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Effect of Advanced Catalysts on Tire Waste Pyrolysis Oil

R. Miandad[1,2], M.A. Barakat[1,3], M. Rehan[2], A.S. Aburiazaiza[1], J. Gardy[4], A.S. Nizami[2,*]

[1]Department of Environmental Sciences, Faculty of Meteorology, Environment and Arid Land Agriculture, King Abdulaziz University, Jeddah, Saudi Arabia
[2]Centre of Excellence in Environmental Studies (CEES), King Abdulaziz University, Jeddah, Saudi Arabia
[3]Central Metallurgical R & D Institute, Helwan 11421, Cairo, Egypt
[4]School of Chemical and Process Engineering, University of Leeds, Leeds, LS2 9JT, UK

Graphical abstract

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Highlights

- Catalytic and non-catalytic pyrolysis of tire waste was carried out at pilot-scale
- Non-catalytic pyrolysis produced highest liquid oil as compared to catalytic pyrolysis
- Natural zeolite, zeolite (H-SDUSY), Al_2O_3 and $Ca(OH)_2$ catalysts were used
- Use of various catalysts improved the quality of liquid oil
- Oil from both processes mainly contained aromatic with some aliphatic compounds

Abstract

This study aims to examine the effect of various advanced catalysts on tire waste pyrolysis oil using a small pilot-scale pyrolysis reactor with a capacity of 20 L. The catalytic pyrolysis with activated alumina catalyst produced maximum liquid oil (32 wt.%) followed by activated calcium hydroxide (26 wt.%), natural zeolite (22 wt.%) and synthetic zeolite (20 wt.%) catalysts, whereas liquid oil yield of 40% was obtained without catalyst. The gas chromatography-mass spectrometry results confirmed the pyrolysis liquid oil produced without catalyst consist of up to 93.3% of mixed aromatic compounds. The use of catalysts decreased the concentration of aromatic compounds in liquid oil down to 60.9% with activated calcium hydroxide, 71.0% with natural zeolite, 84.6% with activated alumina, except for synthetic zeolite producing 93.7% aromatic compounds. The Fourier-transform infrared spectroscopy data revealed that the mixture of aromatic and aliphatic hydrocarbon compounds were found in all liquid oil samples, which further confirmed the gas chromatography results. The characteristics of pyrolysis liquid oil had viscosity (1.9 cSt), density (0.9 g/cm^3), pour point (-2 °C) and flash point (27 °C), similar to conventional diesel. The liquid oil had higher heating values, key feature of a fuel, in the range of 42-43.5 MJ/kg that is same to conventional diesel (42.7 MJ/kg). However, liquid oil requires post-treatments, including refining and blending with conventional diesel to be used as a transport fuel, source of energy and value-added chemicals.

Keywords: Tire waste; Pyrolysis; Catalyst; Liquid oil; Transport fuel

LIST OF ACRONYMS AND ABBREVIATIONS
BET   Brunauer-Emmett-Teller
PBM   Probability Based Matching
CO   Carbon Monoxide
FT-IR   Fourier Transform Infrared Spectroscopy
GC-MS   Gas Chromatography Coupled with Mass
             Spectrophotometry
HC's   Hydrocarbons
HHV   High Heating Value
KSA   Kingdom of Saudi Arabia
NOx   Nitrogen Oxides
NR   Natural Rubber
O_2 Oxygen
SBR   Styrene - butadiene Rubber
SO_2 Sulfur Dioxide
SOx   Sulfur Oxides
SR   Synthetic Rubber
TGA   Thermogravimetric Analyzer
TIC   Total Ion Chromatogram
USA   United State of America
WTE   Waste-to-Energy
XRD   X-Ray Diffraction

1. Introduction

A sustainable resource recovery of tire waste is one of the critical environmental issues in most of the developing countries (Demirbas et al., 2015). Around 1.0 billion tires are manufactured every year for use in trucks, cars, bicycles, and other transport fleets. A similar number is discarded as tire waste and mainly disposed to the dumpsites or landfills without material or energy recovery (Frigo et al., 2014). Tire waste has a life span of 80 to 100 years in a landfill because of its thermostat polymer composition that neither melts nor separated into its chemical components (Martínez et al., 2013). In addition, they are bulky, and their storage in landfills cause fire outbreaks or toxicity due to trapping of hazardous gasses or habitat of diseases causing vector, flies, and rodents (Sadef et al., 2016; Frigo et al., 2014).

The combustion of tire waste is mostly carried out in cement kiln factories due to its high-energy contents (Conesa et al., 2008). Although the burning process produces energy, but it also causes air and waterborne pollution with detrimental effects on the environment and public health (Miandad et al., 2017a, 2016a; Khan et al., 2017). In addition, since the 1970s increase in the

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concentration of Zn particles in the environment is linked with the combustion of tire rubber (Buekens, 1977). Carrasco et al. (1998) reported an increase in the emissions of sulfur dioxide (SO_2) and carbon monoxide (CO) up to 30 and 47% from a cement plant using coal (80%) and tire waste (20%) respectively. Moreover, open burning of the tire waste increases the mutagenic factors by up to 3-4 times as compared to the use of coal, wood, or oil utility boiler (DeMarini et al., 1994). The methods that are in practice for the management and recycling of tire waste include mechanical grinding, rubber reclamation, tire retreading, combustion, and pyrolysis (Ayanoglu and Yumrutas, 2016; Nizami et al., 2017a,b).

Pyrolysis is a thermochemical tertiary recycling technique in which organic polymers are converted into liquid oil at elevated temperatures (400-600 °C) in the absence of oxygen (O_2) (Miandad et al., 2016b, 2017b). The pyrolysis products of tire waste include liquid oil, char, gasses and steel (Ayanoglu and Yumrutas, 2016), which can be used in several environmental and energy-related applications (Ouda et al., 2016). For instance, liquid oil that is a complex mixture of aromatic and aliphatic compounds can be used for energy generation or as feedstock in petrochemical industries (Rehan et al., 2016a). Produced gasses have potential to be used as an energy carrier, while char can be upgraded as activated carbon for use as pollutant adsorbent or employed in the regeneration of tires (Miandad et al., 2016a, 2017b, 2018).

Pyrolysis of tire waste has been carried out using different reactors, including fixed bed reactors (de Marco et al., 2001), thermogravimetric analysis (Teng et al., 1998), spouted beds (Lopez et al., 2009), fluidized bed pyrolysis (Kaminsky and Mennerich, 2001), vacuum pyrolysis (Roy et al., 1995), and rotary kiln (Li et al., 2004). The primary objective of these studies was to investigate the effect of various process variables such as temperature, reaction time, feedstock size and type, and scale of the reactor on pyrolysis products and how to increase the quantity of produced liquid oil, but not the quality of liquid oil (Kraiem et al., 2016; Wu et al., 2016; Wan et al., 2014). For example, Cunliffe et al. (1998) concluded that increase in temperature from 450 to 600 °C decreased the liquid oil yield from tire waste pyrolysis. Whereas, Kaminsky and Sinn (1980) reported that oil yield from tire waste pyrolysis was decreased when the temperature was increased from 640 to 840 °C. However, Williams et al. (1990) reported an increase in liquid oil yield with an increase in temperature from 300 to 720 °C. Moreover, the yield and quality of

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pyrolysis liquid oil not only depend on the tire types but also on the type and conditions of pyrolysis process including catalytic and non-catalytic pyrolysis coupled with the type of catalyst used (Umeki et al., 2016). The catalytic pyrolysis of tire waste was also carried out by several researchers (Shah et al., 2009; İlkılıç and Aydın, 2011; Islam et al., 2010; Frigo et al., 2014; Umeki et al., 2016; Boxiong et al., 2007; Zhang et al., 2008). For instance, Boxiong et al. (2007) carried out the catalytic pyrolysis of tire waste to examine the effect of zeolite catalysts and temperature on pyrolysis yield. Zhang et al. (2008) reported that the use of basic additives and catalysts decreased the reaction temperature.

The most catalytic pyrolysis studies, similar to above mentioned non-catalytic pyrolysis studies published on tire waste, were focused on pyrolysis products yield and oil composition analysis through GC-MS. In addition, the quality of liquid oil through characteristics such as dynamic and kinematic viscosity, density, high heating value (HHV), and flash, freezing and pour points is less studied (Miandad et al., 2016a,b; Nizami et al., 2016a,b; Labaki and Jeguirim, 2016; Umeki et al., 2016), which has been carried out in this study. Furthermore, no comparative study has been published on comparing the effect of catalytic and non-catalytic pyrolysis for the tire waste using natural zeolite and other synthetic catalysts in a pilot-scale reactor, as employed in this study.

This study aims to examine the effect of various advanced catalysts on tire waste pyrolysis oil, including natural zeolite, zeolite (H-SDUSY), activated alumina (Al_2O_3), and activated calcium hydroxide ($Ca(OH)_2$) catalysts using a small pilot scale pyrolysis reactor. A special focus has been given to the use of natural zeolite, as being a naturally available cheap resource, to examine its potential role in catalytic pyrolysis of tire waste. Furthermore, the produced liquid oil was characterized by its chemical and physical characteristics to valorize its potential applications.

2. Materials and Methods

2.1 Feedstock preparation and reactor startup

The feedstock (tire waste) was collected from landfill site of Jeddah city, Kingdom of Saudi Arabia (KSA). The collected sample was crushed into granules (2-3.5 mm) to get a

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homogeneous mixture. Catalytic and non-catalytic pyrolysis of tire waste was carried out using a pilot scale reactor with different catalysts such as natural zeolite, zeolite (H-SDUSY), Al_2O_3 and $Ca(OH)_2$. The catalyst to feedstock ratio used in all experiments was fixed to 1:10 on a weight basis. The synthetic catalysts, including zeolite (H-SDUSY), Al_2O_3, and $Ca(OH)_2$ was purchased from Zeolyst International, USA and used as received without any further modification. The zeolite (H-SDUSY) and Al_2O_3 were in the form of 2 cm long pellets. The natural zeolite was collected from Harrat Shama located at the north-south of Jeddah, KSA (Nizami et al., 2016a; Rehan et al., 2017). The collected sample was crushed into a fine powder used as it is without any further modification and treatment.

The pyrolysis reactor was commissioned and used for the conversion of the tire waste into liquid oil, char, and gasses (Figure 1). The reactor is made up of stainless steel covered with a loop of an electric heater to achieve the desired temperatures with maximum 600 °C (Table 1). Organic vapors produced within the reactor at high temperatures condensed into liquid oil in a tube type condenser with a length of 860 mm. A water circulating chiller using ACDelco classic coolant with a flow rate of 30 L/min was used to achieve the maximum condensation of produced organic vapors into liquid oil for optimum liquid oil yields. The condensed organic vapors, in the form of liquid oil, were finally collected from the oil collecting assembly at the bottom of the system. While the uncondensed products coming out from the same liquid oil pipe in the form of gasses were exhausted outside (Miandad et al., 2016b, 2017b). The collected pyrolysis liquid oil was further analyzed for its yield, quality, and potential applications.

2.2 Experimental setup and scheme

In all catalytic and non-catalytic pyrolysis experiments, 1000 g of tire waste was used in the reactor as a feedstock. In each run of catalytic pyrolysis, 100 g of catalyst was added to the feedstock, keeping catalyst to feedstock ratio of 1:10. The reactor temperature was increased using heating rate of 10 °C/min from room temperature to an optimum temperature of 450 °C. The pyrolysis reaction was then held at 450 °C for 75 min of optimum reaction time for all the experiments. The determination of these optimum conditions (450 °C and 75 min) was examined by Thermogravimetric analysis (TGA) of the used tires under controlled conditions together with safety considerations of using temperatures well below the maximum achievable temperature of

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the pyrolysis process. These determinations of optimum temperature and retention times on the same pyrolysis reactor along with an explanation of reactor controlled conditions are previously published by same authors (Miandad et al., 2016b, 2017b). The organic vapors produced from feedstock in the heating reactor were condensed into liquid oil at temperatures below 10 °C in the condenser unit and were collected from oil collection assembly (Figure 1). The undecomposed feedstock such as char was collected from the reactor at the end of each experiment after allowing the system to cool down to room temperature. The pyrolysis products such as liquid oil and char were weighed for mass balance analysis at the end of each experiment. The percentage of produced gasses was calculated by deducting the weights of liquid oil and char from input feedstock weight.

2.3 Analytical methods

TGA (Mettler Toledo TGA/SDTA851) was used to examine the thermal decomposition trends of tire waste feedstock. In TGA, 10 µg of tire waste sample was heated from 25 to 900 °C with a heating rate of 10 °C per min under nitrogen flow at a constant rate of 50 ml/min. Proximate analysis of tire waste was carried out to determine its moisture, volatile, fixed carbon and ash contents. The procedure of the proximate analysis was based on the standard ASTM D3172 method. The chemical composition of produced pyrolysis liquid oil was characterized by gas chromatography coupled with mass spectrophotometry (GC-MS) and Fourier transform infrared spectroscopy (FT-IR) and the high heating value (HHV) by bomb calorimeter by using the standards ASTM protocols. FT-IR Perkin Elmer's was used to examine the presence of the functional groups in feedstock as well as in the produced pyrolysis liquid oil. A minimum of 32 scans was made at an average signal of IR with a resolution of 4 cm^{-1} in the ranges of 500-4000 cm^{-1}. Bomb calorimeter (Parr 6200 Calorimeter) was used to assess the HHV of liquid oils by following the ASTM D-240 method.

The pyrolysis liquid oils were also analyzed by GC-MS using a Hewlett-Packard HP 7890 with a 5975 quadrupole detector. The length and diameter of GC capillary columns were 30 m and 0.25 mm, respectively, which was coated with a film of 5% phenyl-methypolysiloxane (HP-5) having 0.25 µm thickness. Helium was used as a carrier gas for GC/MS system at a constant flow rate of 1 mL per minute. The GC oven initial temperature was set to 50 °C for a time interval of 2 min

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and then increased gradually to 5 °C per min to 290 °C with an isothermal held for 10 min. The splitless injection with a split ratio of 2:1 was applied at 290°C. The ion source, and transfer line temperatures were kept at 230 °C and 300 °C, respectively. The data was attained in the full-scan mode between m/z 33-533, and a solvent interval of 3 min was used. Chromatographic peaks were recognized using NIST08s mass spectral data library based on their retention times using standard compounds. The peak identification was carried out by probability-based matching (PBM). Peaks that matched 90% to specific compounds were considered valid, and the obtained results were in agreement with the relevant published studies on pyrolysis of tire waste (Labaki and Jeguirim, 2016). Only the compounds above 3 wt.% were used, and compounds below 3 wt.% were ignored for data clarity and significance. Natural zeolite was crushed into a fine powder before its characterization. Powder X-ray diffraction (Bruker D8, XRD) operated with Cu radiation at 40 kV, and 40 mA was used to analyze the purity and crystal structure of the sample. The scanning electron microscopy (SEM) of the sample was performed to study the particle size, morphology and elemental composition of natural zeolite.

3. Results and Discussion

3.1 Feedstock proximate and TGA analysis

The proximate analysis of feedstock was carried out to find out the potential of feedstock for the pyrolysis process. It converts the feedstock into volatile and non-volatile components. Volatile components include liquid oil and gasses, while moisture, fixed carbon, and ash are the non-volatile or inorganic components (Kumaravel et al., 2016). The proximate analysis of tire waste feedstock found 83.9% volatile matter, 7.3% fixed carbon, 7.6% ash and 1.2% moisture contents (Table 2). These results were in close agreement with other studies, which reported volatile matter ranging from 63-76.1%, fixed carbon 19.4-32%, ash 4.2-5.4% and moisture 0.3-1.4% (Table 2) (Choi et al., 2016; Naim et al., 2016; Li et al., 2016; Ucar et al., 2005; Zhang et al., 2008). The differences in the proximate analysis results affect the products yield of pyrolysis process (Martínez et al., 2013). The high volatile matter of 83.9% found from the proximate analysis confirm tire waste as a potential feedstock for the pyrolysis process.

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The TGA of tire waste was also carried out to determine the optimum temperature for the maximum decomposition of the tire waste (Figure 4). Figure 4 showed two-step decomposition of tire waste. The initial decomposition started from 248 to 330 °C that showed the presence and loss of some volatiles impurities such as plasticizers, and oil along with some additives. However, it was followed by rapid second stage decomposition of the tire waste that could be considered as active pyrolysis zone. It occurred between 330 to 450 °C, and maximum decomposition was achieved at this stage that was due to rapid decomposition and continuous cracking of the primary compounds of tire waste such as synthetic rubber (SR), styrene-butadiene rubber (SBR) and natural rubber (NR) (Juma et al., 2007). Pradhan and Singh (2011) reported maximum decomposition of waste bicycle tires during pyrolysis in the semi-batch reactor at a similar temperature. Afterward, a further 15 - 20% decomposition was also observed in between 450 and 900 °C. All the pyrolysis experiments were carried out at 450°C in this study due to safety considerations, even though the pilot-scale pyrolysis reactor employed could achieve a maximum temperature of 600 °C that would otherwise improve the products yield. Nevertheless, more than 60% of decomposition was achieved at this temperature (Figure 4). Williams and Besler (1995) also reported similar results at the same temperature range (450 °C) for the pyrolysis of tire waste.

3.2 Characterization of natural zeolite catalyst

We conducted characterization of natural zeolite to study the various catalytic features and results were published recently (Nizami et al., 2016a). The ICDD-PDF database was used as a reference data file for XRD pattern indexing. The XRD peaks showed that alumina silicate was dominated together with the presence of some other impurities such as Fe, Mg, Na, K, and so on. Some of the obtained peaks were overlapping, revealing possible combinations of compounds, hence the analysis is qualitative instead of quantitative (Figure 2). The detailed quantitative analysis of amounts of different species present in the natural zeolite sample and to determine the zeolite family will be conducted in the future research through Rietveld analysis. However, the clear, and sharp XRD peaks confirmed that natural zeolite had highly crystalline structure.

SEM data showed that natural zeolite particles had bi-modal size and morphology distributions. The smaller spherical particles were found in size range of 50-100 nm, whereas some larger irregular shaped particles were found in size range of around 200-500 nm (Figure 3). The particle

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size and morphology characteristics are not the intrinsic features of the natural zeolite material itself but mainly depend on the milling process used to grind the particles. The smaller particles have larger surface area and show improved catalytic performance. However, the size and morphology effect of natural zeolite catalyst on pyrolytic products yields and quality could form an interesting future study. Moreover, our previous TGA study also showed that natural zeolite didn't have any weight loss up to a very high temperature of 900 °C that proves its high stability at maximum temperature. Overall these features of natural zeolite found in KSA make it suitable to be used as a catalyst in WTE applications such as pyrolysis process (Nizami et al., 2016a).

3.3 Effect of catalysts on pyrolysis products yield

Tire waste was converted into liquid oil and value-added products such as char and gasses through catalytic and non-catalytic pyrolysis (Figure 5). Maximum liquid oil yield (40%) was obtained from non-catalytic pyrolysis of tire waste with the production of 40% char and 20% gasses. Whereas the use of different catalysts overall decreased the liquid oil yields with mostly increased yields of char and gasses, except in the case of catalytic pyrolysis processes using Al_2O_3 and $Ca(OH)_2$ catalysts respectively. In catalytic pyrolysis processes, the decrease in the liquid yield and increase in the gasses and char yields was mainly attributed to various characteristics of a catalyst that controls the formation and transformation of hydrocarbon molecules through selectivity or adsorption mechanisms (Saeng-arayakul and Jitkarnka, 2013). Catalyst pyrolysis of tire waste was carried out with the different catalyst-feedstock ratio. However, Ateş et al. (2005) reported that 10% catalyst-tire ratio produced maximum liquid oil.

Several studies reported similar results to our study for the non-catalytic pyrolysis of tire waste. Roy et al. (1990) carried out non-catalytic pyrolysis of tire waste at 450 °C and reported 59 wt.% liquid yield with 5 and 33.8 wt.% gasses and char yields respectively. Qu et al. (2006) carried out pyrolysis of tire waste at 430 °C and reported 33.3, 17.7 and 49 wt.% of liquid oil, gasses, and char yields respectively. However non-catalytic pyrolysis carried out at a much higher temperature of 890 °C decreased the liquid yield to only 5 wt.% with a significantly high yield of 73 wt.% for gasses along with char yield of 20 wt.% (Zabaniotou and Stavropoulos, 2003). According to Lopez et al. (2009), an increase in gasses at higher temperatures above a certain

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point was due to the increase in thermal cracking, which resulted in lighter carbon chain compounds being released as gasses.

In catalytic pyrolysis processes, maximum liquid oil yield was obtained from the process with Al_2O_3 (32%) catalyst, while the minimum yield of liquid oil was produced from zeolite (H-SDUSY) (20%) followed by natural zeolite (22%) and $Ca(OH)_2$ (26%) catalysts. Shah et al. (2009) and Shah and Jan (2014, 2015) also reported similar results for catalytic pyrolysis of tire waste with Al_2O_3 that produced maximum liquid oil along with the high amount of gasses. Higher liquid oil yields by using the Al_2O_3 catalyst as compared to other catalysts was due to its mild acidity (Saeng-arayakul and Jitkarnka, 2013). However, use of zeolite catalysts for tire waste pyrolysis yielded lower liquid oil with higher gasses and char production due to their higher surface activity and large pore size (Williams and Brindle, 2003). William and Brindle (2002) reported that use of Y- zeolite (CBV-400) and zeolite ZSM-5 catalysts in catalytic pyrolysis of tire waste with 1:5 catalyst to feedstock ratios significantly decreased the liquid oil yields with an increase in the gasses yield.

Ayanoglu and Yumrutas (2016) carried out non-catalytic pyrolysis of tire waste in rotary kiln reactor and obtained 37% liquid oil yield, together with 8% wax, 20% gasses and 35% char. Later on, they distilled heavy oil and wax in a batch reactor with calcium oxide (CaO) and natural zeolite to get the desired products. Saeng-arayakul and Jitkarnka, (2013) used $NiMoS/Al_2O_3$ catalyst for the catalytic pyrolysis of tire waste. All of these studies concluded that use of catalyst decreased the liquid oil yields due to the catalysts characteristics that enhanced decomposition process of tires into lighter products (gasses). Moreover, catalytic pyrolysis of tire waste with $Ca(OH)_2$ catalyst produced maximum char (55.6%) with less amounts of liquid oil (26%) and gasses (18.4%). High deposition of char on the surface of the catalyst was due to its low surface area, less acidic nature and macro-porous structure that enhanced the deposition of char and reduced the catalytic activity of the catalyst. Overall char production was high in catalytic and non-catalytic pyrolysis of tire waste due to the presence of carbon black in the feedstock of tire waste (Alsaleh and Sattler, 2014).

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3.4 Effect of Catalysts on liquid oil quality

Catalytic and non-catalytic pyrolysis of tire waste showed the presence of mainly aromatic with some aliphatic compounds in all of the produced liquid oils. The pyrolysis liquid oil produced without catalyst consist of up to 93.3% of mixed aromatic compounds as confirmed by the GC-MS results (Figure 6). The use of catalysts decreased the concentration of aromatic compounds in liquid oil down to 60.9% with $Ca(OH)_2$, 71.0% with natural zeolite, 84.6% with Al_2O_3, except for synthetic zeolite (H-SDUSY) that produced liquid oil consisted of 93.7% aromatic compounds. Table 3 shows the single and multiple ring aromatic hydrocarbon compounds found in pyrolysis liquid oil without catalyst and with using various catalysts. The use of catalysts not only decreased the overall aromatic hydrocarbons but also formed multiple ring aromatic compounds, except for synthetic zeolite (H-SDUSY). The liquid oil produced with Al_2O_3 catalyst consisted of the maximum amount of 35.5% multiple ring aromatics as compared to 32.5 and 7.4% multiple ring aromatics from natural zeolite and $Ca(OH)_2$ catalysts respectively. This shows that highest conversion of single to multiple ring aromatics of 45.8% was obtained by natural zeolite catalyst followed by 42.0% and 12.2% using Al_2O_3 and $Ca(OH)_2$ catalysts respectively.

The aromatics hydrocarbon compounds found in liquid oil without catalyst were all single ring compounds including α-methylstyrene (32.5%), styrene (27.1%), benzene (12.8%), ethylbenzene (16.7%), benzene, 2-propenyl (4.2%) (Figure 6). Roy et al. (1990 and 1999) carried out the non-catalytic pyrolysis of tire waste in vacuum reactor and reported the similar GC-MS results for the produced liquid oil. Similarly the liquid oil produced using synthetic zeolite (H-SDUSY) catalyst produced only single ring aromatic hydrocarbon compounds including styrene (19.7%), benzene, 1,4-diethyl (19.4%), o-xylene (16.5%), ethylbenzene (10.4%), benzene, 1,2,4-trimethyl (9.6%), α-methylstyrene (7%), benzene, 1-ethyl-3-methyl (6.1%), benzene, 1-ethenyl-2-methyl (5.1%) (Figure 6). Different researchers carried out catalytic pyrolysis of tire waste with different types of zeolite catalysts and reported similar results for liquid oil composition (Williams and Brindle, 2003; Qu et al., 2006; Boxiong et al., 2007). Liquid oil produced from catalytic pyrolysis of synthetic zeolites produced mostly the aromatic compounds due to their large surface area and high catalytic activity (Williams and Brindle, 2003). San Miguel et al. (2006) carried out catalytic pyrolysis of tire waste with three different types of zeolite catalysts along with non-

zeolite catalysts. They concluded that all types of zeolite catalysts favored the production of aromatics compounds during the tire waste catalytic pyrolysis.

The three other catalysts, natural zeolite, Al_2O_3, and $Ca(OH)_2$, not only reduced the overall aromatic hydrocarbon contents in liquid oil but also formed a mixture of single and multiple ring aromatics compounds. The oil with natural zeolite catalyst contained single ring aromatic of styrene (14.9%), o-xylene (10.1%), ethylbenzene (5.1%), α-methylstyrene (4.5%), benzene 1,2,4-trimethyl (3.8%) and multiple ring aromatics of azulene (10.0%), naphthalene, 1-methyl (7.6%), naphthalene, 2-methyl (4.7%), 1H-indene (3.6%), phenanthrene (3.3%), 2-methylindene (3.2%) (Figure 6). The oil produced using Al_2O_3 catalyst contained single ring aromatics of tetracosamethyl-cyclododecasiloxane (23%), 1,2-benzenedicarboxylic acid (21.9%), 3,4-difluorobenzoic acid, dodecyl ester (4.2%) and multiple ring aromatics of phenol (17.1%), naphthalene, 1,8-dimethyl (5.6%), naphthalene, 1-methyl (5.3%), naphthalene, 2-ethenyl (4%), naphthalene, 1,4-dimethyl (3.6%) (Figure 6). Shah et al. (2009) also carried out pyrolysis of tire waste with activated alumina, and SiO_2 and reported similar results. Catalytic pyrolysis with Al_2O_3 produced a high concentration of polar hydrocarbons with less concentration of aliphatic compounds (Shah et al., 2009). A typical GC-MS chromatogram of produced liquid oil from catalytic pyrolysis of tire waste with Al_2O_3 is shown in Figure 7. The liquid oil produced using $Ca(OH)_2$ catalyst contained only one single aromatic compound of 1,2-benzenedicarboxylic acid, mono(2-ethylhexyl) ester (53.5%) and one multiple aromatic compound of phenol, 2,2'-methylenebis[6-(1,1-dimethylethyl)-4-methyl (7.3%) together with tetracosamethyl-cyclododecasiloxane (28.6%) (Figure 6). İlkılıç and Aydın. (2011) carried out pyrolysis of tire waste with $Ca(OH)_2$ and reported similar results. Moreover, use of $Ca(OH)_2$ improved the oil quality and decreased the concentration of sulfur (İlkılıç and Aydın, 2011).

FT-IR analysis was carried out to find out the presence of different functional groups in the produced liquid oils from catalytic and non-catalytic pyrolysis (Figure 8). The FT-IR analysis revealed many clear peaks ranges from 660 to 3000 cm^{-1} in the produced liquid oils from catalytic and non-catalytic pyrolysis. Overall mixture of aliphatic (alkanes, alkenes, aldehydes) and aromatic hydrocarbon compounds was found in all liquid oil samples, which further confirmed our GC-MS results. However, liquid oil from catalytic processes with synthetic and

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natural zeolite showed higher production of aromatics compounds that was clearly seen between the frequencies of 1400-1500 cm^{-1}. These FT-IR results were in agreement with the GC-MS results. Islam et al. (2010) reported the similar results for the liquid oil produced from catalytic and non-catalytic pyrolysis of tire waste.

Physical characterization of liquid oil produced from catalytic and non-catalytic pyrolysis was carried out and compared with conventional diesel and published studies on tire waste pyrolysis (Table 4). The fuel properties such as density, kinematic viscosity, HHV, flash point, and cold flow properties were critical to examine the quality of the liquid oil. Density is one of the important physical properties of any liquid fuel. The density of liquid oil from tire waste had a value of 0.9 g/cm^3 similar to other reported studies (Table 4). However, this value of density was slightly higher but comparable to the value of conventional diesel (0.8 g/cm^3) (Syamsiro et al., 2014). Viscosity is another key physical property of any liquid fuel. High viscosity results in a poor optimization that may lead to affect the engine start-up and reduces its performance. Furthermore, high viscous oil leads to reduced flow especially during the winter season with the fall of temperature. This may create problems in fuel injection in engine startup and vehicle running (Miandad et al., 2016b, 2017b). The produced liquid oil had a kinematic viscosity of 1.9 cSt that is in close agreement with other reported studies (Table 4). Ali et al. (2014) reported that the produced liquid oil of tire waste distilled with water and Fe catalyst had a kinematic viscosity of 0.9 cSt. However, some studies reported higher values such as Frigo et al. (2014) who reported 2.9 cSt, while Pradhan and Singh (2011) reported 5.3 cSt. The conventional diesel has a kinematic viscosity has a range between 2.0-5.0 cSt (Syamsiro et al., 2014).

Cold flow properties that include freezing and pour point are one of the essential characteristics of any fuel (Gardy et al., 2015, 2017). These fuel properties become more critical in countries having cold weather all year round. The produced liquid oil had a freezing point (-5 °C) and pour point (-2 °C). Islam et al. (2010) also reported similar value (-4 °C) for pour point of the tire waste liquid oil. The lower the pour and freezing point values the better the fuel will function, especially in cold weather. The higher pour and freezing points of fuel will lead to the formation of wax if left for an extended period of time, which will result in blockage of the fuel system and may cause problems in engine operations (Miandad et al., 2016b; Rehan et al., 2016b).

Furthermore, the produced liquid oil had a flash point value of 27 °C that is in line with reported studies on oil produced from tire waste (Table 4). The flash point of conventional diesel is higher (-55 to -60 °C) than pyrolysis liquid oil (Syamsiro et al., 2014). The lower flash point value of tire waste pyrolytic liquid oil is probably due to its higher aromatic contents and other compounds that are not present in conventional diesel. The flash point of any liquid fuel is beneficial for its storage and energy applications (Miandad et al., 2016b). The flash point of pyrolysis liquid oil can be further improved by further distillation and refining the oil as well as with blending it with diesel (Islam, 2010). The HHV of any fuel is also critical as it determines the amount of energy available in fuel for its performance in the engine and other applications. The HHV of liquid oil from non-catalytic pyrolysis was found to be 42.5 MJ/kg, whereas the HHV from catalytic pyrolysis were found to be 42.0, 43.5, 43.1 and 43.0 MJ/kg by using natural zeolite, zeolite (H-SDUSY), Al_2O_3 and $Ca(OH)_2$ catalysts respectively. The HHV of liquid oil produced by using synthetic catalysts were slightly higher than the HHV of liquid oil by natural zeolite. This indicates the synthetic catalysts results in more refined products than the natural zeolite due to their much higher purity, surface area, and pore volume. Nevertheless, the HHV for all liquid oils were higher than the HHV (37.3 MJ/kg) of tire waste feedstock as expected.

3.5 Potential applications of liquid oil and char

Liquid oils produced from catalytic and non-catalytic pyrolysis of tire waste contained a mixture of mostly aromatic with some aliphatic compounds and showed similar physical characteristics as compared to conventional diesel. Frigo et al. (2014) used the pyrolysis liquid oil from tire waste and blended with conventional diesel with 20:80 and 40:60 ratios and used in a single cylinder diesel engine. Effect of blended oil was compared with conventional diesel against engine performance, exhaust emissions and cytotoxicity and genotoxicity effects of particulate matter produced from exhaust emissions. The study concluded that 20:80 ratio of liquid oil from the tire waste and conventional diesel showed similar results in comparison to conventional diesel. However, with an increase in the ratio of liquid oil (40:60) showed negative results in the performance of the engine. Furthermore, increasing the pyrolysis liquid oil to diesel resulted in increased NO_x and SO_x exhaust emissions. The decrease in the performance of engine might be due to the delay in ignition time as an increase in liquid oil ratio increases the viscosity of the

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liquid fuel. Therefore, poor optimization of liquid fuel was observed. Moreover, Umeki et al. (2016) blended the liquid oil of tire waste with conventional diesel with the ratios of 20:80 and 40:60 and examined its effect on the physical characteristics of the liquid oil. The study concluded that increase in blend ratio increased the overall kinematic viscosity of the blended liquid oil. Furthermore, kinematic viscosity of conventional diesel at 10 °C was 4.6 mPa-s, while pure pyrolytic tire waste oil has a kinematic viscosity of 8.7 mPa-s at the same temperature. However, at 60 °C, variation among the kinematic viscosity was 0.7 mPa-s while all the blended liquid oil viscosity were measured between 1.6 mPa-s and 2.3 mPa-s. Furthermore, a linear decrease in HHV was also observed with an increase in the blend ratio.

Char is a by-product of pyrolysis that has potential to be used in several environmental applications (Miandad et al., 2016b; Esfandiari et al., 2012). Pyrolysis of tire waste produced a significant amount of char that can be used as an adsorbent material after its activation. Activation of char can be carried out by physical or chemical methods (Antoniou et al., 2013). Physical activation can be achieved via partial gasification by using steam and CO_2 as the activating agents. Steam activation is carried out at high temperature (> 900 °C) with long residence time while, CO_2 activation is performed at low temperature (800 °C) with a shorter residence time (2-3 hr) (Mui et al., 2004). However, in chemical activation, char was impregnated with a dehydrated activating agent such as KOH, and H_3PO_4 (Antoniou et al., 2013). With the use of these activating agents, a rigid matrix is promoted by cross-linking reactions that resulted in further carbonization (Teng et al., 1998). Lopez et al. (2009) carried out pyrolysis of the tire waste in conical spouted bed reactor at 500 °C temperature. The produced char from tire pyrolysis was activated with steam at 850 and 900 °C in a fixed bed reactor. Steam activation produced a mesoporous activated char with the high surface area above 500 m^2/g and pore diameter of 500 Å. Furthermore, sulfur content was also decreased with the activation procedure. Furthermore, chemical activation with nitric acid (HNO_3), hydrogen peroxide and ammonium persulfate were carried out by Heras et al. (2014). Chemical oxidation increased the higher porosity in the mesoporous region with a higher burn-off in the material. However, HNO_3 showed much higher mesoporous value along with some micro-porosity. Moreover, char produced from co-pyrolysis of plastic waste with tires and biomass was upgraded and used for

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the adsorption of dyes. Upgraded char showed the significant removal of methylene blue dyes (3.6 - 22.2 mg/g) from aqueous solution (Bernando, 2011).

3.6 Future work

Pyrolysis is an efficient process to convert the tire waste into liquid oil and other value added products. The use of synthetic catalysts may increase the cost of the pyrolysis process. Thus, considering the economic value of the process, natural zeolite was used for tire waste catalytic pyrolysis. Natural zeolite catalyst showed significant results for the conversion of tire waste. However, its low BET surface area, pore volume, and low acidity affect its catalytic activities. Thus, the modification is required to enhance its overall catalytic activities. In future, natural zeolite modification will be carried out via physical or chemical treatments that will increase its catalytic performance. In addition, the produced char activation and its application for various environmental applications will also be carried out.

4. Conclusions

The pyrolysis of tire waste can be used as an alternative waste management solution. The GC-MS results revealed that pyrolysis liquid oil produced without catalyst consist of up to 93.3% of mixed aromatic hydrocarbon compounds with few aliphatic hydrocarbons. The use of catalysts decreased the concentration of aromatic compounds in liquid oil down to 60.9% with $Ca(OH)_2$, 71.0% with natural zeolite, 84.6% with Al_2O_3, except for synthetic zeolite (H-SDUSY) catalyst that produced liquid oil consisted of 93.7% aromatic compounds. Moreover Al_2O_3, natural zeolite and $Ca(OH)_2$ catalysts formed multiple ring aromatic hydrocarbons compounds in liquid oil in significant amounts of 35.5, 32.5 and 7.4% respectively. The FT-IR data also showed a mixture of aromatic and aliphatic hydrocarbon compounds that were found in all studied samples, which further confirmed the GC-MS results. Furthermore, the values for the physical characteristics of pyrolysis liquid oil such as HHV (42-43.5 MJ/kg), kinematic viscosity (1.9 cSt), density (0.9 g/cm^3), pour point (-2 °C), and flash point (27 °C) were found close to the standard values of the conventional diesel. Thus, the produced liquid oil has the potential to be used as an alternative source of energy and as a transport fuel, after cleaning and post-treatments.

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Acknowledgment

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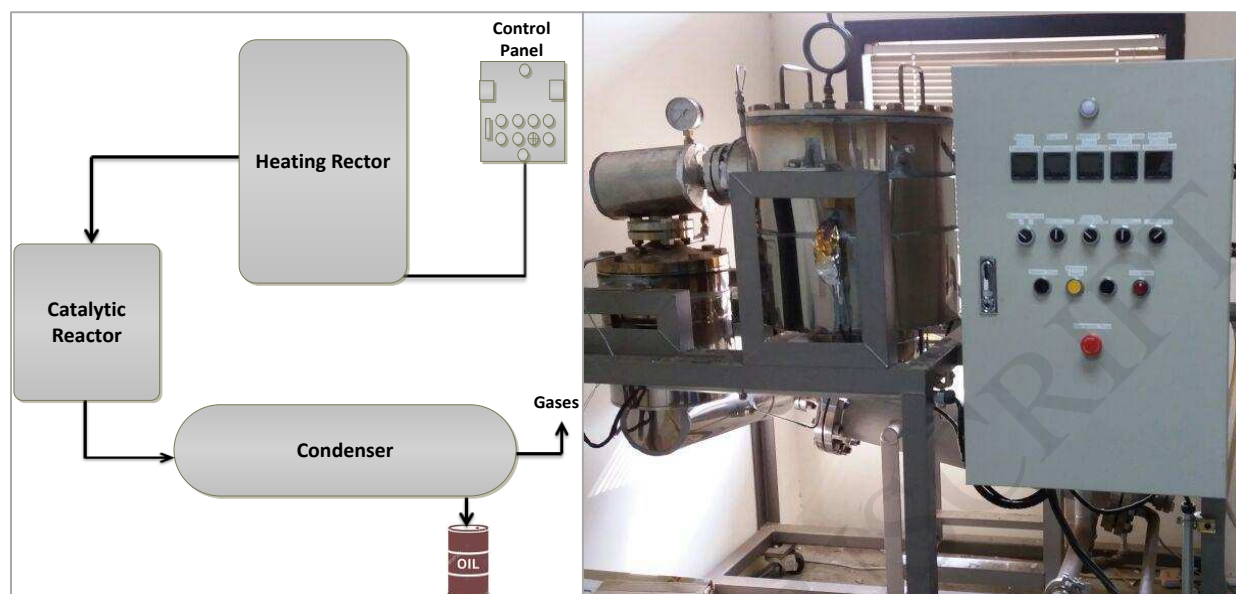
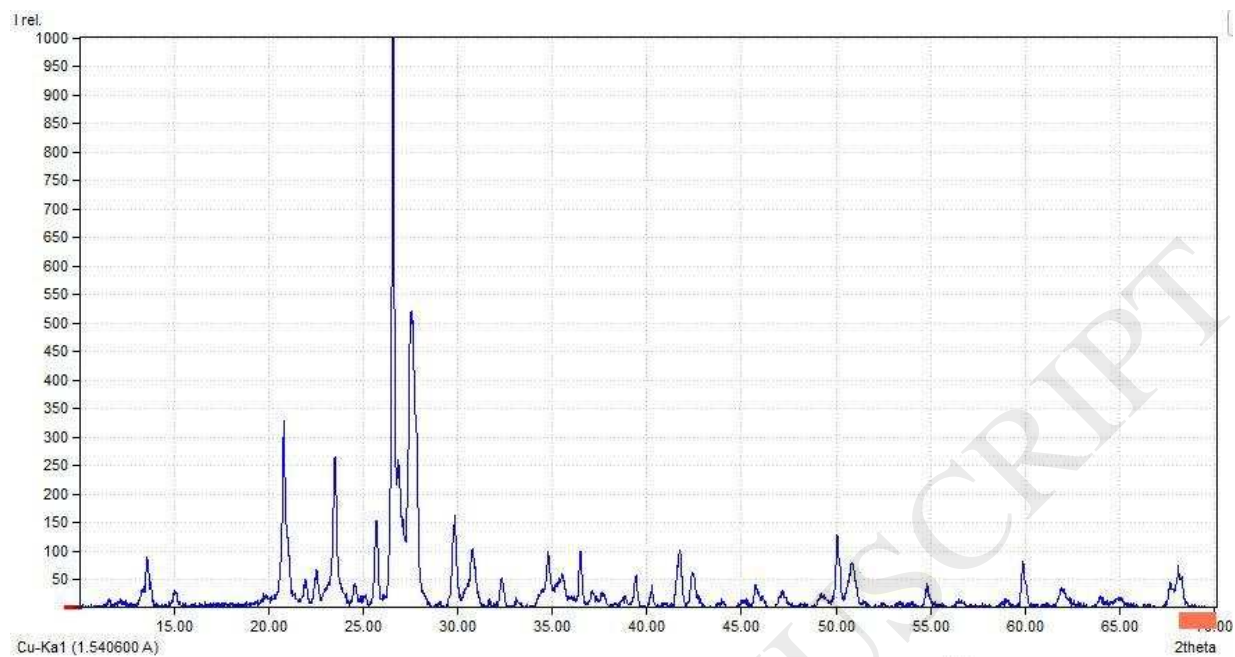Figure 1. Pilot-scale pyrolysis reactor (Miandad et al., 2016b, 2017b)

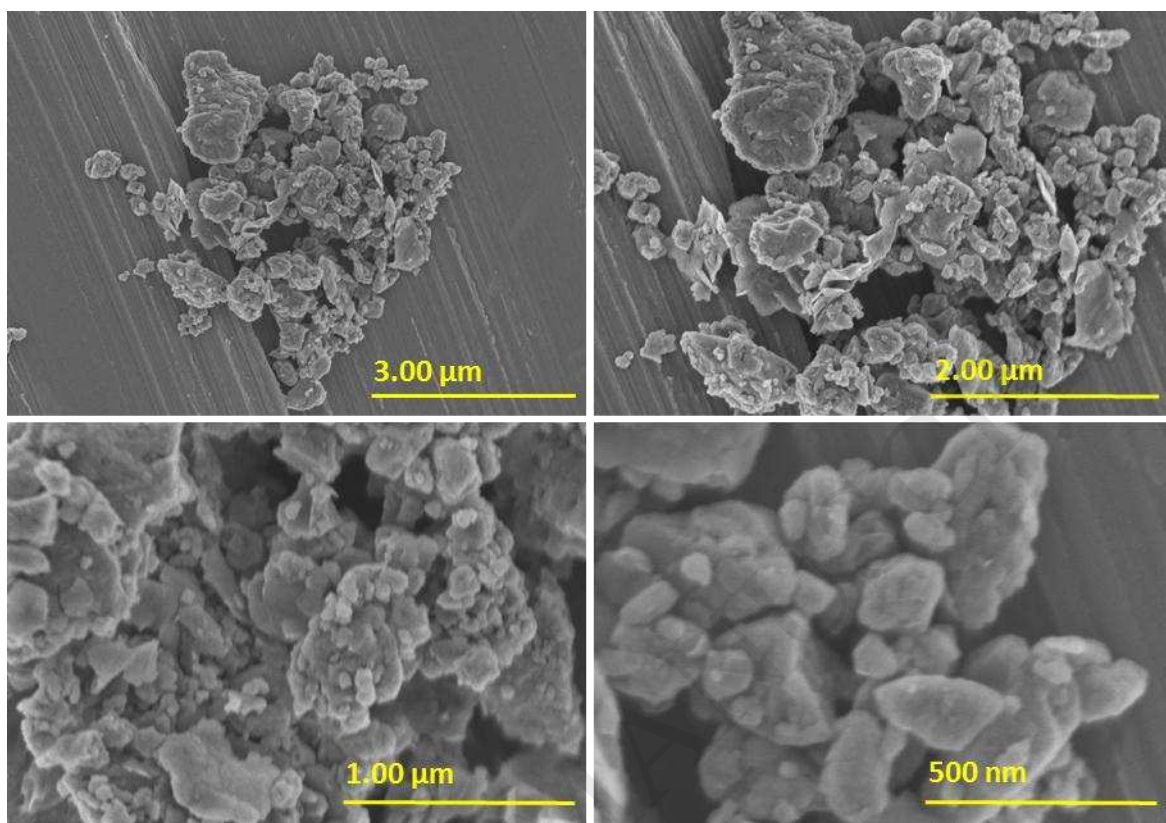Figure 2. XRD pattern of natural zeolite catalyst

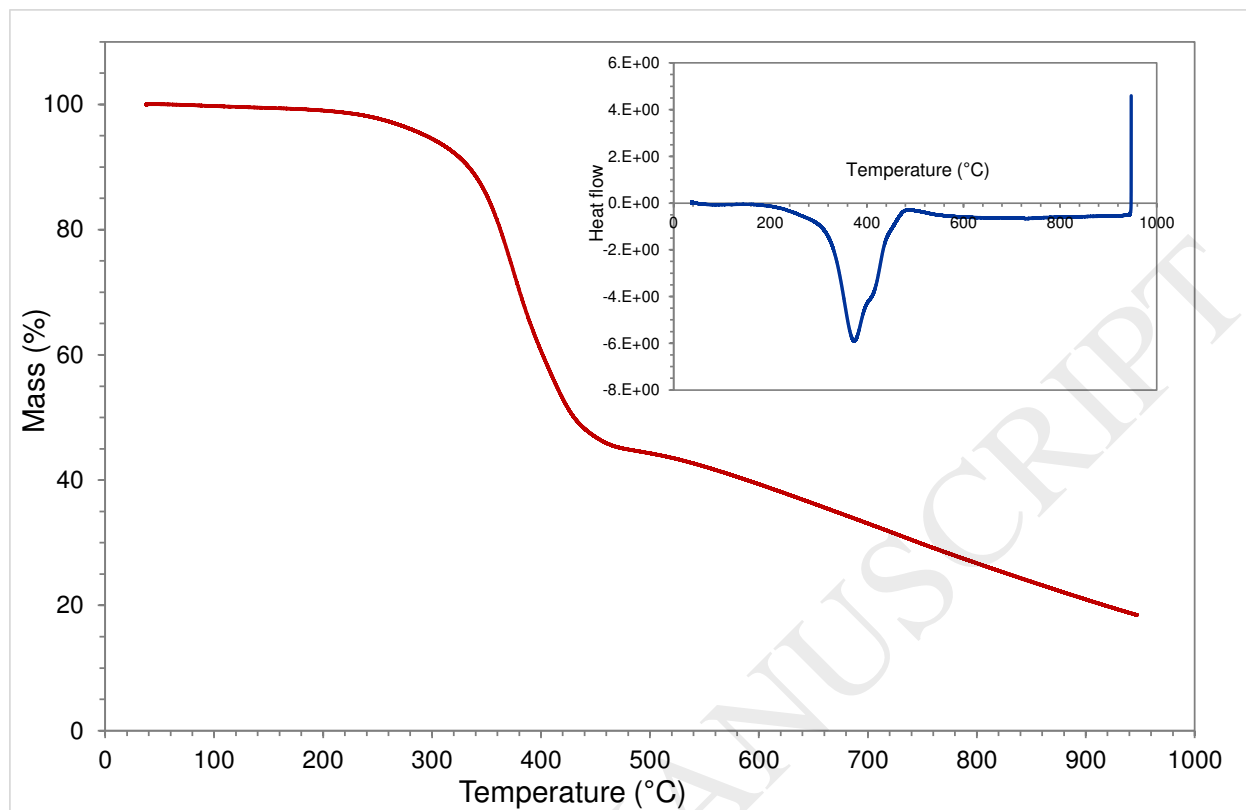Figure 3. SEM images of natural zeolite catalyst

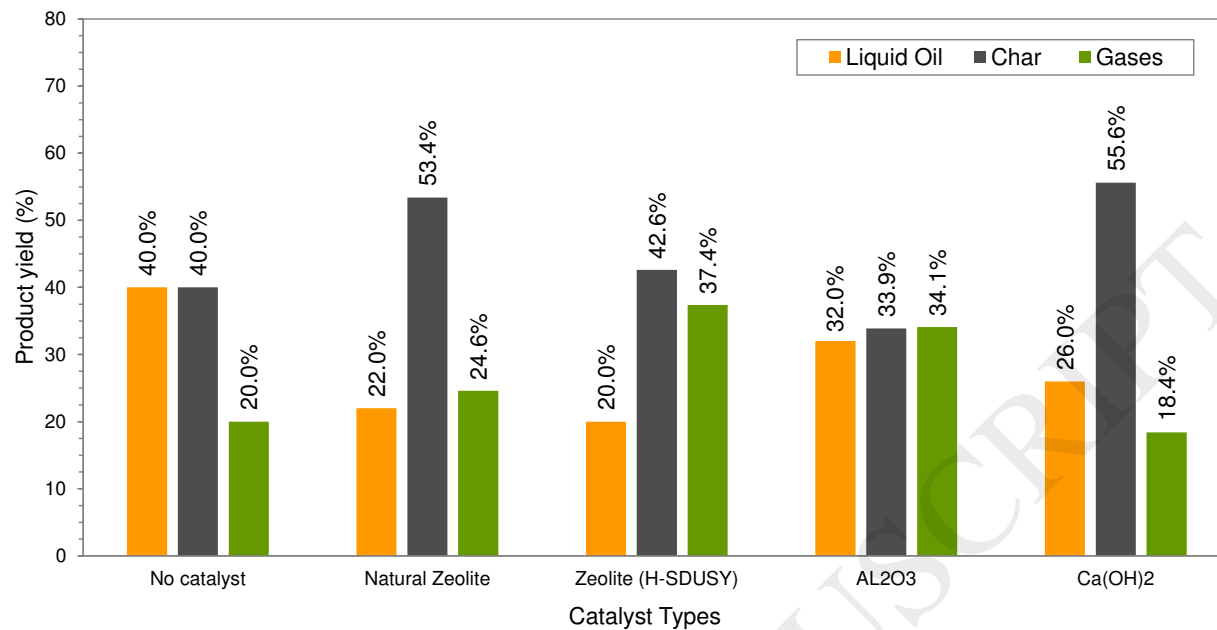Figure 4. TGA and DSC (inset) profiles of tire waste feedstock

Figure 5. Effect of catalytic and non-catalytic pyrolysis on products yields
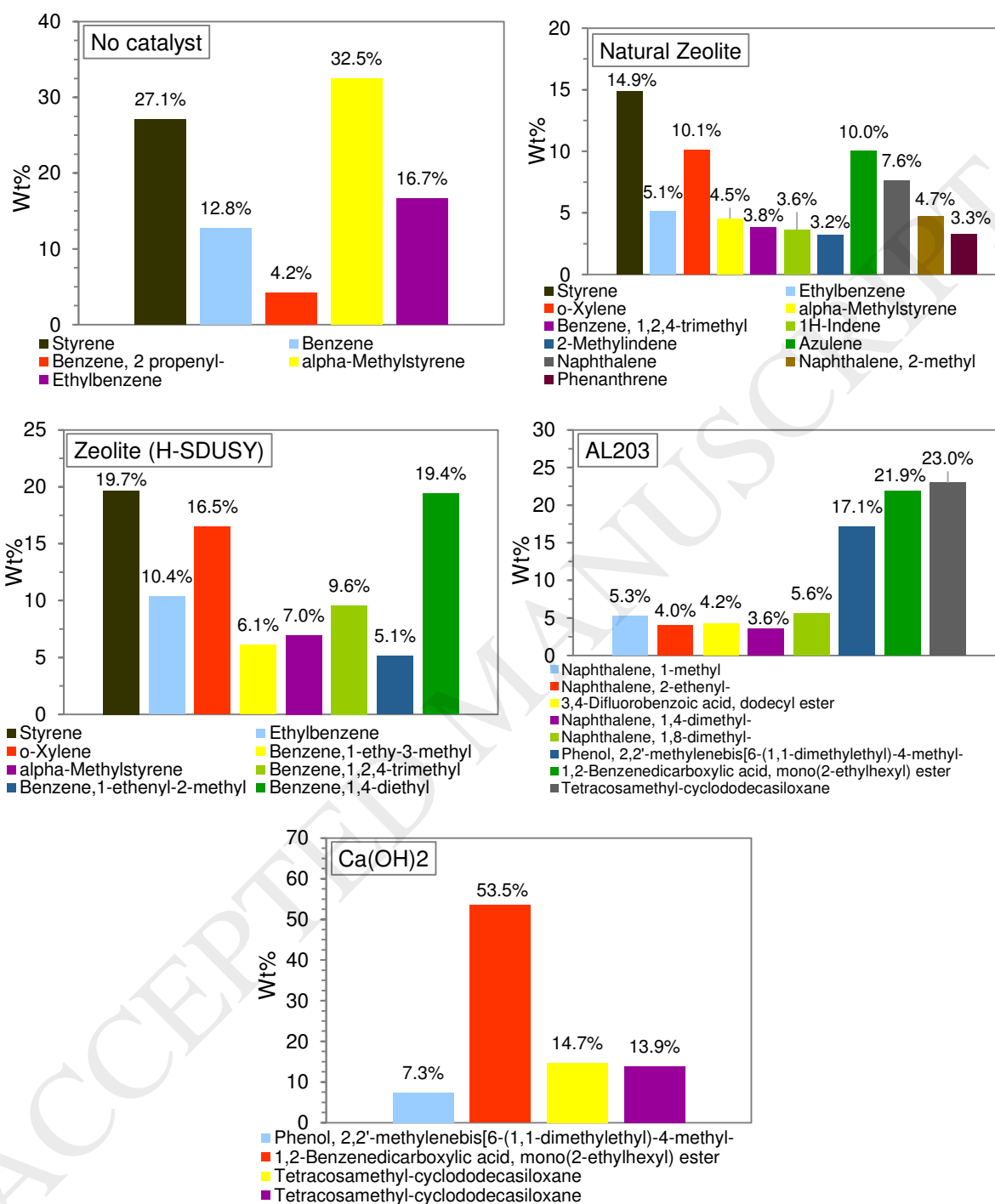
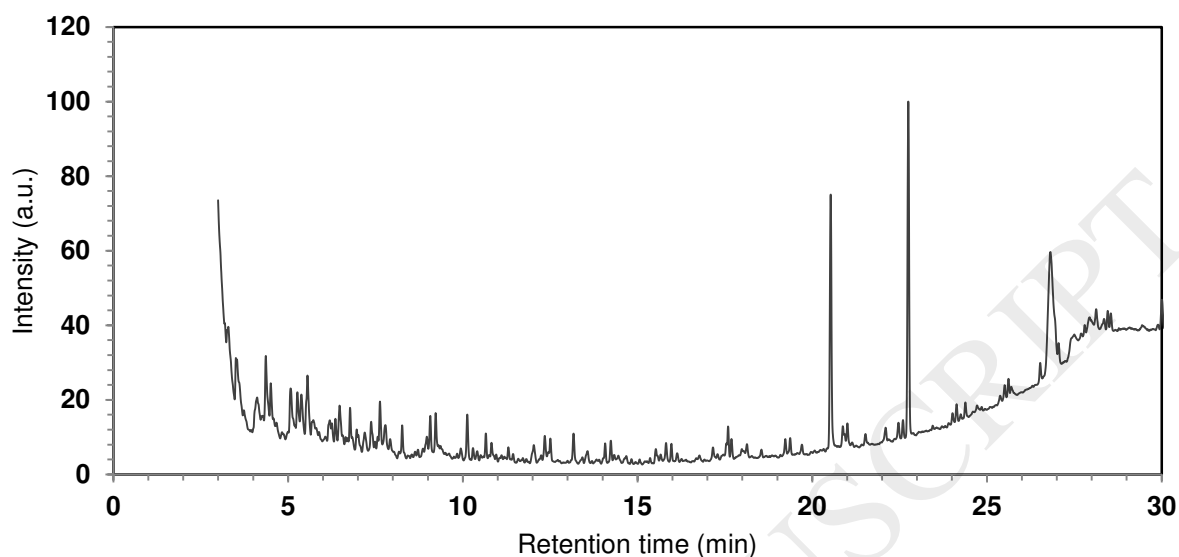Figure 6. GC-MS results of liquid oil produced from catalytic and non-catalytic pyrolysis of tire waste

Peak No	Retention time	Compound name	Compound formula	Molecular weight	Area
1	3.512	Azulene	$C_{10}H_8$	136.22	2.9
2	4.365	Naphthalene, 1-methyl	$C_{11}H_{10}$	142.2	5.3
3	4.508	Naphthalene, 2-methyl-	$C_{11}H_{10}$	142.2	2.1
4	5.078	Naphthalene, 2-ethenyl-	$C_{12}H_{10}$	154.20	3.9
5	5.269	3,4-Difluorobenzoic acid, dodecyl ester	$C_{19}H_{28}F_2O_2$	326.42	4.2
6	5.384	Naphthalene, 1,4-dimethyl-	$C_{12}H_{12}$	156.22	3.6
7	5.559	Naphthalene, 1,8-dimethyl-	$C_{12}H_{12}$	156.228	5.6
8	6.777	Naphthalene, 2,3,6-trimethyl-	$C_{13}H_{14}$	170.25	1.5
9	7.633	1-Heneicosanol	$C_{21}H_{44}O$	312.58	2.8
10	9.072	n-Nonadecanol-1	$C_{19}H_{40}O$	284.52	1.6
11	9.227	Methoxyacetic acid, 4-hexadecyl ester	$C_{19}H_{38}O_3$	314.51	1.9
12	10.131	Anthracene	$C_{14}H_{10}$	178.23	2.6
13	20.53	Phenol, 2,2'-methylenebis[6-(1,1-dimethylethyl)-4-methyl-	$C_{23}H_{32}O_2$	340.49	17.1
14	22.751	1,2-Benzenedicarboxylic acid, mono(2-ethylhexyl) ester	$C_{16}H_{22}O_4$	278.34	21.9
15	26.816	Tetracosamethyl-cyclododecasiloxane	$C_{24}H_{72}O_{12}Si_{12}$	889.84	22.9

Figure 7. A typical example of GC-MS chromatogram of liquid oil produced from catalytic
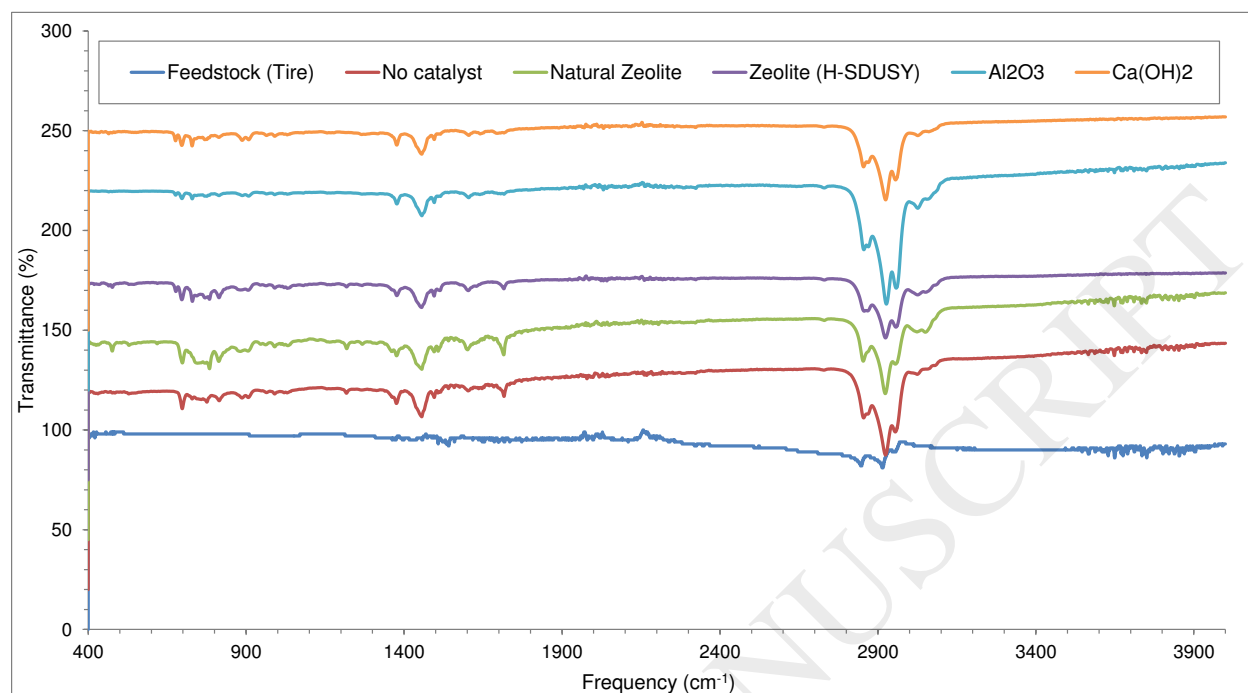
pyrolysis using Al_2O_3 catalyst

Figure 8. FT-IR of tire waste feedstock and liquid oil produced from catalytic and non-catalytic pyrolysis of tire waste

Table 1. Reactor parameters (Miandad et al., 2016b, 2017b)

Reactor component	Features
Height of heating tank	360 mm
Diameter of heating tank	310 φ
Height of catalyst tank	200 mm
Diameter of catalyst tank	165 φ
Reactor capacity for substrate	20 L
Catalyst tank capacity	1 L
Length of condenser	860 mm
Diameter of condenser	147 φ
Maximum temperature	600 ℃

Table 2. Proximate analysis of tire waste in comparison to other published works

Moisture	Volatile matter	Fixed carbon	Ash	Reference
1.2	83.9	7.3	7.6	Present study
0.6	63.3	30.7	5.4	Naim et al. (2016)
0.8	64.9	30.1	4.6	Zhang et al. (2008)
1.4	66.1	27.5	4.2	Ucar et al. (2005)
0.3	76.1	19.4	4.2	Choi et al. (2016)
0.8	63.0	32.0	4.2	Li et al. (2016)

Table 3. Aromatic hydrocarbon compounds found in pyrolysis liquid oil produced using various catalysts and without catalyst

Aromatic types	No catalyst (%)	Natural zeolite (%)	Synthetic zeolite (H-SDUSY) (%)	Al_2O_3 (%)	$Ca(OH)_2$ (%)
Single ring aromatics	93.3	38.5	93.7	49.1	53.5
Multiple ring aromatics	0	32.5	0	35.5	7.4
Total aromatics	93.3	71.0	93.7	84.6	60.9

Table 4. Comparison of pyrolysis liquid oil properties with conventional diesel and other reported data

Liquid oil properties	Our study	Conventional diesel (Ayanoglu and Yumrutas, 2016)	Ayanoglu and Yumrutas (2016)	Islam et al. (2010)	Al-Lal et al. (2015)
Kinematic viscosity (cSt)	1.9	2-4.5	3.2	4.6	2.4
Density g/cm^3	0.9	0.82-0.85	0.8	0.9	0.9
Flash point (°C)	27	>55	28	<30	23
Pour point (°C)	-2	NR	NR	-4	NR
HHV (MJ/kg)	42.5	42.7	41	41.6	42.7

NR= Not Reported