, it further proceeds step by step into light hydrocarbon molecules. The higher molecules are degraded on the external surface of the catalyst, while microporous catalyst hinders their entrance that results in the formation of high carbon chain compounds and large char/coke deposition (Lopez et al., 2011).

Liquid oil produced by the catalytic pyrolysis of mixed plastic wastes with natural and synthetic zeolite catalysts showed the presence of most of the compounds that were produced from their individual pyrolysis (Table 3). The hydrocarbon compounds found in different samples of mixed plastic changed in their types and composition. Most of the samples showed aromatic hydrocarbon compounds. The detailed compounds' names and their amounts from each sample are shown in Table 3. There were many more compounds below 3% which have not been included in Table 3 and Figs. 4 and 5 due to the possibility of errors at such low concentrations and for clarity purpose.

Liquid oils produced from the catalytic pyrolysis of plastic waste with natural and synthetic zeolite contain high concentrations of polycyclic aromatic hydrocarbons (PAHs). PAHs presence in petroleum products is relatively high as they are fossil fuels natural ingredients (Qi et al., 2017). PAHs found in pyrolysis liquid oils originate from the plastic feedstock chemical structure such as PS. PAHs are hydrocarbons, organic compounds consist of carbon and hydro-

gen structured in multiple aromatic rings, and some are classed as carcinogenic and may cause serious health problems (Budhwani, 2015). The conversion of these PAHs compounds into their other value-added products (oxygenated species) such as aldehydes, carboxylic acids, and ketones have been carried out by various researchers (Rivas et al., 2000). Budhwani (2015) used bio-adsorbents for the removal of PAHs from the liquid oil produced from pyrolysis of waste tires. Rivas et al. (2000) carried out the conversion of PAHs into its oxygenated species by using hydrogen peroxide, UV radiation, and ozonation. To avoid the hazards of PAHs, its conversion into low molecular harmless compounds can be carried out before utilizing the pyrolysis liquid oil in various applications.

The presence of functional groups in the produced liquid oils from catalytic pyrolysis of plastic wastes was examined using FT-IR analysis. In this analysis, chemical bonds in liquid molecules produce an infrared adsorption spectrum that leads to the identification of functional groups in the liquid oils (Rehan et al., 2017). The produced liquid oil from individual and mixtures of plastic waste feedstocks in the presence of both natural and synthetic zeolite catalysts at 450 °C and 75 min contained aromatic, alkanes and alkenes along with a small amount of phenol group (Figs. 6 and 7). The aromatic compounds were found in all liquid oil samples, which is in line with the results of the GC-MS (Figs. 4 and 5). Overall, a sharp peak was identified at the start of each analysis of produced liquid oil from natural zeolite that refers to the presence of aromatic compounds (C—H “oop”). While at the middle, alkanes (C—H stretch), alkenes (=C—H bend) and aromatic (C—C stretch in the ring) compounds were dominant (Fig. 6). A strong peak of

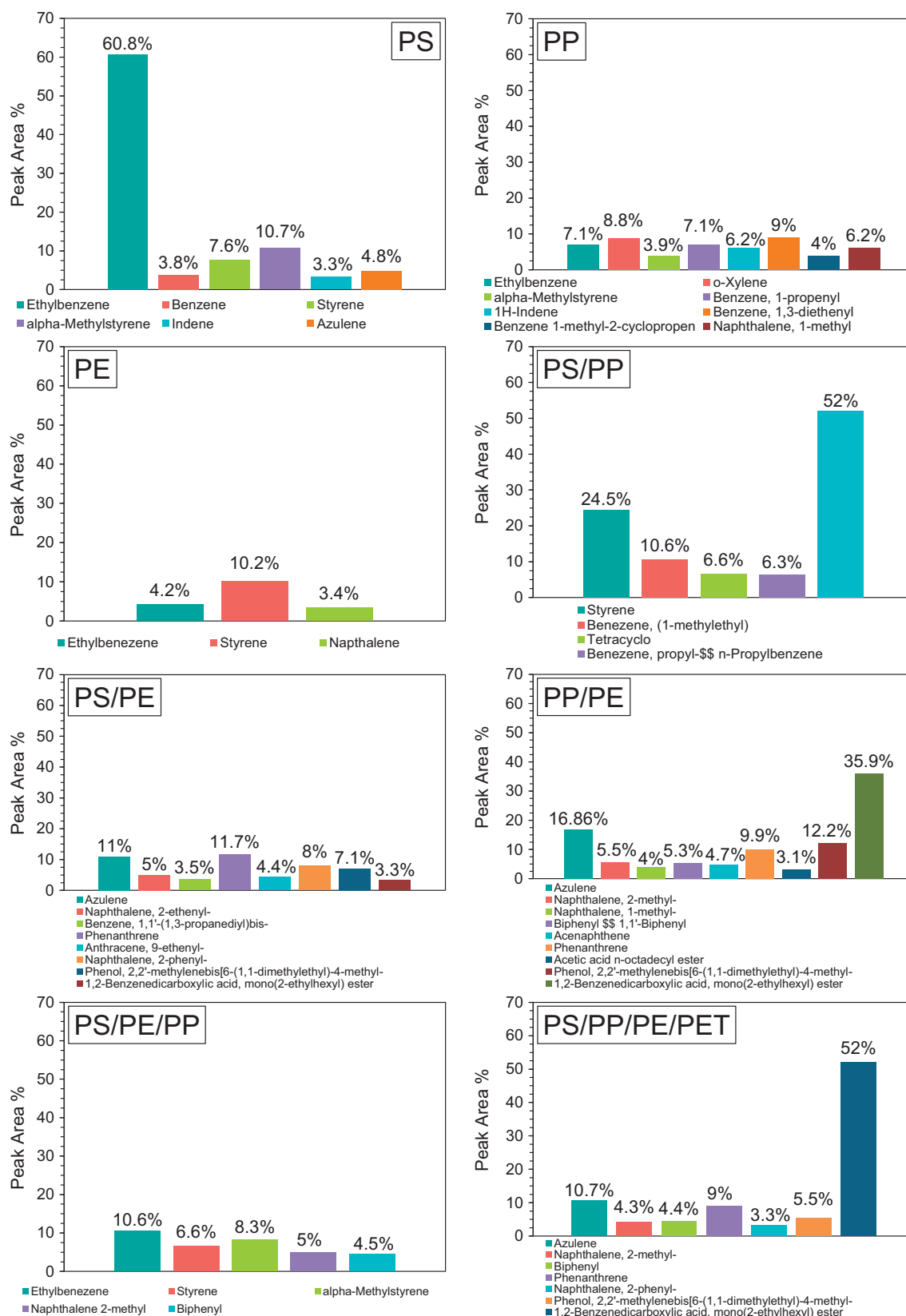


Fig. 4. GC-MS results showing liquid oil compositions from natural zeolite pyrolysis.

alkanes (C–H stretch) was identified at a wavelength of 2930 cm^{-1} in all liquid oil samples (Figs. 6 and 7). In the end, a weak or medium peak of phenol and alcohols (O–H stretch, H-bonded) functional group was identified in the produced liquid oil of PE, PP,

and mixture of all plastic types using both natural and synthetic zeolite catalysts.

Liquid oil produced from the catalytic pyrolysis with synthetic zeolite contained alkanes, alkenes, aromatic, alkynes, alkyl halides

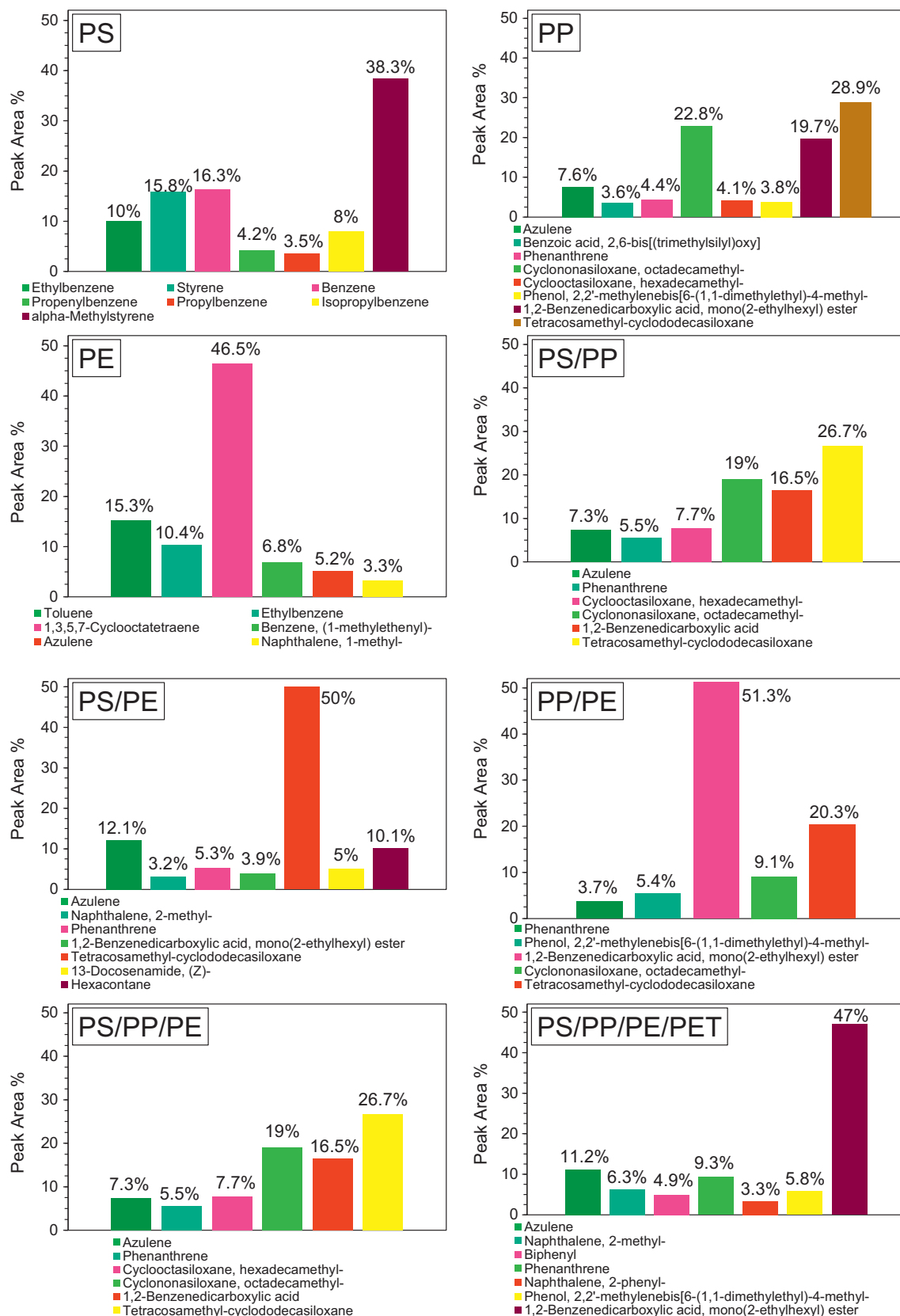
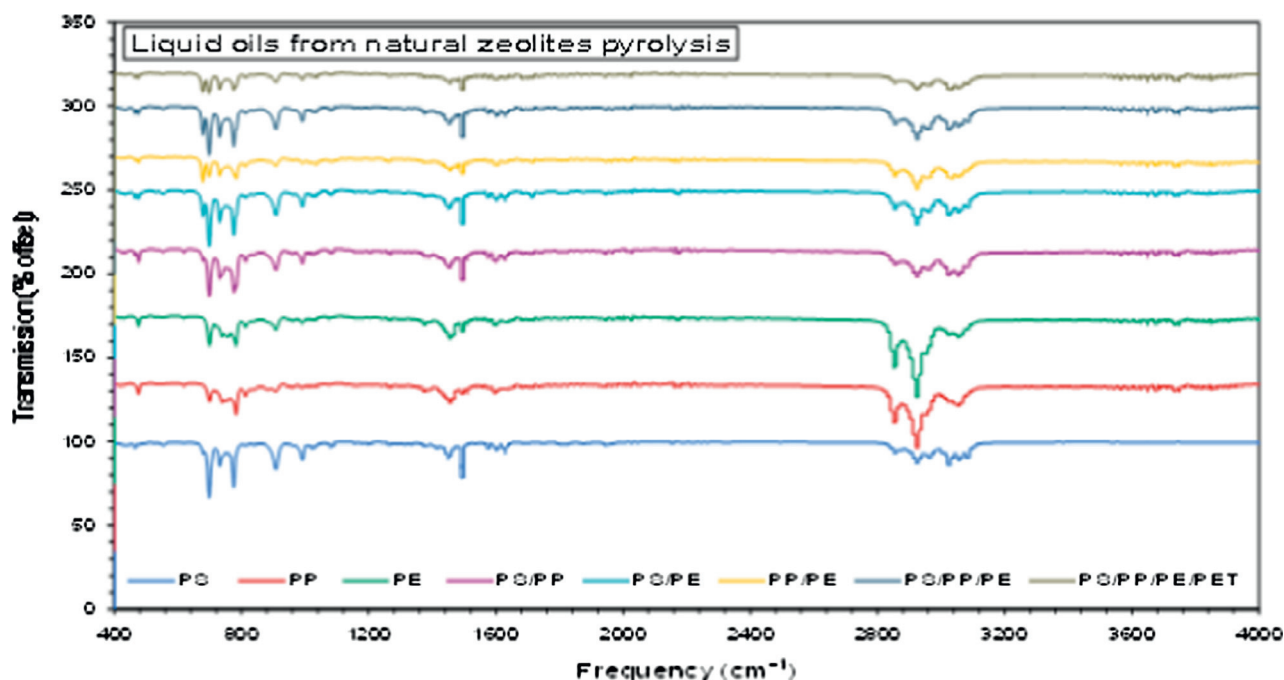


Fig. 5. GC-MS results showing liquid oil compositions from synthetic zeolite pyrolysis.

and phenol and alcohols functional groups (Fig. 7). Aromatic compounds were also dominant that showed the high aromatization capability of the synthetic catalyst. At the start, a weak peak of

alkynes ($\text{—C}\equiv\text{C—H}$:C—H bend) was found in all liquid oil samples except individual PS and combined pyrolysis of all plastic waste types. Overall, at a wavelength of 697 cm^{-1} , a strong peak of

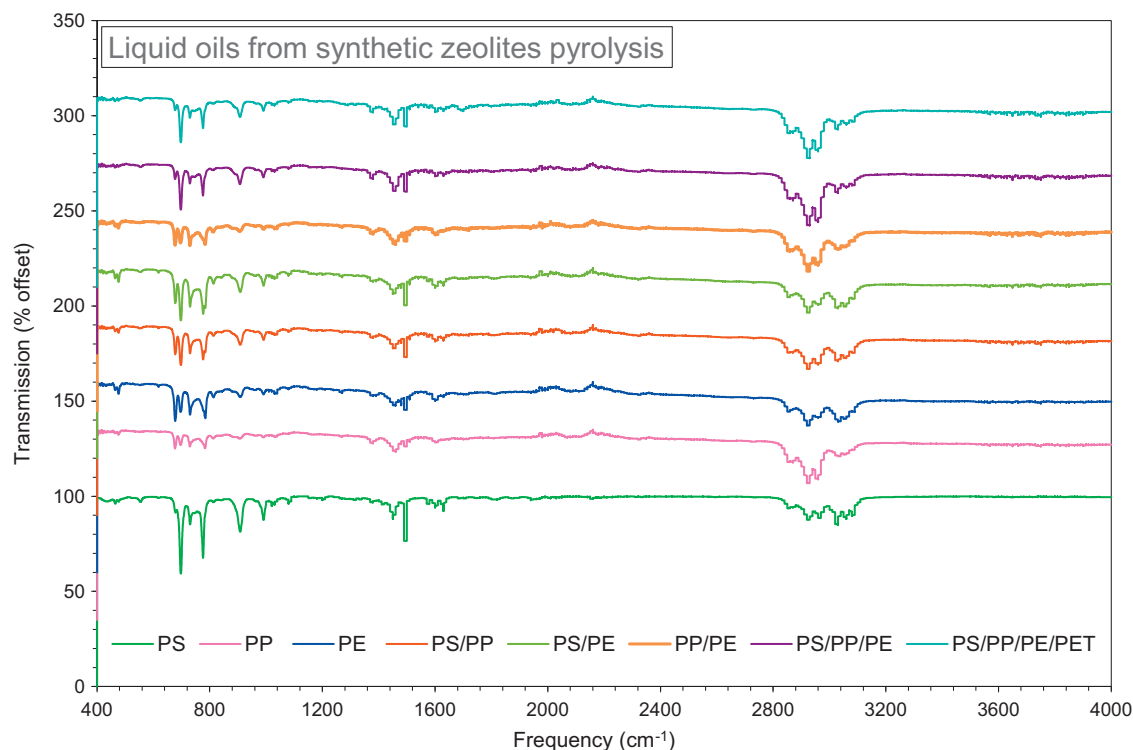


Peaks	PS	PP	PE	PS/PP	PS/PE	PE/PP	PS/PP/PE	PS/PP/PE/PET	Bond	Functional Group
697	✓	X	✓	✓	✓	X	✓	✓	C-H “oop”	Aromatics
776	✓	X	✓	✓	✓	X	✓	X	=C-H bend	Alkenes
910	✓	X	✓	✓	✓	X	✓	X	=C-H bend	Alkenes
990	✓	X	X	✓	✓	X	✓	X	=C-H bend	Alkenes
1,450	✓	✓	✓	✓	✓	X	✓	X	C-C stretch (in ring)	Aromatics
1,500	✓	X	X	✓	✓	X	✓	X	C-C stretch (in ring)	Aromatics
2,860	X	✓	✓	X	X	X	X	X	C-H stretch	Alkanes
2,930	X	✓	✓	X	X	X	X	X	C-H stretch	Alkanes
3,030	✓	X	X	✓	✓	✓	✓	✓	C-H stretch	Aromatics
3,060	X	✓	✓	✓	X	X	X	✓	O-H stretch, H-bonded	Alcohols, phenols

Fig. 6. FT-IR analysis of liquid oil produced from catalytic pyrolysis of plastic waste with natural zeolite.

aromatic was identified in almost all liquid oil samples. At the wavelength of 785 cm^{-1} , a medium peak of 1° , 2° amines (N–H wag) was found in PE, PP and PE/PP liquid oils (Fig. 7). The alkenes ($=\text{C–H}$ bend) and aromatic (C–C stretch in the ring) compounds were dominant in the middle range of wavelength. At the wavelength of 2860 and 2930 cm^{-1} , a medium peak of alkanes (C–H stretch) was identified in all liquid oil samples using synthetic zeolites. Another strong peak of aromatic (C–H stretch) was identified at the wavelength of 3030 cm^{-1} . Nevertheless, a weak peak of alcohol and phenol (O–H stretch, H-bonded) was identified in PE, PP and their mixture with PET (Fig. 7). Siddiqui and Redhwi (2009) and Sarker and Rashid (2013) reported the presence of aromatic, alkanes and alkenes compounds in the liquid oil produced by PS plastic. Tekin et al. (2012) and Panda and Singh (2013) carried out the FT-IR analysis of liquid oil produced by PP and confirmed the presence of mostly aromatic compounds with some alkanes and alkenes.

HHV is one of the key features of any liquid oil especially in the context of energy generation (Rehan et al., 2016a,b). Higher the values of HHV, higher will be energy content in achieving the required energy production with a less consumption of fuel (Miandad et al., 2016b). HHV of liquid oil produced by the catalytic pyrolysis of different plastic types in the presence of both natural and synthetic zeolite catalysts was in the range of $40.2\text{--}45\text{ MJ/kg}$ (Table 4). This HHV value range of produced liquid oil by plastic waste is similar to the value of conventional diesel (43.06 MJ/kg) (Kamal and Zainuri, 2015). Kim et al. (2006) indicated that liquid oil produced from mixed plastic waste had HHV of 44.4 MJ/kg , while Syamsiro et al. (2014) found that liquid oil from PE plastic bag had HHV of 41.5 MJ/kg . High HHV of produced liquid oil shows its potential as an alternative source of energy and conventional diesel as well. Saptoadi and Pratama (2015) concluded that liquid oil produced from pyrolysis of plastic waste has the potential to be used as an alternative to kerosene oil.



Peaks	PS	PP	PE	PS/PP	PS/PE	PE/PP	PS/PP/PE	PS/PP/PE/PET	Bond	Functional Group
677	X	✓	✓	✓	✓	✓	X	X	-C≡C-H: C-H bend	Alkynes
697	✓	X	X	✓	✓	X	✓	✓	C-H “oop”	Aromatics
729	✓	✓	✓	✓	✓	✓	✓	✓	C-Cl stretch	Alkyl halides
776	✓	✓	X	✓	✓	X	✓	✓	=C-H bend	Alkenes
785	X	✓	✓	X	X	✓	X	X	N-H wag	1°, 2° amines
910	✓	X	X	✓	✓	X	✓	✓	=C-H bend	Alkenes
990	✓	X	X	✓	✓	X	✓	✓	=C-H bend	Alkenes
1,460	✓	✓	✓	✓	✓	✓	✓	✓	C-C stretch (in ring)	Aromatics
1,500	✓	X	X	✓	✓	X	✓	✓	C-C stretch (in ring)	Aromatics
2,860	✓	✓	✓	✓	✓	✓	✓	✓	C-H stretch	Alkanes
2,930	✓	✓	✓	✓	✓	✓	✓	✓	C-H stretch	Alkanes
3,030	✓	✓	✓	✓	✓	✓	✓	✓	C-H stretch	Aromatics
3,060	X	✓	✓	✓	X	X	X	✓	O-H stretch, H-bonded	Alcohols, phenols

Fig. 7. FT-IR results of liquid oils produced in the presence of synthetic zeolite.

Table 4

High heating values (HHV) of liquid oils in MJ/kg produced from catalytic pyrolysis with natural and synthetic catalysts.

Feedstock types	HHV (MJ/kg) Natural zeolite	HHV (MJ/kg) Synthetic zeolite
PS	41.9	40.6
PE	45.0	41.0
PP	41.7	42.2
PS/PP	40.2	41.6
PS/PE	41.7	41.2
PE/PP	40.8	41.8
PS/PE/PP	41.7	42.9
PS/PE/PP/PET	40.5	42.1

3.5. Potential applications of liquid oil and char in KSA

The use of both natural and synthetic zeolite catalysts has improved the quality of liquid oil by increasing the light hydrocar-

bon compounds (Table 3). Post-treatment through distillation and refining or blending with conventional diesel is required, to utilize this liquid oil as a transport fuel due to the presence of high aromatic compounds. Islam et al. (2010) and Gardy et al. (2014) have successfully used the pyrolysis liquid oil as a transport fuel after blending it with conventional diesel. Nileshkumar et al. (2015) blended plastic waste pyrolysis liquid oil with conventional diesel with different ratios of 10, 20, 30, 40 and 50% and reported that 20% ratio showed similar results as conventional diesel. At the above ratio, the engine had similar consumption as with conventional diesel. There was an increase in NO_x, SO_x and CO_x emissions with the increase in the ratio of pyrolysis liquid (Frigo et al., 2014). Lee et al. (2015) achieved a satisfactory engine performance with 20% blend ratio but reported a decrease of engine performance at blend ratios of 13 and 17%. Increase in blending ratio decreased the physical characteristics of liquid oil that may delay the ignite time and decrease the produced torque. The use of pyrolysis liquid in a diesel engine for electricity

production is a promising way (Lee et al., 2015). The recovered aromatic compounds present in liquid oil can also be utilized as raw materials in the chemical industries for plastic monomer polymerization (Shah and Jan 2014). The produced liquid oil from PS can also be used for the synthesis of a biodegradable and biocompatible plastic (Nikodinovic-Runic et al., 2011).

In KSA, the current electricity generating capacity is about 55 GW and is estimated to cross 120 GW by 2032 with the current annual rate of 8% (Ouda et al., 2016). More than 50% of the generated electricity in KSA is only consumed in the residential sector for fulfilling the air-conditioning demand due to warm and arid conditions (Nizami et al., 2015b). In this regards, the produced liquid oil from catalytic pyrolysis of plastic waste can play a significant role in substituting the conventional fuels. Rehan et al. (2016a) presented a detail case study on converting plastic waste into liquid oil through pyrolysis in the city of Makkah, KSA. They have estimated that the produced liquid oil from plastic waste pyrolysis can generate about 87.91 MW of electricity in 2017. This electricity is expected to cross 172.80 MW by 2040 if all of the plastic waste generated in the Makkah city is utilized in the pyrolysis facility. A global warming potential (GWP) of 199,700 Mt.CO₂ eq. will be attained with savings of around 7.9 kt emission of methane (CH₄) from this facility. A total savings of US \$79.34 M from landfill diversion, electricity generation, and carbon credits respectively would be possible to attain in 2017 from the pyrolysis facility (Rehan et al., 2016a). This case study presented only one city of KSA that shows the country has potentially tremendous economic and environmental benefits from plastic waste pyrolysis in order to achieve the objectives of the circular economy in the country (Nizami et al., 2017b).

3.6. Future work

Pyrolysis is a promising technology for converting plastic waste into liquid oil and other value added products such as char and gases. Pyrolysis is preferred over other thermal technologies like incineration and plasma arc gasification with a lower annual capital cost (US \$17–25 per ton) and net operational cost (US \$2–3 per ton products) (Ouda et al., 2016). Considering the economic optimization of the process, natural zeolite was used as a cheap catalyst for various plastic waste catalytic pyrolysis in this study. The natural zeolite catalyst showed significant results for the conversion of plastic waste, its low BET surface area, microporous structure and low acidity affect its catalytic activities. The modification of the surface and structure of natural zeolite is needed to enhance its catalytic activities in the pyrolysis process. The modification of natural zeolite could be carried out by acid leaching, and thermal treatment and wet impregnation, as the next step via physical or chemical treatments in order to increase its catalytic performance. For instance, Sriningsih et al. (2014) carried out doping of Ni, Ni-Mo, Co and Co-Mo metals on natural zeolite and observed that doping increased the catalytic properties of natural zeolite. Char activation and its application for adsorbing heavy metals from wastewater will also be carried out in the near future. Life cycle assessments (LCA) studies (Rathore et al., 2016) of different plastic waste types, catalytic process and products are vital for understanding the economic, technical and environmental aspects of catalytic pyrolysis and its upscaling and commercialisation. For example, Wang et al. (2015) investigated the LCA of pyrolysis process and concluded that pyrolysis is one of the optimum practices for plastic waste management among the wastes disposal techniques.

4. Conclusions

The study showed the potential of Saudi Arabian natural zeolite as an alternative promising cheap catalyst in pyrolysis technology.

Natural and synthetic zeolite catalysts were used in a small pilot scale reactor for catalytic pyrolysis of four major types of plastic wastes such as PE, PS, PP, and PET. The liquid oils, produced by all types of plastic wastes using both catalysts, mainly consisted of aromatic hydrocarbons such as styrene, ethylbenzene, benzene, azulene, naphthalene, and toluene with a few aliphatic hydrocarbon compounds as confirmed by GC–MS and FT-IR analysis. Liquid oils produced from all plastic wastes using both catalysts had high HHV (40.2–45 MJ/kg) that is similar to conventional diesel. Catalytic pyrolysis can be a promising technology for conversion of plastic waste into liquid oil and value-added products like char for potential energy and environment-related applications. The liquid oil requires post-treatments such as refining or blending with conventional diesel to make it suitable as a transport fuel, energy source or valuable chemicals.

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