Journal of the Energy Institute 92 (2019) 1831–1841

Contents lists available at ScienceDirect

Journal of the Energy Institute

journal homepage: http://www.journals.elsevier.com/journal-of-the-energy-institute

Microwave-induced pyrolysis of waste truck tyres with carbonaceous susceptor for the production of diesel-like fuel

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ARTICLE INFO

Article history:
Received 27 August 2018
Received in revised form
22 November 2018
Accepted 26 November 2018
Available online 29 December 2018

Keywords:
Microwave
Pyrolysis
Catalytic
Waste truck-tyre
Energy yield

ABSTRACT

Microwave-induced pyrolysis technique was utilised to pyrolyse waste truck tyres (TT) into useful pyrolysis oil with the aid of activated carbon. The effect of temperature was studied to determine the truck-tyre pyrolysis oil (TTPO) yield, hydrocarbon fractions, chemicals composition, energy yield and fuel properties. The activated carbon functions as microwave absorber to elevate the pyrolysis temperature for enhancing production of pyrolysis oil. The optimal pyrolysis temperature of 500 °C produces highest TTPO yield of 38.12 wt% with calorific value of 42.39 MJkg^{-1} and energy yield of 40.55 wt%. Detailed analysis shows the TTPO contained large amount of aromatic hydrocarbons and limonene (14.29%) compared to pyrolysis oil from personal car tyre. Among the important chemical compounds also discovered in TTPO are benzene, toluene, xylene (BTX). The relative yields of toluene obtained at 400 °C is 14.85%, whereas the relative yields of benzene and xylene at 450 °C were 0.85 and 7.60%, respectively. The physiochemical properties of TTPO500 are rather similar to conventional diesel, except the slightly lower flash point and calorific value for the former. This work shows that microwave-induced pyrolysis is a promising technique to recover diesel-like fuel for use as supplemental alternative fuel.

1. Introduction

The growing number of vehicles on the road worldwide generates millions of used tyres annually. The improper management of waste tyre creates huge environmental problem due to the artificial and non-biodegradable polymer. Waste tyre is difficult to decompose in natural environment and improper incineration will cause air pollution due to release of hazardous pollutants that affect human health, including polycyclic aromatic hydrocarbons (PAHs), benzene, styrene, phenols, and butadiene [1]. Further, landfilling waste tire poses a serious fire hazard. Uncontrolled combustion of waste tyres have potentially effect on hot fire resulting in the release of black smoke in an enormous volume. Moreover, sulphur content and additives also pollute the environment [2,3]. The waste tyres are being recycled for energy recovery [4,5], but drawbacks of processing waste tyre and high operating cost remain issues to be tackled.

The need to dispose the waste tire efficiently in the context of circular economy has provided the impetus for researchers to explore pyrolysis research on waste tyre [3,4]. Generally, pyrolysis is a thermal decomposition of material at elevated temperature (300–700 °C) in an oxygen-free environment to decompose solid wastes into char, oil, and gases [2,3]. The quality and yields of the pyrolysis oil are strongly dependent on operating conditions such as particle size, temperature, heating rate, reaction atmosphere and type of reactor as well as the properties of the feedstock [4,5]. The polymeric compounds (natural and synthetic rubber) of waste tyre affect the pyrolysis oil composition. The composition of pyrolysis oil depends on the type of tyre, i.e. personal car tyre (PCT) or truck-tyre (TT). TT has larger natural rubber content than PCT, while the synthetic rubbers, such as butadiene and styrene butadiene represent a third of the rubber in the TT and two-thirds in PCT [5,6]. Sienkiewicz et al. (2012) reported that based on US and EU standards, the natural rubber content in PCT and TT is 14–22 wt% and 27 to 30 wt%, respectively. The synthetic rubber in PCT is about 27–30 wt% while for TT is about 14–15 wt% [6]. The difference in polymeric composition in waste tyre results in different thermal degradation characteristics, hence the quality of pyrolysis oil produced is varied [6,22].

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https://doi.org/10.1016/j.joei.2018.11.009
1743-9671/

Seidelt et al. (2006) examined the thermal properties of natural and synthetic rubber which are derived from styrene–butadiene-rubber and polybutadiene rubber respectively. Results revealed that there exists a relationship between the polymeric composition and thermal degradation of three different rubbers, thus giving different pyrolysis oil composition [7]. Pyrolysis of waste tyre allows the degradation of polymeric compounds into lower molecular weight of oil that can be used as alternative fuels or chemicals feedstock [8]. The pyrolysis oil has high calorific value (40–45 $MJkg^{-1}$) which typically consists of a mixture of aliphatic, olefinics and aromatic hydrocarbons depending on the process conditions and tyre composition [2,4]. Many studies reported that the pyrolysis oil contains a significant amount of nitrogen and sulphur compounds, making pyrolysis oil inferior as compared to fossil fuel and prohibits direct usage in engine [3,5]. Pyrolysis oil has poor physical properties such as high viscosity, low flash point and low density that affects the spray injection system. Das et al. (2018) reported that high viscosity and low volatility of liquid fuel results in inferior atomization and reduced fuel vaporization. [9], whereas high fuel density leads to the increase in spray penetration that results in the increase of emissions of unburnt hydrocarbon and CO [9,10]. High moisture content in oil affects the energy content [9], while high sulphur content causes corrosion of the internal components of the engine, such as piston ring, valves, and cylinder liners [11]. Thus, it is necessary to improve the pyrolysis oil quality to enable direct application in existing engines.

Research has shown that upgrading pyrolysis oil is not commercially viable to compete with petroleum-derived fuels due to high production costs incurred from pyrolysis reactor plant as well as the cost of material collection, storage and handling, drying, cutting and grinding [12]. Thus, to improve the competitiveness of pyrolysis oil as fuel, many researchers are investigating novel methods to maximise the recovery of valuable chemicals from pyrolysis oil before reusing the remaining pyrolysis oil as fuel [4,5]. Aromatic hydrocarbons from pyrolysis oil are valuable feedstock for the production of value-added chemicals and polymers. In addition, pyrolysis oil contains valuable chemicals such as benzene, toluene, xylene (BTX) and D-limonene that could be used as feedstock in petrochemical industry [3,5,13]. BTX is widely used in the chemical industry for the production of a large range of bulk chemicals and plastics derivatives [3,5]. While, D-limonene is widely used as a solvent for the production of resins and adhesives as well as in the cosmetic industry [13]. The high calorific value and high concentration of valuable chemicals present in the pyrolysis oil makes it a potential alternative fuel and chemical feedstock. Studies have been conducted to characterize the performance of waste tyre pyrolysis oil in internal combustion engines. Ilkilic and Aydin (2011) investigated the performance of tyre pyrolysis oil in a diesel engine. It was reported that up to 75% of the oil can be blended with diesel without modification to the engine. However, they observed an increase of unburnt hydrocarbon, CO and SO_x emissions compared to baseline diesel [14]. Tudu et al. (2016), also examined the performance of diesel engine operated with tyre-derived fuel blended with diesel. Result indicates that 40% light fraction pyrolysis oil (LFPO) blended with diesel showed better performance with reduced ignition delay and lower NO_x emissions [15].

There have been some attempts to recover high value products via pyrolysis of waste tyres [5]. Cunliffe and Williams (1998) reported the chemical fractions pyrolysed from waste tyre at the temperature 450–600 °C. They found that aromatic and aliphatic fractions increased and decreased, respectively with increasing pyrolysis temperature. The fractions of aliphatic and aromatic produced at 450 °C were 51.3 and 36.7 wt%, respectively, but as the pyrolysis temperature increases to 600 °C, the latter increased to 45.6 wt% while the former decreased to 36.1 wt% [16], indicating the strong influence of pyrolysis temperature. Lopez et al. (2017) examined the chemical composition of oil produced from waste truck tyre between 452 and 575 °C. They reported that aliphatic production peaks at 425 °C with 23.87 wt% but the aromatics were only 7.02 wt%. Increasing the pyrolysis temperature to 575 °C reduces the aliphatic yield to 2.28 wt% [17].

Microwave-induced pyrolysis (MWIP) is one of the promising technologies suitable for the production of fuel and chemicals [18–20]. Microwave is used to induce heating of materials when dielectric heating transfers electromagnetic radiation to thermal energy [18,20]. The microwaves can penetrate the materials to enable the heat to propagate from inside of the material. Microwave-assisted heating exhibits many advantages over other conventional heating methods, including simple heating system favorable for large-scale industrial technology, ease of operation and maintenance, fast, high-efficiency, selective heating and precise control. This leads to improvement in the oil quality as well as an increase in the production efficiency of pyrolysis oil [21,22].

In the present work, a microwave-induced pyrolysis system is utilised to pyrolyse waste tyres for the production of pyrolysis oil and recovery of high-value aromatics hydrocarbons. Previous pyrolysis researches on waste tyre were mostly performed using personal car tyre (PCT) [22], but study of waste truck-tyre pyrolysis using microwave-heating technique has never been done, to the best of authors' knowledge. The synthetic rubber content in the personal car tyre, i.e. butadiene and styrene butadiene, is two times more than truck tyre [6], hence it is expected that the thermal degradation behavior and the pyrolysed oil produced from waste truck tires will differ from that of personal car tire. By using a microwave reactor, waste truck tires are pyrolysed under different devolatilization temperatures ranging from 300 to 600 °C with the aid of activated carbon as microwave absorber. Chromatographic analyse for pyrolysis oil is performed to determine the fraction of hydrocarbon composition especially aliphatic, olefnic and aromatic hydrocarbons. This work contributes to the database of waste truck tire pyrolysis apart from and contributing to the understanding of pyrolysis oil production and energy recovery.

2. Materials and methods

2.1. Materials

The grinded waste truck-tyre (TT) with size ranging from 5 to 10 mm is sourced from Eco Power Synergy Sdn Bhd. The steel threads in the tyre were removed by magnetic separation. The granular activated carbon with particle size of 5–10 mm was used as microwave absorber to assist in elevating the pyrolysis temperature. The activated carbon was preheated to 110 °C for 12 h in a ventilated oven to remove the moisture prior to experiment.

2.2. Experimental procedure

The experiments were carried out in a 1.0 kW modified multimode digital microwave operated at the frequency of 2.45 GHz. The experimental setup consists of microwave, cylindrical quartz glass reactor, N_2 supply, glass condensers, water chiller, pyrolysis oil collector and data acquisition system as illustrated in Fig. 1.

The three-neck glass cover at the reactor top was used to insert an R-type thermocouple, stirrer and N_2 gas inlet. The R-type thermocouple with small diameter was coated with ceramic to avoid interference with the microwave field. A water bath chiller was used to

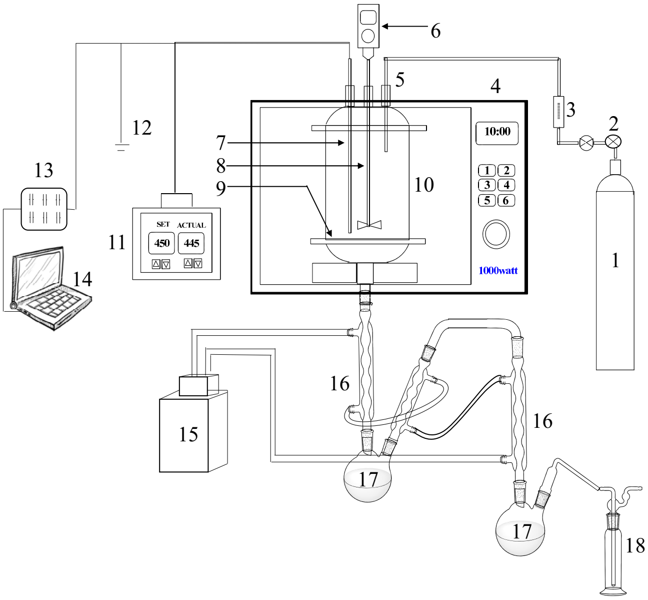

Fig. 1. Schematic diagram of microwave-induced pyrolysis system.

circulate water at ±5 °C in the glass condenser to avoid thermal stresses. The pyrolysis experiments were carried out using 100 g of TT and 100 g of activated carbon (AC), which were mixed homogenously. Nitrogen gas was supplied from the top of glass reactor as carrier gas to facilitate the removal of volatiles from the pyrolysis sample through a single-neck glass at a fixed flow rate of 300 mL min^{-1}. The thermocouple was inserted into the middle of TT and AC to measure the temperature ranging from 300 to 600 °C. The modified digital microwave was set to a maximum power level to acquire a maximum output capacity. Microwave power and reactor temperature has been calibrated according to the standard method [23]. From the calibration data, it was found the actual microwave power output used was 695 W with an efficiency of 69.5% (Fig. 2). The details calibration of each power level were supplied in a supplement data as shown in Fig. S1.

For each run of experiments, the pyrolysis temperature was held constant at the set temperature for 1 h until the pyrolysis process completes. The thermocouple was connected to a data acquisition system for real time monitoring of the process temperature. The pyrolysis oil, char and gas yields were determined by using equations (1)–(3) as follows:

$$\text{Oil yield (wt.\%)} = \frac{\text{Weight of Oil (g)}}{\text{Weight of Feedstock (g)}} \times 100\% \tag{1}$$

$$\text{Char yield (wt.\%)} = \frac{\text{Weight of Char (g)}}{\text{Weight of Feedstock (g)}} \times 100\% \tag{2}$$

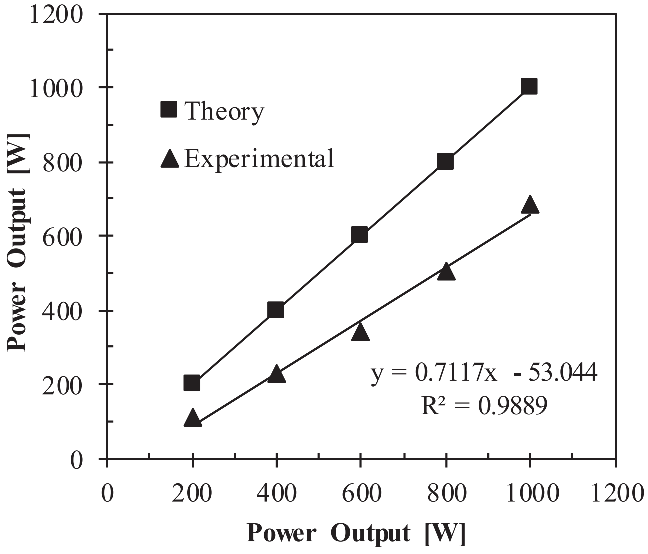

Fig. 2. Calibration curve of microwave power used.

$$\text{Gas yield (wt.\%)} = 100 - (\text{Oil yield} + \text{Char yield}) \tag{3}$$

The energy yield of oil is an index of conversion of energy stored in the feedstock to the pyrolysis oil generated through pyrolysis. Thus, the energy yield is defined by using equation (4) [24] as below:

$$\text{Energy yield (wt.\%)} = [\text{Oil yield (wt.\%)}] \times \frac{\text{HHV of Oil (MJ/kg)}}{\text{HHV of Feedstock (MJ/kg)}} \tag{4}$$

2.3. Material characterization

The proximate analysis of raw materials was conducted to determine the moisture content, volatile matter, fixed carbon and ash content. The proximate analyses were determined using TGA-DTG (Mettler-Toledo TG50) coupled with in-situ FTIR in compliance with ASTM standard (ASTM D3172). All analyses required a re-drying process at 105 °C to completely evaporate the initial moisture content. While, for the post pyrolysis products, FTIR spectrometer (Agilent Cary 640) was used to determine the type of elements released during the decomposition of TT. For the TGA analysis, the material was heated from 50 to 500 °C at a heating rate of 10 °C min^{-1} and held for 30 min before proceeding to heat from 500 to 900 °C. The experiments were carried out in a nitrogen atmosphere with a flow rate of 30 ml min^{-1}. The properties of the TT are shown in Table 1. The ultimate analysis was determined using a 2400 CHNS/O Perkin Elmer analyser. The sulphur content in pyro-oil was determined by using the X-ray fluorescence (AXIOS, PANalytical). The calorific values of the raw material and pyrolysis oil were determined via a bomb calorimeter (IKA C2000).

The nitrogen physisorption analysis of fresh and used activated carbon was carried out by using a Micromeritics ASAP 2020. Prior to the measurement, the sample was put into a sample tube holder, followed by evacuation at 300 °C for 1 h. Then, adsorption of nitrogen was carried out at 196 °C. Surface area, pore size distributions and pore volumes were determined from the sorption isotherms using a non-local density functional theory (NLDFT) method. The density of pyrolysis oil was tested at the temperature of 15 °C while the kinematic viscosity was tested using viscometer (Brookfield Viscometer DVII + Pro) at the temperature of 40 °C. The flash point of oil was tested using a flash point tester (NORMALAB NPM 440) at the temperature between 10 and 60 °C. The moisture content was measured using Karl Fischer moisture meter titration.

2.4. Product analysis

The chemical composition of the pyrolysis oil was analyzed using a gas chromatography-mass spectroscopy-flame ionization detector (Agilent Technologies 6890) with a HP-5MS capillary column of 30 m in length and 250 μm in diameter. The GC oven temperature was raised from the initial temperature of 90–280 °C and was held constant for 10 min, while the helium gas flow rate supplied to the GC was maintained at 2 mL min^{-1}. The gas chromatograph was connected to a mass spectroscopy (MS) (Agilent Technologies 5975 series) equipped with an inert mass selective Detector (MSD) at scanning acquisition mode. The mass spectroscopy was set to electron ionization mode with the ion source temperature of 230 °C, emission current of 34.6 μA, ionization energy of 70 eV, full scan range of 50–550 and quantization by selected ion monitoring mode. The Agilent Chemstation software was used to identify the chemical compounds and peaks with the help of NIST library.

3. Results and discussion

3.1. Characteristics of waste truck-tyre

The chemical composition of waste truck tyre plays a major role in determining the pyrolysis oil yield and qualities [17]. From the proximate analysis (Table 1), the moisture content of the TT is approximately 0.92 wt%, while the volatile, fixed carbon and ash contents are approximately 65.35, 29.53 and 4.02 wt%, respectively. The combustible (volatile and fixed carbon) content was approximately 95.0 wt%. It has been reported that the volatile matter of the waste truck tyre consists mainly of polymeric compounds that come from natural and

Table 1
Proximate, ultimate analyses and high heating values of waste truck-tyre (TT).

Content	TT
Proximate analysis (wt %)	
Moisture	0.92
Volatile matter	65.35
Fixed carbon	29.53
Ash (at 900 °C)	4.20
Ultimate analysis (wt %, dry basis)	
Carbon	80.33
Hydrogen	7.66
Nitrogen	0.35
Sulphur	0.87
Oxygen*	10.79
HHV(MJkg^{-1})	39.87
LHV ((MJkg^{-1})	38.14

* by difference.

synthetic rubber [3,6,17]. The elemental analysis result shows high carbon content of 80.33 wt%, followed by oxygen (10.79 wt%), hydrogen (7.66 wt%), sulphur (0.87 wt%) and nitrogen (0.35 wt%).

The thermal degradation behavior of TT was determined using a TGA-FTIR. The TGA-DTG profiles of sample are shown in Fig. 3a. Deconvolution peak of DTG result with predicted elements are shown in Fig. 3b. From the TGA-DTG profiles (Fig. 3a), it was indicated that the sample started to decompose between 180 and 600 °C after losing 65.0% of its weight in a two-step process. The DTG results were fitted to a multi-component model (Fig. 3b) to evaluate the thermal degradation of polymeric compounds in waste truck-tyres. The overlapped curve of DTG can be approximately divided into three main peaks through deconvolution, which was also an indicator of the complexity of reactions. The degradation behavior of pseudo-components considered are the additives and rubbers typically contained in the truck tyres, i.e., natural and synthetic rubbers [17,25]. The decomposition of natural rubber (NR) usually takes place at lower temperature between 300 and 500 °C. While, the synthetic rubber (SR) is identified by higher thermal decomposition as compared to natural rubber with the degradation peak occurs at temperature between 400 and 550 °C. The same degradation thermal behavior of TT has also been observed from previous study [17,25]. From the peak fit model, it was determined that the content of the present TT is approximated as 34.93 wt% of natural rubber, 27.71 wt% of synthetic rubber and 2.36 wt% of additives, with the balance of 35.0 wt% of ashes and carbon black.

The normalized FTIR spectra of devolatilization polymeric of TT under inert condition are illustrated in Fig. 3c. The IR analysis elucidates the absorptions of alkane/alkyl, alkene and aryl groups, as indicated by the frequencies of alkanes at 2929 (s) (H_2C—H asymmetric stretching) and 2866 (s) (HC—H asymmetric/symmetric stretching), 1456 (m) (HC—H bending). Absorptions of aromatic groups were found to be present at 1605 (w) (aromatic ring stretching), 1374 (m), and 991 (w) (Aromatic C—H in-plane bending) [17,22].

3.2. *Analysis of waste truck-tyre pyrolysis oil (TTPO)*

3.2.1. *Yield of TTPO*

The influence of temperature on the distribution of products obtained from TT pyrolysis was studied in the range of 300–600 °C. Fig. 4a shows the yield distribution of TTPO, char and gas obtained at different pyrolysis temperature. The TTPO is dark in appearance with a pungent smell. TTPO exhibits two distinct immiscible layers of oil and water in the glass collector. The TTPO was dissolved in pre-weighted dichloromethane (analytical grade) solvent. The residual water content in the TTPO was observed to be less than 5 wt%. The yield of TTPO at 300 °C is lowest (7.46 wt%) due to low pyrolysis reaction that took place. Insufficient energy provided by the heat source results in the inability to degrade the polymeric compounds into heavy oil fraction. According to Miranda et al. (2013), the direct conversion of initial polymer in the waste tyre begins at the temperature of 370 °C for the formation of heavy oil fraction [26]. As the pyrolysis temperature increased to 400 and 450 °C, the yield of TTPO increased to 20.51 and 27.25 wt%, respectively. The maximum yield obtained at the temperature of 500 °C is 38.12 wt%. Further increase in pyrolysis temperature from 550 to 600 °C resulted in a net decrease of oil yield (Fig. 4a). Barbooti et al. [25] reported that the highest pyrolysis oil yield was obtained at the pyrolysis temperature of 500 °C, but the yield decreased when the pyrolysis temperature increased.

A different pattern of gas yield was observed in Fig. 4a. As the pyrolysis temperature increased from 300 to 600 °C, the yield of gas increased monotonically. Similar trends have been observed for the pyrolysis of different types of materials [27,28]. This is because the primary decomposition of rubber polymer takes place at a lower pyrolysis temperature and, as the temperature increases, the pyrolytic vapors are further cracked into low molecular weight organic compounds [16,29,32]. At temperature beyond 500 °C, the low molecular weight organic compounds decompose into gaseous products. Thus, the yield of TTPO started to decrease at temperature 550 and 600 °C [16,29,32].

3.2.2. *Effect of activated carbon (AC) towards the yield of TTPO*

The yield of TTPO is significantly affected by the presence of activated carbon (AC). Fig. 4b shows the TTPO yield is higher when TT is pyrolised with AC at 500 °C (500-wt AC). As compared to reaction without AC (500-wo AC), the TTPO yield was reduced to 16.76 wt%.

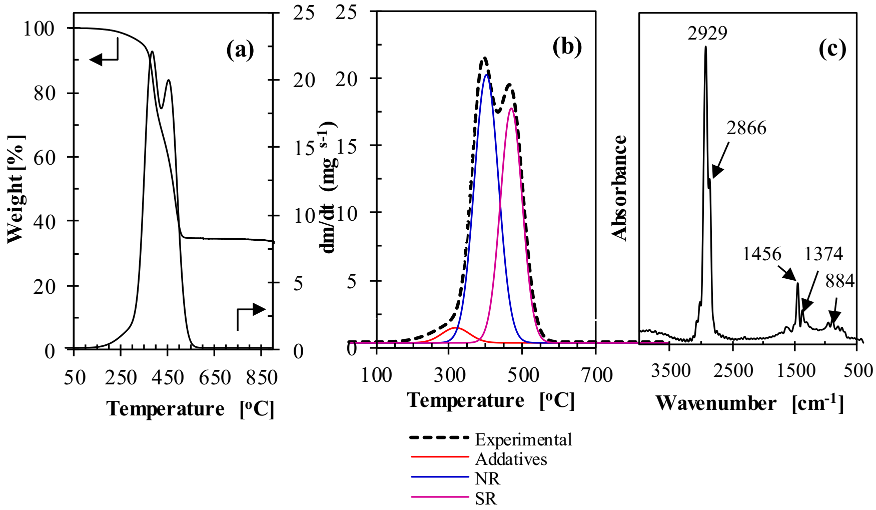

Fig. 3. (a) TGA-DTG profile of TT, (b) deconvolution peak of DTG result and predicted elements using peak fit model software, and (c) normalized FTIR spectra of decomposition TT under inert condition.

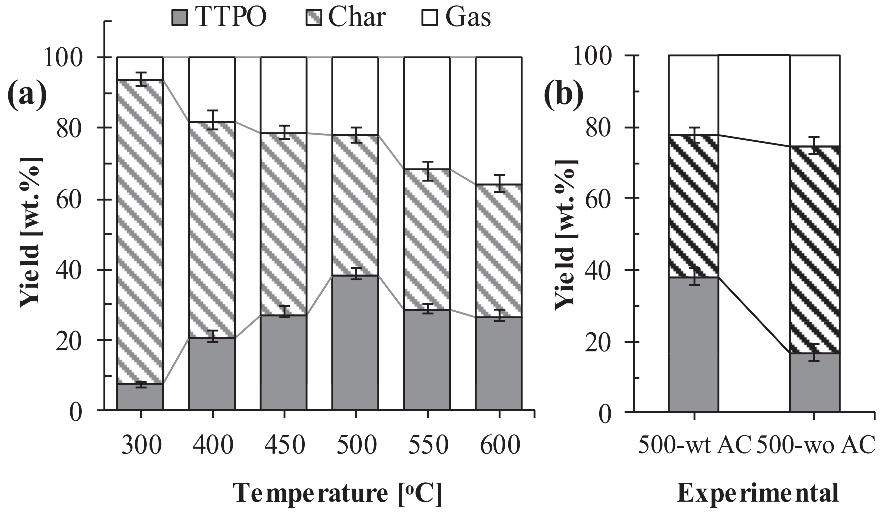

Fig. 4. Yield distribution of TTPO, char and gas from pyrolysis of TT at (a) 300–600 °C (b) with and without of AC at 500 °C.

However, the yield of char was increased to 57.9 wt% and the amount of gas produced was almost similar. It showed that the activated carbon enhanced the microwave absorption and assisted in heating the TT. The AC also acts as insulator that reduced heat losses rate from the surface of the material [30]. Thus, the yield obtained from reaction with AC (500-wt AC) is higher as compared to reaction without AC (500-wo AC). This justifies the need to use microwave absorber. In this study, activated carbon was chosen as a microwave absorber due to its abundance and low cost as compared to other materials such as graphite, silica carbide or alumina [30].

The N_2 adsorption–desorption isotherms of activated carbon before and after reaction are shown in Fig. 5a and b, respectively. The average surface area of fresh AC was 1202.34 m^2g^{-1}. The isotherm shows that type I micro porous materials with the pore size of less than 10 nm. In contrast, the surface area of used AC reduced to 416.49 m^2g^{-1} after reaction. It revealed that the adsorption process occurred inside the micro pores structure. However, there was no significant change in the pore size distribution. The thermal behavior of the fresh activated carbon was determined using TGA (Fig. 5c). The result shows that the AC has high oxidation temperature with approximate weight loss of 8.0 wt% at high temperature (850 °C). Therefore, result confirms that AC does not combust during the pyrolysis process.

3.2.3. *FTIR analysis of TTPO*

The FTIR analysis allowed the evaluation of the functional groups present in the TTPO. Fig. 6 shows the FTIR spectrums of the TTPO obtained at 300–600 °C. The FTIR has been compared to those of different authors and summarized data are presented in Table 2. As shown in Fig. 6a, all spectrums are quite similar although some differences are visible in the absorbance strength of some peaks (Fig. 6a). The weak absorption band between 3500 and 3200 cm^{-1} is assigned to O-H stretching vibrations, indicating limited presence of water and hydroxyl groups, such as alcohols, phenols or carboxylic acids (Fig. 6a) [31,32]. The bands in the range from 3050 to 2850 cm^{-1} are due to C-H stretching present of alkanes group, whereas those from 3000 to 2700 cm^{-1} (Fig. 6b) corresponds to aliphatic compounds [31,32]. In addition, the peaks around 1710 to 1600 cm^{-1} (Fig. 6c) corresponded to C=O stretching vibration attributed to carbonyl/carboxyl groups mainly derived from the additives of the tyres [31,32]. The bands observed between 1650 and 1600 cm^{-1} and 1598 to 1505 cm^{-1} (Fig. 6c) are due to C=C stretching vibrations indicative of the presence of alkenes and aromatics, respectively [31,32]. Peak present at 1453 cm^{-1} is assign to aromatic compounds containing sulphur [31,32]. While, peak present between 1460 and 1380 cm^{-1} (Fig. 6d) are assigned to alkene group with CH_2 and CH_3 compounds [31,32]. From the FTIR spectrum (Fig. 6a), it was observed that the intensity of the peak at region 1270

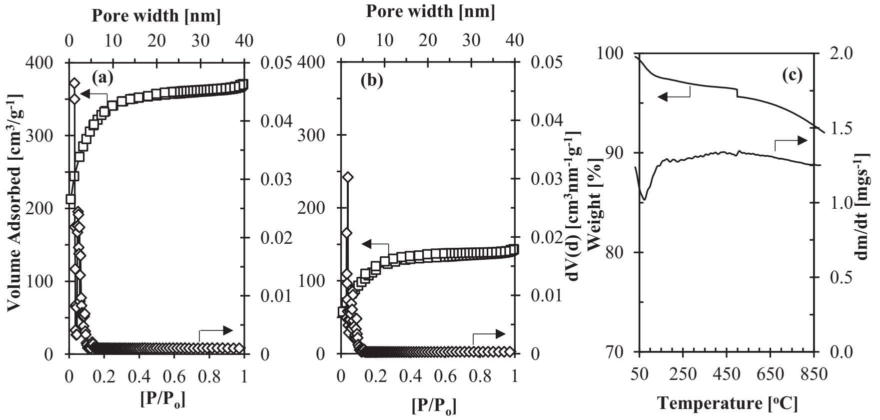

Fig. 5. BET surface area of (a) fresh activated carbon, (b) used activated carbon and (c) TGA-DTG profile of fresh activated carbon.

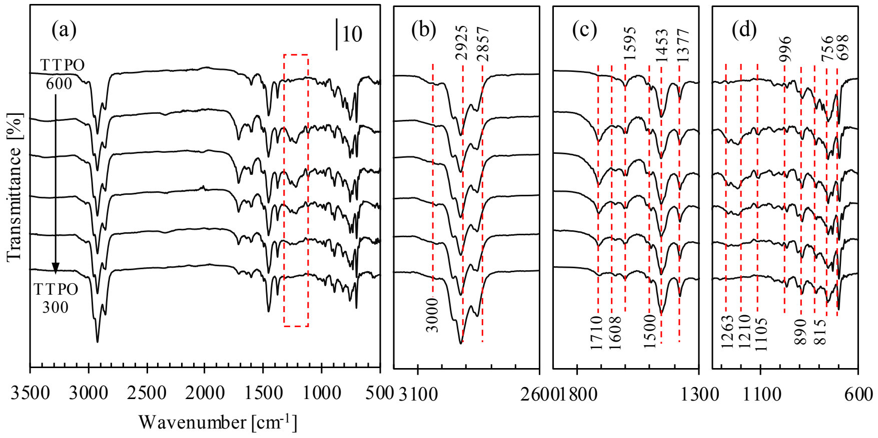

Fig. 6. FTIR spectra of the TTPO obtained at 300–600 °C, (a) overview of spectrum (b) region 3200 to 2600 cm^{-1}, (c) 1850 to 1300 cm^{-1} and (d) 1300 to 650 cm^{-1}.

Table 2
The FT-IR functional groups and the indicated compounds of pyrolysis oil.

Frequency range (cm^{-1})			Functional groups	Class of compounds
This study	Islam et al. [31]	Williams et al. [32]		
–	3100–3005	–	C=C stretching	Alkenes
3050–2850	3000–2800	3000–2800	C-H stretching	Alkanes
1710–1600	–	1750–1650	C=O stretching	Aldehydes or ketones
1646–1600	1675–1605	1675–1575	C=C stretching	Alkenes
1598–1505	1600–1545	1625–1575	carbon-carbon stretching	Aromatic compounds
1460–1380	1520–1115	1475–1350	C-H bending	Alkanes
1270–1100	–	–	C-H in-planes bending	Aromatic compounds
964–880	1020–845	950–875	C=C stretching	Alkenes
900–680	810–660	900–675	C-H out-of-planes bending	Aromatic compounds

to 1100 cm^{-1} increased with the enhancement of the reaction temperature from 400 to 550 °C (Fig. 6a and d). The peak was assigned to C-H in-planes bending, indicating the presence of aromatics compounds. The peak was disappeared when the temperature increased to 600 °C. As compared to the previous study, the peak present in this area have not been reported due to different polymeric compositions [31,32]. Hence, it can be concluded that the waste truck-tyre pyrolysis oil consist of high aromatic compounds as compared to the other tyres. The result is in agreement with the hydrocarbon fraction studied as showed in Fig. 7a. From the figure, it can be seen that the TTPO consist of high aromatic hydrocarbon at temperature 400–500 °C. Akkouchea et al. (2017) studied the pyrolysis waste truck tyre using a fixed-bed reactor. They found the pyrolytic oil from truck tire mainly consists of up to 65 wt% of aromatic hydrocarbons [33]. Finally, the peak at region 970 to 880 cm^{-1} assigned to C=C stretching indicates the alkenes compounds; while, the peak between 900 and 680 cm^{-1} (Fig. 6d) corresponds to the C-H out-of-plane bending peaks derived from aromatic compounds.

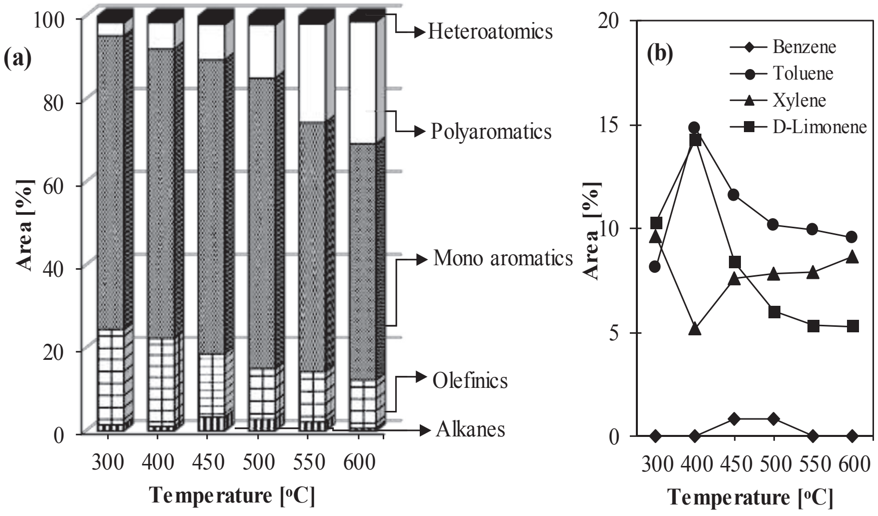

Fig. 7. Effect of temperature on (a) hydrocarbons fractions (b) benzene, toluene, xylene (BTX) and D-limonene.

3.2.4. *Hydrocarbon fractions*

Fig. 7 depicts the hydrocarbon fractions and chemical compounds in TTPO, while Table 3 shows the detail of chemical amounts present in TTPO ranging from 300 to 600 °C. About 34 chemical compounds were detected by GC-MS (Table 3). Relatively, the TTPO contains mixture of aliphatic, olefinics and aromatic hydrocarbons (Fig. 7a). The aliphatic and olefinics hydrocarbons are abundant in TTPO at lower pyrolysis temperature (300 and 400 °C) with maximum yield of 24.49 and 22.35%, respectively. The amount gradually decreases with increasing temperature. At 450 °C the yield decreased to 18.49% and reached a minimum yield of 12.17% at 600 °C. In contrast, yield of mono aromatics hydrocarbon increased from 72.45 to 73.14% as the temperature increased from 300 to 500 °C (Fig. 7a). Akkouche et al. [33] reported pyrolytic oil from truck-tyre using fixed bed reactor consists of up to 65.0% of aromatic hydrocarbon. This result in agreement with the FTIR result as shown in Fig. 6a and d. The FTIR study showed an increase of light aromatic hydrocarbon in the range of temperature 450–500 °C, but a decreasing trend when the temperature was increased to 600 °C. The increasing yield of aromatic hydrocarbon has been reported by several researchers. They claimed that the increase of aromatic hydrocarbon was due to the thermal decomposition of limonene above 500 °C to a range of products including benzene, xylene, toluene, trimethylbenzene, styrene and methylstyrene [16,34]. This explains the maximum yield of limonene range between 400 and 500 °C before decreasing to 600 °C [13,16]. However, the yield of light aromatic hydrocarbon started to decreased at 550 and 600 °C, to 62.19 and 58.58%, respectively. This might be due to the aromatization caused by Diels-Alder reaction that involves the pyrolysis of alkanes to alkenes and subsequent cyclisation to aromatic compounds for the formation PAH in the post-cracking reaction of the rubber materials [16,35,36]. A decrease in mono aromatic hydrocarbon between 600 and 900 °C was also reported as a result from the post-pyrolysis cracking of olefins by the Diels Alder reaction. Thus, at higher temperature (600 °C), the yield of PAHs was increased to a maximum of 29.89%. The PAHs compounds consist of naphthalene, naphthalene derivatives, fluorene and phenanthrene (Table 3). Cunliffe and Williams (1998), reported the Diels-Alder mechanism of alkane dehydrogenation to alkene, followed by cyclisation and aromatization by the results of pyrolytic gas analysis. The pyrolysis model for aliphatic compounds was proposed as the route to naphthalene formation by the Diels-Alders reaction in post-pyrolysis cracking reactions [16,35,36], as illustrated in Fig. 8.

Among mono aromatics hydrocarbon, important chemical compounds obtained in TTPO are benzene, toluene and xylene, BTX (Fig. 7b). The yields of toluene (8.18%) and xylene (9.66%) were significant at 300 °C. The highest yield of toluene was observed to be 14.85% at 400 °C; while, benzene and xylene was observed at 450 °C with value 0.85 and 7.6%, respectively. The yield of BTX decreases with increase in temperature to 550 °C due to generation of low hydrocarbons and reduction of these compounds by alkylation reaction [16]. Karagoz et al. [37] reported that the relative yields of benzene and toluene at 400 °C were 6.8 and 21.5%, respectively.

Table 3
Relative contents of chemical compounds in TTPO at different temperatures (°C).

Relative contents (%)	300	400	450	500	550	600
Alkanes						
Pentadecane	–	–	0.75	0.58	1.34	–
Heptadecane	–	–	0.77	0.63	–	–
Alkenes						
1,3,5-Hexatriene, 3-methyl-, (Z)-	1.51	1.12	1.01	1.07	–	–
Terpenes						
D-Limonene	9.29	14.29	11.37	6.02	5.33	5.29
Cyclo Alkenes						
Cyclobutene, (1-methylethylidene)-	–	–	0.85	0.85	–	–
Cyclohexene, 4-ethenyl-	1.66	1.18	1.71	0.94	0.66	0.56
1,3,5,7-Cyclooctatetraene	8.67	5.76	3.64	3.84	5.20	4.96
Cyclohexene, 1-methyl-4-(1-methylethenyl)-, (S)-	2.36	–	1.08	0.92	0.81	0.70
Mono Aromatics						
Benzene	–	–	0.85	0.85	–	–
Toluene	8.16	14.85	11.57	10.19	9.91	9.56
Ethylbenzene	7.98	11.40	8.17	8.25	5.91	4.77
o-Xylene	9.66	–	–	–	–	–
p-Xylene	–	5.20	7.60	7.80	7.90	8.67
Benzene, 1,3-dimethyl-	3.27	2.52	2.53	2.67	2.64	2.70
Benzene, (1-methylethyl)-	1.95	1.94	1.80	1.61	1.06	0.64
Benzene, 2-propenyl-	4.16	–	0.11	2.38	0.98	0.69
Benzene, 1-ethyl-3-methyl-	7.02	9.34	7.89	10.55	11.38	10.21
α–Methylstyrene	4.32	2.39	1.96	2.74	1.72	1.37
Benzene, 1,2,3-trimethyl-	19.56	18.98	14.96	14.55	10.66	9.72
Benzene, cyclopropyl-	1.62	–	1.09	0.95	0.86	0.70
Benzene, 1-methyl-4-(1-methylpropyl)-	3.28	3.11	5.06	4.75	2.36	3.88
Indene	1.82	–	2.88	2.72	3.7	3.06
1H-Indene, 1,3-dimethyl-	–	–	2.13	2.48	1.95	1.76
Polyaromatics						
Biphenyl	–	–	1.68	1.78	1.98	2.54
1,1′-Biphenyl, 4-methyl-	–	–	–	1.19	2.09	2.73
Naphthalene	1.25	2.88	1.70	1.85	3.93	4.74
1H-Cyclopropa(b)naphthalene, 1a,2,7,7a-tetrahydro-	–	–	0.63	0.58	0.86	1.83
Naphthalene, 1-methyl-	0.95	3.54	2.61	2.13	6.76	6.66
Naphthalene, 1,5-dimethyl-	–	–	1.71	2.45	5.73	5.77
Naphthalene, 1,6,7-trimethyl-	–	–	–	0.71	–	1.19
Fluorene	–	–	–	–	1.49	1.82
Phenanthrene	–	–	–	–	1.02	2.22
Heteroatomics						
1,2-Benzisothiazole	1.51	1.49	1.47	1.29	1.15	0.86
Quinoline, 4,8-dimethyl-	–	–	0.42	0.68	0.62	0.39

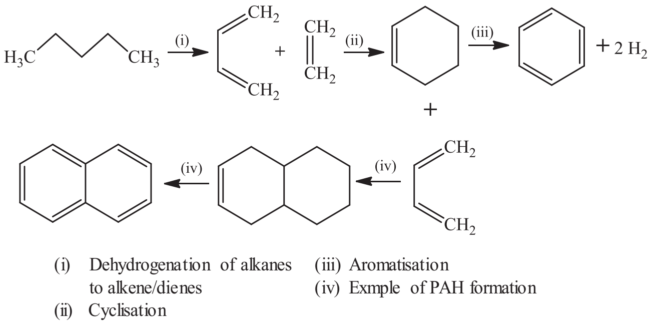

Fig. 8. Proposed mechanism of Diels–Alder reaction for the formation of polycyclic aromatic hydrocarbons in waste tyre pyrolysis [16,35,36].

One of the valuable chemicals obtained in TTPO is D-limonene (Fig. 7b). D-limonene was formed by intermolecular cyclisation of the allylic radicals produced by random scission of polyisoprene chain [13,38]. Several studies were conducted to investigate the influence of pyrolysis temperature on D-limonene yield, but the yields of D-limonene varied significantly. Danon et al. [13] reported that D-limonene production from waste-tyre pyrolysis was optimal between the pyrolysis temperatures of 400–500 °C. In this study, a maximum D-limonene yield of 14.29% was obtained at 400 °C, while a further increase of temperature to 450 and 500 °C resulted in the reduction of yield to 11.37 and 6.02%, respectively. Lopez et al. [17] reported the yield of D-limonene from pyrolysis of truck-tyre of 14.1% at temperature 475 °C using a spouted bed reactor, which is rather similar to the yield obtained in this study. It is should be noted that the optimum temperature of the current work was slightly lower as compared to the condition by Ref. [17] and the difference in the reactor used might have affected the result.

3.3. Energy recovery

Fig. 9 shows the calorific value of TTPO and energy yield at different pyrolysis temperatures. The energy yield was calculated based on Eq. (4). The value represents the conversion of energy stored in TT into pyrolysis oil during pyrolysis process [24]. From the figure, it is shown that higher calorific value is observed at 300 °C (TTPO300); however, the value decreased with increasing temperature. The difference in energy yield between TTPO300 (43.05 MJkg^{-1}) and TTPO400 (42.39 MJkg^{-1}) is 7.16 wt%. The reduction of calorific value may be due to some factors, such as the decrease if aliphatic fraction as well as the increase of aromatic fraction, water content, sulphur and oxygen content in the pyrolysis oil [2,4,18]. Cunliffe and Williams (1998) studied the influence of temperature towards the aromatic and aliphatic fraction in the waste tyre pyrolysis. As the temperature increased from 450 to 600 °C, they found the gross calorific value decreased slightly from 42.6 to 41.2 MJkg^{-1} due to the increase of aromatic fraction and decrease of aliphatic fraction [16]. From Fig. 7a, it was clearly shown that as the temperature increases, the aliphatic fraction decreases while the aromatic fraction increases, which could be one of the factors that contribute to the decrease of calorific value of TTPO. Williams et al. (1995) suggested that the decreasing fraction of aliphatic fraction is due to the volatilization of hydrocarbons which are degraded from limonene [34]. Hence, the decrease of limonene concentration in the pyrolysis oil is observed at higher temperature (>550 °C) [13,16,37]. The energy yield of the oil peaks at 500 °C (TTPO500) with the calorific value of 42.39 MJkg^{-1} before decreasing at 550 and 600 °C. The highest energy yield in pyrolysis oil relative to the feedstock in percentage are TTPO500, followed by TTPO550 and TTPO450 with 40.55, 29.97 and 28.97 wt%, respectively. The lowest calorific value of TTPO obtained at pyrolysis temperature 600 °C was 41.90 MJkg^{-1}, whereas, the TTPO300 contains the lowest energy yield of 8.06 wt% owing to low yield of pyrolysis oil.

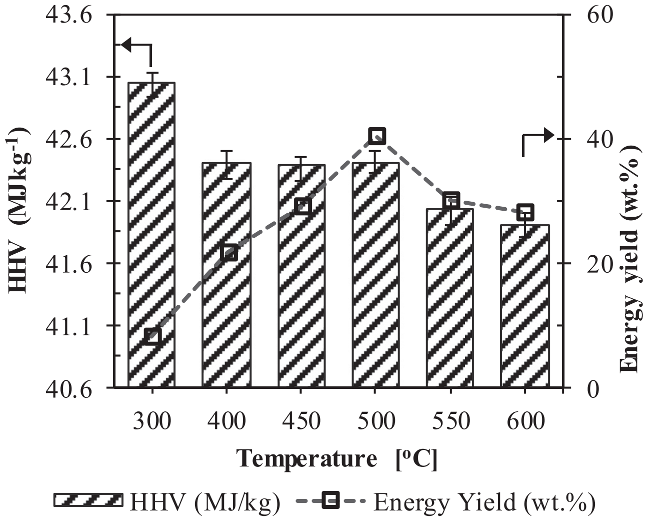

Fig. 9. Calorific value and energy yield of TTPO at different temperature (°C).

Table 4
The comparative study between TTPO500 with conventional diesel.

Characteristics	TTPO500	Diesel [14,15]
Carbon, C (wt.%)	87.75	86.58
Hydrogen, H (wt.%)	10.63	13.29
Nitrogen, N (wt.%)	0.60	0.01
Sulphur, S (wt.%)	0.67	0.01
Oxygen, O* (wt.%)	0.35	0.11
Kinematic viscosity at 40 °C	3.53	3–7.5
Density at 15 °C (kgL^{-1})	0.90	0.85–0.89
Flash Point (^{o}C)	<30	60–98
Water Content (%)	0.47	nd
HHV (MJkg^{-1})	42.39	45.6
LHV (MJkg^{-1})	40.12	40.3

* by difference.

3.4. *Fuel properties*

The elemental analysis, kinematic viscosity, density, flash point, and calorific value of TTPO at temperature 500 °C (TTPO500) were measured. Table 4 shows the comparison of physiochemical properties of TTPO500 with conventional diesel. From the CHNOS analysis, TTPO500 has higher carbon content compared with conventional diesel. However, the higher and lower heating value (HHV and LHV) of TTPO500 is slightly low as compared to conventional diesel but still consider high for the potential used as an alternative liquid fuel by blending with petroleum diesel [14,15]. The density and kinematic viscosity of TTPO500 is slightly higher as compared to conventional diesel. However, the kinematic viscosity of TTPO is still in the range of petroleum fuel standard, hence it would not incur the problem of injector clogging when blending with conventional diesel fuel. The flash point of fuel is a measure of the maximum temperature at which it can be stored and handled without serious fire hazard. The flash point of pyrolysis oil measured was shown to be within the range of 40–110 °C [39]. Table 4 shows that the volatility of TPPO is lower compared to petroleum diesel, indicating the pyrolysis oil needs to be upgraded in order to be utilised for direct application.

Several studies have been conducted in diesel engines using waste tyre pyrolysis oil as operating fuel. Lopez et al. [17] produced waste truck-tyre pyrolysis oil with good characteristics, in particular oil with high heating value. Yet, high sulphur contents limit the direct application of pyrolysis oil. In order to overcome this limitation, hydro treating process have been proposed [40,41]. The present TTPO produced shows high potential as alternative fuel, but further post-processes are needed to remove sulphur and nitrogen compounds.

4. Conclusion

The pyrolysis oil from waste truck-tyre was obtained by using microwave-assisted heating technique at different pyrolysis temperatures. The process involved the use of activated carbon as microwave absorber. Results show that activated carbon enhanced the TTPO yield. Highest yield of TPPO of 38.12 wt% was achieved at pyrolysis temperature of 500 °C. TTPO at pyrolysis temperature 400–500 °C contains high fractions of mono aromatics hydrocarbon with average yield of 73.14%. The calorific value of TTPO500 is 42.39 MJkg^{-1} with energy yield of 40.55%. Among the important chemical compounds observed in TTPO are benzene, toluene, xylene (BTX) and D-limonene. The relative yield of toluene and D-limonene was obtained at 400 °C with value of 14.85 and 14.29%, respectively. While, the relative yield of benzene and xylene observed at 450 °C with the amount of 0.85 and 7.60%. From the elemental analysis, the TTPO500 consist of high carbon content of 87.75% as compared to commercials diesel despite the presence of sulphur and nitrogen compounds inherited from the feedstock. This work shows that pyrolysis oil (TPPO) can effectively be derived from waste truck tyre using microwave heating technology. Detail characterization of the physiochemical properties of TTPO shows that it is a potential alternative fuel suitable for blending with conventional diesel, albeit further desulphurization process is needed to enhance its quality.

Acknowledgment

This research was financially supported by the University Grant of UMS (Grant No. RACE16-TK-2014) as well as the Research University Grant of UTM (Grant No. 4L653 and 17H70). Authors gratefully acknowledge the Eco Power Synergy Sdn Bhd for the supply of waste truck-tyre. R. Idris is funded by Ministry of Higher Education under the SLAB scholarship.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.joei.2018.11.009.

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