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Effect of Zeolite Catalysts on Pyrolysis Liquid Oil

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Abstract

The aim of this study was to determine the quality and applications of liquid oil produced by catalytic pyrolysis of polystyrene (PS) plastic waste in comparison to thermal pyrolysis, using a small pilot scale pyrolysis reactor. Thermal pyrolysis produced maximum liquid oil (80.8%) with gases (13%) and char (6.2%), while catalytic pyrolysis using synthetic and natural zeolite decreased the liquid oil yield (52%) with an increase in gases (17.7%) and char (30.1%) production. The lower yield but improved quality of liquid oil through catalytic pyrolysis are due to catalytic features such as microporous structure and high BET surface area. The liquid oils, both from thermal and catalytic pyrolysis consist of around 99% aromatic hydrocarbons, as further confirmed by GC-MS results. FT-IR analysis showed chemical bonding and functional groups of mostly aromatic hydrocarbons, which is consistent with GC-MS results. The produced liquid oils are suitable for energy generation and heating purposes after the removal of acid, solid residues and contaminants. Further upgrading of liquid oil or blending with diesel is required for its use as a transport fuel.

Keywords: Energy; Natural zeolites; Pyrolysis oil; Polystyrene (PS); Thermal pyrolysis; Catalytic pyrolysis

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LIST OF ACRONYMS AND ABBREVIATIONS

AD: Anaerobic digestion
BET: Brunauere-Emmete-Teller
Btu: British thermal units
EDS: Energy dispersive spectrometer
FT-IR: Fourier transform infrared spectroscopy
GC-MS: Gas chromatography-mass spectrophotometry
GHG: Greenhouse gases
HDPE: High density polyethylene
HHV: Higher heating values
HR-TEM: Higher resolution transmission electron microscopy
ICP: Inductively coupled plasma
KSA: Kingdom of Saudi Arabia
LCA: life cycle assessments
LDPE: Low density polyethylene
MSW: Municipal solid waste
O_2: Oxygen
PE: Polyethylene
PP: Polypropylene
PS: Polystyrene
PTF: Plastic-to-fuel
RDF: Refuse derived fuel
SAED: Selected area electron diffraction
SCAPE: School of Chemical and Process Engineering
SEM: Scanning electron microscopy
WTE: Waste-to-energy
XRF: X-ray fluorescence

1. Introduction

The recent volatility in crude oil prices, shortages and unsustainable future supply, along with environmental pollution generated especially by greenhouse gas emissions (GHG), all support the development of alternatives to petroleum (Gardy et al., 2014; Demirbas et al., 2016). Treaties like the Kyoto Protocol and Agenda 21 are also forcing fossil fuel-based economies towards renewable energy-based economies (Ouda et al., 2016). Renewable energy sources like wind, solar, geothermal, waste-to-energy (WTE), and biomass are attracting significant attention to bridge the ever-increasing energy demand and supply gap (Lam et al., 2016). Technological advancements, and cost effective techniques along with governmental incentives are further increasing the growth of renewable energy sector (Nizami et al., 2016a, b; Rathore et al., 2016).

The pyrolysis of plastic waste has emerged as an effective WTE technology (Table 1) as a solution for plastic waste management and to generate energy (liquid oil) and value-added products (char and gases) (Sharma et al., 2014). The pyrolysis process involves thermal and catalytic cracking of complex organic molecules into smaller molecules or short chain hydrocarbons (Demirbas et al., 2015a; Kartal et al., 2011). The overall process mechanism is complicated but mainly involves four steps: initiation, transfer, decomposition and termination (Faravelli et al., 2001). Computer simulation studies consider hundreds of possible reactions happening during the thermal cracking of substrate (Zhang et al., 2015). The process depends on a series of factors including temperature, residence time, heating rates, feedstock composition, presence of moisture or toxic elements and the use and types of catalysts (Miskolczi et al., 2009, Miandad et al., 2016a, d, e). Similarly, a wide range of reactors are employed e.g. fixed bed reactor, tube reactor, rotary kiln reactor and batch, semi-batch and pyrex batch pyrolysis reactors (Syamsiro et al., 2014).

In catalytic pyrolysis, the plastic waste is depolymerized into an improved liquid oil at lower temperature (~400 °C) in comparison to thermal pyrolysis, which is carried out in absence of catalyst at higher temperature (~500 °C) (Miandad et al., 2016b). The liquid oil of thermal pyrolysis is often unstable, low-grade, acid-corrosive, tarry and discoloured (Al-Salem et al., 2009; Hernandez et al., 2007). While the catalytic pyrolysis although decreases the liquid oil yield, but increases its quality (Table 2). The selection of catalyst in catalytic pyrolysis depends on the desired products such as liquid oil, char and gases and their quality (Walendziewski et al., 2001).

Polystyrene (PS), polyethylene (PE) and polypropylene (PP) are the most used plastic types in pyrolysis studies (Miandad et al., 2016a, b). Zeaiter (2014) obtained liquid oil from catalytic pyrolysis of high density polyethylene (HDPE) waste using modified zeolites. The liquid oil can be used in modified diesel engine vehicles after upgrading its gasoline range hydrocarbons (C_4 - C_{12}) through refining and blending with conventional fuels. Furthermore, the liquid oil can be used in heat generation and electricity production after removing the acid, solid residues, and contaminants present in the oil (Demirbas et al., 2015a). The value-added products such as styrene, benzene, toluene and other condensed aromatic hydrocarbons either cyclic or arenes can also be obtained by distillation and refining process of liquid oil (Demirbas 2004; Mohammed et al., 2015; Kobayashi et al., 2016).

In the Kingdom of Saudi Arabia (KSA) and in Gulf region, there exists no WTE facility to convert the plastic waste into energy and value-added products. Similarly, the plastic waste and natural zeolite have not been characterized for their potential role as an energy source and catalyst in pyrolysis technology. This study aims to determine the quality of liquid oils produced from thermal and catalytic pyrolysis using PS plastic waste in a small pilot scale pyrolysis reactor. The effect of synthetic and natural zeolite catalysts were studied on the fractions of liquid oils, gases and char in comparison to thermal pyrolysis. The quality of produced liquid oil is evaluated based on its physico-chemical properties and energy contents.

1.1. Energy demands and plastic waste management in KSA

KSA is one of the world’s largest energy consuming countries due to its rapid population growth (around 3.4% per year), urbanization (around 1.5% per year) and a rise in living standards resulting from high economic growth. In 2013, the total energy consumption in KSA surpassed 9 quadrillion British thermal units (Btu) making the country one of the 12 largest primary energy consumers in the world (Nizami et al., 2015a, b). Currently, around 55% of KSA energy demands are satisfied by petroleum and the remaining 45% by natural gas. The KSA government wants to generate about half of the country’s energy (about 72 GW) from renewable sources like nuclear (17.6 GW), solar (41 GW), wind (9 GW), geothermal (1 GW) and WTE (3 GW) by 2032 (Nizami et al 2016b; Demirbas et al., 2015b). In the KSA, 15.3 million tons of municipal solid waste (MSW) was produced during 2014 (average 1.4 kg/capita/day) and it is estimated that figure will almost double to 30 million tons per year by 2033. Every year, around 6 million metric tons of plastic products are produced in KSA, and thus it is the second largest waste stream of MSW (up to 17%) with total annual waste generation of 2.7 million tons. All of the plastic waste, along with other MSW fractions, are disposed in landfills or dumpsites. The plastic waste has detrimental environmental and operational effects at landfill sites due to slow degradation rates and the presence of toxic dyes and additives. Plastic waste is managed through different approaches, including reducing, reusing, recycling and WTE. Conventional mechanical recycling techniques such as sorting, grinding, washing and extrusion can recycle only 15-20% of all plastic waste. Beyond this level, the plastics become contaminated with materials like soil, dirt, aluminium foil, food waste and paper labels. Air and waterborne pollutants are emitted from uncontrolled plastic combustion. In recent years, WTE technologies including gasification, pyrolysis, and refuse derived fuel (RDF) and chemical recycling methods such as hydrolysis, methanolysis, and glycolysis have been gaining significant attention.

2. Material and methods

2.1. Experimental setup

A small pilot scale pyrolysis reactor has been designed and used for thermal cracking of plastic waste into liquid oil, gases and char (Figure 1). The reactor is a closed system to operate in the absence of O_2 and has a capacity to achieve up to 600 °C using desired heating rates. The reactor is made of stainless steel and has a height of 360 mm with 310 mm diameter and a capacity of 20 L (Table 3). There is also a pressure gauge connected with pyrolysis reactor to monitor the pressure to switch off in case of excess pressure build-up. The system can work both as a thermal or catalytic pyrolysis process. During the catalytic pyrolysis, the powder catalyst was mixed with the feedstock in the pyrolysis reactor to study its effect on the final products yield and quality. The sample was heated and melted in the reactor, producing organic vapours. These vapours moved to a condenser unit and were converted into liquid oil by using a chiller system attached to the condenser unit. ACDelco classic coolant was used in the chiller to achieve maximum condensation of organic vapours for optimized liquid oil yields. The condensed organic vapours (liquid oil) were collected from the oil collector assembly at the bottom of the system. While the uncondensed products (gases) coming out from the same liquid oil pipe were exhausted outside. The collected liquid oil was further analysed for its yield, quality and potential applications.

2.2. Sample preparation and experimental scheme

PS disposable plates were used as plastic waste and treated in the pyrolysis process to produce liquid oil, gases and char. 1 kg of PS sample was used for each experiment, including thermal pyrolysis, catalytic pyrolysis with natural zeolite and synthetic zeolite catalysts. 100 g of both natural and synthetic zeolite catalysts were used, which gives the catalyst to feedstock ratio of 1:10. This ratio was fixed based on the recently published research (Ateş et al., 2005; Lopez et al., 2011). The synthetic zeolite catalyst (ZEOLYST^{TM} CBV 780 CY (1.6) Zeolite SDUSY Extrudate) was purchased from Zeolyst International (Zeolyst, 2015) and used as received without any further treatment. The chemical name of this synthetic zeolite catalyst is Zeolite type SDUSY, hydrogen form, aluminium oxide and it has a specific gravity of greater than 1 with negligible solubility in water. The natural zeolite was extracted from the Harrat Ash-Shamah area located in the northwest of KSA (Nizami et al., 2016a). The samples were collected for research purpose without requiring any specific permission from Government or any other agencies. It also confirm that the field studies did not involve endangered or protected species. This catalyst was simply milled to micron sized particles and used without any other pre-treatment or surface modification.

The raw material (PS plastic waste) was prepared by cutting the disposable plates into small pieces to achieve sample homogeneity. Each sample was heated from room temperature to 450 °C using heating rate of 10 °C/min and the reaction time was fixed to 75 min. The fractions of liquid oil, gases and char were estimated on their weight basis. The produced liquid oil was further characterized to study the effect of thermal and catalytic pyrolysis under presence of synthetic and natural zeolite catalysts. The optimum conditions of 450 °C and 75 min for non-catalytic pyrolysis process was first determined by TGA (Mettler Toledo TGA/SDTA851) analysis of the PS plastic sample under controlled conditions. The analysis was carried out by heating 10 µg of PS sample at the rate of 10 °C per min from 25-900 °C under nitrogen flow at a constant rate of 50 ml/min. The detailed experiments on effect of temperature and reaction time on pyrolysis products and choosing optimum conditions as well as TGA results and analysis have been published earlier by the authors (Miandad et al., 2016d).

2.3. Analytical characterization

The characterization of natural zeolite was carried out at the School of Chemical and Process Engineering (SCAPE), University of Leeds, UK and detailed results have been published earlier by the authors (Nizami et al., 2016a). The Brunauere-Emmete-Teller (BET) surface area, pore size and volume of natural zeolite catalyst were analysed by using Micromeritics TriStar 3000 (UK) surface analyser and the experimental details are provided in earlier study (Nizami et al., 2016a). The particle size and morphology distribution of natural zeolites was examined by Hitachi scanning electron microscopy (SEM). The elemental analysis of natural zeolite was carried out by energy dispersive spectrometer (EDS) attached with SEM. A homogeneous suspension of sample was prepared by mixing zeolite powder in acetone using ultrasonic batch. Few drops of this homogenous diluted sample was then added on SEM stubs and the stubs were dried and transferred to a cleaning zone. UV-Ozone radiation unit was used at pressure 1 Pa for 10 min to remove any possible contamination. The cleaned samples were finally installed in SEM and images at different magnifications and EDS were collected for detailed analysis. The produced liquid oils from thermal and catalytic pyrolysis with natural and synthetic zeolite catalysts were further characterized by a number of analytical techniques. The chemical structure and the functional groups present in PS plastic raw material and produced liquid oil samples were studied by Fourier transform infrared spectroscopy (FT-IR), Perkin Elmer's, UK. A minimum of 32 scans were performed at average signal of IR with a resolution 4 cm^{-1} in the ranges of 500-4000 cm^{-1}.

Gas chromatography coupled with mass spectrophotometry (GC-MS) of Hawlett-Packard HP 7890 was used to analyse the chemical composition of produced liquid oils by both thermal and catalytic pyrolysis. The produced liquid oils were mixed with polar solvent dichloromethane and injected to GC-MS for analysis. The GC-MS system used a 30 m long with 0.25 mm diameter capillary column coated with 0.25 µm thick film of 5% phenyl-methypolysiloxane and worked with a 5975 quadrupole detector. The initial temperature of the oven was kept at 50 °C for 2 min and then increased to 290 °C at the rate of 5 °C per min at holding rate of 10 min. The ion source and transfer line temperatures were kept at 230 °C and 300 °C respectively. The GC-MS was operated in full scan mode between m/z 33-533 using splitless injection function at 290 °C and solvent interval of 3 min. The obtained peaks based on their retention times were matched with standard compound peaks in NIST08s mass spectral data library. The percentage fractions of different hydrocarbon and other compounds present in the liquid oil samples were determined by total ion chromatogram peak areas using the software. The energy contents, in terms of higher heating values (HHV) of the PS plastic raw material and produced liquid oil, were analysed by bomb calorimeter (Parr 6200 Calorimeter, US) based on the ASTM D 240 method.

The characteristics of pyrolysis liquid oils were determined by relevant techniques based on standard ASTM methods. The viscosities of the liquid oil were measured by a Discovery Hybrid Rheometer (HRI 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 was set to 40 °C and the shear rate range was set between 1-500 1/s. The rheometer was first calibrated using viscosity standard liquid followed by actual liquid viscosity measurements. Flash point of produced liquid oil was determined by Automatic

Pensky-Martens Closed Tester (Koehler, US) based on the ASTM D 93 method. For pour point, AWD-12 Pour Point Tester was used with temperature of -10 °C for one tank (left tank) and the temperature of -56 °C for other tank (right tank). The sample was poured in the sample tube up to the mark. The sample was first put in the left 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 seconds. This process was continued until the pour point was reached. For density measurement, a portable density meter (DMA 35 from Anton Paar) was used, which was first calibrated with distilled water and then rinsed with acetone and allowed to dry between each sample, before taking the next measurements.

3. Results and discussion

3.1. *Characteristics of KSA's* natural zeolite

The SEM images revealed that mostly spherical shaped particles were between 50-200 nm size-range (Figure 2). However, some larger grains with irregular morphology were also observed in 0.5-1 nm size range. The BET surface area, pore size and volume of natural zeolite were found to be 4.3 m^2/g, 18.7 Å and 0.02 cc/g respectively (Nizami et al., 2016a). The microporous nature of zeolite plays a vital role in thermal cracking reactions by adsorbing selective larger hydrocarbon chain molecules and other impurities to produce improved liquid oil. The surface area and pore volume of the catalyst can be increased significantly by chemical treatment such as acid leaching or thermal activation that will further enhance its catalytic functions (Sriningsih et al., 2014). Similarly, the impurities present in natural zeolite catalyst can also be removed by chemical or thermal treatment (Syamsiro et al., 2014). To study the in-depth microporous structural features of natural zeolites, samples must be milled to below 100 nm size range. Higher resolution transmission electron microscopy (HR-TEM) analysis can be used to obtain detailed structural features including particle size, clear morphology, crystallographic phases from HR-TEM images, atomic fringes, selected area electron diffraction (SAED) and EDS analysis (Rehan et al., 2011, 2015). This would be the subject of our future studies.

Natural zeolites are alumina-silicates complex structured minerals containing a number of earth metals such as Na, Ca, K, Mg, and Fe (Nizami et al., 2016a). The energy dispersive spectra

(EDS) were taken from different regions of the SEM image, which showed some differences in the weight percentage composition, and spectrum 4 is presented in figure 3. The weight percentage of major components were found to be O (57.2%), Si (26.7%) and Al (7.0%). The minor components included Na (2.2%), Mg (0.6%), S (0.4), K (2.7%), Ca (0.5%), Ti (0.2%) and Fe (2.5%) (Figure 3). The elemental analysis of compounds like zeolites are generally performed by SEM-EDS with enough degree of accuracy, however the results obtained do vary from sample to sample. This is because the spectrum is taken from one single point that may not always be a true representative of the whole sample. However, the most accurate quantitative elemental analysis including all major and minor components including impurities can be achieved by inductively coupled plasma (ICP) and X-ray fluorescence (XRF).

3.2. Analysis of pyrolysis products yield

Figure 4 and table 4 show the results for amounts of liquid oil, gases and char produced from thermal and catalytic experiments. Thermal pyrolysis produced maximum liquid oil (80.8%) with gases (13%) and char (6.2%), while catalytic pyrolysis decreased the liquid oil yields to 54% and 50% from natural zeolite and synthetic zeolite respectively. Natural zeolite having BET surface area of 4.3 m^2/g produced 54% liquid oil yield, while synthetic zeolite with surface area of 780 m^2/g produced 50% liquid oil yield. The char produced from catalytic pyrolysis, 32.8% with natural zeolite and 27.4% with synthetic zeolite, was higher than 6.2% from thermal pyrolysis. Similarly, gases production was at a maximum with synthetic zeolite 22.6% and 12.8% with natural zeolite as compared to 13% from thermal pyrolysis (Figure 4). Lopez et al. (2012) and Syamsiro et al. (2014) also reported similar products yield trends that use of the catalyst decreased overall liquid oil yield with an increase in char and gases production.

The lowest liquid oil yield and highest gas production in catalytic pyrolysis with synthetic zeolite can be due to its microporous structure and high BET surface area (Figure 5). Seo et al. (2003) also reported that use of microporous catalyst with high BET surface area will lead to an increase in gas and decrease in liquid oil yields. The natural zeolite has lower BET surface area and microporous structure as compared to synthetic zeolite, thus increasing the char production. Lopez et al. (2011) reported the similar results by using ZSM-5 and red mud catalysts having BET surface area of 412 m^2/g and 27.1 m^2/g respectively. Moreover, catalysts with higher acidity increase the cracking process that also increases the gases production and decreases liquid oil yield (Sriningsih et al., 2014). The synthetic catalyst used in the present study was more acidic than natural zeolite, thus it increased the gases production with a decrease in liquid oil (Figure 4 & 5).

3.3. Analysis of pyrolysis liquid oil quality

The chemical composition of PS plastic raw material and pyrolysis liquid oils were studied by using FT-IR spectra and are drawn on the same graph (Figure 6). This technique identifies the chemical bonds in a molecule by producing an infrared absorption spectrum, leading to identification of functional groups. Many clear peaks were generated, ranging from 697-3070 cm^{-1}. The FT-IR spectra for all three pyrolytic liquid oils are very similar for peak positions except for minor differences in some peak intensities possibly due to the variations in percentage compositions of different aromatic hydrocarbons found in these liquid oils (Figure 6). The FT-IR peaks were characterized and matched with the standard characteristic IR absorption peaks given in Orgchem (2015). The two strongest sharp peaks found at 697 and 775 cm^{-1}, attributed to the =C-H out of plane bending vibrations for mono-substituted benzene rings. Another medium peak found at 1490 cm^{-1} falls within the 1500-1400 range corresponding to C=C stretch for substituted aromatic hydrocarbons. One weak peak at 1450 cm^{-1} can be assigned to C-H bend in alkanes. Two sharp peaks appeared at 905 and 989 cm^{-1} are corresponding to =C-H bend in alkenes. Many weak absorption peaks found at the higher frequency range from 2800-3100 cm^{-1} and were at 2850, 2920, 2940 cm^{-1} and 3020, 3030, 3070 cm^{-1} fall within standard ranges of 3100-3000 for sp^3 C-H stretch in alkanes and 3100-3000 cm^{-1} for sp^2 C-H stretch in aromatics, respectively (Figure 6). These FT-IR results presented strong evidence that aromatic hydrocarbons were the major components found in the liquid oils produced from both thermal and catalytic pyrolysis.

The FT-IR analysis of the PS plastic raw material was also carried out and its spectrum is shown in figure 6. Most of the peaks found for raw material matched closely with the FT-IR peaks of pyrolytic liquid oils. The minor differences in the peak frequencies and intensities in raw material to liquid oil samples were possibly due to different phases and degree of crystallinity of styrene, some impurities or additives present in the plastic feedstock. The other strong peak at 533 cm^{-1} might be attributed to the =C-H OOP of mono-substituted benzene ring. This absorption band also observed for the native styrene (raw material), but it has not been previously reported in the literature (Pavia et al., 2008). These results (Figure 6) are also consistent with other related studies, where it is reported that the liquid oil obtained from PS plastic feedstock mainly produce aromatic hydrocarbons with paraffins (alkanes), olefins (alkenes) and naphthenes (cycloalkanes) in minor quantities (Siddiqui et al., 2009; Lee et al., 2002; Ramli et al., 2011; Kim et al., 2002).

The GC-MS results also showed the presence of aromatic hydrocarbons as being dominant compounds in liquid oils from both thermal and catalytic pyrolysis (Figure 7). In thermal pyrolysis, styrene was the main compound (48.3%) with ethylbenzene (21.2%), toluene (25.6%) and benzo(b)triphenylene (1.6%). In catalytic pyrolysis with natural zeolite, styrene was also the major compound (60.8%) with methylstyrene (10.7%), azulene (4.8%), 1H-indane (2.5%) and ethylbenzene (1.3%) (Figure 7). In catalytic pyrolysis with synthetic zeolite, the following compounds were found in descending concentrations: alpha-methylstyrene (38.4%), benzene (16.3%), styrene (15.8%), ethylbenzene (9.9%), isopropylbenzene (8.1%), propenylbenzene (4.2%) and propyl benzene (3.5%) (Figure 7). These findings are in agreement with other studies that observed the chemical composition of liquid oil produced from MPW mainly consists of aromatic hydrocarbons with some paraffins (alkanes: C_nH_{2n+2}), olefins (alkenes: C_nH_{2n}), and naphthenes (cycloalkanes) (Shah and Jan, 2014; Ukei et al., 2000). Moreover, the chemical composition of liquid oil depends on plastic types and various process conditions, including temperature reaction time, and type and amount of catalyst used. For example, benzene, styrene, ethylbenzene, toluene, α-methylstyrene and indane derivate are the major compounds reported by many researchers (Shah and Jan, 2014; Ukei et al., 2000; Lee et al., 2002). Lee et al. (2002) reported that liquid oil produced from catalytic degradation of PS consists more than 99% of aromatic compounds with minor quantities of n-paraffin (0.02%), iso-paraffin (0.1%), olefins (0.03%) and naphthenes (0.1%), which is in agreement with our findings (Figure 7). Similarly, the liquid oil produced by Ramli et al. (2011) from thermal and catalytic pyrolysis contained 80% and 85-90% of aromatic hydrocarbons respectively. The high ratio of aromatic compounds found in the pyrolytic liquid oil from thermal and catalytic degradation of PS is due to the high stability of these compounds, which inhibit the further cracking or hydrogenation into paraffin and olefins (Saptoadi et al., 2015). The GC-MS results revealed that pyrolysis liquid oils mainly consist of aromatic hydrocarbons, which is in agreement with FT-IR results (Figure 6).

In both thermal and catalytic pyrolysis of PS, styrene was the main compound found in produced liquid oils with some other aromatic compounds such as ethylbenzene, toluene and methylstyrene. Styrene production in thermal pyrolysis oil was 48.3%, while in catalytic pyrolysis oil there was an increase in the production of styrene (60.8%) using natural zeolite. The styrene with synthetic zeolite however decreased down to 15.8% with an increase in its derivatives alpha-methylstyrene (38.4%). Many researchers reported similar results that styrene, ethylbenzene, toluene and methylstyrene were the major compounds from the degradation of PS (Aguado et al., 2003; Artetxe et al., 2015; Bartoli et al., 2015). According to Onwaduili et al. (2009), there is no direct production of toluene and ethylbenzene from the plastic waste raw material and they may be produced by the reaction of styrene itself. Moreover, production of styrene initially increases with an increase of temperature but further increase in temperature to above 500 °C showed a declining trend in the styrene production. Beyond 500 °C, it is reported that styrene production decreases with the increase in the production of toluene and ethylbenzene, which shows further decomposition of styrene at high temperature (Demirbas, 2004; Onwudili et al., 2009).

It has been reported by many researchers that increase in pyrolysis temperature and reaction time decreases the production of styrene with the increase of toluene and ethylbenzene. (Agudo et al., 2003; Artetxe et al., 2015; Bartoli et al., 2015). This increase in the production of ethylbenzene, toluene and methylstyrene is attributed to the hydrogenation of styrene at high temperature due to secondary reactions (Ukei et al., 2000). In addition increase in reactor pressure also decreases the production of styrene with the increase in toluene and ethylbenzene which is due to the hydrogenation of styrene into its derivate (Shah and Jan, 2014). Overall decrease in styrene production with the increase in ethylbenzene, toluene, methylstyrene or production of high molecular weight hydrocarbon (benzene, 3-butynyl) either may be due to further cracking of styrene via hydrogenation (Lee et al., 2002) or recombination of styrene to higher molecular weight via H-abstraction followed by cyclization (Hu and Li, 2007). Overall secondary reactions are responsible for the decrease in the production of styrene (Karaduman, 2002).

Styrene production is also effected by the selection of catalyst. Styrene production is higher in catalytic pyrolysis as compared to thermal pyrolysis when solid base catalyst was used (Shah and Jan, 2014). Ukei et al. (2000) used solid base catalyst (BaO) for the degradation of PS and achieved maximum styrene recovery. Adnan et al. (2014) used Cu base catalyst and achieved up to 60% of styrene recovery. However use of solid acid catalyst decreases the production of styrene and increase the production of ethylbenzene, toluene and methylstyrene. Audisio et al. (1990) reported the very low production of styrene (below 5% weight) by using silica alumina, REY or HY zeolite at 350 °C. Lee et al. (2003) reported that use of solid acid catalyst decreases the production of styrene as compare to thermal pyrolysis. Thermal pyrolysis achieved 52.2% of styrene recovery however it decreases with the use of solid acid catalyst such as NZ (50.8%), HNZ (48.1%), HSCLZ (47.7%) and SA (36.1%). The decrease in styrene production is may be due to high acidity of catalyst which increases the rate of secondary reactions. This is possibly the reason for a decrease in styrene production in liquid oil from synthetic zeolite catalytic pyrolysis in this study (Figure 6). Since the structure of the synthetic zeolite would be more pure and highly crystalline than natural zeolite, it is therefore probably more acidic in nature as well. This observation is in line with the work of Nizami et al. (2016a) and Miandad et al. (2016a, b).

The energy content is one of the most important characteristics of any fuel in its applications and it can be characterised by its HHV. The higher the HHV value of a fuel, the higher the energy content of the fuel, meaning the required performance can be achieved with less fuel quantity (Saptoadi et al., 2015). In this study, the average HHV of PS plastic raw material, liquid oils produced from thermal and catalytic pyrolysis with natural and synthetic zeolite catalysts were found to be 39.3, 41.6, 41.7 and 40.6 MJ/kg respectively (Table 5). The slightly lower HHV of raw material to liquid oils can be due to its solid phase form. Similarly, the minute difference in HHV of oil from synthetic zeolite catalyst to other oils may be due to the presence of ash or catalyst particulates in final product. These results are in agreement with many other studies such as Syamsiro et al. (2014) that reported the HHV of 36.3 MJ/kg for liquid oil produced from pyrolysis of PS plastic raw material at 450 °C. Lopez et al. (2011) reported a HHV of 41.5 MJ/kg for liquid oil produced from pyrolysis of packaging plastic waste at 440 °C. Moreover, the HHV of pyrolytic liquid oils are very close to HHV (43.1 MJ/kg) of conventional diesel (Table 5), which further affirms its suitability to be used for energy production. Some studies have also suggested that pyrolytic oil, having slightly lower HHV then diesel, can be suitably utilized as it is as a fuel or after mixing it with kerosene oil (Saptoadi et al., 2015).

The thermal pyrolysis oil was further characterized for various parameters such as dynamic viscosity, kinematic viscosity, density, pour point and flash point and compared with reported conventional diesel values (Table 6). The dynamic and kinematic viscosity was found to be 1.8 mPa.s and 1.9 cSt, which are comparable to 1-4.1 mPa.s and 2.0-5.0 cSt ranges of conventional diesel respectively. The density was found to be 0.9 g/m^3 which is also close to reported density range of 0.8-0.9 g/m^3 for conventional diesel. The flash point was found to be 30.2 °C, which is below the conventional diesel range of 55-60 °C. One of the possible reason for this lower flash point could be that pyrolysis liquid oil mainly consist of aromatic hydrocarbons.

3.4. Potential applications of pyrolysis technology in KSA and other developing countries

There is a huge potential applications for pyrolysis technology in KSA and other developing countries of Asia, Africa and Latin America. The liquid oil produced by pyrolysis process is suitable to be used as a feedstock for value-added chemicals production, energy generation, transport fuel and heating purposes (Islam et al., 2010; Ouda et al., 2016; Rehan et al., 2016). The consumption and generation of plastic waste in these countries have increased to an alarming rates (Ouda et al., 2016). For instance, in KSA, around 6 million metric tons of plastic products are produced every year and therefore, it is the second largest waste category of MSW with total generation of 2.7 million tons per year.

Rehan et al. (2016) have recently described a case study of Makkah on the amounts of liquid oil that can be generated from all the plastic waste produced in Makkah city together with details on achieving economic savings and other environmental benefits. Rehan et al. (2016) estimated that around 87.91 MW of electricity can be produced along with global warming potential savings of 199.7 thousand Mt.CO_2 eq. in Makkah city by utilizing all of the plastic waste in the pyrolysis process. A total economic savings of 297.52 million SAR or 79.33 million USD will be achieved from carbon credits, landfill diversion and electricity production from pyrolytic liquid oil. Moreover, the pyrolysis has an advantage over other WTE technologies including incineration and plasma arc gasification due to less annual capital cost ($17-25/ton) and net operational cost ($2-3/ton) (Table 1).

The quality of liquid oil produced needs to be improved further in terms of removing some of the heavy hydrocarbons and impurities (Figure 8). Many studies have been recently published on improving the pyrolytic liquid oil quality by various methods such as filtration, chemical treatment, by blending it with conventional fuels and distillation and refining (Islam et al., 2010; Mohebali and Ball, 2016; Chong and Hochgreb, 2015). Pyrolysis has also been reported to be an effective way to recover the styrene from PS plastic. Several researchers have reported the production of styrene, ethylene benzene and toluene with some other styrene monomers from the thermal degradation of PS plastic (Jung et al., 2013; Artetxe et al., 2015). Recovered styrene can be used as feedstock in various industries for PS polymerization (Achilias et al., 2007). Biodegradable plastic i.e. polyhydroxyalkanoate can also be produced from pyrolytic liquid oil produced from thermal degradation of PS plastic wastes (Nikodinovic-Runic et al., 2011).

The oil produced in this study was found to have similar chemical composition and HHV values as conventional diesel (Table 7). Thus produced liquid oil has the potential to be used as alternative of conventional diesel. However produced liquid oil should be upgraded or blended with conventional diesel as it contains high aromatic content. The high percentage of styrene found in liquid oils from both thermal and catalytic pyrolysis could be used as valuable chemicals for improving the octane number of petrol fuel produced from crude oil by blending them in different proportions. The octane number of petrol fuel mainly depends on their hydrocarbon composition such as n-paraffins and olefins are less desirable compared to iso-alkanes, naphthenic and aromatic compounds. Furthermore, higher octane number is favoured for prevention of early ignition which leads to cylinder knock (Andras et al., 2007; Corma 1996; Madon 1991).

Several studies have reported the mixing and blending of pyrolytic oil with conventional fuel in different ratios to further improve its quality (Sharuddin et al., 2016; Li et al., 2016; Kumara et al., 2013). For example, the produced liquid oil was blended with the diesel oil with different ratios i.e. 5%, 10%, 20%, 30%, 40% and 45% (Frigo et al., 2014; Nileshkumar et al., 2015; Lee et al., 2015). Wongkhorsub and Chindaprasert (2013) directly injected the pyrolytic liquid oil produced from wastes tires and wastes plastic into diesel engine. All aforementioned studies reported the successful use of pyrolytic liquid oil for energy generation. Engine performance and exhaust emissions were also examined with the use of pyrolytic liquid oil. The results concluded that among all the used ratios 20/80% (pyrolytic liquid oil/conventional diesel) ratio showed similar performance as conventional diesel. Lee et al. (2015) reported 13% decrease in engine performance at 2450 rpm while it reaches to 17% at 3500 rpm with 20/80% ratio. Nileshkumar et al. (2015) also recommended the same ratio for the better performance of engine. However fuel consumption increased with the increase in blending ratio due to slightly lower calorific value of pyrolytic liquid oil (Cleetus et al., 2013). In addition exhaust emissions also increased as blending ratios increased reaching to its maximum at 50/50% blending ratio. Nileshkumar et al. (2015) reported that at 20/80% blending ratio, COx and NOx emissions were (0.5 and 0.7 g/km) and (0.3 and 0.4 g/km) for low and full load respectively. However for conventional diesel the reported emissions were 0.5 and 0.7 g/km for COx while, 0.3 and 0.4 g/km for NOx respectively. More comprehensive studies are required to fully understand the transformation of pyrolytic liquid oil into pure clean transportation fuel and its effect on internal combustion engine performance, stability and structural damage as well as the type and impact of gases emissions.

3.5. Future perspective

There is much scope in the optimization of the pyrolysis process on a large scale by detailed investigations of the effect of various process parameters, feedstock type, and type of catalyst used. Most of the pyrolysis plants at pilot and commercial scale use synthetic catalysts intensively in order to improve the yield and quality of liquid oil and to overall optimize the pyrolysis process. Despite the recent advancements in pyrolysis technology, several issues and scope for further process optimization still remain. For example, the use of synthetic catalysts in pyrolysis technology is making the overall process more energy intensive and economically expensive. In such scenario, a significant research is underway on exploring new and cheap catalysts, reusing catalyst, using natural minerals as catalysts, and using of catalysts in less quantities. Another area of further research would be to study the activation of produced char with steam and other appropriate gases and to study its various potential applications such as removal of heavy metals and other toxic contaminants from wastewater and soil (Aktaş and Çeçen, 2007; Qin et al., 2013). Jindaporn and Lertsatitthanakorn et al. (2014) reported that the char produced from pyrolysis of HDPE waste has a calorific value of 4,500 cal/g and its surface area and volume increased by thermal activation at 900 °C for 3 hours.

Natural zeolite catalysts are used successfully in the pyrolysis process; however, there is scope for further improvement in their catalytic performance by removing some of the impurities present and by increasing their surface area and volume. This surface and structural modifications can be carried out by acid leaching, and thermal treatment and wet impregnation (Nizami et al., 2016a). Syamsiro et al. (2014) reported that the natural zeolite's catalytic performance was improved by removing the volatile impurities through thermal treatment at

500 °C for 3 hours. Similarly, the catalytic performance of natural zeolites was improved by removing impurities and increasing the overall catalyst acidity via HCl leaching process (Sriningsih et al., 2014). Wet impregnation method is an important technique widely used to modify and generate heterogeneous catalysts (Adnan et al., 2014). The life cycle assessments (LCA) of feedstock, products and process are also recommended (Nizami, 2015; Shahzad et al., 2015; Singh et al., 2010; Nizami and Ismail, 2013) that are very important to fully understand the economic, technical and environmental aspects of pyrolysis technology before its installation at a commercial scale.

4. Conclusions

The GC-MS results showed that around 99% aromatic hydrocarbons were found in liquid oils produced by both thermal and catalytic pyrolysis. In thermal pyrolysis oil, the major compounds were styrene (48.3%), ethylbenzene (21.2%), toluene (25.6%) and benzo (b) triphenylene (1.6%). In catalytic pyrolysis with natural zeolite, the major compounds were styrene (60.8%), methylstyrene (10.7%), azulene (4.8%), 1H-indane (2.5%) and ethylbenzene (1.3%), while, in catalytic pyrolysis with synthetic zeolite, the major compounds were alpha-methylstyrene (38.4%), styrene (15.8%), benzene (16.3%), ethylbenzene (9.9%), and isopropylbenzene (8.1%). The FT-IR analysis also revealed chemical bonding and functional groups of mostly aromatic hydrocarbons found in all samples, which is in agreement with GC-MS results. The average HHV of PS plastic feedstock, liquid oil produced from thermal and catalytic pyrolysis with natural zeolites and synthetic zeolites were found to be 39.3, 41.6, 41.7 and 40.6 MJ/kg respectively. The produced liquid oils are suitable for heating and energy generation applications after post-treatment. However, the high percentage of aromatic compounds (up to 99%) in liquid oil make it less suitable as a transportation fuel until it further goes through refining stages including blending with diesel. This will upgrade the liquid oil to gasoline range hydrocarbons (C_4 - C_{12}).

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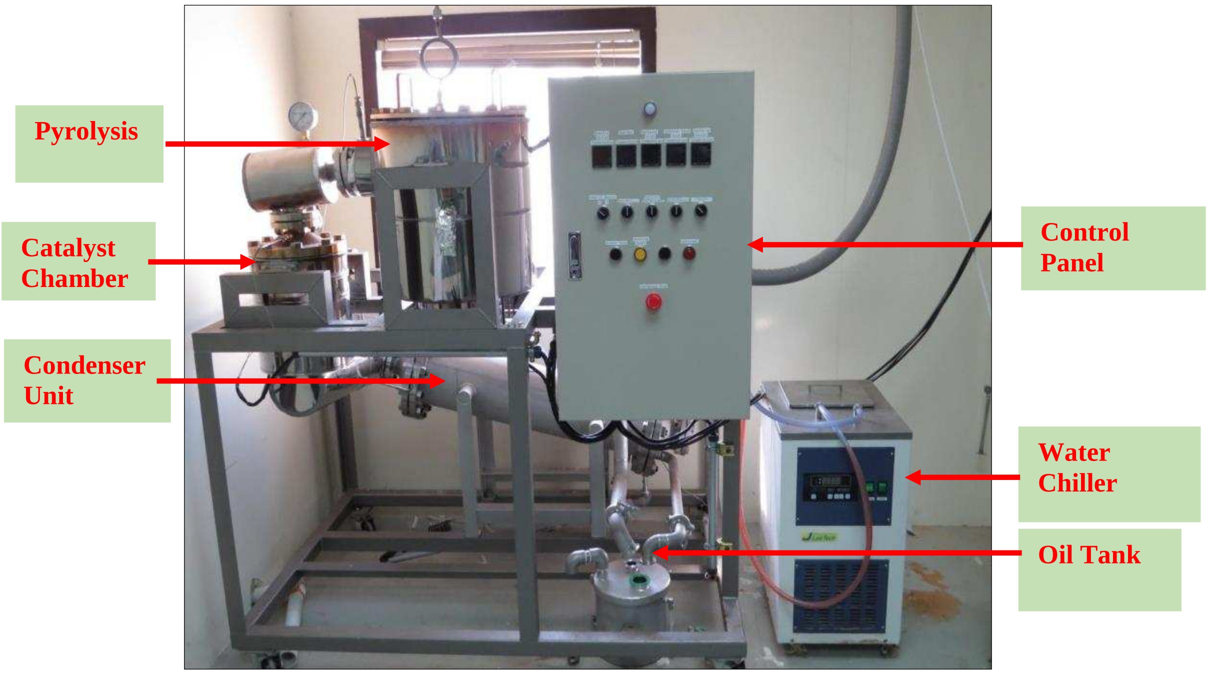


Figure 1. Small pilot scale pyrolysis reactor (Miandad et al., 2016d).

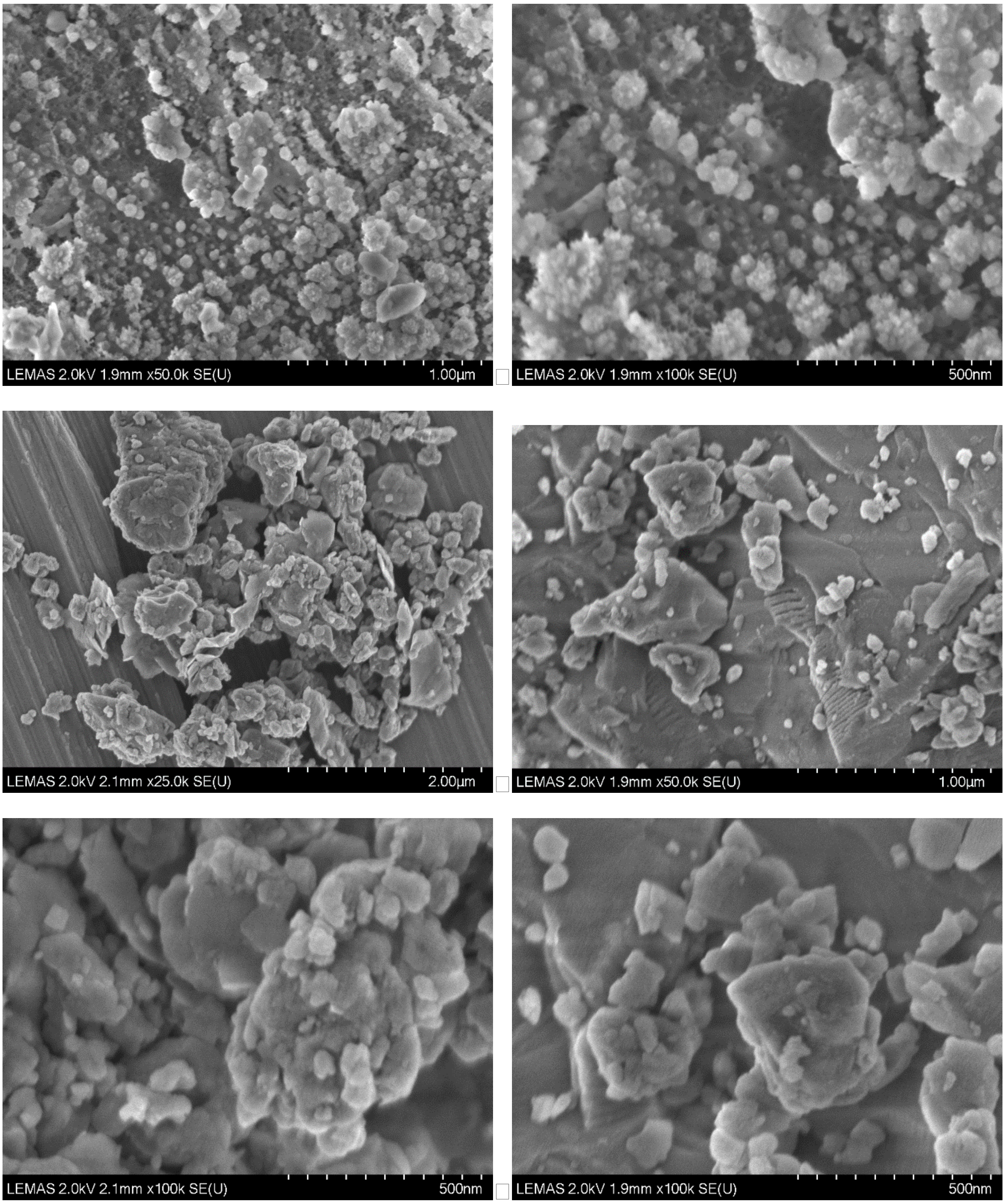
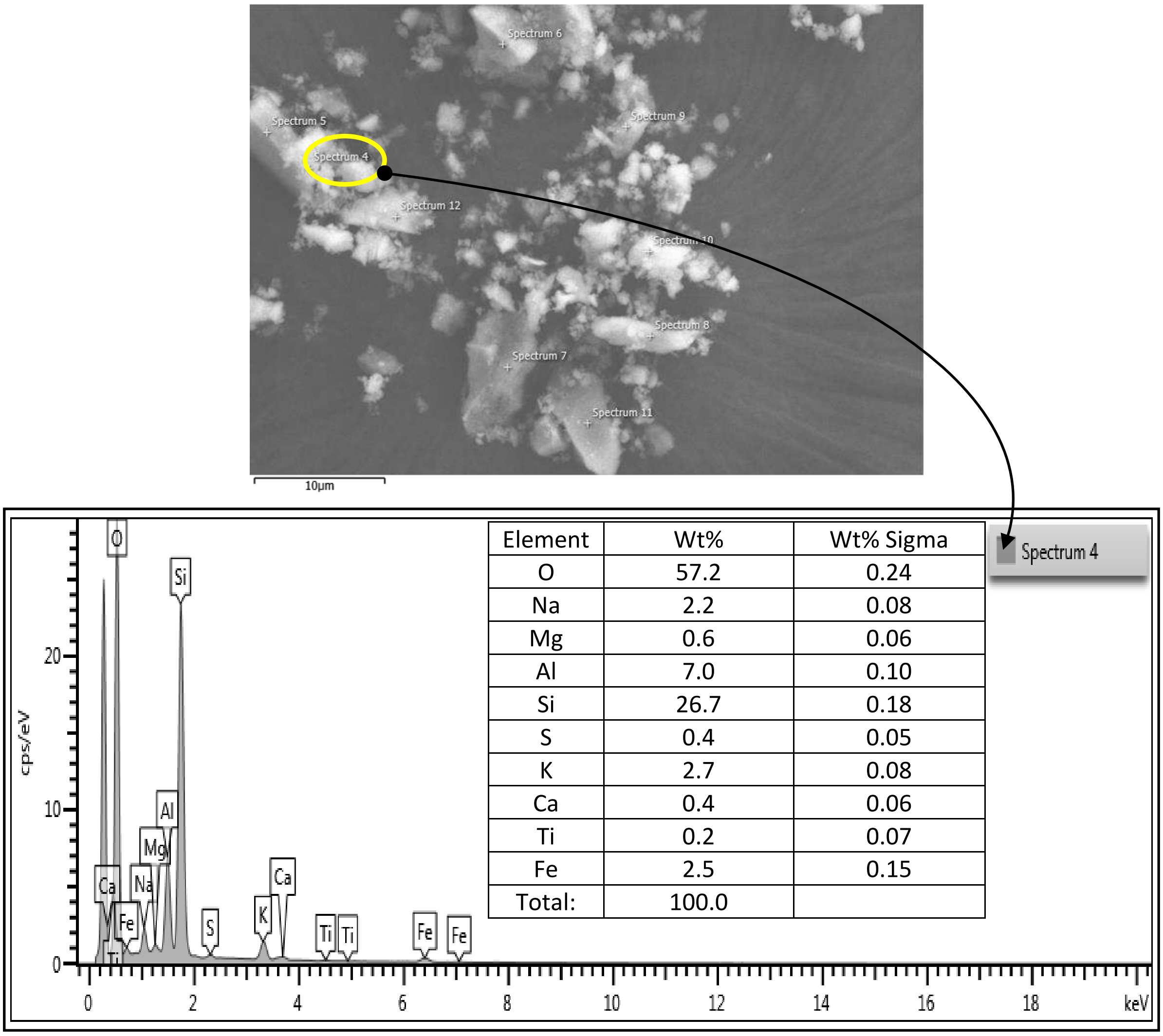


Figure 2. SEM images of the Saudi Arabian natural zeolites.



Element	Wt%	Wt% Sigma
O	57.2	0.24
Na	2.2	0.08
Mg	0.6	0.06
Al	7.0	0.10
Si	26.7	0.18
S	0.4	0.05
K	2.7	0.08
Ca	0.4	0.06
Ti	0.2	0.07
Fe	2.5	0.15
Total:	100.0	

Figure 3. SEM-EDXS of Saudi Arabian natural zeolite showing elemental composition and quantities in wt% for certain location (Spectrum 4).

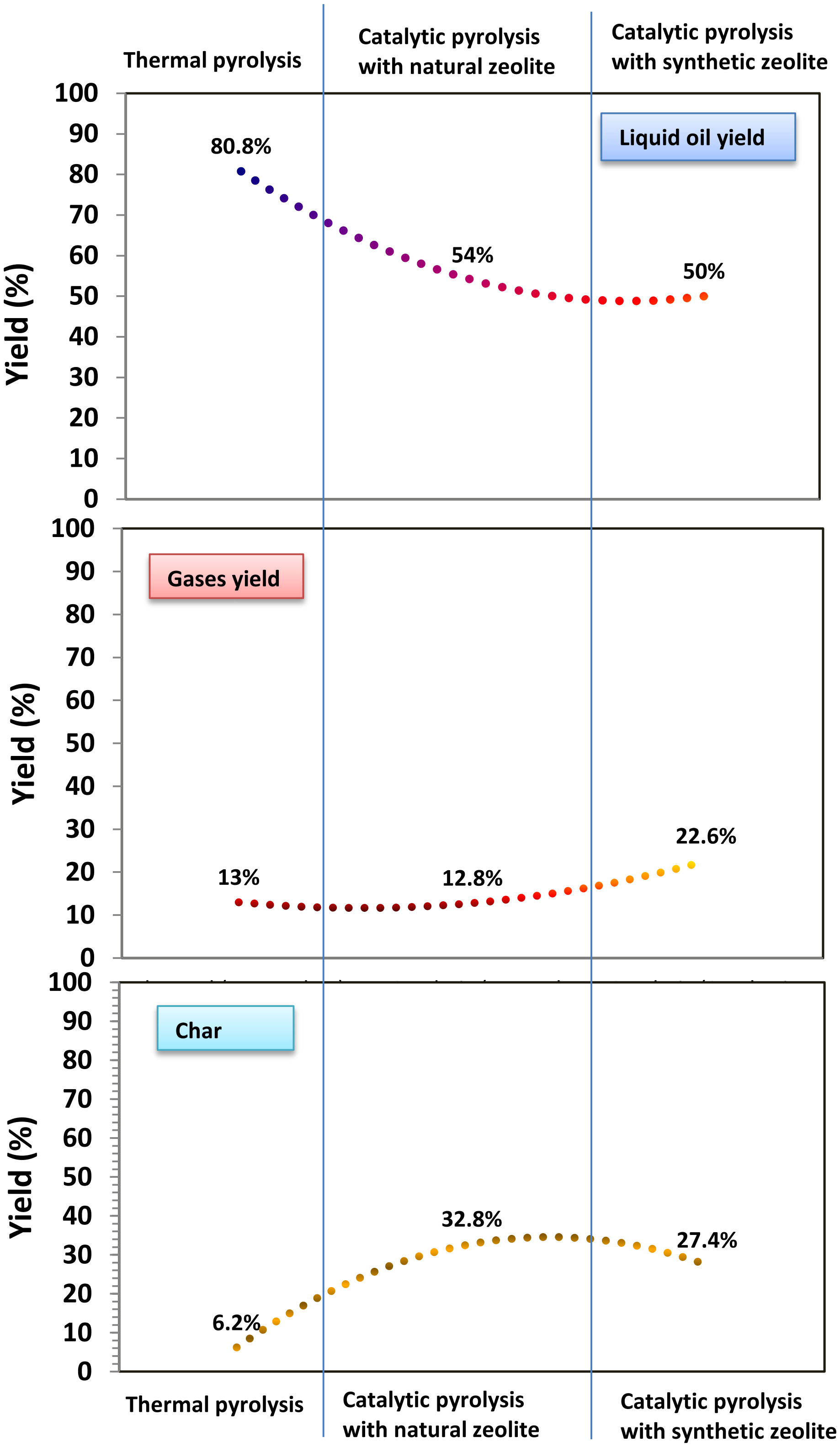


Figure 4. The yield of liquid oils, gases and char from thermal and catalytic pyrolysis with natural and synthetic zeolite.

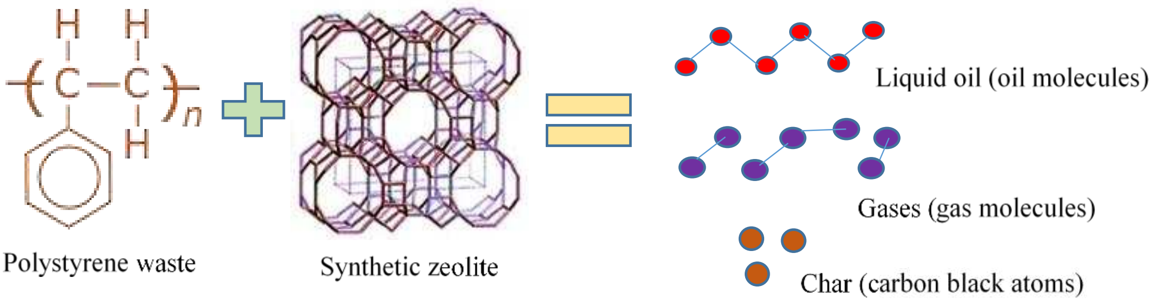
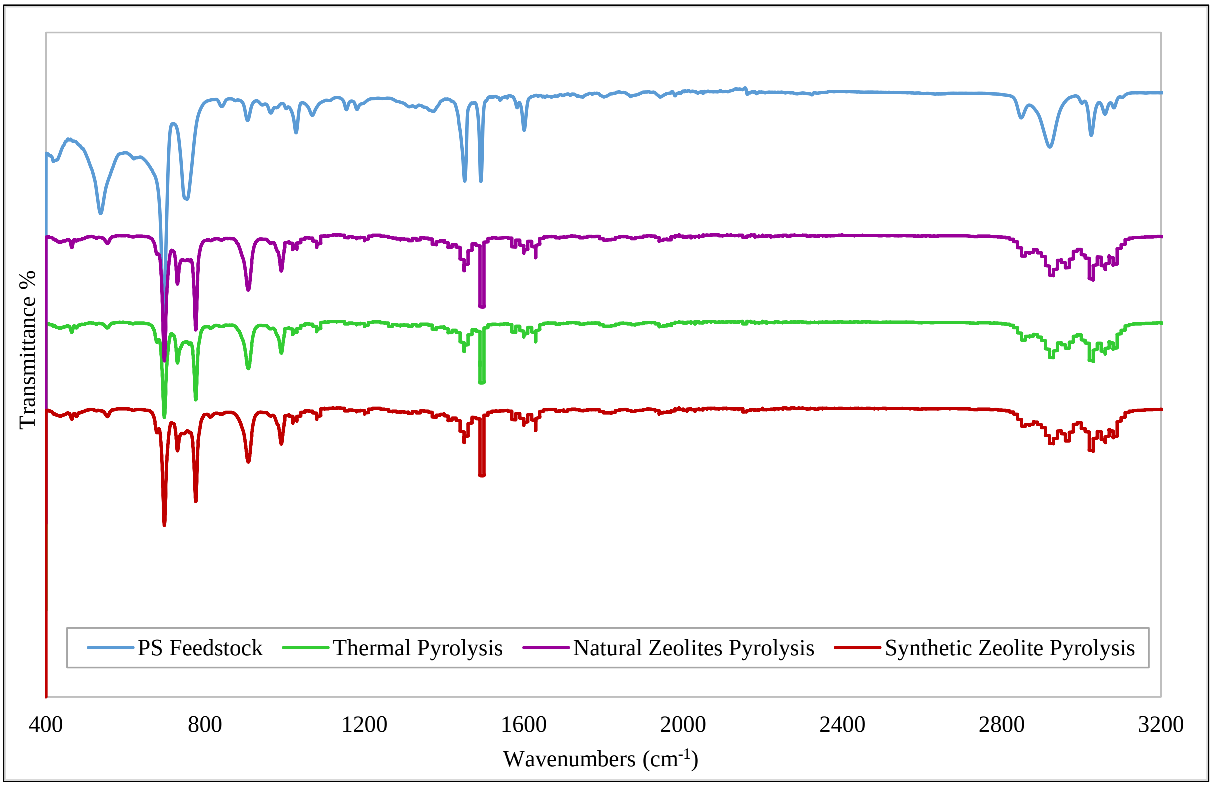


Figure 5. Reaction of polystyrene plastic waste with synthetic zeolite



Frequency cm^{-1}	Bond	Functional group
3020, 3030, 3070	=C-H stretch	Aromatics
2850, 2920, 2940	C-H stretch	Alkanes
1450, 1490	C-C stretch (in-ring)	Aromatics
905, 989	=C-H bend	Alkenes
697, 775	C-H “oop”	Aromatics
533.71	C-Br stretch	Alkyl halides

Figure 6. FT-IR spectrum of PS plastic raw material and thermal and catalytic pyrolysis liquid oils.

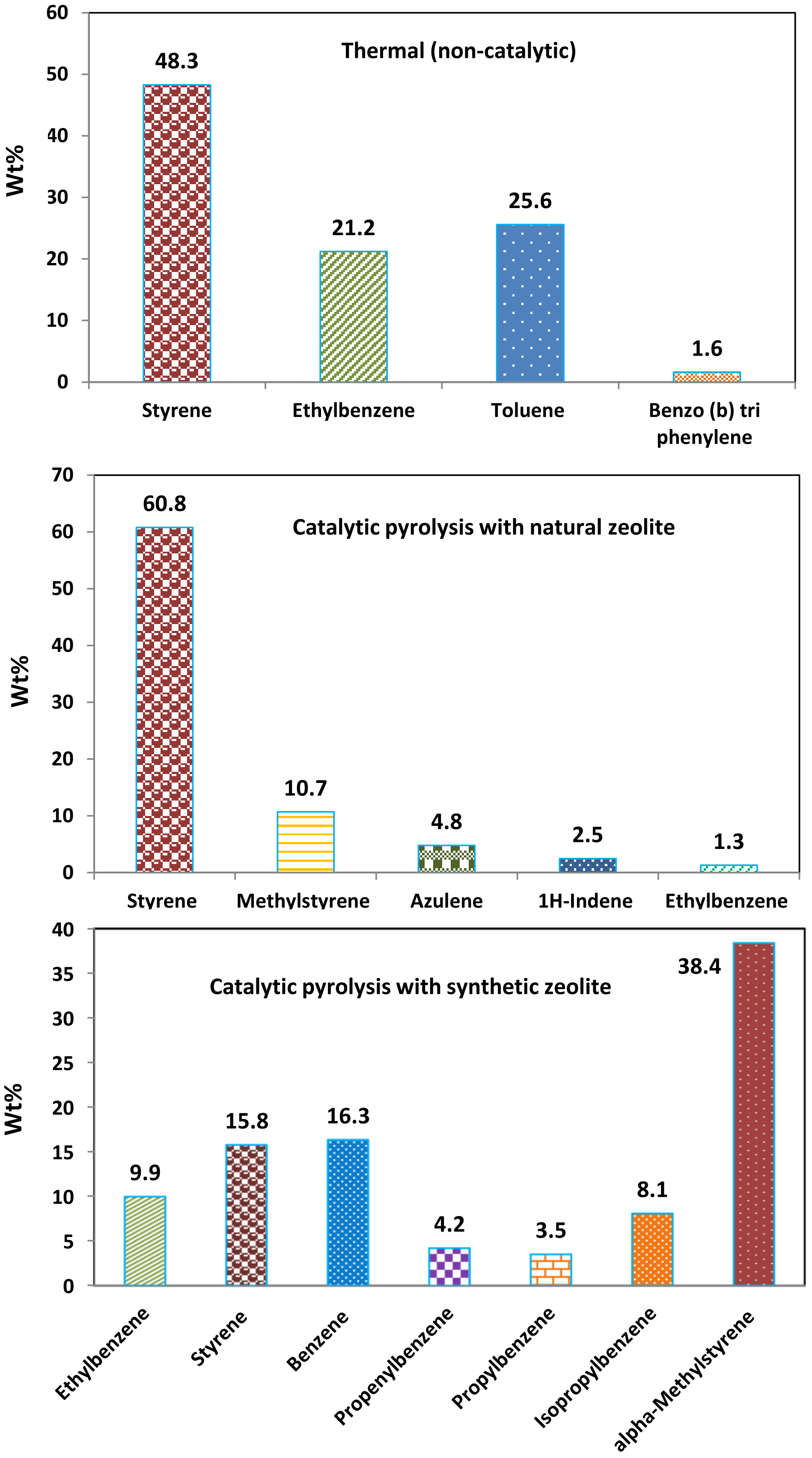


Figure 7. GC-MS analysis showing the effect of thermal and catalytic pyrolysis on liquid oil

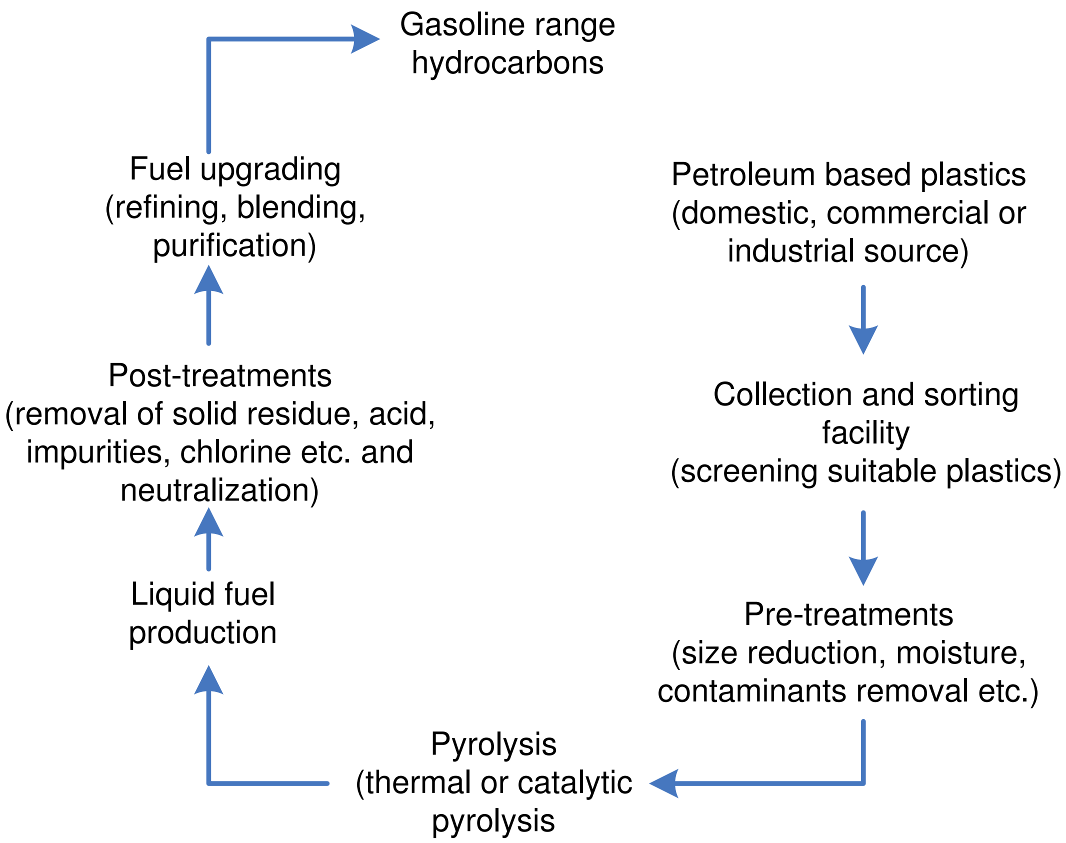


Figure 8. Recovery of petroleum based plastics into gasoline range hydrocarbons

Table 1. Technical and economical comparison of pyrolysis with others WTE technologies (Ouda et al., 2016a, Nizami et al., 2015c; Sadef et al., 2016; Rahmanian et al., 2015; Eqani et al., 2016; Munir et al., 2016)

WTE technologies	Capital cost/ ton/year	Net operational cost /ton	Merits	Limitations
Incineration	$14.5-$22	$1.5-$2.5	- Up to 80% of volume reduction - Up to 70% of mass reduction - Large amounts of waste can be treated - Fast treatment	- Air and water pollution - Carcinogenic chemical (dioxins) release - Public opposition - Produce solid waste (slag)
Pyrolysis	$17-$25	$2-$3	- Up to 80% energy recovery from waste - Reduced land requirement - High calorific value products - Liquid products easily separated from vapor phase - Up to 50-90% reduction in MSW volume	- Lower liquid products yields - Moisture produced from organic matter - Coke formation from liquid products - By-products cleaning - Corrosion of pyrolysis metal tubes
Plasma arc gasification	$19.5-$30	$2.5-$4	- No GHG emissions - All waste types can be treated - Easy technology expansion	- Higher energy consumption - High capital and operating cost
Refuse derived fuel (RDF)	$7.5-$11.3	$0.3-$0.6	- Stabilized waste - Reduced waste volume - RDF pellets having high calorific values	- Air pollution by RDF fuel - Ash formation - Land requirement
Anaerobic digestion (AD)	$0.1-$0.14	Minimal	- Lower solid produced - High rate anaerobic composting with energy - Nutrient rich digestate as an organic fertilizer - Cost effective technology	- Impurities - Not suitable at larger scale - Vulnerability to overloads and shocks - Space requirement

Table 2. Comparison of thermal and catalytic pyrolysis and their impacts on fuel characteristics

	Thermal pyrolysis	Catalytic pyrolysis	Impact on fuel
Classification	Classification is simple	Technology classification is unclear	Poor market acceptance
Temperature	High temperature demand leads to production of some diolefins	Decomposition of feedstock at low temperature	Effect fuel cost on product selectivity
Reaction time	High reaction time	Low reaction time is required	Effect on fuel cost
Gas formation	Increase production of CH_4 and C_2H_6	Increase the concentration of C_3 and C_4 hydrocarbons	Effect the quantity and quality of gas production
Solid residue	High solid residue production	Less solid residue production	Effect the quality and quantity of oil
Impurities	High impurities in the form of S, N, P, and acid	Impurities removed via adsorption	Effect on the quality of liquid oil
Aromaticity	Less aromatic hydrocarbon formation	High aromatic hydrocarbon formation	Aromatic cyclization
Paraffins formation	Less formation of paraffin	Paraffin production via hydrogen transfer	Effect on the gasoline selectivity
Reactivity	Less reactivity	More reactive especially for larger molecules	Effect on radical formation
Distribution of molecular weight	Large distribution of hydrocarbon with less short chain hydrocarbon	High production of short chain hydrocarbons	Effect on gasoline selectivity

Table 3. Pyrolysis reactor features

Heating tank (height)	360 mm
Heating tank (diameter)	310 mm
Catalytic chamber (height)	200 mm
Catalytic chamber (diameter)	165 mm
Reactor (total capacity)	20 L
Catalytic chamber (total capacity)	1 L
Condenser (length)	860 mm
Condenser (diameter)	147 mm
Temperature (maximum)	600 ℃

Table 4. Pyrolysis products yield and liquid oil composition of thermal and catalytic pyrolysis

Pyrolysis type	Pyrolysis products (%)			Liquid oil
	Liquid oil	Gases	Char	(Composition %)
Thermal pyrolysis	80.8	13	6.2	• Styrene (48.3) • Ethylbenzene (21.2) • Toluene (25.6) • Benzo (b) tri phenylene (1.6)
Catalytic pyrolysis (natural zeolite)	54	12.8	32.8	• Styrene (60.8) • Methylstyrene (10.7) • Azulene (4.8) • 1H-Indene (2.5) • Ethylbenzene (1.3)
Catalytic pyrolysis (synthetic zeolite)	50	22.6	27.4	• Ethylbenzene (9.9) • Styrene (15.8) • Benzene (16.3) • Propenylbenzene (4.2) • Propylbenzene (3.5) • Isopropylbenzene (8.1) • Alpha-Methylstyrene (38.4)

Table 5. Higher heating value (HHV) in MJ/kg of the feedstock and produced liquid oil and char

Feedstock (PS plastic)	Thermal pyrolysis		Catalytic pyrolysis			
			Natural zeolite		Synthetic zeolite	
	Liquid	Char	Liquid	Char	Liquid	Char
39.3	41.6	20.1	41.7	11.1	40.6	9.7

Table 6: Comparison of present study liquid oil with conventional diesel

Parameters	Our results	Conventional diesel	Reference
Dynamic viscosity (mPa.s)	1.8	1-4.1	Wongkhorsub and Chindaprasert, 2013
Density@15 °C (g/cm^3)	0.9	0.8-0.9	Syamsiro et al., 2014
Kinematic viscosity @40 °C (cSt)	1.9	2.0-5.0	Syamsiro et al., 2014
Pour point (°C)	-60	Max 18	Syamsiro et al., 2014
Flash point (°C)	30.2	Min 55-60	Syamsiro et al., 2014

Table 7. Heating value of different fuel types according to their hydrocarbon chains (Lee et al., 2015).

Fuel type	Hydrocarbons	HHV (MJ/kg)
LPG	C_3 - C_4	46.1
Petrol	C_4 - C_{12}	44.0
Kerosene	C_{12} - C_{15}	43.4
Diesel	C_{12} - C_{24}	43.0
Heavy fuel oil	C_{12} - C_{70}	41.1