

Modification of Clinoptilolite as Catalyst for Waste Tyre Pyrolysis to Liquid Oil

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Abstract—This study investigates the modification of clinoptilolite with kaolin as a suitable catalyst and its effect on the properties of produced pyrolytic oil from waste tyres. The natural and modified clinoptilolites were characterized by Scanning Electron Microscopy (SEM) and Fourier transform infrared (FTIR). The influencing factors of the pyrolysis process including the temperature and particle size were evaluated. The results showed that the yield of pyrolytic oil increased from 20 to a value of 40 wt% at 400 °C and increased from 25 to 30 wt % for 2–10 mm particle size. The Composition of Pyrolytic Oil gave a benzene yield higher than that of non-catalysed pyrolytic oil. The catalyst also improved the yield of other valuable chemicals such as ethylbenzene, o- and p-xylene, styrene, toluene, quinoline, pyrene, thiophene, P-cresol, phenol, and limonene in the pyrolytic oil.

Keywords— Catalyst, clinoptilolite, liquid oil, waste tyre.

I. INTRODUCTION

The rapid industrialization and large amount of solid waste generated quotidian have contributed to energy crisis and environmental degradation challenges facing humanity today. The waste tyre is non-biodegrade and one of most important hazardous solid waste. Land filling the waste tyre leads to highly flammable toxic chemicals infiltrating the surrounding environment, while incineration produces a large amount of air pollutants [1]. Therefore, it is important to reduce waste tyres from the environment by implementing efficient innovative recovery methods. Among these, pyrolysis is a common method of processing waste tyres to produce fuel that is both efficient and economical [2]. Pyrolysis can recover ~70% of energy, which has high economic and environmental benefits [3]. Pyrolysis involves the thermal decomposition of waste tyres at high temperatures in the absence of oxygen [4, 5]. Pyrolysis offers an environmentally friendly method for the decomposition of large amount of waste tyres. Pyrolysis the waste tyres as a thermal degrading process has been regarded as the most promising method for the utilization of the waste tyres since the process is to reduce the weight of the waste tyres by up to 90 % of its original weight [6]. It results in the production of products such as waste tyre pyrolysis oil having a higher heating value than petroleum products and can be burned directly or mixed in with them, pyrolysis char and gas [7]. The pyrolysis process necessitates the use of a catalyst, which can upgrade the yield, quality and quantity of the products obtained from waste tyre pyrolysis [8]. The

impact of several types of natural and modified catalysts on the pyrolysis of waste tyres was investigated, with study results demonstrating an improvement in the pyrolytic oil's physicochemical qualities and chemical composition. This has been validated by the use of clinoptilolite as a catalyst in the pyrolysis waste tyres due to its unique properties including low cost, environmental friendliness, large specific area, high exchange capacity, micro porous structure, excellent selectivity to change, size and shape of cationic species, high chemical, thermal and mechanical stability [9]. Clinoptilolite is an excellent catalyst for a variety of key organic molecular processes. Cracking, isomerisation, and hydrocarbon synthesis are the most important. Clinoptilolite can promote a diverse range of catalytic reactions including acid-base and metal induced reactions [10]. Clinoptilolite is not used only in its natural state, but also in its modified state. Numerous studies have contributed to the issue of clinoptilolite modification in recent years. It was stated that the functionalization of both the external and internal surfaces of clinoptilolite could greatly expand the field of application. Surfactants, organic compounds, and inorganic substances can all be used to carry out the modification [11]. Related studies also stated that some clinoptilolite alterations alter its chemical composition and structure. Specific ions in the clinoptilolite are replaced with exchangeable ions that were previously within the clinoptilolite, making the clinoptilolite more accessible and increasing efficiency [12]. The objective of this work is to modify clinoptilolite to obtain viable catalyst. Various attempts have been undertaken to modify clinoptilolites utilizing low-cost raw materials such as clay minerals, slag and sludge, fly ash, and mining leftovers in order to address environmental and economic concerns [13]. Among them, kaolin appears to be the best option. Kaolin is a white hydrated aluminosilicate crystalline mineral with pseudo-hexagonal symmetry and a chemical composition of $\text{Si}_2\text{Al}_2\text{O}_5(\text{OH})_4$ [14]. Kaolin also has a high molecular stability, with isomorphous substitutions being rare or non-existent and environmentally friendly. Several researchers have modified the chemical and physicochemical properties of zeolite with kaolin to create catalyst [15-17]. Nevertheless, as zeolites have different properties affecting their capability, further research is required to evaluate the potential of other types of zeolites such as clinoptilolite. The literature shows no investigation on modification of clinoptilolite as a catalyst in pyrolysis process to convert waste tyres to liquid oil. Therefore, the present investigation is focused on the characterization and chemical composition of pyrolytic oil.

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II. METHODOLOGY

A. Materials and methods

A.1 Preparation of catalyst

All reagents and materials used in this study were of analytical or extra pure grade. Clinoptilolite and kaolin were provided, respectively by Pratley mining company in South Africa and Beihai, Guangxi, China. Clinoptilolite was first washed twice with distilled water to remove fine particles and impurities, then dried in the oven at 60°C for 24 h. Clinoptilolite was heated at 70°C in distilled water with a magnetic stirrer for 8 hours to remove magnetic impurities. The sample was dealuminated with 8.5 mL of HCl solutions (0.1M) at 80°C for 4 h then washed with distilled water until no Cl⁻ ions could be detected in the solution and dried at 80°C. The resultant sample was crushed, milled and sieved at 75 µm for analysis. The kaolin was washed, dried in an oven at 105°C for 10 h then milled at the size as clinoptilolite. The kaolin was refined for the removal of iron and performed the metakaolinization step at 600°C during 3 h, the metakaolin produced was then modified to clinoptilolite via the conventional hydrothermal process. The produced catalyst was kept in a desiccator for analysis and waste tyre pyrolysis.

A.2. Preparation of waste tyres

After washing the waste tyre with distilled water to remove debris, sand and stones, the tyre material was dried in an oven for 24 h at 100°C. Heavy duty was used to cut small pieces of tyre (5 and 10 mm) (GMF 8). The waste tyre was crushed into powder using a band saw (PCB DM 9500). All particle sizes were washed with acetone, soap, and distilled water before drying for 24 h at 45°C. A mass of 5 g of waste tyre was milled at 50 µm for characterization analysis. The proximate analysis of waste tyre consists of determination, by American Society for Testing and Materials (ASTM) standard methods, of moisture content, volatile content, ash and fixed carbon was done using STA 6000 Simultaneous Thermal Analyzer. The ultimate analysis was conducted with the thermo Scientific Flash 2000 elemental analyzer.

B. Pyrolysis Process

This work was carried out in a batch reactor. The waste tyres were used as feedstock in the pyrolysis process, which resulted in pyrolysis liquid oil and gas. Each experiment used 20 g/batch of waste tyre sample, including thermal pyrolysis and catalytic pyrolysis with modified clinoptilolite. A mass of 5 g of modified clinoptilolite catalyst was used, which gives the catalyst to feedstock ratio of 1:10 by weight loaded on a crucible and introduced into the reactor chamber. Nitrogen was used as carried gas to ensure the inert atmosphere at the constant flow rate of 100 mL/min (see Fig. 1). Each sample was heated in the pyrolysis reactor from room temperature to 600°C using heating rate of 15°C/min, once the process reached the desired temperature and the reaction time was fixed to 30 min or until there was no visible flow of liquid, before being cooled to 20°C. These allowed all liquid and vapour products to exit the reactor and reach the collection unit. The pyrolytic oil and gas fraction were both introduced into the flask via a flexible hose from the reactor outlet. The

ice aided in cooling the condensable fraction of the gas. When the pyrolysis was finished, the N₂ gas flow was stopped, and the reactor power was turned off. The round bottom flask was disconnected from the reactor after cooling, and the pyrolytic oil was collected in a glass vial, weighed, and stored for analysis.

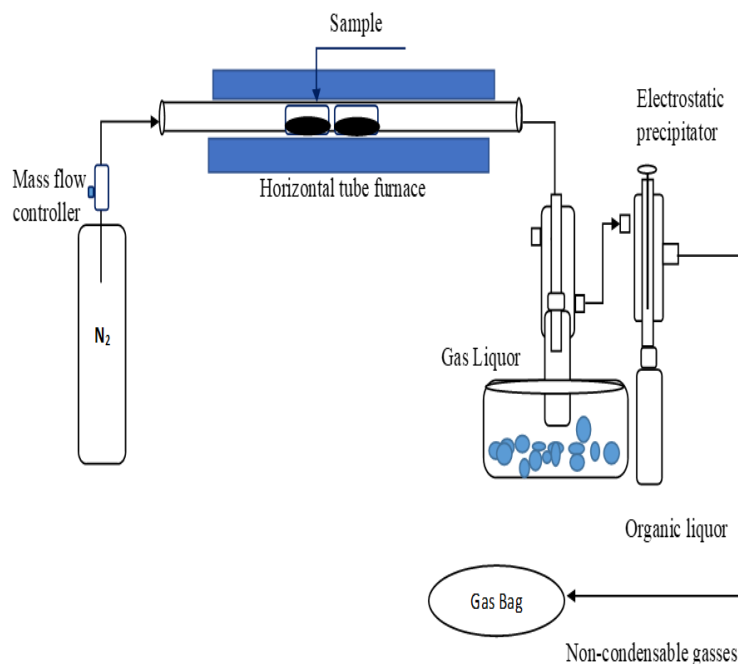


Fig. 1 Schematic diagram of the fixed bed pyrolysis unit

III. RESULTS AND METHODOLOGY

A. Characterizations of natural and modified clinoptilolites

A.1 Fourier transform infrared spectroscopy (FTIR)

Fourier Transform Infrared (FTIR) spectroscopy is used to specify the structure of clinoptilolite and to monitor reactions in the clinoptilolite framework.

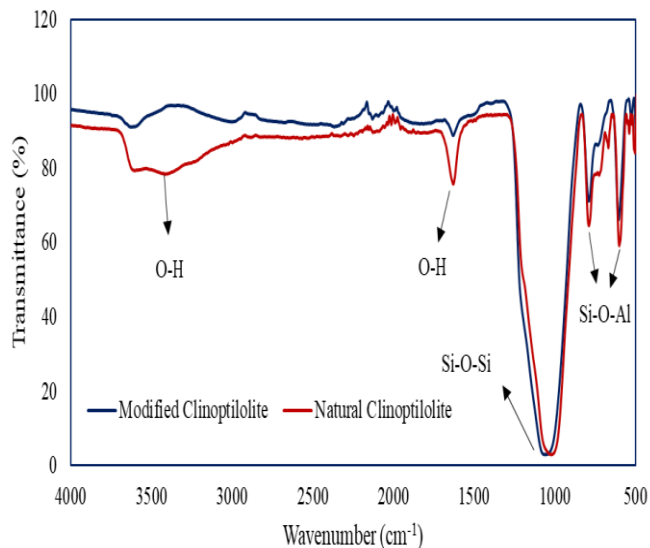


Fig. 2 FTIR spectra of natural and modified clinoptilolites

Figure 2 illustrates the FTIR spectra of the natural and modified Clinoptilolites. The peak at 3400 cm^{-1} in Figure 2 for the natural clinoptilolite represents the bonding O-H, which is the stretching and bending vibrations of hydroxyl groups. Weak peak at 3400 cm^{-1} should be due to the presence of kaolin in the modified clinoptilolite [14]. The peak at 1600 cm^{-1} for natural and modified clinoptilolites also represents the bonding O-H, which is the bending vibration. According to Mohamed Abatal et al. [18] the band at 1051 cm^{-1} is the most affected, this also appears widened and shifted to 1070 cm^{-1} , this behaviour has been attributed to a decrease in the relative content of Si/Al ratio in clinoptilolite framework with the increase in the length of the bonds Si-O-Si, and with the formation of structured effects. The peak at 1000 cm^{-1} could be assigned to antisymmetric stretching of Si-O bonds in aluminosilicates with clinoptilolite structure SiO_2 and Al_2O_3 are transformed to aluminosilicates during the reaction. The broad band in the spectral range from about ($700\text{--}600\text{ cm}^{-1}$) are assigned to Al-O bonds in Al_2O_3 .

A.2. Scanning Electron Microscopy (SEM)

The surface morphology of natural and modified clinoptilolites was also determined using SEM.

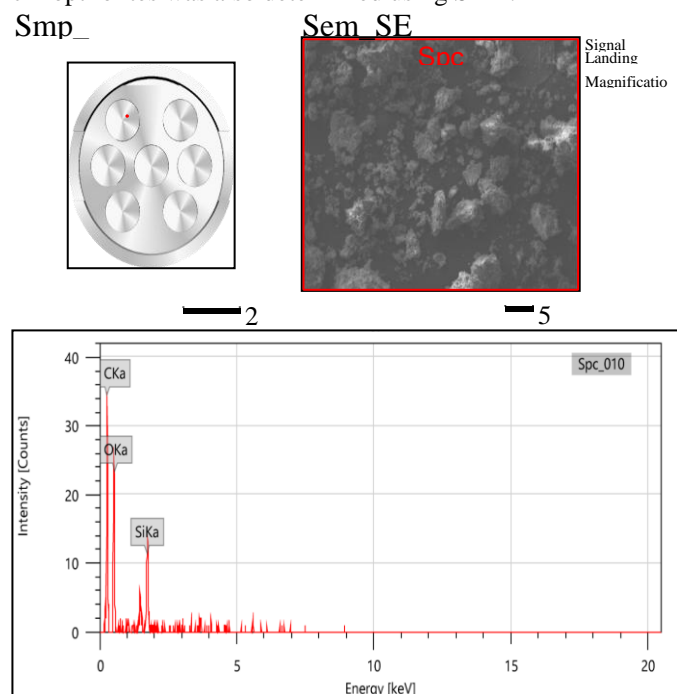


Fig. 3a SEM -EDS of natural and modified clinoptilolites

The natural and modified clinoptilolites are also depicted in Figs 3a and 3b, respectively. The natural clinoptilolite has large and small globular particles with random forms having a large space between them, while the modified clinoptilolite has also random globular particles but small space between them with white deposits, indicating the presence of kaolin. It also showed that the natural clinoptilolite elements are Carbon (C), Oxygen (O) and Silicate (Si) after modification of

clinoptilolite with kaolin ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), there is presence of Aluminium this indicated its higher kaolin content.

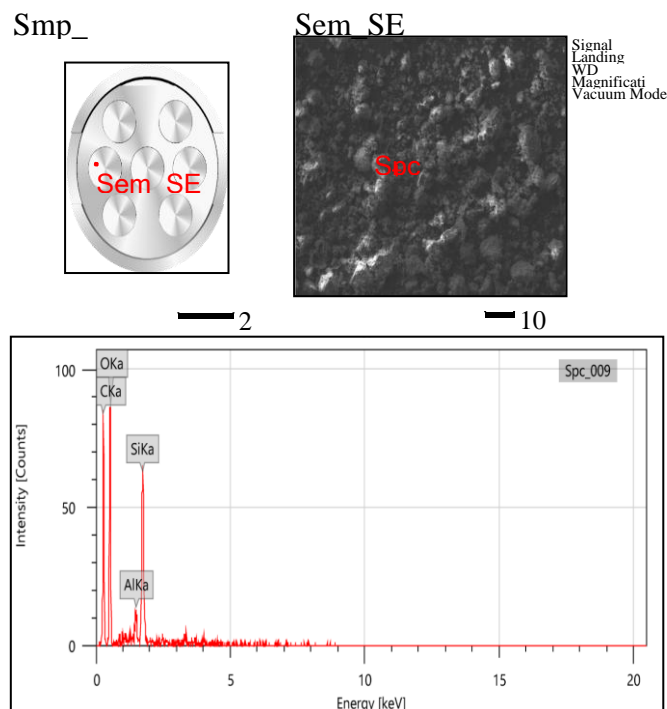


Fig. 3b SEM-EDS of natural and modified clinoptilolites

B. Waste tyre (WT) analysis

B.1 Proximate and Ultimate analysis of waste tyre

The proximate and ultimate analysis of waste tyre has been done to determine the residue contents. Proximate analysis was used to determine the moisture, ash, volatile, and fixed carbon content whereas the ultimate analysis was used to determine the elemental composition in terms of Carbon, Hydrogen, Sulphur, Nitrogen and Oxygen. The obtained results in Table I indicate the suitability of the waste tyre for the pyrolysis process as it was within the value range for the pyrolyzed tyre by Song et al. [19]. The substantial variance in the ash content could be attributed to the difference in the amount of inorganic compounds such as clay, silica, antioxidants, stabilizers and other additives introduced into the tyre rubber during production subject to the manufacturer exclusive formulation [20]. The presence of fixed carbon content indicates the amount of char formation in the pyrolysis process [21], it does not mean the total carbon in the feedstock as some might have escaped along with the volatile content during the thermal decomposition. Lower moisture and ash content recorded for the used tyres could be an added advantage than coal as a solid fuel. For the ultimate analysis, the results of hydrogen and nitrogen contents presented in Table I correlate with values reported in literature [21], but a little variation was observed in the values obtained for Carbon and Sulphur contents. Gross calorific value (GCV) of waste tyres obtained in this study was lower than that of conventional diesel but higher than that of lignite coal and

wood, making waste tyres a better source of solid fuel than lignite coal and wood [22].

TABLE I
PROXIMATE ANALYSIS (WT, %)

	This study	[17]	[23]	[24]	[25]	[26]	[27]
Moisture content	0.5	0.5	0.7	1.72	3.57	2.35	0.37
Ash	14	16	8	19.13	15.33	12.32	8.27
Fixed carbon	27	27.1	29.5	18.45	-	-	-
Volatile content	56.2	56.4	61.9	59.69	12.78	16.14	7.78

TABLE II
ULTIMATE ANALYSIS (WT, %)

	This study	[17]	[23]	[24]	[25]	[26]	[27]
Carbon	84.6	85	86.7	67.08	85.31	82.17	88.19
Hydrogen	5.2	5.5	8.1	6.12	1.77	2.28	0.9
Nitrogen	0.3	0.21	0.4	0.17	0.34	0.61	0.1
Sulphur	1.4	1.2	1.4	2.05	2.13	2.32	1.9
Oxygen	8	8.09	1.3	24.58	-	-	-
GCV (MJ/kg)	56.2	31.22	36.2	27.37	30.5	31.5	30.8

B.2 Waste tyre SEM

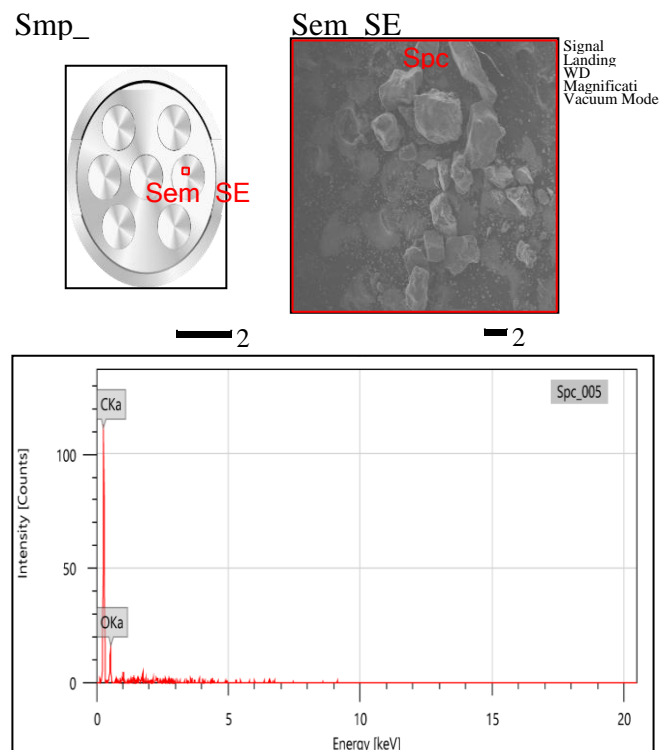


Fig. 4 SEM image of waste tyre

Fig. 4 shows the SEM images of waste tyre obtained at 750°C. The image was taken at a magnification of (X55) and acceleration voltage 10.00 kV with different pore diameter ranges (20 nm, 200 μm). The figure shows the heterogeneous distribution of pore and rough texture on surface. The image reveals about high surface area created during the process.

B.3 TGA analysis of waste tyre

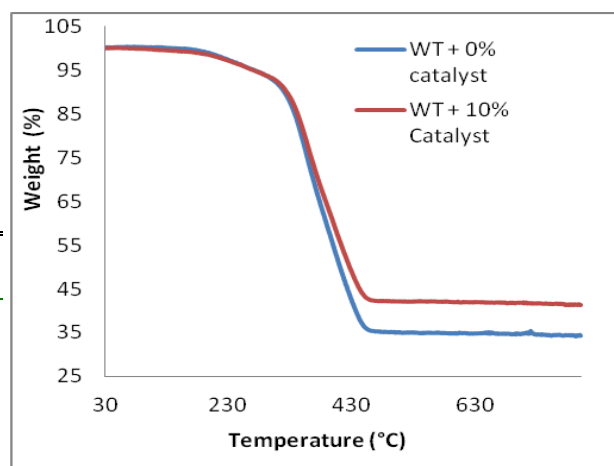


Fig. 5 Waste tyre and catalyst degradation

The pre-information regarding the thermal decomposition process of both waste tyre and catalyst was determined using thermo gravimetric analysis of waste tyre and catalyst in Fig. 5. The findings are inconclusive because they indicate that the catalyst slowed the process, but it was speculated that the reason for this was the more incombustible clinoptilolite that could be accounted for. Over a temperature range of 30 to 800°C, four radiation zones were found throughout the investigation. The first step, dehydration (loss of moisture), took place between 30 and 200°C, the second stage, early breakdown loss of hydrocarbons, took place between 200 and 220°C, and the third stage took place between 220 and 420°C. This stage is known as the pyrolytic zone, where maximum decomposition is achieved due to continuous cracking and rapid decomposition of rubber compounds such as natural rubber, styrene-butadiene rubber, and synthetic rubber [28], and it is stable between 420 and 800°C.

C. Factors affecting the pyrolysis process

C.1. Effect of Temperature

Temperature has a great influence on the pyrolysis product of tyre decomposition. The product distribution of the thermal pyrolysis of 10 g of waste tyre at a heating rate of 15°C/min at a temperature between 400 and 600°C at a particle size of 6 mm was investigated. The product yield of the process (pyrolysis oil, gas, and char) changes as temperature varies. Figure 6 shows that an increase in temperature from 300 to 600°C resulted in an increase in the yield of pyrolytic oil from 20 to a value of 40 wt% at 400 °C due to a decrease in the sulphur content in the oil. Furthermore, the yield reduced to

17 wt% at 600°C. The solid char yield decreased from 40 wt% to 30 wt% over the entire temperature range, while the gas yield increased from 34 to 40 wt%. It is obvious that a maximum yield exists at the temperature, where the optimum yield of pyrolytic oil was obtained possibly because of effective decomposition of the waste tyre at this temperature, 500°C, followed by secondary reactions that occurred within the reactor. This occurrence could have led to the formation of more gases at higher temperatures more than 500°C. This is also in agreement with the optimum temperature reported by Pradhan and Singh [29] and Osayi et al., [22]. The high-temperature process favours the production of gases while the low to medium temperature pyrolysis process favours the production of tyre pyrolysis oil.

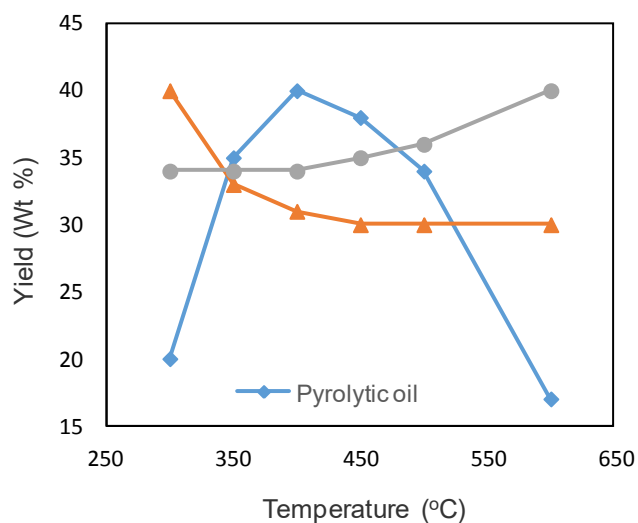


Fig. 6 Effect of temperature on waste tyre pyrolysis product yield (heating rate of 10 °C/min, N₂ flow rate of 100 mL/min)

C. 2. Effect of Particle size

Figure 7 shows the effect of feed size on waste tyre pyrolysis product yield conducted at 600°C at a heating rate of 10°C/min. The pyrolytic oil yield increased from 25 to 30 wt % for 2–10 mm particle size, respectively. The increase from 30 to 55 wt % in solid residue for particles from size 2–10 mm could be attributed to the less exposed surface area, which reduced the breaking of hydrocarbon molecules. Furthermore, the size increase could lower the thermal conductivity within the waste tyre, thereby preventing even distribution of heat within the entire waste tyre for more reaction [30]. This occurrence might lead to carbonization or incomplete degradation of the larger sizes of waste tyre, resulting in an increase in chars produced and a reduction in pyrolytic oil and gas yields. However, for the smaller size of 2 mm, the observed increase in gas yield may be attributed to the larger surface area available for reaction, enhancing the rate of heat transfer and degradation of the waste tyre. Small particle sizes aid the reduction of char due to more reaction surface, which led to more gas products. Particle size increased, the gas yield

steadily reduced as the solid increased. This is due to the low thermal conductivity and less exposed surface areas.

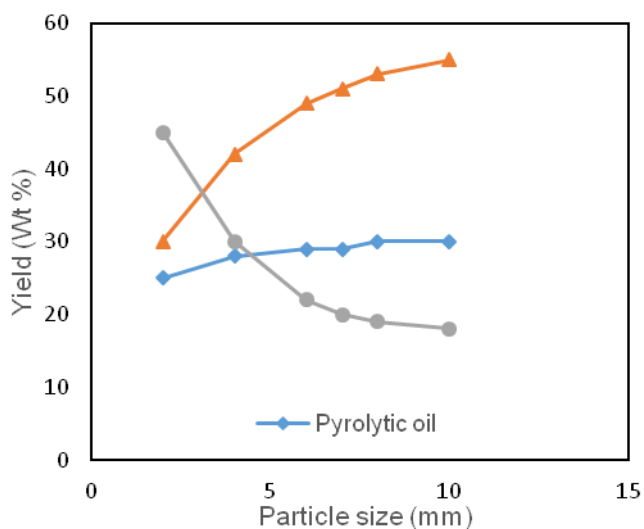


Fig. 7 Effect of Effect of particle size on waste tyre pyrolysis product yield.

D. Characterization of produced pyrolysis oil

The fuel properties such as density, Higher heating value (HHV), flash point, pH value, pour point, sulphur content, refractive index, and viscosity, were determined using American Society for Testing and Materials (ASTM) methods for its suitability as a liquid fuel. Table II presents the fuel properties of the waste tyre pyrolytic oil obtained in comparison with those reported by other researchers.

TABLE III
FUEL PROPERTIES OF WASTE TYRE PYROLYTIC OIL

	This study	[22]	[29]	[21]	Light Fuel oil	Commercial No2 diesel
Density (kg/m ³)	870	890	917	970	890	820-860
HHV (MJ/kg)	42	42.72	34.61	40.80	44.8	44-46
Flash point (°C)	30	30	-	32	79	> 55
pH value	6	5.76	-	4.80	N/A	N/A
Pour point (°C)	-10	-12	-87	-3	-10	-30
Sulphur Content (wt %)	0.0035	0.0035	1.38	1.36	30	1.2
Refractive Index	1.48	1.52	-	N/A	<1.49	1.45-1.1475
Viscosity (Cst)	4.98	5.18	5.31	4.90	21	2.0-4.5

As shown in Table III, the density of waste tyre pyrolytic oil is higher than that of commercial diesel and less than that of light fuel oil. Since high density is dependent on the molecular weight of the fuel molecules, this implies that the pyrolytic oil has higher fuel molecules than that of the conventional

gasoline and diesel [22]. The viscosity of waste tyre pyrolytic oil is above the maximum range for commercial diesel, this could be attributed to the presence of heavy compounds in the pyrolytic oil [31]. The refractive index of 1.480 was obtained for waste tyre pyrolytic oil which is within the acceptable values for commercial diesel. The pH value for the waste tyre pyrolytic oil is 6, this indicates that storage of the pyrolytic oil is safe and environmentally friendly due to its weak acidic nature [32]. The pour point obtained for the waste tyre pyrolytic oil is -10°C , making the oil useful where temperature could be below 0°C [22]. The sulphur content obtained for the waste tyre pyrolytic oil is lower than the sulphur content range of 0.11–1.54 wt% for used tyre pyrolytic oil [33] and that of light fuel oil. The flash point is low due to the fact that the pyrolytic oil is composed of a mixture of compounds with a wide distillation temperature range. The HHV of the waste tyre pyrolytic oil is at close range to that of a commercial diesel. The high HHV of the waste tyre pyrolytic oil makes it a viable alternative source of liquid fuel [34].

E. Influence of Modified clinoptilolite on chemical composition of pyrolytic oil

Table IV presents the influence of the modified clinoptilolite activity on the pyrolytic oil yield of chemical compounds of industrial significance. The results of all the Composition of Pyrolytic Oil gave a benzene yield higher than that of non-catalysed pyrolytic oil as follow: Composition of Pyrolytic Oil (5 wt.%) > Composition of Pyrolytic Oil (1 wt.%) > Composition of Pyrolytic Oil (10 wt.%) > Composition of Pyrolytic Oil (7.5 wt.%) > non-catalysed pyrolytic oil. This increase of benzene yield could be attributed to the modified clinoptilolite ability to enhance chain scission that occurs mostly for the pyrolysis of the various components of used tyres. Modified clinoptilolite must have favoured the Diels–Alder reaction that promotes the generation of benzene ring chemical species at elevated temperature. Modified clinoptilolite also improved the yield of other valuable chemicals including ethylbenzene, o- and p-xylene, styrene, toluene, quinoline, pyrene, thiophene, P-cresol, phenol, and limonene. These could be attributed to the catalyst-cracking ability of the tyre molecules, dehydrogenation, and transalkylation reaction that occurred during the pyrolysis process [35]. The presence of limonene and phenol in high amount in the Composition of Pyrolytic Oil is an advantage to the market value of the pyrolytic oil due to the wide industrial application of these compounds.

TABLE IV
INFLUENCE OF MODIFIED CLINOPTILOLITE ON PYROLYTIC OIL CHEMICAL SPECIES

Chemical species	Non-catalytic pyrolytic oil	1 wt% catalyst	5 wt% catalyst	7.5 wt% catalyst	10 wt% catalyst
Benzene	1.94	11.34	11.86	9.10	10.68
Toluene	-	-	-	-	0.19
Ethylbenzene	0.19	1.59	0.21	0.01	0.28
o-xylene	0.007	-	0.46	-	0.33
p-xylene	-	-	1.07	1.95	1.24
Styrene	0.08	-	-	-	0.80
Naphtalene	2.64	2.59	2.01	2.96	2.66
Quinolene	0.92	0.60	0.50	1.05	1.00
Pyrene	0.46	0.06	0.09	0.03	0.07
Thiophene	0.39	0.22	0.20	0.37	0.17
Limonene	0.08	9.72	2.85	2.96	5.00
p-cresol	0.10	0.75	0.25	0.26	0.45
Phenol	1.24	3.47	1.99	6.43	6.65

IV. CONCLUSION

The present study reports the effectiveness of a modified clinoptilolite catalyst from kaolin for waste tyre pyrolysis to liquid oil. The SEM and FTIR analysis for natural clinoptilolite were compared with the modified. The proximate and ultimate analysis of waste tyre were compared with the ones reported in literature. GCV of waste tyres obtained in this study was lower than that of conventional diesel but higher than that of lignite coal. The results showed that the yield of pyrolytic oil increased from 20 to 40 wt% at 400°C and increased from 25 to 30 wt % for 2–10 mm particle size. The product yield of the process (pyrolysis oil, gas, and char) changes as temperature varies while the pyrolytic oil yield increased from with the particle size. The physical properties of the produced pyrolytic oil are comparable with that of other pyrolytic liquids reported in the literature and that of the commercial diesel, strengthening the ability to use the liquid fuel as a source of energy. The addition of the catalyst in the pyrolysis of waste tyres gave a remarkable influence on the formation and content of some valuable industrial chemical compounds in the Composition of Pyrolytic Oil. It was found that all the Composition of Pyrolytic Oil gave a benzene yield higher than that of noncatalysed pyrolytic oil. This can be ranked as Composition of Pyrolytic Oil (5 wt.%) > Composition of Pyrolytic Oil (1 wt.%) > Composition of Pyrolytic Oil (10 wt.%) > Composition of Pyrolytic Oil (7.5 wt.%) > noncatalysed pyrolytic oil. In addition, the catalyst also improved the yield of other valuable chemicals such as ethylbenzene, o- and p-xylene, pyrene, quinoline, P-cresol, phenol, styrene, thiophene, toluene, and limonene in the pyrolytic oil.

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