

# **Research** Article

# Thermal Pyrolysis of Used Tyres to Produce Liquid Fuel: Process Optimization and How It Compares to Microwave Pyrolysis

Ronald K. Bett <sup>(1)</sup>,<sup>1,2,3</sup> Anil Kumar <sup>(1)</sup>,<sup>4</sup> Zachary O. Siagi <sup>(1)</sup>,<sup>1</sup> and Zeddy C. Mibei <sup>(1)</sup>,<sup>2</sup>

<sup>1</sup>Department of Mechanical, Production and Energy Engineering, School of Engineering, Moi University, Uasin Gishu County, P. O Box 3900-30100, Eldoret, Kenya

<sup>2</sup>Africa Centre of Excellence II in Phytochemicals, Textiles and Renewable Energy (ACE II PTRE), Moi University, Uasin Gishu County, P. O Box 3900-30100, Eldoret, Kenya

<sup>3</sup>Kenya Ordnance Factories Corporation, Department of Quality Assurance Research & Development, P. O Box 6634-30100, Eldoret, Kenya

<sup>4</sup>Department of Chemical & Process Engineering, School of Engineering, Moi University, Uasin Gishu County, P. O Box 3900-30100, Eldoret, Kenya

Correspondence should be addressed to Ronald K. Bett; kipkemoironald@gmail.com

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Used tyres are not biodegradable, and the current methods of disposal pose a threat to the environment. Such tyres can be valorised through decomposition to produce liquid fuel, an alternative diesel fuel, using thermal pyrolysis technique. Microwave pyrolysis is an alternate method which uses microwave irradiation, saves energy, and is better environmentally. The main objective of this study was to perform microwave pyrolysis of used tyres to produce liquid fuel and compare with thermal pyrolysis. The specific objectives were to study the effects of pyrolysis operating variables and optimization of liquid fuel yield for thermal pyrolysis, compare with microwave pyrolysis, and characterize the liquid fuel. Thermal pyrolysis variables were reaction temperature, reaction time, and particle size. Thermal pyrolysis reaction temperatures were 200, 300, 400, 500, 600, and 700°C; reaction time 10, 20, 30, 40, 50, 60, 70, 80, 100, and 120 minutes. Particle sizes were 25, 50, 60, 100, 125, and 200mm<sup>2</sup>. Thermal pyrolysis was carried out in furnace fabricated using furnace clay rated 600 W. A 500 ml round bottomed flask was used as a reactor. Design Expert 13 was used for data analysis and optimization, gas chromatography-mass spectrometry (GC-MS) was used for chemical composition analysis, while physiochemical properties were tested using standard methods. The yield of the liquid product was correlated as a quadratic function of the reaction variables. Response surface methodology (RSM) was used to study the effects of operating variables and identify points of optimal yields. The yield decreased as particle size increased. Yield increased with increase in temperature optima being 500°C. Yield increased with increase in reaction time, and the pyrolysis time was 80 minutes. The highest liquid yield of 40.4 wt. % corresponded to temperature of 500°C, time of 80 min for 60 mm<sup>2</sup> size. The calorific value for liquid fuel was 47.31 MJ/kg and GC-MS analysis showed that the oil comprised of complex mixtures of organic compounds with limonene, toluene, and xylene as major components. When compared to the published literature on microwave pyrolysis, both processes gave similar maximum yield but microwave process was superior due to a 77.5% reduction in reaction time, resulting in a 73.02% saving in energy requirement.

# 1. Introduction

The production of vehicles is increasing as a result of fast industrialization around the globe since it is the popular mode of transport. As a result, the use of petroleum oil is increasing leading to a rapid depletion in nonrenewable petroleum fuels [1]. In the recent decades, alternative energy sources such as biodiesel and waste to energy fuels such as waste plastics pyrolysis oil have been of great interest to energy researchers [2]. Due to the desire to conserve environment from pollution, researchers are doing researches on conversion of wastes to energy using various waste to energy technologies [3]. Used tyres is one of the categories of wastes that are nonbiodegradable and, when they are disposed in environment or burnt in an open air, leads to environmental pollution. Thermal pyrolysis of tyres is the cracking of tyre molecules at higher temperatures in absence of oxygen to produce liquid, solid, and gaseous products [4]. The liquid product is of great interest in waste to energy because of its fuel properties. It has a higher calorific value compared to fossil fuels and therefore can be used as an alternative source of cheaper energy. According to Bett et al. [5], tyre pyrolysis oil has a calorific value of 48.99 MJ/kg while that of diesel is 44.8 MJ/kg according to Osueke et al. [6].

Several studies on catalytic thermal pyrolysis have been done to investigate the yield of pyrolysis products. According to research by Durak et al. [7], a cumin seed cake was transformed to liquid and solid products with and without catalyst. The pyrolysis was performed at temperatures of 300, 400, and 500°C. The aim was to investigate the liquid yield and the effects of catalyst on the process. The highest liquid yield was 30% in presence of  $Al_2O_3$  catalyst and less than 30% without catalyst. This clearly indicates that catalyst improves the yield of the liquid products. The high heating values (HHV) for the pyrolysis oil was found to be between 32.44 and 36.19 Mj/kg.

Another research was done to investigate the effects of temperature and catalyst on the production of biooil and biochar from avocado seeds by Durak and Aysu [8]. The reaction was performed in a fixed-bed reactor using KOH and Al2O3 as a catalyst and another without catalyst. The temperature range was between 400°C and 600°C, and the heating rate was 50°C/min. Temperature and catalysts were determined to be the main factors that affect the thermal cracking of avocado seeds to liquid and gaseous products. In this research, the highest liquid fuel yield of about 37.5% was obtained using 10% KOH as a catalyst at pyrolysis temperature of 600°C and heating rate of 50°C/min.

Aysu and Durak [9] did a research in 2015 to study the effects of temperature and catalyst on thermal pyrolysis of liquorice (*Glycyrrhiza glabra* L.). Experiment was performed with different catalysts (ZnO, FeCl<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, and Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>.10H<sub>2</sub>O) and without a catalyst at three different reaction temperatures (350, 450, and 550°C). The experiment was performed in a tubular fixed-bed reactor with a constant heating rate of 40°C/min. The highest liquid yield of 34.35% was at a temperature of 550°C with Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>.10H<sub>2</sub>O catalyst.

A research to study the primary products from thermal pyrolysis of lignin, cellulose, and hemicellulose was performed in 2020 by Senneca et al. [10]. After volatilization, the volatiles were quenched via a cold pyrex bridge, and the solid residue remains in the reactor strip. The results indicated that fast pyrolysis of lignin produces light tar that contains vanillin, aliphatics, and PAHs. At 1573 K, cellulose produces light tar containing levoglucosan as a result of depolymerization, and as the temperatures increases, the tar produced becomes heavier. Hemicellulose produces light tar similar to cellulose, and at higher temperatures, the tar becomes heavier. Thermal and catalytic pyrolysis of waste plastics was performed in 2020 by Kasar et al. [11] to study the properties of liquid fuel and gaseous products produced. The calorific value of the liquid products was found to be between 44 and 47 MJ/kg while that of gaseous products was between 27 and 32 MJ Nm<sup>-3</sup>. Other properties of liquid fuel were found to be similar to those of conventional fuels such as diesel and therefore recommended to be used as a fuel.

There are various pyrolysis technologies that can be used to recover the useful oil from used tyres. This research focuses on thermal pyrolysis and how it compares to microwave pyrolysis. Microwave pyrolysis is the use of microwave irradiation [12] instead of external heating source which is the case for thermal pyrolysis. There is need to compare various technologies to enable the pyrolysis industrial players choose an efficient system in terms of energy requirement, pyrolysis time, and waste to energy conversion efficiency. Despite the need to compare pyrolysis technologies, there is also need to clearly define the variables that affect each technology and identify the points of optimal yields. Thermal pyrolysis process will be compared to microwave pyrolysis by Bett et al. [5]. The microwave pyrolysis research by Bett et al. examined the effects of variables on the process and optimized the yields using response surface methodology. The microwave pyrolysis variables were microwave power, reaction time, and particle size. According to Bett et al. [5], the liquid fuel yield increased with increase in microwave power optima being 50% power. Yield increased with increase in reaction time while decrease in particle size increased the yield of tyre pyrolysis oil. The highest liquid yield of 39.1 wt % was at 50% power, 18 min reaction time, and particle size of 25 mm<sup>2</sup>.

The present research studied the effects of operating variables on thermal pyrolysis and optimized the liquid fuel yield using central composite design. Besides, the energy requirements for both processes were analyzed. However, the calculation of energy requirements for microwave pyrolysis was based on the parameters of microwave experimental set up by Bett et al. [5]. The type of reactor used in this study is a fabricated fixed bed reactor. A fixed bed reactor is a pyrolysis reactor where the feedstock is allowed to be heated for a given period on a bed which is stationary. It has heat source and condensing unit where the liquid products condenses [13].

### 2. Materials and Methods

2.1. Experimental Set-Up. The experimental set up was done as illustrated in Figure 1. A heating furnace was fabricated using furnace clay. Furnace clay was chosen because of its ability to retain heat and to withstand higher heating temperatures. The furnace clays were arranged in such a way that they form a cavity where the reactor is heated. Two electrical heating coils each rated 300 W were inserted on the furnace clays on the inner side of the heating cavity. The coils were then connected to a temperature controller to monitor the temperature of the heating cavity. A 500 ml round bottomed flask connected to a glass Liebig condenser was used as a reactor. The feedstock is fed into the reactor,



FIGURE 1: Thermal pyrolysis set up.

and when the power is switched on, the feedstock is heated to the set temperatures. The fumes are formed at higher temperatures, and they flow out of the reactor through the condenser where they are condensed, and the liquid products are collected at the sample bottle. The condenser comprises of flowing cold water at an average temperature of 10°C. A temperature gradient exists between the hot products of pyrolysis in the inner tube of the glass Liebig condenser and the circulating cold water. A heat transfer occurs, and the products of pyrolysis condense, and the liquid products are collected.

The thermal oven comprises of heating coil rated 600 W, a thermocouple probe with maximum temperature of 1300°C, and a temperature controller each with a range of 0-1000°C.

2.2. Feedstock Preparation. The feedstock used in this study was used tyre particles that were shredded into desired particle size using a sharp knife. The thickness of the tyre particles were similar with a dimension of 2 mm; therefore, crosssectional area was used as a measure of particle size in mm<sup>2</sup>. Since this study was a prototype, small quantities of used tyre particles were required, and therefore, sizes could be measured using a meter rule. For a mass production and industrial set-up, use of sieve with different mesh sizes is recommended similar to the method by Paczkowski et al. [14]. The feedstock is then sorted and sun dried to remove foreign particles and moisture that could interfere with pyrolysis process. Low temperature preheating of feedstock to about 100 to 110°C is recommended to vaporize all the moisture that could be in the tyre particles since the boiling point of water is about 100°C [15].

2.3. Effects of Operating Variables on Thermal Pyrolysis. There are several factors that affects thermal pyrolysis [16], but the present study focuses on the variables: reaction temperature, particle size, and reaction time. The effect of each variable was studied by conducting an experiment.

2.3.1. Effects of Reaction Temperature. The temperature of the furnace was set using an automated temperature controller coupled to a thermocouple probe each with a temperature range of 0-1000°C. When the temperature set is attained, it automatically stops and maintains the tempera-

ture. The furnace was allowed to achieve the required temperature before feeding the feedstock into the reactor. The temperature considered were 200°C, 300°C, 400°C, 500°C, 600°C, and 700°C. The liquid products and solid products from each run were weighed and recorded for analysis. In each experimental run, 100 g of 25 mm<sup>2</sup> feedstock was used.

2.3.2. Effects of Particle Size. Tyre (Triangle 1000 R 20 10.00X20 Truck Tyre) manufactured in China was shredded into various sizes using a knife, and 100 g feedstock was used in each experimental run. The sizes used in this experiment were cubic with uniform thickness of 2 mm. The crosssectional area of various sizes was varied for the purpose of investigating the effect of particle size of the feedstock on the yield of thermal pyrolysis process. The cross-sectional areas considered were 25 mm<sup>2</sup>, 50 mm<sup>2</sup>, 100 mm<sup>2</sup>, and 200 mm<sup>2</sup>. The temperature was set to 500°C and when there is no more liquid condensing and no more gaseous products, the heating furnace was stopped, and liquid fuel collected are weighed. The solid residue was also weighed, and the mass of the gaseous products is obtained using the following relation as per the law of conservation of mass [17]: Mass of the gaseous products (g) = 100 g - mass of liquid fuel(g) - Massof solid residue(g).

2.3.3. Effects of Reaction Time. A stop watch was used to measure time, and the first step was to determine the time taken for the condensable products to condense at set temperature. The temperature considered was 500°C. The sample size was 100 grams of 25 mm<sup>2</sup> feedstock, and the liquid fuel yield was monitored after every 10 minutes.

2.4. Thermal Pyrolysis Process Optimization. This research was mainly focused on the liquid fuel yield. The three variables reaction temperature, reaction time, and particle size were optimized using the central composite design (CCD) [18]. The central values, the step sizes, and the range of variables were as follows: central reaction temperature of 400°C, step of 100°C, and range of 300°C-500°C; central reaction time of 60 mins, step of 20 mins, and range of 40 mins-80 mins; and central particle size of 112.5 mm<sup>2</sup>, step of 52.5 mm<sup>2</sup>, and range of 60 mm<sup>2</sup>-165 mm<sup>2</sup> as shown in Table 1.

TABLE 1: CCD matrix.

Factors	Units	$-\alpha$	-1	0	+1	+α
Reaction temperature	°C	231.8	300	400	500	568.18
Reaction time	Mins	26.36	40	60	80	93.64
Particle size	mm <sup>2</sup>	24.21	60	112.5	165	200.79

TABLE 2: Microwave pyrolysis energy requirement [5].

Microwave energy consumption (power × time)	$(50/100) \times (900/0.62) \times (17.5/60) = 211.7 \text{ Wh}$
Stirrer energy consumption (power × time)	$50 \times (17.5/60) = 14.6 \mathrm{Wh}$
Total energy consumption	226.3 Wh
Total energy consumption per liter of tyre pyrolysis oil	$226.3/\{(39.1/1000) \times (1/0.91)\} = 5266.8 \text{ Wh}$
Total energy consumption per kg of tyre pyrolysis oil	5266.8/0.91 = 5788 Wh = 5.788 kWh

TABLE 3: Thermal pyrolysis energy requirement.

Heating element energy consumption (power × time)	$(2 \times 300) \times (80/60) = 800 \mathrm{Wh}$
Stirrer energy consumption (power × time)	$50 \times (80/60) = 66.67 \text{ Wh}$
Total energy consumption	866.67 Wh
Total energy consumption per liter of tyre pyrolysis oil	$866.67/\{(40.4/1000) \times (1/0.91)\} = 19521.53$ Wh
Total energy consumption per kg of tyre pyrolysis oil	1951.53/0.91 = 21452.23  Wh = 21.452  kWh

Design Expert 13 Trial Version was used to develop the runs for optimization, and the factorial, axial, and centre point runs were obtained. A total of 45 experimental runs were obtained using the software since 3 replications were done on the axial, factorial, and centre point runs. For a full factorial rotatable design,  $\alpha = [2^k]^{1/4} = [2^3]^{1/4} = 1.682$  [19]. 0<sub>1</sub>, 0<sub>2</sub>, and 0<sub>3</sub> are the centre points while  $-\alpha$  (1.682) and  $+\alpha$  (1.682) are the axial points.

2.5. Characterization of Liquid Products for Fuel. The physiochemical and chemical analysis of the liquid products were performed using standard methods. Gas chromatography-mass spectrometry (GC-MS) was used to analyze the chemical composition and compared to pure standards of various components being analyzed using standard GC-MS procedure [20]. Analysis of tyre oil from thermal pyrolysis was subjected to the same tests done by Bett et al. [5] for microwave pyrolysis since the same type of tyre was used in both cases.

2.6. Energy Requirements for Optimal Thermal Pyrolysis and How It Compares to Microwave Pyrolysis. To calculate the energy requirement per kg of tyre pyrolysis oil for thermal pyrolysis, the following key parameters were considered: heating element energy consumption (power  $\times$  time) and stirrer energy consumption (power  $\times$  time). Similarly, for microwave pyrolysis [5], the microwave power level for optimal yield (power  $\times$  time) and the stirrer energy requirement (power  $\times$  time) were considered. Magnetron efficiency of a microwave oven is taken to be 62% according to Devine and Leadbeater [21]. The detailed calculations of energy requirements are as indicated in Table 2 and Table 3 for microwave and thermal pyrolysis, respectively.

# 3. Results and Discussion

3.1. Effects of Reaction Temperature. An experimental run was done using particle size of  $25 \text{ mm}^2$ . 100 g sample was weighed and subjected to pyrolysis at different temperatures for 70 minutes. The temperature range was between  $200^{\circ}$ C and  $700^{\circ}$ C and for  $25 \text{ mm}^2$  particle size; there was an increase in liquid fuel yield from 18.4 (wt.%) at  $200^{\circ}$ C to an optimum value of 38.0 (wt.%) at  $500^{\circ}$ C. After  $500^{\circ}$ C, there was a continuous decrease in the liquid fuel yield up to 30.6 (wt.%) at  $700^{\circ}$ C as illustrated in Figure 2. On the other hand, there was a continuous decrease in gas yield from  $200^{\circ}$ C to  $400^{\circ}$ C from 13.3 (wt.%) to 8.5 (wt.%). This was followed by a continuous decrease in the solid yield as illustrated in Figure 2 from 68.3 (wt.%) at  $200^{\circ}$ C to 39.6 (wt.%) at  $700^{\circ}$ C.

The results are in agreement with the published literature as reported by Hossain and Rahman [22]. The maximum yield was probably due to better cracking at 500°C. The thermal cracking was not complete at lower temperatures; hence, the pyrolysis process was not complete. Beyond 500°C, there was a decrease in the liquid fuel yield because of elevated temperatures that cracks further the liquid products to gaseous products. That explains why the gas products increase after 500°C. At lower temperatures, the pyrolysis



FIGURE 2: Effects of reaction temperature on yield.

process was partial, and less oil and volatiles were produced, and therefore, there was maximum retention of material in form of solid char [22]. According to Varma et al. [23], the complexity of the temperature graphs is as a result of the primary and secondary reactions. At lower temperatures, the primary reactions predominate, and as the temperature rises, the formation of vapours increases, and as condensation takes place, more oil products are formed [23]. As temperature increases, the secondary reaction takes place, and thus, after a certain temperature (500°C) when the secondary reaction predominate, the production of biooil decreases [24].

3.2. Effects of Particle Size. To study the effects of particle size, 100 grams of different particle sizes were subjected to pyrolysis process for 75 minutes at 50% microwave power. The yield of the liquid fuel decreased continuously from 39.1 (wt.%) for  $25 \text{ mm}^2$  to 30.6 (wt.%) for  $200 \text{ mm}^2$ . The solid residue had a similar trend from 46.2 (wt.%) for 25 mm<sup>2</sup> to 32.2 (wt.%) for 200 mm<sup>2</sup>. On the other hand, the gaseous products increased with increase in particle size from 14.7 (wt.%) for 25 mm<sup>2</sup> to 37.2 (wt.%) at 200 mm<sup>2</sup>. They are as illustrated in Figure 3. The results are in agreement with the published literature [22]. The decrease in liquid fuel yield with increase in particle size is probably due to reduction in surface area for the pyrolysis process [25]. The increase in gas yield with increase in particle size implies that as heating continues; the small quantities of liquid products that were formed were further cracked to form gaseous products. The quantity of solid residue is dictated by the trend of liquid and gaseous products.

3.3. Effects of Reaction Time. A 100 g particle size of  $25 \text{ mm}^2$  was used for this particular experiment while temperature was held constant at 500°C. The liquid and gaseous yield increased continuously up to about 60 mins where the yield remained constant. The liquid products increased from 5.2 (wt.%) at 10 mins to 38.2 (wt.%) at 60 mins. It then remained constant up to 120 mins. On the other hand, the gaseous



FIGURE 3: Effects of particle size on yield.



FIGURE 4: Effects of reaction time on yield.

products increased from 8.4 (wt.%) at 10 mins to 43.4 (wt.%) at 60 mins then remained constant. Finally, the solid char was maximum at the beginning with 86.4 (wt.%) at 10 mins to 18.4 (wt.%), then remained constant. The results are in agreement with the published literature by Shah et al. [26]. At 10 mins, the pyrolysis process is not yet complete, and a few hydrocarbons in the tyre have been cracked to form liquid and gas. The cracking continues up to 60 mins which is the optimum time for the pyrolysis process. After 60 mins, the cracking of complex molecules in the tyre is complete, and therefore, no more cracking takes place, hence the constant trend as illustrated in Figure 4.

3.4. Thermal Pyrolysis Process Optimization. Central composite design (CCD) was used for optimization. The required runs were obtained using Design Expert 13-Trial Version software. The results are as tabulated in Table 4

TABLE 4: Optimization runs for thermal pyrolysis process	ation runs for thermal pyrolysis proce	ermal pyrol	therma	uns fo	ptimization	Op	ABLE 4:	T
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Std	Run	X1: reaction temperature (°C)	X2: reaction time (mins)	X3: particle size (mm <sup>2</sup> )	Exp. liquid fuel yield (wt. %)	Predicted liquid yield (wt. %)	Residual
31	1	400	26	112.5	28.5	28.5	-0.0012
38	2	400	60	25	39.3	39.31	-0.0126
8	3	300	80	60	34.3	34.3	0.0041
5	4	500	40	60	35.6	35.59	0.0078
21	5	300	80	165	31.5	31.5	-0.0041
6	6	500	40	60	35.6	35.59	0.0078
44	7	400	60	112.5	37.4	37.4	0.0009
1	8	300	40	60	30.8	30.8	0.0029
4	9	500	40	60	35.6	35.59	0.0078
9	10	300	80	60	34.3	34.3	0.0041
10	11	500	80	60	40.4	40.39	0.0091
11	12	500	80	60	40.4	40.39	0.0091
30	13	568	60	112.5	36.7	36.71	-0.0085
41	14	400	60	200	33.5	33.49	0.0071
27	15	232	60	112.5	27.9	27.9	0.0032
23	16	500	80	165	37.2	37.2	0.0009
3	17	300	40	60	30.8	30.8	0.0029
29	18	568	60	112.5	36.7	36.71	-0.0085
20	19	300	80	165	31.5	31.5	-0.0041
24	20	500	80	165	37.2	37.2	0.0009
40	21	400	60	200	33.5	33.49	0.0071
28	22	568	60	112.5	36.7	36.71	-0.0085
37	23	400	60	25	39.3	39.31	-0.0126
7	24	300	80	60	34.3	34.3	0.0041
13	25	300	40	165	27	27.01	-0.0053
36	26	400	94	112.5	36.4	36.4	-0.0041
15	27	300	40	165	27.1	27.01	0.0947
45	28	400	60	112.5	37.4	37.4	0.0009
35	29	400	94	112.5	36.4	36.4	-0.0041
34	30	400	94	112.5	36.4	36.4	-0.0041
32	31	400	26	112.5	28.5	28.5	-0.0012
19	32	300	80	165	31.5	31.5	-0.0041
33	33	400	26	112.5	28.5	28.5	-0.0012
22	34	500	80	165	37.2	37.2	0.0009
39	35	400	60	25	39.3	39.31	-0.0126
25	36	232	60	112.5	27.9	27.9	0.0032
12	37	500	80	60	40.4	40.39	0.0091
16	38	500	40	165	31.4	31.4	-0.0004
26	39	232	60	112.5	27.9	27.9	0.0032
43	40	400	60	112.5	37.4	37.4	0.0009
17	41	500	40	165	31.4	31.4	-0.0004
2	42	300	40	60	30.8	30.8	0.0029
18	43	500	40	165	31.4	31.4	-0.0004
42	44	400	60	200	33.5	33.49	0.0071
14	45	300	40	165	26.9	27.01	-0.1053

Source	Sequential <i>p</i> value	Lack of fit <i>p</i> value	Adjusted R <sup>2</sup>	Predicted R <sup>2</sup>		
Linear	< 0.0001	<0.0001	0.8404	0.8283		
2FI	0.6758	< 0.0001	0.8345	0.8338		
Quadratic	<0.0001	0.794	1	1	Suggested	
Cubic	0.7215	0.573	1	0.9999	Aliased	
Sequential model sum	of squares [type I]					
Source	Sum of squares	df	Mean square	Fvalue	pvalue	
Mean vs. total	51592.48	1	51592.48			
Linear vs. mean	628.84	3	209.61	78.25	< 0.0001	
2FI vs. linear	4.28	3	1.43	0.513	0.6758	
Quadratic vs. 2FI	105.53	3	35.18	57067.7	<0.0001	Suggested
Cubic vs. quadratic	0.0014	4	0.0003	0.5203	0.7215	Aliased
Residual	0.0202	31	0.0007			
Total	52331.15	45	1162.91			

TABLE 5: Summary for model fit-sequential model sum of squares for thermal pyrolysis.

TABLE 6: ANOVA for response surface quadratic model for thermal pyrolysis.

Source	Sum of squares	df	Mean square	F value	p value	
Model	738.65	9	82.07	1.331 <i>E</i> +05	< 0.0001	Significant
X1-reaction temperature	281.53	1	281.53	4.567 <i>E</i> +05	< 0.0001	
X2-reaction time	223.35	1	223.35	3.624 <i>E</i> +05	< 0.0001	
X3-particle size	123.96	1	123.96	2.011 <i>E</i> +05	< 0.0001	
X1.X2	2.53	1	2.53	4112.66	< 0.0001	
X1.X3	0.2400	1	0.2400	389.36	< 0.0001	
X2.X3	1.50	1	1.50	2433.53	< 0.0001	
$(X1)^{2}$	58.96	1	58.96	95654.80	< 0.0001	
$(X2)^{2}$	55.28	1	55.28	89690.31	< 0.0001	
$(X3)^{2}$	2.26	1	2.26	3668.04	< 0.0001	
Residual	0.0216	35	0.0006			
Lack of fit	0.0016	5	0.0003	0.4721	0.7940	Not significant
Pure error	0.0200	30	0.0007			
Cor Total	738.67	44				

for the 45 optimization runs comprising of 3 replications of the axial, factorial, and centre point runs. The predicted yields are obtained from Equation (1).

The data in Table 4 were tested for fit considering linear, two-factor interaction (2FI), quadratic, and cubic polynomials. The results are as shown in Table 5; the highest adjusted  $R^2$  was for quadratic model, and it was not aliased. Putting into consideration the *F* value and the *p* value, a quadratic model was suggested.

The selected quadric model was in the form  $Y = b_0 + \sum_{i=1}^{n} C_i X_i + \sum_{i=1}^{n} C_{ii} X_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} C_{ij} X_i X_j$ , where Y is the liquid fuel yield,  $X_i$  is the coded variables. The analysis of variance (ANOVA) for the quadratic model is given by Table 6. As illustrated, the model F value of 133149.35 implies the model is significant. There is only a 0.01% chance that an F value this large could occur due to noise.

TABLE 7: *R*-square values for thermal pyrolysis.

Parameter	Value
Std. Dev.	0.0248
Mean	33.86
C.V. %	0.0733
$R^2$	1.0000
Adjusted R <sup>2</sup>	1.0000
Predicted R <sup>2</sup>	1.0000
Adeq precision	1143.7156

*p* values less than 0.0500 indicate that model terms are significant. In this case, X1, X2, X3, (X1.X2), (X1.X3), (X2.X3),  $(X1)^2$ ,  $(X2)^2$ , and  $(X3)^2$  are significant model terms. Values greater than 0.1000 indicate the model terms are not



FIGURE 5: RSM plot on effect of reaction temperature and reaction time on yield.

significant. The lack of fit F value of 0.47 implies the lack of fit is not significant relative to the pure error. There is 79.4% chance that a lack of fit F value this large could occur due to noise. The p value for lack-of-fit was greater than 0.05, and therefore, it was not significant.

Table 7 gives the *R*-square values for the model.

As illustrated in Table 7, the "predicted  $R^2$ " of 1.0000 is in reasonable agreement with the "adjusted  $R^2$ " of 1.0000; i.e., the difference was less than 0.2. "Adeq precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. In this particular case, the ratio of 1143.7156 indicates an adequate signal.

The quadratic equation is given by:

$$Y = -17.61552 + 0.163074 X1 + 0.537908 X2 - 0.010641 X3 + 0.000162 X1.X2 - 0.000019 X1.X3 + 0.000238 X2.X3 - 0.000181 (X1)2 - 0.004279 (X2)2 - 0.000130 (X3)2. (1)$$

Equation (1) can be used to make predictions about the response for given levels of each factor. Here, the levels should be specified in the original units for each factor.

3.4.1. Response Surface and Contour Plots for Thermal Pyrolysis. Equation (1) was used to plot response surface and contours for optimization of liquid fuel yield. Figure 5 is a plot for yield as a function of reaction temperature and reaction time. The optima lie close to a reaction temperature of 500°C and reaction time of 80 minutes.

Figure 6 gives a plot for yield as a function of reaction temperature and particle size. The optima lie close to a reaction temperature of  $500^{\circ}$ C and particle size of  $60 \text{ mm}^2$ .

Figure 7 gives a plot for yield as a function of particle size and reaction time. The optima lie close to a particle size of  $60 \text{ mm}^2$  and reaction time of 80 minutes.

From the optimization, the optimal yield of liquid fuel for thermal pyrolysis was 40.4 (wt. %) and was achieved at a reaction temperature of 500°C, particle size of  $60 \text{ mm}^2$ , and reaction time of 80 minutes. Particle size of  $60 \text{ mm}^2$ was among the smallest particle sizes for this specific study, and even smaller particle sizes can be achieved and are likely to give better results. On the other hand, for microwave pyrolysis according to Bett et al. [5], the optimal yield of liquid fuel (39.1 wt. %) was achieved at a microwave power of 50%, particle size of  $25 \text{ mm}^2$ , and reaction time of 17.5 minutes.  $25 \text{ mm}^2$  was the smallest particle size for this specific study, and even smaller particle sizes can be achieved and are likely to give better results.

#### 3.5. Characterization of Thermal Tyre Pyrolysis for Fuel

3.5.1. Physiochemical Properties. The physiochemical properties were conducted using standard methods at Lab Works East Africa Ltd., Nairobi, Kenya. Table 8 summarizes the results of the physiochemical properties tests for thermal pyrolysis and how it compares to that of microwave pyrolysis according to Bett et al. [5].

From Table 8, the properties of oil from both processes are similar since the same type of tyre was used. The calorific value of oil from microwave pyrolysis is 48.99 MJ/kg [5] while that from thermal pyrolysis is slightly lower at 47.31 MJ/kg. According to the experiment by Osueke et al., 2018 [6], the gross calorific value of commercial diesel is 44.8 MJ/kg. Besides, Hariram et al. [27] reported a calorific and 43.9 MJ/kg for commercial diesel. This implies that the



FIGURE 6: RSM plot on effect of reaction temperature and particle size on yield.



FIGURE 7: RSM plot on effect of particle size and reaction time on yield.

TPO has calorific value higher than that of commercial diesel. Upon further purification, TPO can be used directly in internal combustion engines instead of diesel. The calorific value of heavy fuel oil (HFO) is at 39 MJ/kg according to Senčić et al. [28]. The recommended properties of HFO [28] include: maximum kinematic viscosity @ 288 K of 5 Pa•s, sulphur content of 0.45% maximum, and a net calorific value of 39 MJ/kg. Therefore, TPO qualifies to be used directly as an HFO.

3.5.2. GC-MS Analysis. The TPO optimal sample for thermal pyrolysis about 1 litre was collected in the laboratory for analysis and comparison with that from Bett et al. [5]. Specific pure standards of the components to be analyzed were

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Demonstran	Mathad	Results	
Parameter	Method	Microwave pyrolysis [5]	Thermal pyrolysis
Viscosity @ 40°C (cSt)	AOAC	3.07	3
Ash content (%)	AOAC	1.9	1.5
Density @ 15°C (kg/l)	AOAC	0.91	0.91
Pour point (°C)	ASTM D2015	6.7	6.5
Flash point (°C)	ASTM D2015	61	59
Fire point (°C)	ASTM D2015	65	62
Sulphur content (%)	AOAC	0.08	0.08
Carbon residue (%)	ASTM D2015	0.75	0.68
Calorific value (MJ/kg)	ASTM D2015	48.99	47.31

TABLE 8: Physiochemical properties of tyre pyrolysis oil from thermal pyrolysis and how it compares to that from microwave pyrolysis by Bett et al. [5].

TABLE 9: GC-MS analysis of thermal pyrolysis TPO and its comparison to that of published microwave pyrolysis [5].

		Microwave p	yrolysis [5]	Thermal pyrolysis	
Components	Molecular formula	Retention time (RT) (mins)	Peak area %	Retention time (RT) (mins)	Peak area %
D-limonene	C <sub>10</sub> H <sub>16</sub>	13.46	20.23	13.45	14.55
Toluene	$C_7H_8$	7.03	10.65	7.02	7.45
m-Xylene	$C_8H_{10}$	8.82	7.31	8.83	6.82
1-Methylnaphthalene	$C_{11}H_{10}$	27.09	5.8	27.08	4.45
Naphthalene	$C_{10}H_{8}$	15.59	5.42	15.6	5.4
Estradiol, 3-deoxy	$C_{18}H_{24}O$	28.88	3.5	28.88	2.5
3,4-Dihydro-1-methylnaphthalene	$C_{11}H_{12}$	15.72	2.74	15.72	3.2
Naphthalene,2,7 -dimethyl	$C_{12}H_{12}$	25.09	2.5	25.1	2.32
Naphthalene 1,7-dimethyl	$C_{12}H_{12}$	20	1.96	20.01	2.05
o-Xylene	$C_8 H_{10}$	11.33	1.4	11.33	1.45
Naphthalene, 1,2-dihydro	$C_{10}H_{10}$	19.44	1.2	19.45	1.75
Cyclohexane, 1-methyl-5-(1-methylethenyl)-(R)	$C_{10}H_{16}$	12.64	1.1	12.63	1
Benzene	$C_6H_6$	5.62	0.92	5.61	1
Ethylenzene	$C_8H_8$	4.94	0.6	4.9	0.68
Fluoranthene	$C_{16}H_{10}$	30.33	0.45	30.32	0.62
2,4-Dimethyl-quinolin	$C_{11}H_{11}N$	7.96	0.41	_	Not detected

first run in the GC. The retention time these standards were registered in the GC. The pyrolysis oil samples were diluted in an ethanol solvent before analysis and the tyre pyrolysis oil to solvent ratio being 1:10. The GC detector then identified the components in the sample based on the stored information from the standards. It is the peak area that determined the concentration of a component in the sample. The retention time shows the identity of the component. The machine used for analysis was Thermo Scientific TM Trace Gold TG-1MS. The inert carrier gas used was helium, and FID detector was used. The temperature settings was an initial temperature of 100°C and final temperature of 380°C. The results of GC analysis are as illustrated in table below: from the analysis, it is evidenced that the TPO from thermal pyrolysis comprises a complex mixture of hydrocarbons with major components being limonene, toluene, and xylene which is similar to the published literature for microwave pyrolysis. The proportions of tested components are as illustrated in Table 9. The results are in agreement with the published literature [5, 29].

#### 3.6. Energy Requirements

*3.6.1. Microwave Pyrolysis.* The results from Bett et al. [5] are used for comparison purposes to that of thermal pyrolysis. A 39.1 g of liquid fuel with a density of 0.91 kg/l was produced in 17.5 minutes using 50% power level for a microwave oven ratted 900 W [5]. Assume a magnetic stirrer rated 50 W was used, and the magnetron efficiency of a microwave oven was taken to be 62% according to Devine Leadbeater [21]. Therefore, the microwave energy requirement can be summarized as shown in Table 2.

3.6.2. Thermal Pyrolysis. A 40.4 g of tyre pyrolysis oil was produced using two heating elements each having a power rating of 300 W. The density of the liquid produced was

0.91 kg/l and was produced after 80 minutes. Electric stirrer rated 50 W was used. The energy requirement can be summarized as shown in Table 3.

From Tables 2 and 3, it can be concluded that the microwave pyrolysis requires less energy compared to thermal pyrolysis process to produce 1 kg of liquid fuel. The energy requirement is reduced by  $(21.452 - 5.788)/21.452 \times 100\%$ = 73.02% compared to thermal pyrolysis.

#### 4. Conclusion and Recommendations

The reaction temperature affects the yield of thermal pyrolysis process. The liquid fuel yield increases with increase in temperature up to an optimal yield at about 500°C beyond which the liquid fuel yield decreases. On the other hand, the gas yield decreases with increase in temperature up to 500°C beyond which the gas yield starts to increase. The solid residue is dependent on the liquid and gas yields, and it portrays a decreasing trend as temperature rises. Reaction time affects thermal pyrolysis where the liquid and gas yields increase with increase in reaction time while the solid residue decreases uniformly. At about 60 minutes and beyond, the solid, liquid, and gaseous products remain constant, and that is a clear indication that the pyrolysis process is completed. Particle size affects the thermal pyrolysis process as where the liquid and solid products yields reduce with increase in particle sizes while the gaseous products increases with increase in particle size. The optimal yield of liquid fuel for thermal pyrolysis was achieved at a reaction temperature of 500°C, particle size of 60 mm<sup>2</sup>, and reaction time of 80 minutes.  $60 \text{ mm}^2$  was among the smallest particle sizes for this specific study, and even smaller particle sizes can be achieved and are likely to give better results. Both microwave pyrolysis and thermal pyrolysis give almost the same results in terms of optimal liquid fuel yield. However, microwave pyrolysis is preferred because it uses less time to complete pyrolysis process for a similar amount of feedstock where it reduces reaction time from 80 minutes to about 18 minutes. The percentage reduction in reaction time can be calculated as  $((80 - 18)/80) \times 100 = 77.5\%$ . This is in agreement with a research by Kumar et al. [30]. Besides, microwave pyrolysis reduces the energy requirement by 73.02% compared to thermal pyrolysis.

4.1. Recommendations for Further Research. Upscaling, purification of tyre pyrolysis oil, and use of appropriate catalyst are recommended for further research.

#### **Data Availability**

The article contains all the relevant data. The corresponding author would provide any additional data upon request.

## **Conflicts of Interest**

The authors declare that they have no conflicts of interest.

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