

Pyrolysis of Waste Tyre

Nur Atiqah Mohd Rafee, Rusmi Alias

Faculty of Chemical Engineering, Universiti Teknologi Mara

Abstract—Millions of tyre were produced each and every year and end up as waste tyres because of developing population and fast industrialization. One of the method to convert waste tyre into a valuable product is pyrolysis. The aim of this study is to characterize the liquid product produced by pyrolysis of waste tyre and their characteristics under process parameter such as temperature. In this study, a series of tests were carried out at a various process temperature from 300°C to 500°C. The degradation of the waste tyre used was identified by TGA analysis and the liquid oil produced were analysed through FTIR and GC-MS analyzer. The oil yield was found to decrease with increasing final pyrolysis temperature and the yield of the gas increased. The highest oil yield was found at 400°C which is 58.3wt.%. The pyrolysis of used tyre at atmospheric pressure commences at about 340°C and completes at around a temperature of 460°C. The influence of temperature showed an increase in the aromatic content of the oil with increasing temperature. However, the aliphatic content decreased. As the temperature was increased from 300°C to 500°C, it was observed that the amount of aliphatic fraction in the oil decreased from 7.8wt.% to 5.4wt.%. In the meantime, the amount of aromatic compounds increased from 37.4wt.% to 51.2wt.%. The main aromatic compounds were limonene, xylene, styrene, toluene, trimethylbenzene, ethylbenzene and benzene.

Keywords— Liquid, oil, pyrolysis, tyre

I. INTRODUCTION

Waste such as municipal solid waste, industrial wastes and biomass are increasing every day. A lot of research has been conducted to recoup the energy from these waste. Fast depletion of fossil fuel also demands another ways to provide energy. Waste from tyres are causing a big problem since it is not biodegradable. Most of waste tires are discarded via landfilling or even stockpiling. This utilized lots of our land spaces. Illegal dumping of waste tyres is also increasing into a large stockpiles. In fact, illegal dumping of tyres have been increasing because of the surprising expense of legitimate dumping.

Tyres are fabricated to profoundly impervious to physical, chemical and biological impacts. Thus, making tyres extremely hard to apply methods for their recycling as well as further processing. Few alternatives have also been made to diminish the quantity of waste tyres, for example, utilizing them as a dock bumper, playground equipment, artificial reefs and others [1]. Pyrolysis, incineration and gasification processes are viewed as increasingly appealing and useful strategies for recovering energy. However, pyrolysis is getting a great deal intrigue and regard for handle the waste tyre discarded problem at the same time permitting energy recovery. Pyrolysis has various focal points as a method alternative since the derived oils might be utilized straightforwardly as fuels or added to petroleum refinery feed stocks. Plus, they may likewise be a critical hotspot for refined chemicals.

The pyrolysis oils have been had all the earmarks of being an ability source of light aromatics in addition to their utilization as fuels. For example, benzene, toluene and xylene (BTX) direction a higher market an incentive than the raw oil [2]. Correspondingly, the oils seemed to comprise limonene. Limonene is a valuable product utilized in industrial applications such as resin, as dispersing agent for pigments, formulation of industrial solvents, adhesives, as a fragrance in cleaning products and as an environmentally acceptable solvent [3]. The objectives of this research are to produce liquid oil from waste tyre by using fix bed reactor and to characterize the produced liquid oil. The process is done in a fixed bed reactor with temperature from 300°C to 500°C.

II. METHODOLOGY

A. Preparation of raw material

The raw material that was used in this research of study was waste tyre. The waste tyre was collected from tyre shop. The tyre was cut into smaller part and the steel inside the tyre was removed. The tyre was cut into approximately 1.5cm each including the textile.

i. Thermogravimetric analysis

Thermogravimetric analysis (TGA) was conducted to check for the thermal degradation of the tyre by using thermogravimetric analyzer (model Mettler Toledo). The sample of the tyre was in powdered form and collected from Faculty of Civil Engineering. This is because tyre powder is one of the research material provided at the faculty. The powder was about <1mm approximately. 100mL/min of nitrogen gas was used to remove all oxygen in this analysis. The temperature and heating analysis that was run for this analysis is from 25°C to 800°C and 10°C/min respectively.

ii. Proximate analysis

This analysis is to determine the proximate composition as far as moisture, ash, volatile matter and fixed carbon of the raw material which is the waste tyre. The analysis is depends on estimations of the mass difference of the sample as a function of a controlled/indicated temperature profile. This analysis was conducted by using thermogravimetric analyzer. The analyzer was run in presence of nitrogen from 25 to 950°C then with presence of air from 950 to 1200°C. The heating rate was 10°C/min with nitrogen flow rate of 50 ml/min and 20mg of powdered waste tyre was used. The powder was about <1mm approximately. The result is shown in Table 1.

Table 1. Result of proximate analysis of waste tyre

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

B. Pyrolysis

The process was conducted in a vertical fixed bed reactor in a nitrogen atmosphere. The reactor consists of condenser to collect the gas. The products that were produced including liquid oil, char and also gas. The gas was released to the atmosphere since it is not the objective of this research to study about the gas. The liquid oil was collected together with the char. The char, and liquid were weighed. The gas weight was obtained by subtracting total weight with char and liquid obtained. The heating of the waste tyre was conducted in a few temperatures which were 300°C, 400°C, and 500°C in 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.

C. Liquid oil analysis

FTIR equipment (model Perkin Elmer/ Spectrum One and GC-MS equipment were used to analyze the liquid oil product from the pyrolysis.

III. RESULTS AND DISCUSSION

A. Thermal degradation of tyre

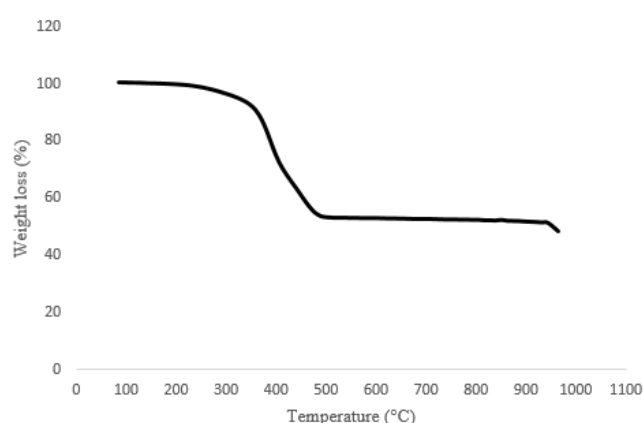


Figure 1. TGA curve for waste tyre

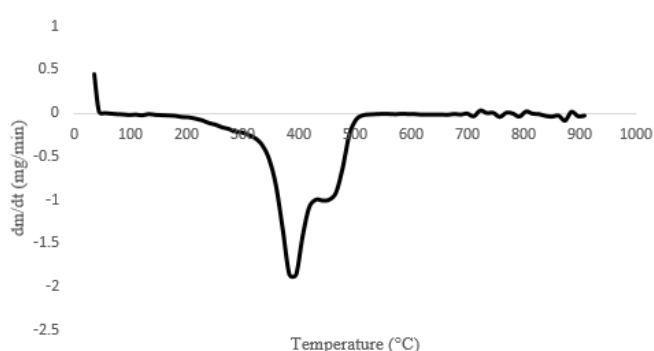


Figure 2. DTG curve of the waste tyre

From Figure 1, it can be seen that it is one-step degradation graph. The pyrolysis of used tyre at atmospheric pressure begins at about 340°C and finishes at around a temperature of 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 [4]. 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 Berruoco et al [5] at temperature 400°C to 700°C and gained three main products which were oil, gas and char. They noticed an increment in oil product 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.

Figure 2 shows the DTG curve of waste tyre which shows the weight loss per time as a function of temperature. From the graphs, the optimum condition for 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 shows the first weight loss 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). 410°C to 500°C was the final weight loss due to the decomposition of polybutadiene (PBR).

A TGA analysis was done by previous study to study the thermal decomposition of three samples of known rubber composition and the three major rubber components of the tyre which were NR, SBR and PBR. The thermogram indicated two decomposition regions. 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 [6].

B. Pyrolysis yields

The oil, gas and char yields (wt.%) gained in the tyre pyrolysis experiments carried out at 300, 400, and 500°C are presented in Figure 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 contents of oil and gas increases as the temperature is increased to 400°C. The tyre pyrolysis was completed at 480°C considering that higher increment in temperature would only give a little difference of the yields gained from the tyre. 400°C seems to be the optimum temperature for pyrolysis of tyres, since decomposition is finished and the amount of yields obtained are not much different as at higher temperatures. Anyway, 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. The carbon black filler is the source of the char from the tyre pyrolysis [6].

A pyrolyzed car tyre was pyrolyzed in nitrogen atmosphere from 300°C to 700°C. The products gained were collected and characterized. From their experiments, there was no temperature impact above 500°C was seen on the quality and amount of the products [7]. Tyre pyrolysis could be compromised of three phases. They are, the arrival of volatile and dampness at lower temperature prevailing by the thermal decomposition of NR and the decomposition of PBR and SBR at higher temperature, separately [8]. The yield of oil, char and gas were not essentially affected by the type of the tyre [9]. However there were observable differences in the composition of the derived oil and gas.

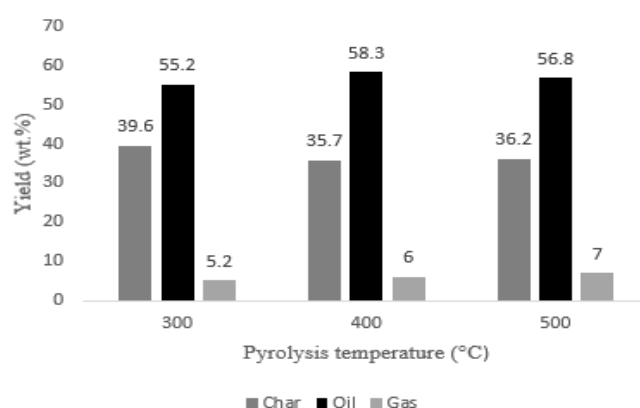
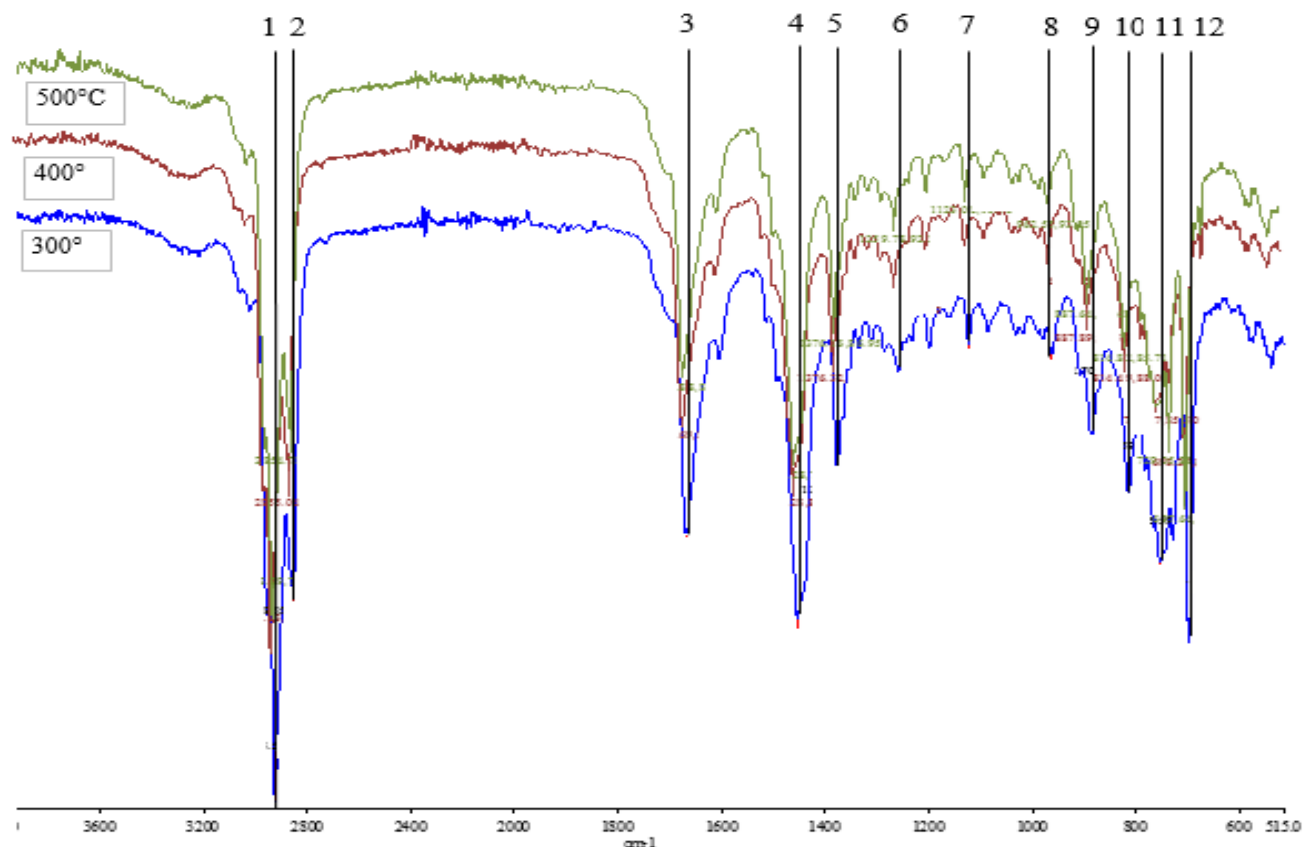


Figure 3. Yield of products on various temperature



A similar result of the product has been gained in study of thermal degradation of used tyre [10]. They stated that as the temperature increases, the char decreases. Meanwhile, the increment of gas fraction and corresponding decrease in pyrolytic oil was due to the cracking at high temperature. In Figure 3, the yield of pyrolytic oil from the pyrolysis gained a maximum at nearly 400°C with a yield of 58.3wt.%. The oil yield is then decreased with increasing temperature. On the other hand, the gas yield of the waste tyre shows a corresponding increment from 5.2wt.% at 300°C to 6wt.% at 400°C and 7wt.% at 500°C. Similar oil yield result was found by Williams et al [3]. They gained a maximum of 58.8wt% of their waste tyre oil by using nitrogen purged static bed reactor. In addition, other studies have observed the decrease in oil yield with increasing temperature and corresponding increase in gas yield. For example, Williams et al [3], Kaminsky et al [11] and Lucchesi et al [12].

C. 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 utilized elemental analysis, FT-IR, and GC-MS analytical

techniques to distinguish and evaluate potential compounds in the liquid oils derived from various types of waste tyres. The liquids

gained in tyre pyrolysis, which are usually termed oils, are dark-brown coloured products, which looks like petroleum fractions [7].

Results by Martínez et al [13] showed that oil from the pyrolysis of waste tyre can achieve 44MJ/kg of energy content relying upon the composition of the tyre and the condition of the process. This means that the oil has a higher calorific value than the waste tyre from which is recovered. It could also resembles 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.

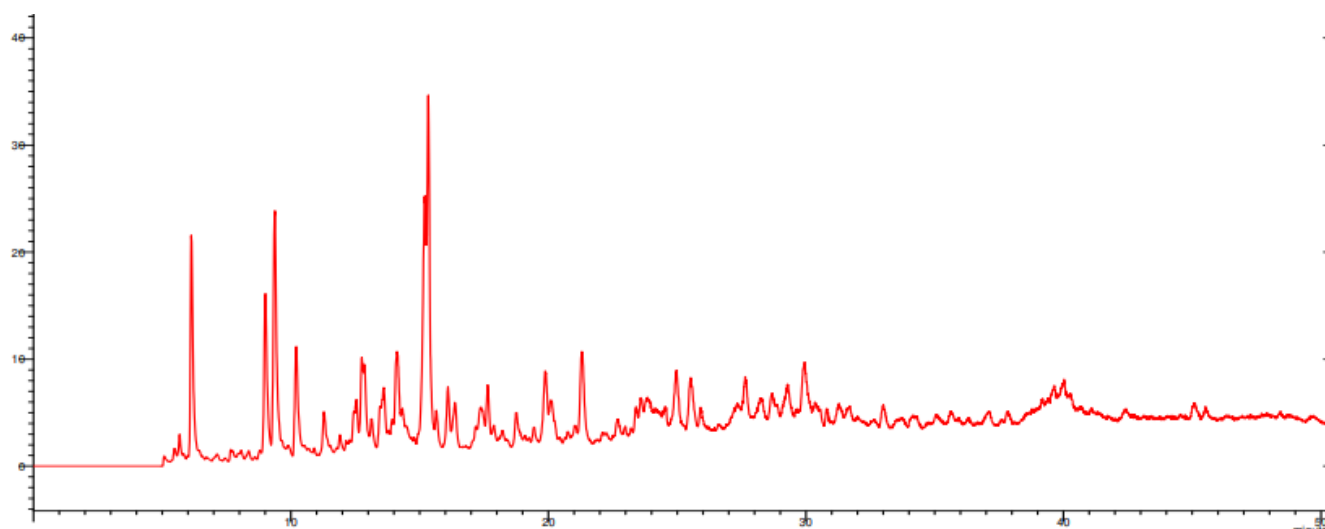
i. Fourier-transform infrared spectroscopy (FTIR) analysis

The oil composition was determined at 300°C, 400°C 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 temperature demonstrates the presence of alkanes, alkenes, alkyls and aromatic groups. The results of the analysis was shown in Figure 4 and a series of absorption bands summarized 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 stretching of C=C in alkene. Band 4 corresponded to stretching of aromatic C=C. Band 5 seems to be corresponded to bending of C–H in alkane. Band 6 observed at

Table 2. Classification of 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 compound
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



1259 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 cm^{-1} and 698 cm^{-1} respectively.

Studies by Dai et al [14] showed that a tyre oil composition from the pyrolysis of tyre consists of 26.8wt.% alkanes, 42.1wt.% aromatics, 26.7wt.% on non-hydrocarbons and 4.05wt.% asphalt. At 600°C, Aylón et al [15] reported a polar fraction of 27.8wt.%. Other than that, as the temperature was increased from 300°C to 700°C, Laresgoiti et al [16] showed an increase in aromatic content of the pyrolytic oil from 53.4wt.% to 74.8wt.%.

ii. Gas chromatography/mass spectroscopy (GC/MS) analysis

GC/MS 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. Figure 5 shows the gas chromatograms of the oil obtained at 400°C from the pyrolysis of the tyre. Our 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, thiophene, and naphthalene.

Figure 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. From Table 3, it can be said that aromatics were the main components of the oil. About 40-55wt.% of the pyrolytic oil consists of aromatic compound. The main aromatic compounds were limonene, xylene, styrene, toluene, trimethylbenzene, ethylbenzene and benzene. As the temperature was increased from 300°C to 500°C, it was observed that the amount of aliphatic fraction in the oil decreased from 7.8wt.% to 5.4wt.%. In the meantime, the amount of aromatic compounds increased from 37.4wt.% to 51.2wt.%. This results proved that higher temperature favors aromatic compound formation reaction. Some studies on the thermal decomposition reported that NR was the main source of limonene [1, 13, 17].

Table 3. Main components of the pyrolytic oil

Components (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
Naphthothiophene	0.43	0.55	0.42
Dibenzothiophene	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

Broken NR changed into limonene at temperature higher than 400°C, due to the NR fragments met with cyclization and aromatization to create aromatic compounds. Other than that, limonene also disintegrates to a range of products. This includes xylene, trimethylbenzene, benzene, toluene and styrene. This happens at pyrolysis above 500°C and/or with long hot zone residence times [6, 18, 19]. The high concentrations 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 plasticisers, dyes and pigments. In addition, toluene has a broad range of application as a 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 consists of fluorine, naphthalene and phenanthrene. For a fixed bed reactor, it has been reported that the total concentration of PAH in pyrolysis of tyre was 1.72wt.% at 500°C [1]. However, over 16wt.% of total PAH concentration has been reported at the same temperature [19]. Tyre pyrolysis prompts to the generation of propene, ethane and butadiene which react to form cyclic alkenes. The cyclic alkenes were then undergoes dehydrogenation with six carbon atoms. It was then produce aromatic compounds and prompts the formation of PAH such as phenanthrene and naphthalene as a result of subsequent associative reactions [1, 20].

IV. CONCLUSION

Pyrolytic oil from waste tyres is a suitable methods of an alternative renewable energy source that can help caution the fast depletion of crude oil reserves, its fast increasing cost due to high demand, along with its adverse negative environmental effect. This review reports the present stage of research in used tyre pyrolysis. In this study, waste tyre was pyrolyzed at 300–500°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 pyrolysis products yields 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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