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Characterisation of liquid oil from pyrolysis of waste tyre

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Abstract

The aim of this study is to characterise the liquid oil produced from pyrolysis of waste tyre. In this study, a series of experiment were carried out at various process temperature from 300 °C to 500 °C. The degradation study was carried out by using TGA, meanwhile the pyrolysis process was done using a fixed bed reactor. Liquid oil obtained from the pyrolysis was analysed using FTIR and GC-MS. The oil yield was found to decrease with increasing final pyrolysis temperature and the yield of the gas increased. The highest oil yield was 58.3 wt. %. For pyrolysis at 400 °C. The pyrolysis of waste tyre at atmospheric pressure commenced at about 340 °C and completed at 460 °C. An increase in the aromatic content of the oil was observed with increasing temperature. However, the aliphatic content decreased as the temperature increased from 300 °C to 500 °C. It was observed that the amount of aliphatic fraction in the oil decreased from 7.8 wt. % to 5.4 wt. %. In the meantime, the number of aromatic compounds increased from 37.4 wt. % to 51.2 wt. %. The main aromatic compounds were limonene, xylene, styrene, toluene, trimethylbenzene, ethylbenzene and benzene.

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1.0 Introduction

Wastes such as municipal solid waste, industrial wastes and biomass are increasing every day. A lot of research has been conducted to recoup energy from these wastes. Fast depletion of fossil fuel also demands other ways to provide energy (Kumaravel et al., 2016). Waste from tyres are causing environmental effects because of its non-biodegradable properties. Most of waste tires are discarded via landfilling or even stockpiling that resulted in the utilisation of lots of our land spaces. Illegal dumping of waste tyres is also increasing because of the surprising expense of legitimate dumping.

Tyres are designed to withstand harsh conditions such as exposure to ozone, friction, light, and bacteria. This means they do not degrade in landfills; the tyre lifetime in a landfill is estimated between 80 to 100 years. Few alternatives have been made to diminish the quantity of waste tyres, for example, utilising them as a dock bumper, playground equipment, artificial reefs, and others (Canon et al., 2018). Pyrolysis, incineration, and gasification processes are viewed as increasingly appealing and useful strategies for recovering energy. However, pyrolysis is getting a greater interest in dealing and handling the waste tyre problem while at the same time permitting energy recovery. Pyrolysis has been an alternative method since the derived oils can be utilised directly as fuels or added to petroleum refinery feed stocks.

The pyrolysis oils are the source of light aromatics in addition to their utilisation as fuels. For example, benzene, toluene, and xylene (BTX) have higher market incentives than the raw oil (Roy, et al., 1997). Correspondingly, the oils seemed to comprise limonene. Limonene is a valuable product utilised in industrial applications such as resin, dispersing agent for pigments, formulation of industrial solvents, adhesives, fragrance in cleaning products, and as an environmentally acceptable solvent (Alsaleh et al., 2014). The objectives of this research are to produce liquid oil from waste tyre by using a fix bed reactor temperature from 300 to 500 °C and to characterise the produced liquid oil.

2.0 Methodology

2.1 Material

The waste tyre was collected from tyre shops. The tyre was cut into smaller parts of 1.5 cm each and the steel inside was removed.

2.2 Methods

2.2.1 Thermogravimetric analysis

Thermogravimetric analysis (TGA) was conducted to determine the thermal degradation of the waste tyre by using Thermogravimetric Analyser (Mettler Toledo, USA). The waste tyre samples were ground to powder form of approximately <1 mm particle size. The temperature and heating analysis used for the experiments were from 25 to 800 °C and 10 °C/min, respectively.

2.2.2 Proximate analysis

The proximate analysis was carried out to determine the proximate composition of moisture, ash, volatile matter and fixed carbon of the waste tyre. The analysis depends on the estimations of the mass difference of the sample as a function of a controlled/indicated temperature profile. This analysis was conducted by using Thermogravimetric Analyser (Mettler Toledo, USA) in presence of nitrogen from 25 to 950 °C, and then with the presence of air from 950 to 1200 °C. The heating rate was set to be 10 °C/min with nitrogen flow rate of 50 ml/min and 20 mg of powdered sample approximately < 1 mm size was used.

2.2.3 Pyrolysis

The pyrolysis was conducted in a vertical fixed bed reactor in a nitrogen atmosphere. The reactor consists of a condenser to collect and condense the gas. The products of this process include liquid oil, char and gas. The uncondensed gas was released to the atmosphere since it is not the objective of this research to study the gas. The liquid oil was collected together with the char and weighed. The gas weight was obtained by subtracting total weight with char and liquid obtained. The heating of the waste tyre was conducted at temperatures 300, 400, and 500 °C in a nitrogen atmosphere. In a typical run a cross-section tyre portion of about 200 g of waste tyre was placed into the reactor, which was sealed.

Table 1: Proximate analysis of waste tyre

Component	**wt. %**
Ash	11.0
Moisture	0.2
Volatile matter	48.9
Fixed carbon	39.9

3.0 Results and discussion

3.1 Proximate analysis

The proximate composition of moisture, ash, volatile matter and fixed carbon of the waste tyre is shown in Table 1. The analysis depends on the estimations of the mass difference of the sample as a function of a controlled/indicated temperature profile.

3.2 Thermal degradation of tyre

Fig. 1 and Fig. 2 show the TGA and DTG curves of the waste tyre, respectively.

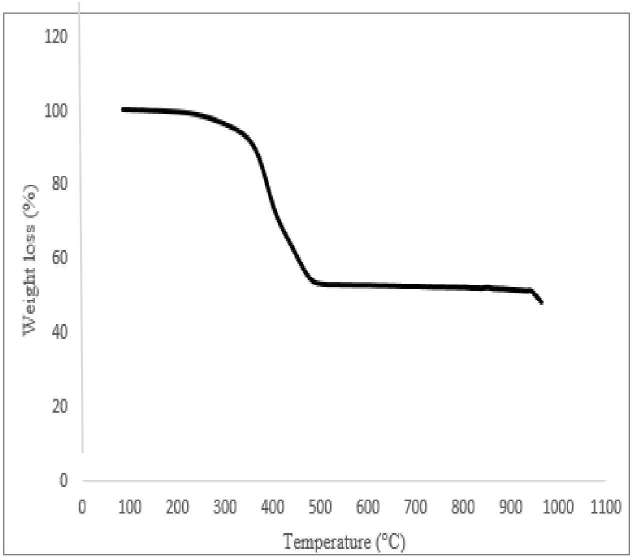

Fig. 1. TGA curve of the waste tyre

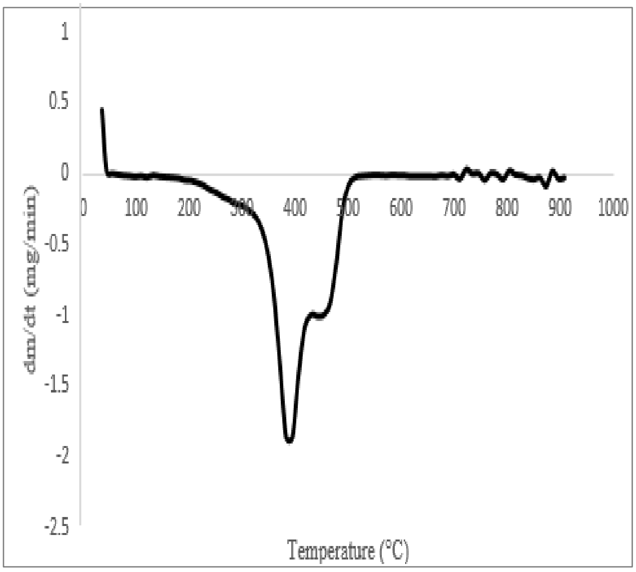

Fig. 2. DTG curve of the waste tyre

From the figures, it can be seen that it is one-step degradation graph. The pyrolysis of waste tyre at atmospheric pressure begins at about 340 °C and finishes at around 460 °C. The midpoint of the degradation is at 398 °C. The rubber degradation was generally assumed to begin at 200 °C. Significant yields of volatiles are discharged at temperature higher than this. The exact degradation temperature of the tyre relies upon the distributions and the contents of the rubber compound of the tyre.

Thermal degradation of waste tyre was carried out by Januszewicz et al. (2017) at temperature 400 °C to 700°C and gained three main products which were oil, gas, and char. In the study, an increment in oil product was noticed as the temperature differed from 400 °C to 500 °C. However, there is no increment of oil seen above 500 °C but a little increment in gas fraction was seen which was explained in terms of cracking of the liquid fraction at high temperature.

Fig. 2 shows the DTG curve of waste tyre which shows the weight loss per time as a function of temperature. From the graph, the optimum condition for the waste tyre degradation would be at its peak at 396 °C. The curve clearly shows that there are three decomposition regions of the sample. At 200 °C to 300 °C, the first weight loss was seen due to the degradation of the additives such as oils and stearic acid. The second weight loss was at 380 °C to 480 °C attributed to the degradation of the main components of the tyre which are natural rubber (NR) and styrene-butadiene rubber (SBR). Temperature around 410 °C to 500 °C was the final weight loss due to the decomposition of polybutadiene (PBR).

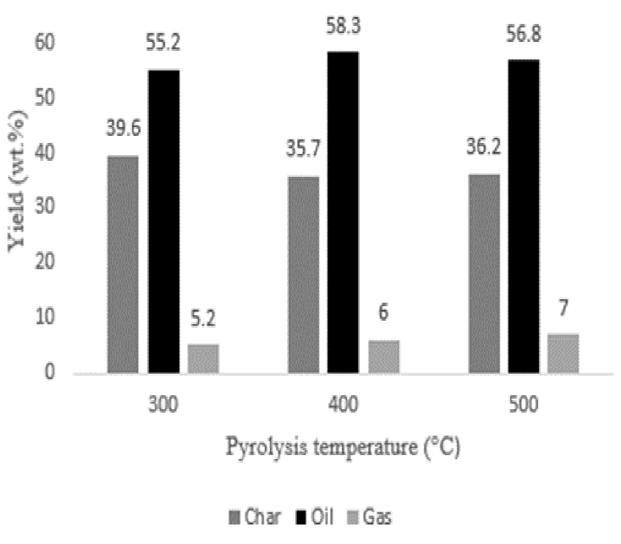

Fig. 3. Yield of products at 300, 400, and 500 °C

According to Li et al. (2016), thermogravimetric analysis was done to study the thermal decomposition of samples of known rubber composition and three major rubber components of the tyre were NR, SBR and PBR. However, Li et al. (2016) reported only two decomposition regions on the thermogram. The SBR decomposed at higher temperature, meanwhile NR decomposed at lower temperature. PBR decomposed mainly at higher temperature yet additionally showed initial decomposition at lower temperature.

3.3 Pyrolysis yields

The oil, gas and char yields (wt. %) of the waste tyre pyrolysis carried out at 300, 400, and 500 °C are presented in Fig. 3. At 200 °C the pyrolysis was not completed. At 300 °C the main product was char with values ranging between 30 and 40 wt. %. The content of oil and gas increases as the temperature is increased to 400 °C. The waste tyre pyrolysis was completed at 480 °C considering that higher increment in temperature would only result a little difference on the product yields. Pyrolysis at 400 °C seems to be the optimum condition, since decomposition is completed and the amount of yields obtained are not much different as at higher temperatures.

Nevertheless, due to higher thermal cracking as a result of consistency rise in the gas yield of the tyre, there is a small reduction in the char yield. The decrease in char yield was due to the increment in devolatilisation of solid hydrocarbon in the char.

Similar work has been reported on the pyrolysis of car tyre in nitrogen atmosphere from 300 to 700 °C by Islam et al. (2017). There was no temperature impact above 500 °C on the quality and amount of the products. Tyre pyrolysis could be comprised of three phases. They are the arrival of volatile and dampness at lower temperature prevailing by the thermal decomposition of NR, the decomposition of PBR and SBR at higher temperature. The yields of oil, char and gas were not essentially affected by the type of the tyre (Kyari et al., 2005). However, there were observable differences in the composition of the derived oil and gas.

A similar result of the product has been mentioned in the study of thermal degradation of waste tyre by Zabaniotou et al. (2003). It stated that as the temperature increases, the char yield decreases. Meanwhile, the increment of the gas fraction and corresponding decrease in pyrolytic oil was due to the cracking at high temperature.

The waste tyre pyrolysis gained a maximum yield of 58.3 wt. % at nearly 400 °C. The oil yield was then decreased with increasing temperature. On the other hand, the gas yield of the waste tyre shows corresponding increment from 5.2 wt. % at 300 °C to 6 wt. % at 400 °C and 7 wt. % at 500 °C. Similar oil yield result was found by Nisar et al. (2018). In addition, other studies have observed the decrease in oil yield with increasing temperature and corresponding increase in gas yield.

3.4 Characteristic of tyre pyrolysis liquids

Since the liquid oil comprises of various and diverse components, it is hard to quantify them. Almost all of the researchers have utilised elemental analysis, FTIR, and GCMS analytical techniques to distinguish and evaluate potential compounds in the liquid oils derived from various types of waste tyre (Ding et al., 2016). The liquids gained in tyre pyrolysis, which are usually termed oils, are dark brown-coloured products, which look like petroleum fractions.

Martínez et al. (2013) reported that oil from the pyrolysis of waste tyre can achieve 44 MJ/kg of energy content relying upon the composition of the tyre condition of the process. This means that the oil has a higher calorific value than the waste from which it is recovered. It could also resemble similar properties to those of a light liquid fuel that has similar calorific value and the content of the sulphur, which can be used as substitution of conventional oil fuels.

3.5 Fourier-transform infrared spectroscopy (FTIR) analysis

The oil composition was determined at 300, 400, and 500 °C. The oils have been fractionated into wide chemical class fractions. A qualitative observation of the FTIR spectra relating to the oil at these temperatures demonstrates the presence of alkanes, alkenes, alkyls and aromatic groups. The results of the analysis are shown in Fig. 4 and a series of absorption bands are summarised in Table 2.

Band 1 corresponded to stretching of C–H in alkane. Band 2 also corresponded to stretching of alkane C–H. Band 3 has observed to be corresponded to the stretching of C=C in alkene. Band 4 corresponded to stretching of the aromatic C=C. Band 5 seems to be corresponded to bending of C–H in alkane. Band 6 observed at 1259 $\mathrm{cm^{-1}}$ corresponded to stretching of ether C–O. Stretching of C–N in amine was observed to correspond to band 7. Band 8, 9, and 10 shows that they are corresponded to the same group which is bending of alkene =C–H. Band 11 and 12 also observed to be corresponded to the same group which is stretching of C–Cl in alkyl halide at 729 $\mathrm{cm^{-1}}$ and 698 $\mathrm{cm^{-1}}$, respectively.

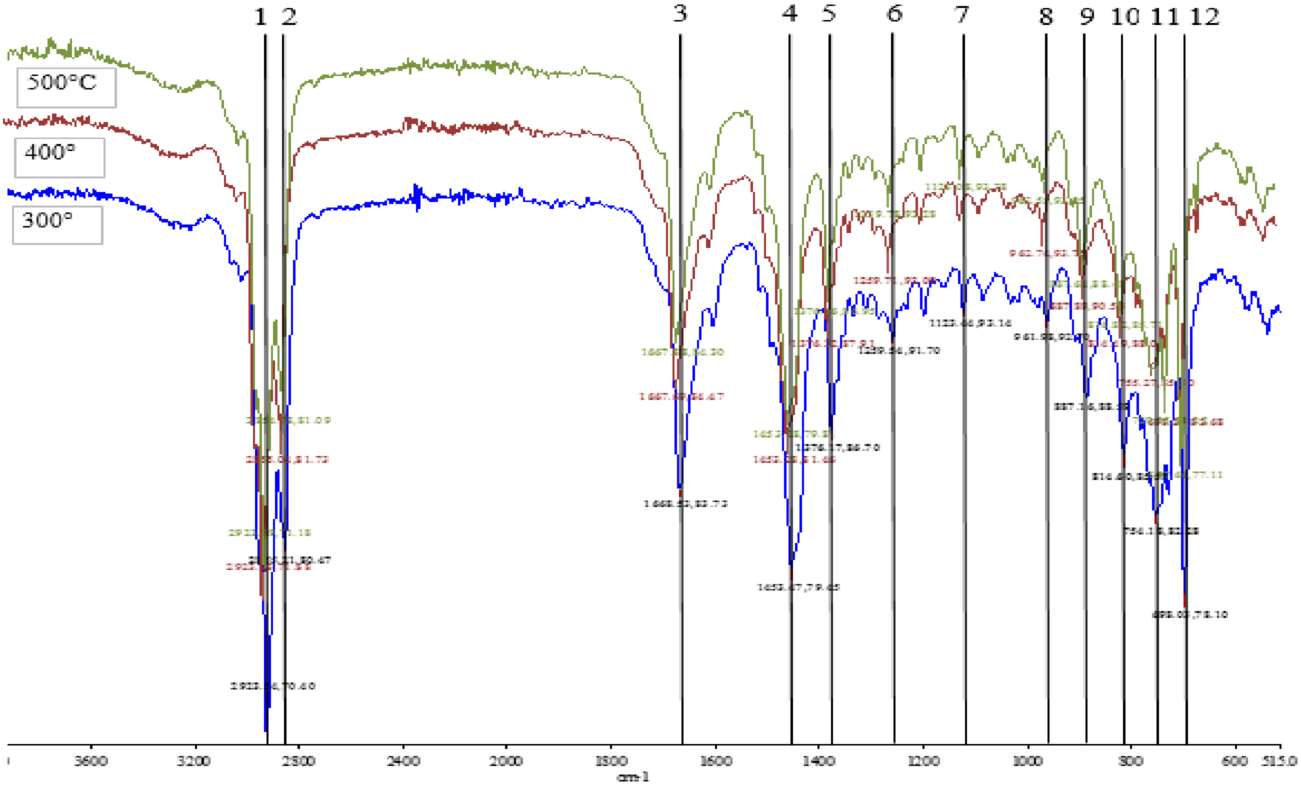

Fig. 4. FTIR of the oil at 300, 400, and 500 °C

Studies by Ding et al, (2016) showed that waste tyre oil composition from the pyrolysis of waste tyre consists of 26.8 wt. % alkanes, 42.1 wt. % aromatics, 26.7 wt. % on non-hydrocarbons and 4.05 wt. % asphalt and at 600 °C, a polar fraction of 27.8 wt. %. On the other hand, as the temperature increased from 300 to 700 °C, Nisar et al., (2018) showed an increase in aromatic content of the pyrolytic oil from 53.4 wt. % to 74.8 wt. %.

3.6 Gas chromatography mass spectroscopy (GCMS) analysis

GCMS analysis were carried out with the pyrolysis oils obtained at every temperature. A profile of the oils gained at these temperature shows that they are qualitatively similar. Fig. 5 shows the GC-MS chromatograms of the oil obtained at 400 °C from the pyrolysis of the waste tyre. The aim was to gain a general idea of the compositions of the oils. The main component identified in this analysis were summarized in Table 3. The main components were benzene, toluene, ethylbenzene, xylene, styrene, limonene, trimethylbenzene, hexane, thiopene, and naphthalene. Fig. 5 shows the GCMS chromatogram of the pyrolytic oil gained at 400 °C. The compositions of the chemical of the pyrolytic oil were complex. This is due to the variety of tyre rubbers and processing additives. The main components of the oil are aromatic compounds which were limonene, xylene, styrene, toluene, trimethylbenzene, ethylbenzene and benzene. As the temperature increased from 300 °C to 500 °C, it was observed that the amount of aliphatic fraction decreased from 7.8 wt. % to 5.4 wt. %. In the meantime, the aromatic compounds increased from 37.4 wt. % to 51.2 wt. %. It shows a favour of aromatic compound formation reaction at higher temperature.

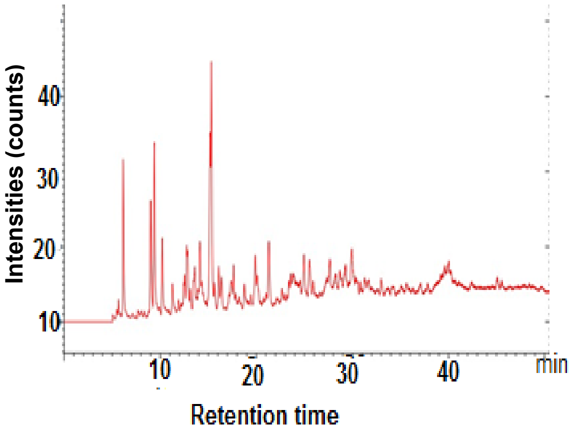

Fig. 5: GCMS chromatogram of pyrolytic oil at 400 °C

Degradation of natural rubber changed into limonene at temperature higher than 400 °C, due to the natural rubber fragments undergo cyclisation and aromatisation reaction to create aromatic compounds. Other than that, limonene also disintegrated to a range of products which includes xylene, trimethylbenzene, benzene, toluene and styrene. This happen at pyrolysis above 500 °C and/or with long hot zone residence times (Williams et al., 2013). The high concentration of the aromatic compounds present in the oil is a potential high value product. For instance, xylenes are major industrial chemicals and are used in plastic industry such as plasticizers, dyes and pigments. In addition, toluene has a broad range of application as chemical feedstock and are used in producing pesticides, solvents and surfactants. Styrene is used in the production of plastic materials.

Pyrolytic oil consists of a broad range of polycyclic aromatic hydrocarbon (PAH). The largest concentration of PAH found consist of fluorine, naphthalene and phenanthrene. For a fixed bed reactor, it has been reported that the total concentration of PAH in pyrolysis of waste tyre is 1.72 wt. % at 500 °C. However, over 16 wt. % of total PAH concentration has been reported at the same temperature.

Table 2. Classification of the main FTIR bands

Band	Frequency range (cm^{-1})	Functional groups	Class of compounds
1	2923	C–H stretching	Alkane
2	2855	C–H stretching	Alkane
3	1667	C=C stretching	Alkene
4	1453	C=C stretching	Aromatic
5	1376	–C–H bending	Alkane
6	1259	C–O stretching	Ether
7	1123	C–N stretching	Amine
8	962	=C–H bending	Alkene
9	887	=C–H bending	Alkene
10	814	=C–H bending	Alkene
11	729	C–Cl stretching	Alkyl halide
12	698	C–Cl stretching	Alkyl halide

Tyre pyrolysis prompts to the generation of propene, ethane and butadiene which react to form cyclic alkenes. The cyclic alkenes then undergo dehydrogenation with six carbon atoms. It then produces aromatic compounds and prompts the formation of PAH such as phenanthrene and naphthalene as a result of subsequent associative reactions, Lewandowski et al, (2019).

Table 3: Main components of the pyrolytic oil

Component (wt. %)	**Reaction temperature (°C)**		
	300	**400**	**500**
Aliphatic			
Stearic acid	0.27	0.25	0.12
Acetic acid	0.3	0.2	-
Heptene	0.09	0.05	0.02
Heptane	0.27	0.14	0.09
Hexane	1.17	1.16	1.03
Others	5.71	4.23	4.16
Hydrocarbons			
Methylcyclohexane	0.17	0.13	-
Cyclobutane	0.21	0.20	0.18
Cyclohexadiene	0.32	0.27	0.22
Cyclopentene	0.9	0.76	0.53
Limonene	6.41	6.52	5.51
Others	10.2	11.3	10.4
Aromatic			
Toluene	3.7	4.1	4.6
Ethylbenzene	1.93	2.22	2.89
Styrene	2.43	2.68	3.01
Xylene	1.57	1.55	2.42
Benzene	5.39	5.44	5.89
Methylstyrene	0.15	0.17	0.26
Indene	0.82	0.83	0.9
Trimethylbenzene	5.18	5.07	5.79
Propyltoluene	0.48	0.51	0.47
Others	15.77	19.36	24.92
Sulphur compound			
Thiophene	4.04	4.01	2.23
Naphthothiopene	0.43	0.55	0.42
Dibenzothiopene	2.24	2.15	1.13
Others	3.12	2.55	2.12
Polyaromatic hydrocarbon			
Fluorene	0.05	0.04	1.89
Naphthalene	1.07	2.76	4.83
Phenanthrene	0.09	2.31	2.43
Pyrene	0.11	0.06	0.24
Others	7.3	7.8	8.1
Unknown	18.11	10.63	3.4

4.0 Conclusions

Pyrolysis of oil from waste tyres is a suitable method to produce an alternative renewable energy source that can support the impact of fast depletion of crude oil reserves, its fast-increasing cost due to high demand, along with its adverse negative environmental effect. In this study, waste tyre was pyrolysed at 300 to 500 °C in a fixed bed reactor to produce pyrolytic oil. Thermogravimetric analysis affirms that the pyrolysis of waste tyre at atmospheric pressure begins at about 340 °C and finishes at around a temperature of 460 °C. It was also seen that the pyrolysis products yield and their characteristics are greatly influenced by the composition of the feed, operating conditions, and the specific properties of the system used.

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