



## Article Info

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## Recycling of Waste Tyres to Liquid Fuel for Automobile Application

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The pyrolysis of waste tyres was carried out in a batch pyrolyzer reactor at a temperature of 500°C and atmospheric pressure. The tyre pyrolyzed oil (TPO) obtained recorded an average yield of 43% and the pyrolyzed carbon black (PCB) was found to be 39% while the steel wire was found to be 9%, the remaining 9% was mainly pyrolyzed gas. The average calorific value of the waste tyre pyrolyzed oil was found to be 40MJ/kg while the average density and viscosity were 0.850g/cm<sup>3</sup> and 3.69Cst respectively. The results obtained from the Gas Chromatography Mass Spectrometer (GC-MS) revealed total of 21 compounds from the uncatalyzed pyrolysis while 20 compounds were found in the catalyst aided pyrolysis. More so, Tricosanoic acid, Cyclotrisiloxane hexamethyl, Phenol-3-ethyl and Tris(ter-butyl dimethylsilyloxy) are the only common compounds found in both catalyzed and uncatalyzed TPO. As such, the catalyst has caused the formation of compounds that are different from the ones found in the uncatalyzed pyrolysis process. More so, based on average oil yield the process is suitable in the generation of diesel like fuel that can be used to power devices that operate on diesel. However, further processes are required to remove the impurities found in the pyrolyzed oils.

**Keywords:** Pyrolysis; tyre waste; pyrolyzed oil; pyrolyzed carbon black; pyrolyzed gas.

## 1. Introduction

The human activities that are directly related to the utilization of fossil fuels caused the generation of carbon dioxide a major greenhouse gas (GHG) as a result of combustion of the fossil fuels. This carbon dioxide results in the formation of a shield in the atmosphere that causes the global warming with climate change consequences. Due to the industrialization, this fossil fuel which is non-renewable is significantly depleting at high rate and projected to become exhausted in the next few decades to come [Akinola and Fapetu, 2015; Yaru et al., 2021]. As such, the renewable energy sources are becoming alternative energy sources world-wide. This renewable energy sources are not exhaustible due to the faster generation or high rate of generation in some cases. The typical examples of this renewable energy are hydropower, wind, solar and recently solid wastes generated from human activities [Akinola, 2012; Arabiourrutia et al., 2021; Yaru et al., 2021]. These solid wastes are either biodegradable and non-biodegradable. However, the non-biodegradable solid wastes such as scrap tyres do not undergo bio-degradation easily in the soil due to the nature and composition of the tyre materials that include

carbon black, rubbers, steel wire, inorganic materials and other organic components [Islam, 2008; Karagoz et al., 2020; Yaru et al., 2021]. Therefore, the scrap tyre pollutes the soil, water and atmosphere thereby becoming breeding places for diseases and their vectors.

Moreover, the tyre material has a durability property that makes it non-biodegradable thereby making its disposal and reprocessing difficult and challenging. Additionally, the quantity of tyres produced recently world-wide generates both environmental and economic problems number as a result of landfilling of the waste tyres in huge quantities (Stelmachowski and Słowiński, 2009). Again, burning of scrap tyres in an open environment releases many air pollutants to the environment which are seriously harmful to the environment (Czajczynska et al., 2020). As such, it is imperative to stop our environment from the impacts related to dumping, landfilling and burning of tyre wastes. Due to this interest it was found that, the pyrolytic conditions are suitable for the transformation of scrap tyres to diesel like fuels. Consequently, the pyrolytic conversion of waste tyres to diesel like fuels is becoming interesting recent, because it seems efficient and

eco-friendly way to mitigate the scrap tyres from the environment (Yaqoob et al., 2021). The pyrolysis of waste tyres, which is the heating of the scrap tyre in the absence of oxygen, generates pyrolytic oil, carbon black, steel wire and pyrolyzed gas (fuel gas). As the pyrolysis process starts the pyrolysis gas generated can be used as fuel in sustaining the pyrolysis process for heat generation. The pyrolytic oils is tested and found to be a useful fuels as it is or can be used as a blending agent to other fuels such as diesel (Yaqoob et al., 2021).

This research investigates the performance of Calcium hydroxide [ $\text{Ca}(\text{OH})_2$ ] waste (catalyst) produced from the local oxy-acetylene gas welding center after pretreatment in the pyrolysis of scrap tyre to liquid fuel at a temperature of  $500^\circ\text{C}$  and atmospheric pressure for the first time.

## 2. Materials and Methods

### 2.1. Materials

The major materials used in this research work were scrap tyre wastes and calcium hydroxide waste (waste from a gas welding center).

### 2.2 Sample and sample pretreatment

#### 2.2.1 Scrap tyre waste

The scrap tyre waste was collected randomly from Sahara area in Sokoto South Local Government Area of Sokoto state. The tyre waste was cut into pieces and a clean towel was used to clean all the pieces before loading into pyrolysis reactor.

#### 2.2.2 Calcium hydroxide waste

The catalyst (calcium hydroxide waste) was locally source from a gas welding center in Buzaye mechanic workshop center and random sampling process was carried out. The catalyst was dried in an oven at a temperature of  $105^\circ\text{C}$  overnight and calcined at  $500^\circ\text{C}$  in muffle furnace for 4 hours.

### 2.3 Calcium hydroxide waste characterization

Fourier transform infrared (FT-IR) spectra of model FTIR-8400S spectrophotometer (Shimadzu) was used in recording the wavelength range of  $400\text{--}4000\text{ cm}^{-1}$ . The X-Ray diffraction (XRD) analysis of the catalysts was determined using an ARL X'TRA X-ray diffractometer (thermoscientific) at a scanning speed  $12^\circ/\text{minute}$  over the  $2\theta$  range of  $20\text{--}90^\circ$ .

### 2.4. Pyrolysis Test

About 5 kg of the pieces of tyre waste was gently loaded into the pyrolyzer. The pyrolysis reaction was conducted at a temperature of  $500^\circ\text{C}$  and

atmospheric pressure in a locally made pyrolysis reactor. The tyre pyrolyzed oil starts to dropped from the reactor outlet after 15 minutes in the absence of catalyst. Same procedure was applied for the catalytic pyrolysis except that 0.12 kg of catalyst was added into the reactor and the oil starts to drop within the first 10 minutes. The tyre pyrolyzed oil was collected at the reactor outlet from the begging of pyrolysis to the end. The total quantity of tyre pyrolyzed oil, steel wire and pyrolyzed carbon black were calculated, while the pyrolysis gas was estimated. The composition of tyre pyrolyzed oil was investigated using GCMS-QP2010SE Gas Chromatography Mass Spectrophotometer (Shimadzu) equipped with a  $30\text{m}\times 0.32\text{mm}$ , Rxi-624 Sil MS capillary column (Restek Corp.).

### 2.4 Characterization of the Pyrolyzed Oil Obtained from Scrap Tyres

The viscometer model 3530 Chandler Engineering and bomb calorimeter model-IKA C2000 were used to investigate the viscosity and calorific value of the nylon sachet pyrolyzed oil.

## 3. Results and Discussion

### 3.1 Results

#### 3.1.1 Results of the FT-IR and XRD pattern of Calcium hydroxide waste

The FT-IR spectrum in Figure 1 exhibits several notable peaks which include a broad peak between  $3640\text{--}3660\text{ cm}^{-1}$ , corresponding to O-H stretching vibrations, which indicates the presence of hydroxide ions ( $\text{OH}^-$ ) and this is in conformity with the findings by Nandhini et al. 2019. Another peak at  $874\text{--}877\text{ cm}^{-1}$ , attributed to Ca-O-H bending vibrations, characteristic of calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ). While a peak at  $1420\text{--}1450\text{ cm}^{-1}$ , assigned to C-O stretching vibrations, suggesting the presence of trace amounts of calcium carbonate ( $\text{CaCO}_3$ ) or other carbonates. These findings collectively suggest that the sample is primarily composed of calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ), consistent with the expected composition of a gas welding station residue. The presence of hydroxide ions and calcium ions further confirms this conclusion.

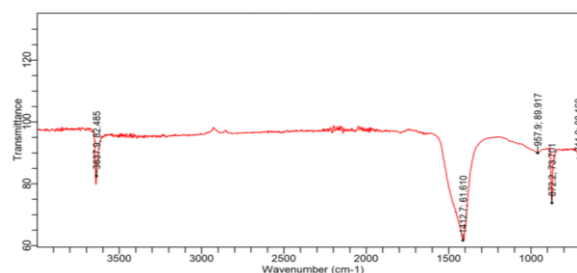
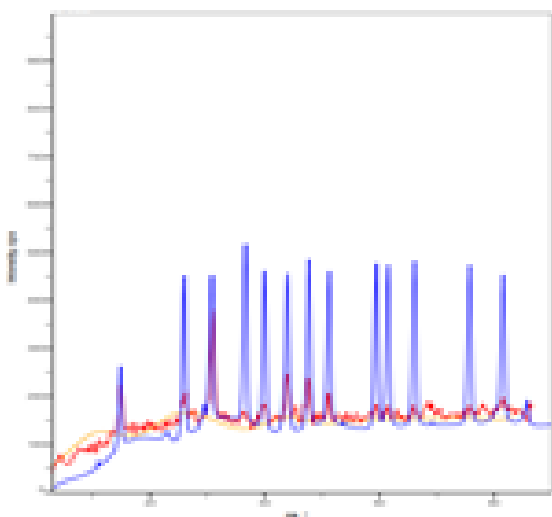


Figure 1: The FT-IR Spectrum of  $\text{Ca}(\text{OH})_2$  from gas welding station

Based on the XRD (X-Ray Diffraction) results for calcium hydroxide waste, the major peaks at  $2\theta$  (degrees) are  $17.1^\circ$ ,  $28.7^\circ$ ,  $34.1^\circ$ ,  $47.1^\circ$ ,  $50.9^\circ$ ,  $54.3^\circ$ ,  $62.5^\circ$ ,  $65.7^\circ$ . The XRD pattern indicates that the sample is primarily composed of calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ), also known as portlandite which agrees with research of Daniele and Taglieri (2012). The observed peaks match the characteristic diffraction pattern of  $\text{Ca}(\text{OH})_2$ . The presence of sharp, well-defined peaks suggests a crystalline structure. While the absence of significant peaks from other phases indicates a high purity of  $\text{Ca}(\text{OH})_2$ . The XRD results confirm that the sample is primarily composed of calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ), consistent with the expected composition of a gas welding station residue.



**Figure 2:** The XRD Spectrum of  $\text{Ca}(\text{OH})_2$  from gas welding station

### 3.1.2 Results of Calorific value and Viscosity

The result of viscosity was found to be 3.55 and 3.82Cst for catalyzed and uncatalyzed pyrolysis oils respectively. While the calorific value was also found to be 40.2 and 39.8 MJ/kg for the catalyzed and uncatalyzed pyrolysis oils respectively. More so, the density of 0.845 and  $0.855\text{g}/\text{cm}^3$  were determined for the catalyzed and uncatalyzed pyrolysis process respectively and these findings are in agreement with the findings of research conducted by Prurapark et al. (2020).

### 3.1.3 Results of GC-MS Analysis of Pyrolyzed Oils

The GC-MS results showing the different compounds present in the pyrolyzed oils with and without the application of catalyst are shown in Tables 1 and 2 respectively.

The GC-MS results of the TPO generated from both catalyzed and uncatalyzed pyrolysis of waste tyre revealed the presence of four (4) common compounds in both TPO samples. These compounds include phenol-3-ethyl; 2(3H)-Furanone-3,4-bis(1,3-benzodioxal-5-methyl) dihydro-3(3R-trans)-; cyclotrisiloxane hexamethyl and tris(tert-butyl dimethylsilyloxy)arsane. The amount of these compounds in the TPO was found to be about 20% of the total compounds. More so, the results showed that ursodeoxycholic acid and acetamide -N-(Cyclopropyl phenyl)-2-(3-methylphenoxy) was found to be in the % area of 20.8 and 6.1% respectively and this amount to 10% of the total compounds found presence in the TPO of uncatalyzed process. Again, the GC-MS results of the TPO established the presence of Arsenous acid tri(trimethylsilyl ester)- which amount to 5% of the total compounds presence in TPO of the catalyzed pyrolysis process, while it is %area was found to be 41.5%. Furthermore, all the other compounds are found to be in both catalyzed and uncatalyzed pyrolysis processes are found to be well below 5%.

It appears from the results that, the catalyst does not influence the production of phenol-3-ethyl and 2(3H)-Furanone-3,4-bis(1,3-benzodioxal-5-methyl) dihydro-3(3R-trans) as both compounds have equal % area in the both TPO from catalyzed and uncatalyzed pyrolysis process. However, the catalyst shows a negative effect in the production of cyclotrisiloxane hexamethyl and tris(tert-butyl dimethylsilyloxy)arsane as their concentration (production) decreased by 71.56% and 38.05% respectively. Again, the catalyst prevents the generation of ursodeoxycholic acid in total as such, the compound does not appeared in the TPO of the catalyzed pyrolysis process. However, Arsenous acid, tris(trimethylsilyloxy)silane in the TPO of the catalyzed pyrolysis process with %area of 41.5% appeared which indicates the catalyst designed another reaction routes that resulted to this compound.

**Table 1:** Peak no., RT, % Area and compound present, molecular formula and qual found in the tyre pyrolyzed oil without application of catalyst (uncatalyzed)

Peak No.	RT	% Area	Compound	Qual	Molecular Formula
1	6.665	0.58	3-Phenyl oxindole, BSTFA derivative	30	C <sub>17</sub> H <sub>19</sub> NOSi
2	8.397	0.4	o-Anisidine, N-trimethylacetyl-	30	C <sub>7</sub> H <sub>9</sub> NO
3	9.455	0.6	Phenol, 3-ethyl-	49	C <sub>8</sub> H <sub>9</sub> OH
4	10.018	1.4	6-mercapto-5-p-tolyl-1,2,3,5-tetrahydro-8-thia-5,7-diazacyclopenta[a]inden-4-one	38	C <sub>16</sub> H <sub>14</sub> N <sub>2</sub> OS <sub>2</sub>
5	10.201	0.4	2-Isopropenyl-4,4,7a-trimethyl-2,4,5,6,7,7a-hexahydro-benzofuran-6-o	35	C <sub>12</sub> H <sub>18</sub> O
6	10.417	0.5	N-(4-Isopropylbenzyl)-3-phenylpropionamide	18	C <sub>19</sub> H <sub>23</sub> NO
7	10.597	0.9	2(3H)-Furanone, 3,4-bis(1,3-benzodioxol-5-ylmethyl)dihydro-, (3R-trans)-	43	C <sub>20</sub> H <sub>18</sub> O <sub>6</sub>
8	11.277	4.2	trans, cis-3-Ethylbicyclo[4.4.0]decane	14	C <sub>12</sub> H <sub>22</sub>
9	11.57	2.7	Tricosanoic acid	25	C <sub>23</sub> H <sub>46</sub> O <sub>2</sub>
10	11.706	1	Bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene	53	C <sub>11</sub> H <sub>10</sub>
11	11.975	3.8	1-(2,6-Dimethyl-phenyl)-1H-tetrazole	25	C <sub>10</sub> H <sub>12</sub> O
12	12.218	1.8	Bicyclo[4.1.0]heptane,-3-cyclopropyl,-7-carbmethoxy, cis-	64	C <sub>10</sub> H <sub>16</sub>
13	12.714	6.1	Acetamide, N-(2-cyclopropylphenyl)-2-(3-methylphenoxy)-	56	C <sub>10</sub> H <sub>13</sub> NO
14	12.981	5	9,19-Cyclolanostan-3-ol, acetate,(3.beta.)-	38	C <sub>32</sub> H <sub>54</sub> O <sub>2</sub>
15	13.334	20.8	Ursodeoxycholic acid	32	C <sub>24</sub> H <sub>40</sub> O <sub>4</sub>
16	20.856	1.8	Ethyl o-acetamidobenzoate	35	C <sub>11</sub> H <sub>13</sub> NO <sub>3</sub>
17	21.166	1.5	2-butenedioic acid, 2,3-bis(phenylamino)-, diethyl ester	35	C <sub>20</sub> H <sub>22</sub> N <sub>2</sub> O <sub>4</sub>
18	22.301	0.1	Benzoic acid, 4-(1,3-dioxolan-2-yl)-, methyl ester	78	C <sub>10</sub> H <sub>10</sub> O <sub>4</sub>
19	27.085	22.47	Cyclotrisiloxane, hexamethyl-	62	C <sub>6</sub> H <sub>18</sub> O <sub>3</sub> Si <sub>3</sub>
20	28.941	20.50	Tris(tert-butyl)dimethylsilyloxy)arsane	50	C <sub>18</sub> H <sub>45</sub> AsO <sub>3</sub> Si <sub>3</sub>
21	29.676	2.65	1,1,1,3,5,5,5-Heptamethyltrisiloxane	50	C <sub>7</sub> H <sub>21</sub> O <sub>2</sub> Si <sub>3</sub>

**Table 2:** Peak no., RT, Area% compound present, molecular formula and qual found in the tyre pyrolyzed oil with application of catalyst

Peak No.	RT	% Area	Compound	Qual	Molecular Formula
1	8.319	1.17	p-Cresol	60	C <sub>7</sub> H <sub>8</sub> O
2	9.422	0.63	Phenol, 3-ethyl-	41	C <sub>8</sub> H <sub>10</sub> O
3	10.012	2.07	Benzene, 1-methoxy-2-methyl-	35	C <sub>5</sub> H <sub>12</sub> O
4	10.551	0.91	2(3H)-Furanone, 3,4-bis(1,3-benzodioxol-5-ylmethyl)dihydro-ns)-, (3R-trans(-	49	C <sub>20</sub> H <sub>18</sub> O <sub>6</sub>
5	10.812	0.31	Ether, 2,4,6-cycloheptatrien-1-ylmethyl	46	C <sub>8</sub> H <sub>10</sub> O

6	11.292	1.36	3-Isopropylthiophenol	49	C <sub>9</sub> H <sub>12</sub> S
7	11.558	0.68	Pregan-20-one, 2-hydroxy-5,6-epoxy-15-methyl-	12	C <sub>22</sub> H <sub>34</sub> O <sub>3</sub>
8	11.951	0.43	2,4,4-Trimethyl-3-hydroxymethyl-5a-(3-methyl-but-2-enyl)-cyclohexene	22	C <sub>15</sub> H <sub>26</sub> O
9	12.691	1.93	.delta.2-Tetrazaboroline, 1,4,5-triethyl-	25	C <sub>3</sub> H <sub>9</sub> BN <sub>4</sub>
10	12.951	0.4	Methane, bis(4-methylphenoxy)sulfonyl-	35	C <sub>13</sub> H <sub>12</sub> O <sub>4</sub> S <sub>2</sub>
11	13.266	1.09	4,7,7-Trimethylbicyclo[2.2.1]heptan-2-one O-allyloxime	38	C <sub>10</sub> H <sub>16</sub> O
12	21.45	1.53	Silane, dimethyl(2-fluorophenoxy)dodecyloxy-	45	C <sub>22</sub> H <sub>39</sub> FO <sub>2</sub> Si
13	21.762	0.15	2-butenedioic acid, 2,3-bis(phenylamino)-, diethyl ester	45	C <sub>20</sub> H <sub>22</sub> N <sub>2</sub> O <sub>4</sub>
14	23.066	0.29	1,2-Bis(trimethylsilyl)benzene	38	C <sub>12</sub> H <sub>22</sub> Si <sub>2</sub>
15	23.605	3.57	Methyltris(trimethylsiloxy)silane	47	C <sub>10</sub> H <sub>30</sub> O <sub>3</sub> Si <sub>4</sub>
16	26.815	41.53	Arsenous acid, tris(trimethylsilyl) ester	52	C <sub>9</sub> H <sub>27</sub> AsO <sub>3</sub> Si <sub>3</sub>
17	26.950	6.39	Cyclotrisiloxane, hexamethyl-	58	C <sub>6</sub> H <sub>18</sub> O <sub>3</sub> Si <sub>3</sub>
18	27.175	3.57	Methyltris(trimethylsiloxy)silane	50	C <sub>10</sub> H <sub>30</sub> O <sub>3</sub> Si <sub>4</sub>
19	27.338	1.85	Tetrasiloxane, decamethyl-	50	C <sub>10</sub> H <sub>30</sub> O <sub>3</sub> Si <sub>4</sub>
20	27.95	12.78	Tris(tert-butyldimethylsilyloxy)arsane	52	C <sub>18</sub> H <sub>45</sub> AsO <sub>3</sub> Si <sub>3</sub>

Two Arsenic containing compounds namely Arsenous acid tris(trimethylsilyl)silane and tris(tert-butyldimethylsilyloxy)arsane with total %area of 54.3% were found in the catalyzed TPO while one compound tris(tert-butyldimethylsilyloxy)arsane with total %area 20.5% was found. The presence of arsenic in the TPO was in conformity with the research conducted by Uguz and Ayanoglu, (2021) on characterization of waste tyre pyrolysis products by GC, ICP-MS, TGA, and DSC The aromatic compounds, aliphatic alkenes, aliphatic alkanes, esters, organic acids, nitrogen containing compounds, ketones, aldehydes, oxygenate and others found in the TPOs aligned with the investigation carried out by Uguz and Ayanoglu, (2021) on chemical characterization of waste tyre products.

The TPO yield was found to be 42% and 46% for the catalyzed and uncatalyzed pyrolysis process respectively. While the carbon black found to be 42 and 36% for the uncatalyzed and catalyzed process respectively. Furthermore, the steel wire found close to 9% for each catalyzed and uncatalyzed pyrolysis process respectively. Again, the gas product was estimated to be 9%

and 7% for the catalyzed and uncatalyzed pyrolysis process respectively and these are in good agreement with research work titled bio-oil production by thermal and catalytic pyrolysis of waste tyres carried out by Khalif *et al.* (2021).

#### 4. Conclusion

Based on the caloric value of the TPOs and oil yield the tyre pyrolysis oil is a cheap eco-friendly liquid fuel that can be used so as to mitigate the way scrap tyres are dumped or burn in an open environment which increase significantly the air pollutants in the atmosphere. More so, the pyrolysis of waste tyres if utilize properly it will create a lot of jobs to the Nigerian population in addition to providing cheaper alternative energy source. However, due to the presence of arsenic, sulfur containing compounds and other unwanted substances in the tyre pyrolysis oils there is need of pretreatment of the oil so as to remove these unwanted materials before the oil can be put to applications in industrial or boiler heating, such as cement factory, steel factory, glass factory, boilers.

### Conflict of interest

The authors declare no conflict of interest.

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