

# Yield Response from the Catalytic Conversion of Parsley Seed Oil into Biodiesel Using a Heterogeneous and Homogeneous Catalyst

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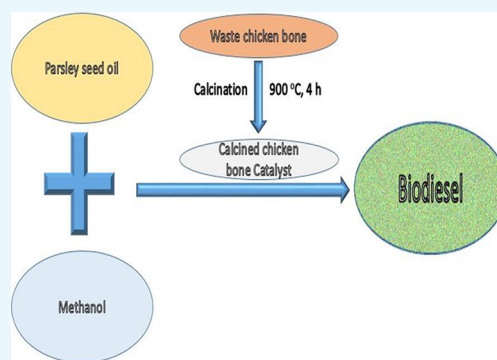
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**ABSTRACT:** This research work is focused on the investigation of the optimum condition for parsley seed oil (PSO) trans-esterification using a heterogeneous (CCB) and homogenous catalyst (KOH). The process parameters (alcohol: oil ratio, temperature, and catalyst loading) were varied to examine their effect on the percentage biodiesel yield using a Box–Behnken design embedded with the response surface methodology (RSM). Also, the heterogeneous catalyst was synthesized by calcining waste chicken bones at 900 °C for 4 h. Thereafter, scanning electron microscopy (SEM), X-ray fluorescence (XRF), energy-dispersive X-ray spectroscopy (EDS), Fourier-transform infrared spectroscopy (FT-IR) and X-ray diffraction (XRD) analysis were utilized to determine the morphology and elemental composition. Thermogravimetric analysis (TGA) was also adopted to assess the effect of calcination temperature on the prepared catalyst. The characterization analysis revealed the presence of hydroxyapatite as the major component, and the reusability test showed that it exhibited good catalytic performance for PSO transesterification. However, the optimization study revealed that the optimum reaction conditions of 9:1 alcohol: ratio, 60 °C reaction temperature, and 3 wt % catalysts gave 90% biodiesel yield, while the homogenous catalyst (used as the control transesterification experiment) under the same conditions gave an average yield of 96.33%. Gas chromatography–mass spectrometry (GC–MS) was utilized to characterize the produced biodiesel. Furthermore, the fuel characteristics of biodiesel were within the specifications of the ASTM D6751.



## 1. INTRODUCTION

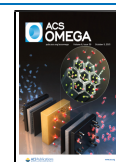
Biodiesel is one of the renewable energy sources that has gained widespread acceptance as a reliable solution to the current energy crisis. This alternative fuel, which appears to be an ideal substitute for diesel fuel, has successfully gained global attention because of its outstanding properties such as lower carbon monoxide emissions, biodegradability, nontoxicity, and lower sulfur content.<sup>1–4</sup> However, the feedstock and catalyst to be used in biodiesel production as well as the yield and quality of the biodiesel should be taken into account. Nonetheless, unconventional oils have gained tremendous popularity in the last ten years as a result of their valuable characteristics in various industries.<sup>5</sup> Few reports suggest that the oils extracted from seeds and kernel byproducts could be utilized to prepare biodiesel instead of being discarded as waste.<sup>6,7</sup> Also, the type of catalyst employed for biodiesel production can influence its quality and quantity. Homogeneous and heterogeneous catalysts can be utilized for biodiesel processing.<sup>8</sup> However, homogeneous catalysts are not cost-effective because they consume so much energy, water, and time. Meanwhile, heterogeneous (solid) catalysts have a number of advantages, including thermal stability, reusability, and low cost of production.<sup>9,10</sup> Initially, the materials such as waste animal bones, from which heterogeneous catalysts can be synthesized,

were thought to be waste products, and their disposal was a great challenge as it can lead to environmental pollution. However, the diversion of these waste materials into heterogeneous catalyst synthesis for biodiesel processing is an innovative green technology. Moreover, animal bones consist of sixty-five to seventy percentage of hydroxyapatite as well as thirty to thirty-five percentage of organic materials with respect to its dry weight.<sup>11</sup> The primary constituent of bones (calcium phosphate) can be converted to hydroxyapatite with excellent stability (chemical and thermal) as well as a high catalytic activity, which supports the processing of environmentally sustainable biodiesel.<sup>12</sup> Nonetheless, one commonly adopted technique utilized for the extraction of hydroxyapatite is the thermal calcination technique.<sup>10</sup> Also, the desirable properties (ion-exchange potential, adsorption capability, and the acid–base characteristics) of hydroxyapatite have fostered its

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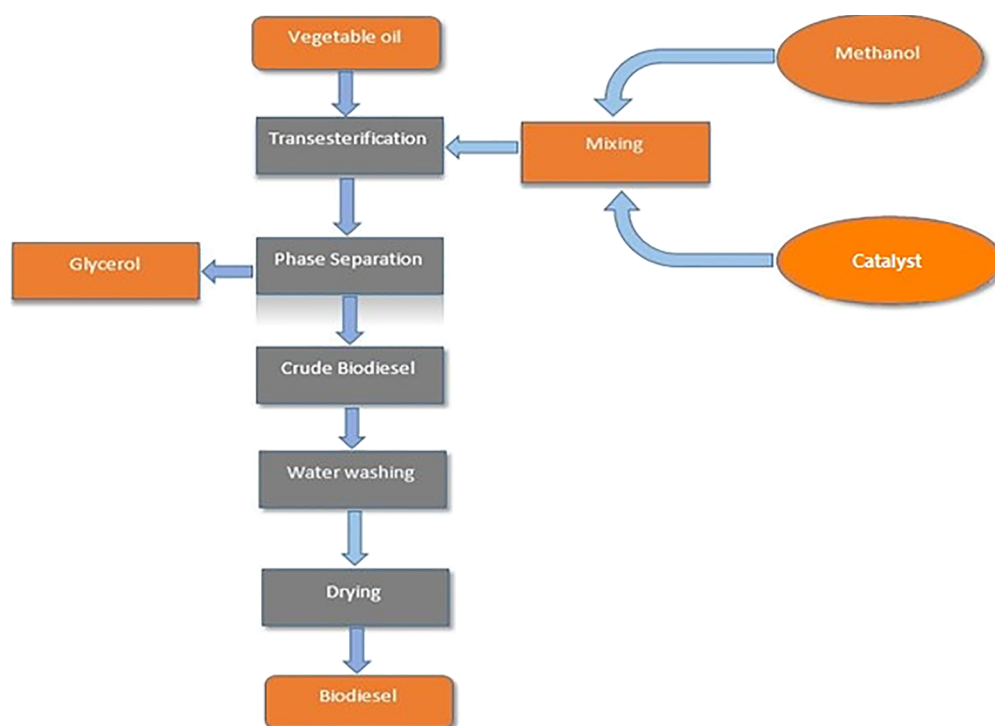


Figure 1. Biodiesel production flowchart.

utilization in so many sectors.<sup>13</sup> Recently, studies have been conducted with the use of waste animal bones for biodiesel production owing to their high basicity. Khan et al. synthesized hydroxyapatite as a heterogeneous catalyst from waste animal bones and utilized it for the transesterification of waste cooking oil to obtain a 90.56% yield of biodiesel.<sup>14</sup> Singh et al. derived the hydroxyapatite catalyst from waste animal bones, which was employed in the transesterification of custard apple seed oil.<sup>15</sup> The authors achieved  $95.82 \pm 0.2\%$  fatty acid methyl ester optimum conversion. The hydroxyapatite catalyst was also synthesized from waste animal bones by Farooq and Ramli for the transesterification of low free fatty acid (FFA) waste cooking oil to obtain a high biodiesel yield of 89.33%.<sup>16</sup> Likewise, Obadiah et al. processed animal bones to obtain hydroxyapatite catalysts, which was employed in the transesterification of palm oil to achieve a high biodiesel yield of 96.78%.<sup>12</sup> Buasri et al. obtained about 94% yield from the biodiesel production from *Jatropha curcas* oil utilizing hydroxyapatite from animal bones.<sup>17</sup> Thus, hydroxyapatite is an efficient solid-base catalyst used for the transesterification of vegetable oil to achieve a high biodiesel yield. This study is focused on the transesterification of parsley seed oil (PSO) using a heterogeneous catalyst derived from animal bones (CCB) and a homogenous (KOH) catalyst to investigate the impact of the process parameters (alcohol: oil molar ratio, temperature, and catalyst loading) on the percentage biodiesel yield so as to ascertain the optimum reaction conditions for high biodiesel yields. The derived catalyst was characterized by scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), X-ray fluorescence (XRF), and X-ray diffraction (XRD), while the produced biodiesel was examined for its fatty acid methyl ester composition and fuel properties by gas chromatography–mass spectrometry (GC–MS). Also, the reusability of the catalyst was investigated. Furthermore, the biodiesel fuel properties were

tested to make sure they meet American Society for Testing and Materials (ASTM) standard specifications.

## 2. MATERIALS AND METHODS

**2.1. Experimental Materials.** Sigma-Aldrich supplied the chemical reagents employed in this analysis. This study utilized potassium hydroxide, *n*-hexane, methanol, and other chemicals. All the chemical reagents were of analytical grade.

**2.2. Experimental Procedure.** **2.2.1. Extraction of PSO.** The parsley oil utilized was extracted from waste parsley seeds using the solvent extraction method adopted by Bitire et al. The extraction process was conditioned for 5 h and later dried for 24 h at room temperature.<sup>18</sup> The solvent of choice for the oil extraction of PSO is *n*-hexane because of its reusability, excellent extraction efficiency, and low cost.<sup>19</sup>

**2.2.2. Catalyst Preparation.** Waste chicken bones were obtained from a local market in Brixton, Johannesburg, South Africa. To remove the impurities, flesh, and gelatinous matter, the waste bones were washed several times with hot distilled water. The bones were dried for 6 h at 110 °C in a hot air oven and then pulverized to the powder form to increase their surface area in order to speed up the reaction process. Afterward, the milled bones were calcined for 4 h at 900 °C in a muffle furnace,<sup>16</sup> and the prepared catalyst was processed for characterization after cooling in a desiccator.

**2.2.3. Characterization of the Catalyst.** To establish the formation of the hydroxyapatite catalyst, XRD, EDX, XRF, and SEM were utilized to analyze the calcined chicken bone (CCB) samples.

**2.2.4. Evaluation of the Physicochemical Properties of PSO.** The Association of Analytical Chemists' standard test methods were utilized to determine the characteristics of the extracted PSO. The viscosity of the seed oil was calculated using a rotational viscometer, and the density of the seed oil was determined using a density bottle. AOAC 920:160, AOAC

920:158, and AOAC Ca5a-40 methodologies were utilized to obtain the iodine, saponification, and acid values, respectively. To determine the total FFA content, the extracted oil was titrated with the potassium hydroxide solution utilizing the phenolphthalein indicator.

**2.3. Biodiesel Production from PSO Utilizing CCB and KOH as Catalysts.** The FFA content of PSO was examined prior to the transesterification reaction. This is because it is necessary to know the FFA value in order to ascertain if an esterification reaction is needed before transesterification so as to reduce the FFA that may be present in the feedstock of choice. Moreover, Stacy et al. revealed that an esterification reaction should be performed prior to transesterification to reduce the FFA content for feedstock with a high amount of FFAs.<sup>20</sup> However, the FFA content of the extracted seed oil was 0.78%, indicating that there is no need for esterification before transesterification because the FFA content is less than 1%. The transesterification of PSO was then conducted by utilizing methanol as the preferred alcohol. The biodiesel production steps are illustrated in Figure 1. The transesterification process was performed in a stainless-steel bioreactor of about 50 mL–100 L capacity, with an optimum temperature of 500 °C (Amar Equipment Pvt. Ltd). The given ratio of the oil, prepared catalyst, and methanol was poured into the bioreactor, and the bioreactor was closed and heated at temperatures ranging from 50 to 70 °C, with various alcohol-to-oil ratios (6:1 to 12:1) and catalyst loadings ranging from 1–3 wt % for 3 h of reaction time. After each run, the mixture (biodiesel and glycerin) was placed in a separatory funnel to settle for 24 h and separated with respect to their different densities. Nonetheless, the CCB were visible at the bottom of the separatory funnel, glycerin was visible in the middle layer, and the formed biodiesel was visible in the upper layer. Thereafter, biodiesel was washed with distilled water, dried, and poured into a sample bottle for testing. The same procedure was employed for KOH but at low, medium, and high levels for the alcohol-to-oil ratio, temperature, and catalyst loading, respectively. However, the optimum reaction condition that gave the highest biodiesel yield when CCB were used as the catalyst was selected from the obtained experimental result and also utilized for the transesterification reaction utilizing KOH as the catalyst. The transesterification process (using KOH) was performed thrice, and the average biodiesel yield obtained was recorded. This was performed in order to effectively compare the efficiency of each catalyst and assess their influence on the yield of the produced biodiesel as well as to determine the optimal reaction conditions for the high biodiesel yield. Furthermore, the parametric reaction condition selected for optimization for the transesterification reaction was derived from related literature studies that examined and tested the best parametric condition for generating biodiesel from waste bones.<sup>21,22</sup> The biodiesel yield was then measured by employing eq 1

$$Y = \frac{D_o}{D_s} \times 100\% \quad (1)$$

where  $Y$  = methyl ester yield (%),  $D_o$  = amount of the methyl esters produced, and  $D_s$  = amount of raw oil utilized.

**2.4. Physicochemical Properties of Parsley Methyl Ester.** The physical and chemical properties of PSO and parsley biodiesel were investigated using the ASTM standard test process. The pH, cetane number, cloud point, specific gravity, kinematic viscosity, pour point acid value, and flashpoint were

among the physicochemical properties assessed. Also, GC–MS was utilized to characterize the biodiesel produced.

**2.5. Optimization Parameters of Biodiesel Production from PSO Using Response Surface Methodology.** In this analysis, Design-Expert 11.1.0.1 software was utilized to determine the best conditions for generating biodiesel from PSO by employing a three-factor three-level Box–Behnken design embedded with the response surface methodology (RSM). The alcohol: oil ratio, temperature, and catalyst loading were defined as A, B, and C, while response (Y) was used to represent the biodiesel yield. As shown in Table 1, the model

**Table 1. Biodiesel Production Experimental Design Layout Using Box–Behnken Design (BBD)**

factor	unit	level	
		low	high
alcohol: oil	mol	6:1	12:1
temperature	°C	50	70
catalyst loading	wt %	1	5

produced approximately 17 experimental runs, which depict the design layout and levels. The high-level values in the model reveal the impact of the optimum conditions on biodiesel yields. Similarly, the biodiesel formation spectrum was revealed by the low-level factor. Its requirements for fewer design points enable versatility in dealing with unusual combinations of variables.

### 3. RESULTS AND DISCUSSION

This section focuses on the results of the physicochemical properties of PSO, biodiesel yield from utilizing the two catalysts, a comparison of the biodiesel yield using CCB and KOH under the same reaction conditions, and the fuel characteristics of the produced biodiesel.

**3.1. Physicochemical Properties of PSO.** The properties of PSO, as shown in Table 2, reveals that the FFA value of PSO is

**Table 2. Physicochemical Characteristics of PSO**

parameters	values
specific gravity	0.991
viscosity (mm <sup>2</sup> /s)	14.9
color	pale yellow
oil yield (%)	25
moisture content (%)	0.55
acid value (mg KOH/g)	1.55
saponification value (mg KOH/g)	194.81
FFA (%)	0.78
pH	6.8
molecular weight	882.68
iodine value (gI <sub>2</sub> /100 g)	103.04
pour point (°C)	−3.0
cloud point (°C)	2.1
refractive index	1.467
high heating value (kJ/kg)	42.99

0.78%, which is less than 1%. Higher levels of FFA in biodiesel-making oils can cause problems during the biodiesel recovery process.<sup>23</sup> The viscosity of methyl esters prepared with CCB as the catalyst was found to be 4.86 mm<sup>2</sup>/s, which is within the ASTM D6751 requirements. The utilization of CCB as a catalyst decreased the viscosity of parsley oil from 14.9 to 4.86 mm<sup>2</sup>/s, indicating that transesterification occurred. In addition, based

on the findings reported in Table 2, all the other physicochemical properties (acid value, saponification value, refractive index, viscosity, higher heating value (HHV), pour point, cloud point, specific gravity, and pH) can also be seen to have a positive impact on the quality of the biodiesel produced.

**3.2. Characterization of the Catalyst.** **3.2.1. Thermogravimetric Analysis.** To efficiently assess the impact of calcination temperature on weight loss, thermogravimetric analysis (TGA) was conducted on the chicken bone samples utilizing SDTQ-600, which is a TA instrument, sourced by advanced laboratory solutions. The starting temperature was the ambient temperature up to about 1050 °C and a heating rate of 10 °C per minute with N<sub>2</sub> purge flow of 20 mL per min. The obtained thermogram displayed in Figure 2 showed that there was mass loss at about

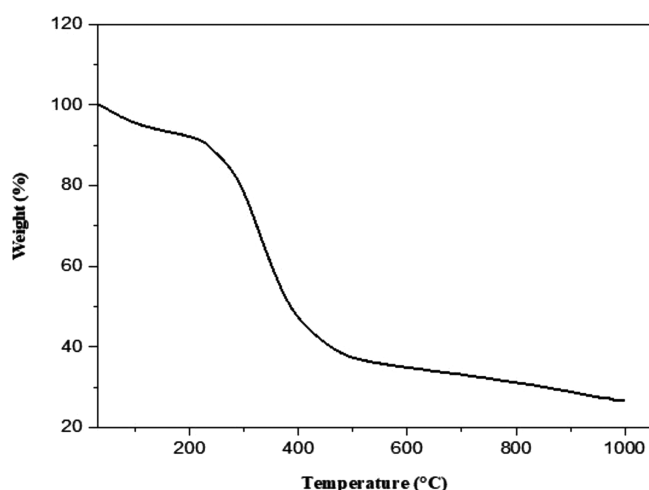


Figure 2. TGA thermogram of powdered chicken bones.

40 to 170 °C, which can be attributed to the disappearance of water molecules. The next phase observed from the thermogram was a broad exothermic peak from 200 to 500 °C, which could be as a result of the loss of the organic materials (collagen and proteins) present in the chicken bone.<sup>24</sup> Also, a consequential loss in weight was seen within the temperature range of 600 to 900 °C, and this can be designated to the creation of gaseous fraction because of the creation of hydroxyapatite.<sup>25</sup> Furthermore, there was no additional weight loss observed at 900 °C temperature and above. This shows that the calcined bone sample is thermally stable at a temperature of 900 °C and above.<sup>26</sup>

**3.2.2. XRD Analysis.** The CCB was derived with the utilization of Cu K $\alpha$  radiation ( $\lambda = 1.54060$  nm) at 40 kV, 40 mA. The XRD spectra of the calcined CCB are shown in Figure 3. The prominent peaks seen at  $2\theta = 10.84, 21.83, 25.90, 32.91, 34.54, 39.81, 46.67, 48.08, 49.50, 52.24, 59.91, 62.98,$  and  $65.11$  denote the presence of hydroxyapatite and correspond with JCPDS file No. 09-0432,<sup>27,28</sup> while peaks  $2\theta = 27.94, 28.91, 31.87,$  and  $51.23$  reveal the presence of beta-tricalcium phosphate (JCPDS card No. 09-0169). Meanwhile, calcium hydroxide peaks were seen at  $2\theta = 17.26$  and  $34.07$  (JCPDS card No. 00-004-0733), and the distinctive characteristics of calcium oxide were observed at peaks  $2\theta = 35.20, 53.12,$  and  $65.32$  (JCPDS 00-037-1497).<sup>29</sup> As a result, the formation of hydroxyapatite is confirmed, and it could serve as a potential catalyst for the transesterification of PSO.

**3.2.3. XRF Analysis.** The XRF results obtained from this analysis revealed the presence and the composition of the oxides

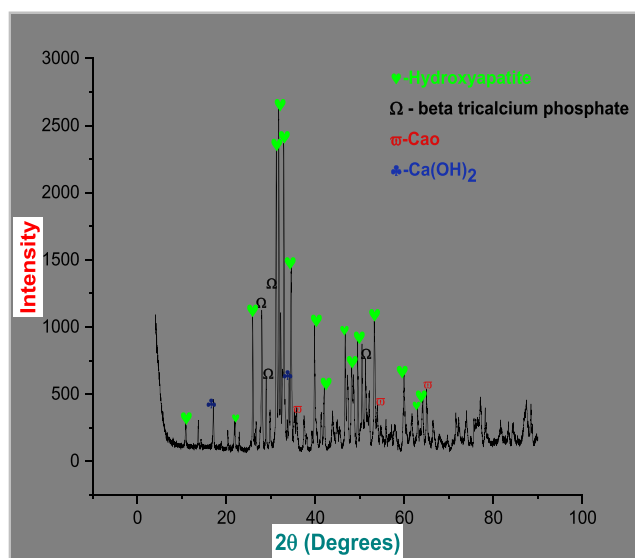


Figure 3. XRD patterns of CCB.

present in the CCB. The oxides (K<sub>2</sub>O, CaO, SO<sub>3</sub>, SiO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub>, Na<sub>2</sub>O, MgO, and Fe<sub>2</sub>O<sub>3</sub>) present are displayed in Table 3.

Table 3. Chemical Composition of CCB Obtained by XRF

elements	weight (%)
CaO	51.620
P <sub>2</sub> O <sub>5</sub>	43.437
K <sub>2</sub> O	0.382
Na <sub>2</sub> O	1.836
MgO	1.478
SO <sub>3</sub>	0.424
SiO <sub>2</sub>	0.053
Fe <sub>2</sub> O <sub>3</sub>	0.395
ZnO	0.023
Al <sub>2</sub> O <sub>3</sub>	0.019

However, CaO (51.620 wt %) and P<sub>2</sub>O<sub>5</sub> (43.437 wt %) are the most abundant oxides present in the CCB, and this confirmed that the calcination of the bones at 900 °C for 4 h completely decomposed to give hydroxyapatite. Also, the presence of trace elements in the CCB could be beneficial in increasing its catalytic activity.<sup>30</sup>

**3.2.4. SEM Characterization.** To investigate the surface morphology of the uncalcined chicken bone and CCB, SEM analysis was adopted, as displayed in Figure 4. The SEM analysis

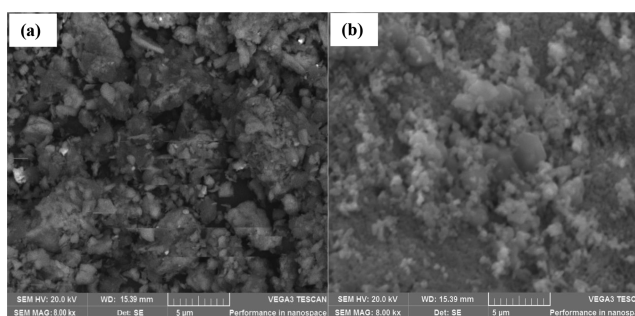


Figure 4. SEM image for (a) uncalcined chicken bone and for (b) CCB at 900 °C for 4 h.

revealed that the uncalcined chicken bone sample is made up of uneven, irregular, and a broad size distribution, unlike the agglomerates of fine particles with regular shapes noticed for the CCB sample. The reduction in the particle size of CCB could be attributed to the calcination at 900 °C for 4 h, as reported by Chingakham et al. that calcination results in a reduction in the particle size and an increase in the surface area.<sup>31</sup> The agglomerates of the fine particles noticed in CCB can be ascribed to the change in the composition as a result of the formation of oxides.

Furthermore, the uniform distribution of the catalyst and the removal of the organic elements present in the bones were favored by calcining CCB at higher temperatures. As a result, the particle sizes decreased greatly, as shown in Figure 3b. Moreover, Madhu et al. found that organic elements (such as fats and proteins) can be removed at a calcination temperature of 800 to 1000 °C, thereby increasing the surface area of the catalyst.<sup>32</sup>

**3.2.5. EDX.** The elemental composition of uncalcined chicken bone and CCB was examined by employing EDX analysis, as illustrated in Figures 5 and 6, respectively. The result showed

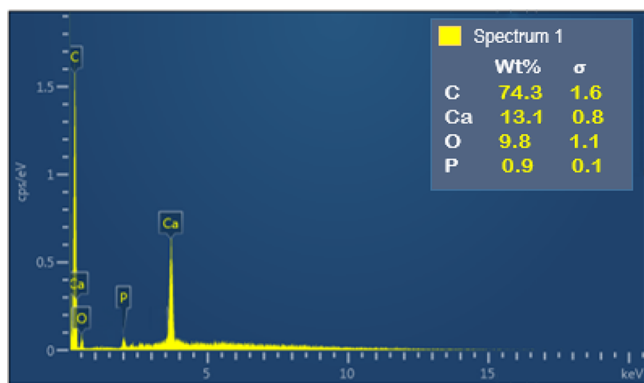


Figure 5. EDX analysis of uncalcined chicken bone.

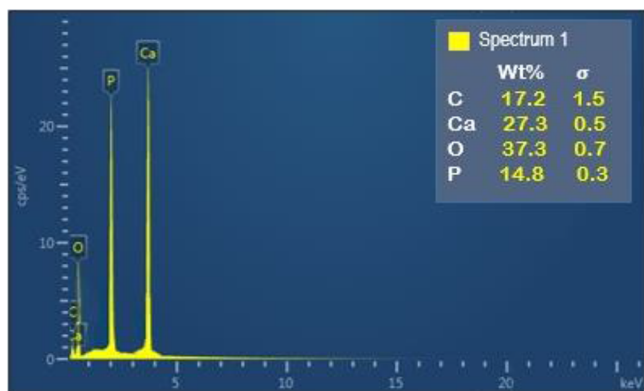


Figure 6. EDX analysis of CCB.

that the uncalcined chicken bone consists of carbon (C), calcium (Ca), oxygen (O), and phosphorous (P) of 74.3, 13.1, 9.8, and 0.9 wt %, respectively, while the uncalcined sample contains the same elements with 17.2, 27.3, 37.3, and 14.8 wt %. A substantial difference in the elemental composition of the two samples was observed. For instance, the carbon peak, which was high before calcination, reduced drastically after calcination and also reduced in percentage weight from 74.3 to 17.2%. A remarkable increase in the calcium, oxygen, and phosphorus

contents was noticed in the uncalcined chicken bones to that in the CCB, that is, for calcium (13.1–27.3 wt %), oxygen (9.8–37.3 wt %), and phosphorus (0.9–14.8 wt %), which indicates an increase in the activity of the catalyst, as a result of the formation of hydroxyapatite.<sup>12</sup>

**3.2.6. Fourier-Transform Infrared Spectrometry Analysis.** The Fourier-transform infrared (FT-IR) patterns of the CCB is displayed in Figure 7. A distinctive absorption peak attributed to the presence of hydroxyapatite was noticed from the IR spectra of the CCB sample.<sup>24</sup> The synthesized catalyst (hydroxyapatite) showed a C–O band seen at 1418 and 880  $\text{cm}^{-1}$ , whereas the phosphate bands were identified at 1086, 1023, 977, 600, and 554  $\text{cm}^{-1}$ . FT-IR spectrometry revealed that the desired catalyst (hydroxyapatite) was generated after the chicken bone was calcined for 4 h. Also, the identification of carbonated hydroxyapatite bands is evident; the 4 h reaction time was sufficient for the conversion of chicken bone to hydroxyapatite. Moreover, few studies have also reported similar findings.<sup>31,33,34</sup> Furthermore, no characteristic peak associated with the presence of collagen was detected in the spectra of the CCB sample, indicating that collagen from bone samples is burned at 900 °C calcination temperature for 4 h.<sup>35</sup>

**3.2.7. Catalyst Reusability.** The reusability of the synthesized catalyst was examined under optimum reaction conditions of 3 wt % catalyst loading, 60 °C reaction temperature, and alcohol: oil molar ratio of 9:1. After each cycle, the catalyst was recovered and treated by washing thoroughly using methanol to eliminate polar compounds (such as glycerol), filtered, and then dried prior to its reuse. The differences in the biodiesel yield with each run are illustrated in Figure 8. The obtained results showed that the catalyst can be utilized for four consecutive runs with good biodiesel yield and little loss in catalyst activity. However, from the fifth run, a substantial loss in the activity of the catalyst as well as the biodiesel yield was observed, and this could be due to the deposition of compounds such as glycerol, unreacted oil, and biodiesel on the catalyst active site.<sup>8</sup> Moreover, Khan et al. reported that hydroxyapatite synthesized from waste animal bones was reused for up to four consecutive cycles, with better biodiesel yield.<sup>14</sup> Farooq and Ramli also stated that hydroxyapatite prepared from CCB showed for four consecutive cycles, and a decline in the yield of biodiesel was noticed from the fifth run.<sup>16</sup> Hence, waste chicken bones are a very good source for the synthesis of hydroxyapatite for the production of biodiesel.

**3.3. Biodiesel Yield from PSO Produced with CCB.** The result of the process parameter optimization for the transesterification of PSO adopting CCB as a catalyst for the experimental runs is displayed in Table 4.

The optimum reaction conditions of 9:1 alcohol: ratio, 60 °C reaction temperature, and 3 wt % catalyst loading gave the highest biodiesel yield (90%), while the lowest yield (55%) was observed with reaction conditions of 12:1, 70 °C, and 5 wt % for alcohol: ratio, reaction temperature, and catalyst loading, respectively. The reaction conditions that gave the maximum biodiesel yield are slightly similar to the maximum reaction conditions adopted by Nisar et al. to obtain 96.1% optimum biodiesel from *Jatropha* oil utilizing waste animal bones as the catalyst.<sup>25</sup> The authors also reported that the bone-based catalyst could be reused up to four times for good biodiesel yield. However, in this study, it was discovered that the parametric medium reaction produced the highest biodiesel yield, and this chemically active reaction was sufficient to break the triglyceride bond. This demonstrates that the reaction conditions were adequate for complete PSO transesterification in 3 h reaction

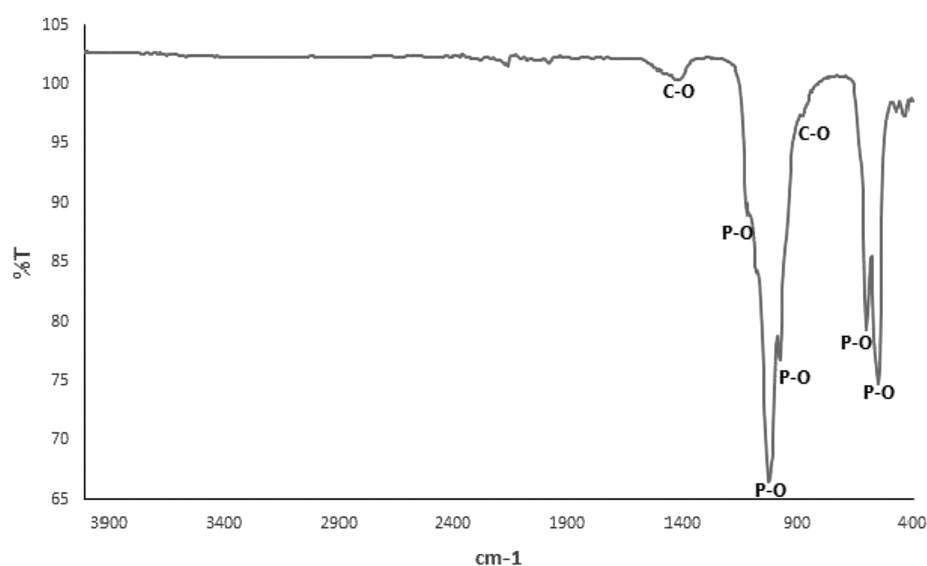


Figure 7. FT-IR spectrometry of CCB.

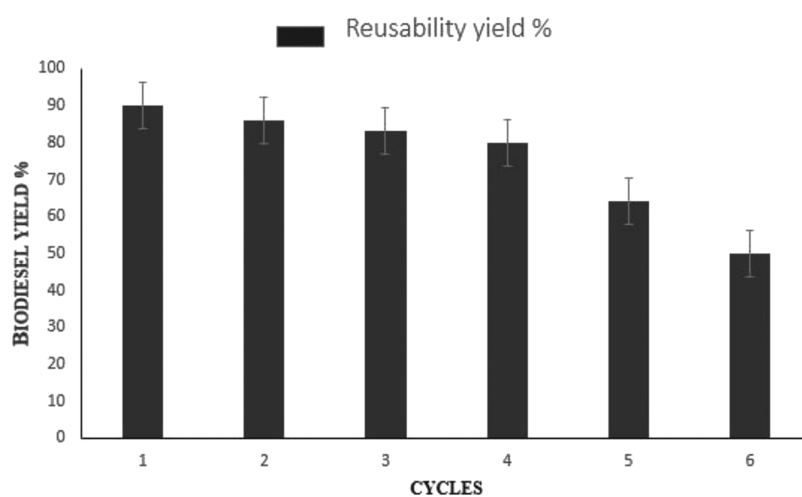


Figure 8. Reusability of the CCB catalyst.

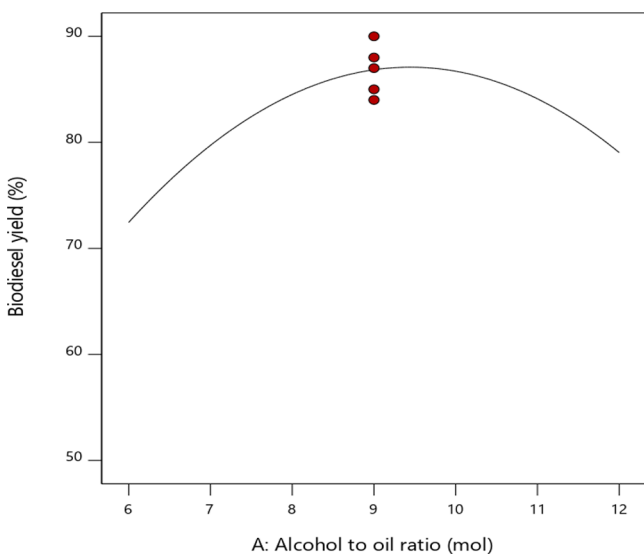
time. A higher reaction parametric variable resulted in a substantial reduction in the biodiesel yield. According to Musa et al., a higher molar ratio of alcohol to oil would affect the interaction of triglyceride molecules on the catalyst's active site, thus lowering its activity.<sup>22</sup> However, when the molar ratio of alcohol to oil is higher, more glycerol is formed, which favors backward reactions, and this can lead to a reduction in the biodiesel yield. Also, the observed changes in the biodiesel yield are due to the effect of reaction parameters employed, which shows that they have an impact on the amount of biodiesel produced. The effect of the process parameters in (the alcohol-to-oil molar ratio, the reaction temperature, and the amount of catalyst) on the biodiesel yield is illustrated in the biodiesel yield as a single factor in Figures 9, 10, and 11, respectively. The red dots in the center of the curves represent points of design (as shown in Table 4 for experimental runs), with a higher percentage yield. It can be seen that the biodiesel yield increases as the reaction parameter increases and suddenly begins to decline at reaction conditions above 9:1, 3 wt %, and 60 °C for alcohol: oil ratio, catalyst loading, and temperature, respectively. As shown in Figure 9, the yield of biodiesel increases as the molar ratio of alcohol-to-oil is increased. This is because a higher ratio

of alcohol-to-oil, which is greater than the stoichiometric ratio (3:1) for the transesterification reaction, is required to enhance the interaction between the alcohol and triglyceride molecules. However, during the transesterification of triglycerides into biodiesel, an elevated amount of alcohol is required to split the linkages (glycerin-fatty acid).<sup>18</sup> However, at a higher alcohol-to-oil ratio greater than 9:1, the biodiesel yield begins to decrease. This is due to the reaction system's low catalyst amount as well as a reduction in triglyceride-catalyst interaction.

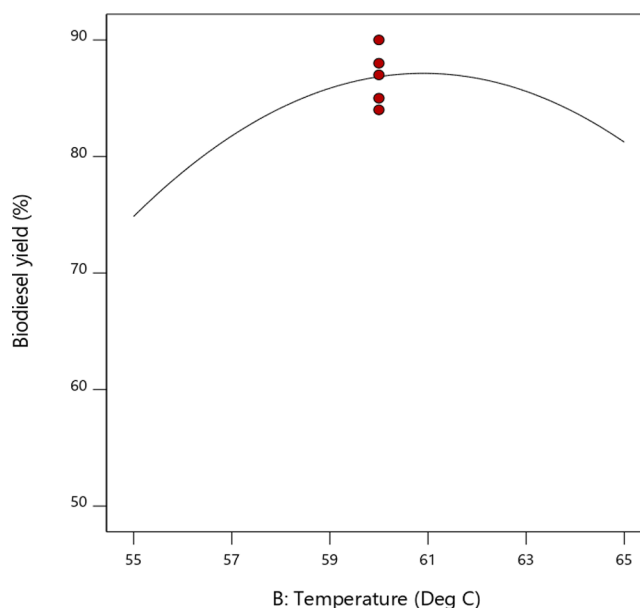
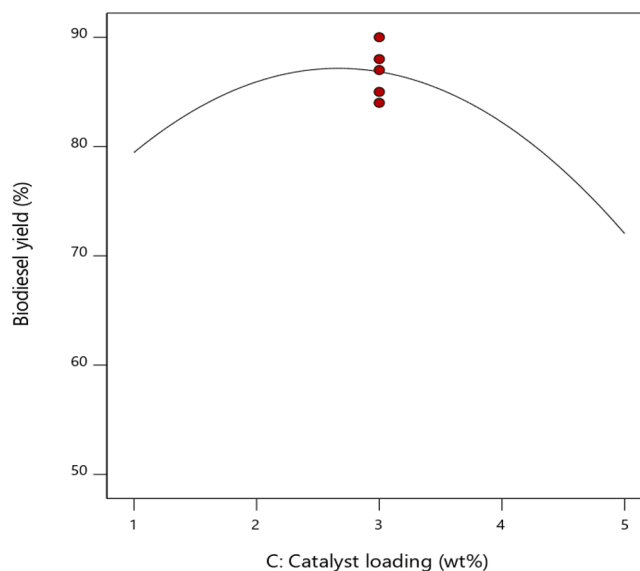
Also, Lin et al. revealed that at higher temperatures, triglycerides attached to FFAs can be destroyed, resulting in a decrease in the biodiesel percentage yield.<sup>36–38</sup> As seen in Figure 10, the biodiesel yield decreased drastically above 60 °C reaction temperature. Likewise, the reduction in the biodiesel yield above 3 wt % catalyst loading, as displayed in Figure 11, can be a result of the reaction mixture becoming very viscous, which requires a higher amount of stirring.<sup>39</sup> Essamlali et al. transesterified rapeseed oil by utilizing modified sodium hydroxyapatite and observed the effect of the adopted reaction parameters on biodiesel yield.<sup>40</sup> The authors discovered that higher parametric reaction conditions would cause a decline in the percentage biodiesel yield, while moderate reaction conditions favored

**Table 4. Yield of Biodiesel from PSO Utilizing CCB as the Catalyst**

std	run	A: alcohol to oil ratio (mol)	factors B: temperature (°C)	C: catalyst loading (wt %)	response biodiesel yield (%)
4	1	12	70	3	76
15	2	9	60	3	88
9	3	9	50	1	73
16	4	9	60	3	85
2	5	12	50	3	65
12	6	9	70	5	70
14	7	9	60	3	87
13	8	9	60	3	84
7	9	6	60	5	66
3	10	6	70	3	67
5	11	6	60	1	57
8	12	12	70	5	55
17	13	9	60	3	90
1	14	6	50	3	60
6	15	12	60	1	80
11	16	9	50	5	57
10	17	9	70	1	68

**Figure 9.** Effect of alcohol: oil ratio on the yield utilizing CCB as a catalyst.

optimum biodiesel yield. Suwannasom et al. also optimized the reaction conditions for the transesterification of waste cooking oil utilizing a bone-based catalyst and reported that higher biodiesel yield was obtained by utilizing a moderate level of the reaction parameters (alcohol:oil ratio, catalyst amount, and temperature).<sup>41</sup> However, at higher reaction conditions, the biodiesel yield decreases as a result of soap and emulsion formation via saponification. This can foster the decline in the quantity of biodiesel produced because of the separation of the biodiesel from glycerin. It can also lead to the production of low-quality biodiesel. Nonetheless, the variation in the yield of the produced biodiesel, as a result of the effect of the utilized process parameter, is evidence that they play an important role in determining the percentage yield of the biodiesel. Also, the optimum biodiesel yield of 88.51%, with the maximum reaction conditions of the alcohol to oil ratio, temperature, and catalyst loading of 9.2:1, 61.3%, and 2.85 wt %, respectively, was achieved via data analysis using the RSM.

**Figure 10.** Effect of temperature on the yield utilizing CCB as a catalyst.**Figure 11.** Effect of catalyst loading on the yield utilizing CCB as a catalyst.

**3.3.1. Statistical Analysis for Biodiesel Production from PSO Using CCB as the Catalyst.** This study employed Design Expert 11.1.0.1 software to investigate the production of biodiesel from PSO. The second-order polynomial equation was adjusted to eliminate the irrelevant coded factors AB, while A, B, C, AC, BC, A<sup>2</sup>, B<sup>2</sup>, and C<sup>2</sup> are significant model terms in the multiple regression analysis of the experimental outcomes.

Therefore, the net equation in terms of the coded variable factors gives the following

$$\begin{aligned}
 Y_{\text{CCB}} = & 86.85 + 3.29A + 3.19B - 3.71C + 0.8822AB \\
 & - 8.41AC + 4.38BC - 11.10A^2 - 8.81B^2 \\
 & - 11.10C^2
 \end{aligned} \quad (2)$$

where  $Y_{\text{CCB}}$  = yield of biodiesel using CCB as the catalyst; A = alcohol to oil ratio; B = temperature; and C = catalyst loading.

Table 5. ANOVA of Biodiesel Yield from PSO Transesterification Using CCB

source	sum of squares	df	mean square	F-value	P-value	
model	2174.89	9	241.65	46.76	<0.0001	significant
A-alcohol to oil ratio	78.20	1	78.20	15.13	0.0060	significant
B-temperature	84.14	1	84.14	16.28	0.0050	significant
C-catalyst loading	99.01	1	99.01	19.16	0.0032	significant
AB	3.32	1	3.32	0.6434	0.4489	not significant
AC	232.08	1	232.08	44.91	0.0003	significant
BC	82.04	1	82.04	15.88	0.0053	significant
A <sup>2</sup>	485.14	1	485.14	93.88	<0.0001	significant
B <sup>2</sup>	267.56	1	267.56	51.78	0.0002	significant
C <sup>2</sup>	485.14	1	485.14	93.88	<0.0001	significant
residual	36.17	7	5.17			
lack of Fit	13.37	3	4.46	0.7820	0.5627	not significant
pure error	22.80	4	5.70			
cor total	2211.06	16			R <sup>2</sup>	0.9836
std dev	2.27				adjusted R <sup>2</sup>	0.9626
mean	72.24				predicted R <sup>2</sup>	0.8706
C.V.%	3.15				adeq precision	17.9963

Furthermore, the analysis of variance (ANOVA) was utilized to assess the biodiesel processing from PSO. The biodiesel yield for the ANOVA model values of PSO transesterification is shown in Table 5.

The *P*-value and the *F*-value can be utilized to verify the nature of the designed model and experimental factors.<sup>42</sup> The 85.70 *F*-value derived from the statistical model indicates the model's relevance. The importance of the model term was also demonstrated by *P*-values of less than 0.0500. As a result, the parametric variables employed in the model, as well as their interactive effects, are significant model terms. However, the catalyst loading, which has the highest *F*-value of 19.16 and the low *P*-value of <0.0001, is the most important parameter for parsley biodiesel production, according to the *F* and *P*-values of the parameters utilized. Furthermore, the precision ratio of 17.9963, which is desirable (above 4), and the "Pred. R-Squared" of 0.9836 shows maximum similarity with the "Adj R-Squared" of 0.9626, with a lesser difference of about 0.2. The lack of fit has no impact on the accepted model, and the *F*-value of 0.7820 indicates that it is negligible when compared to the pure error. Table 5 shows the results of the ANOVA analysis. Furthermore, the normal plots of residuals, as well as the comparison of real and predicted values, can also be attributed to the assertion of this model, as shown in Figure 12. The observed space point centered along the diagonal line is caused by a close relationship between the *R*<sup>2</sup> and the adjusted *R*<sup>2</sup> values. Additionally, the analytical percentage yields and model response yields demonstrated a great fit.

### 3.4. Characterization of the Produced Biodiesel.

**3.4.1. GC Analysis.** The GC-MS study was employed to identify the esters present in the produced biodiesel. The obtained chromatogram (Figure 13) illustrates the chromatogram of parsley biodiesel. Table 6 depicts the fatty acid methyl esters present, as determined by GC-MS. Figure 14 shows the fragmentation spectrum of the obtained methyl esters. The chromatogram in Figure 13 shows a total of six peaks that equate to the methyl esters present in the produced biodiesel. The methyl ester of hexadecanoic acid is the first peak detected, with a composition of 10.55%. The presence of *cis*-13-octadecenoic acid methyl ester with a composition of 12.10% was discovered in the second peak. The third peak contains 32% 11-octadecenoic acid methyl ester, whereas the fourth peak

contains 20.11% 9-octadecenoic acid methyl ester. The percentage composition of heptadecanoic acid, 16-methyl-, methyl ester and octadecenoic acid, methyl ester was 1.40 and 5.18% for the fifth and sixth peaks, respectively.

**3.4.2. FT-IR Spectrometry of PSO and Parsley Biodiesel.** The FT-IR spectrometry analysis was employed to further validate the conversion of PSO into biodiesel. The obtained spectra are displayed in Figures 15 and 16. A noticeable dissimilarity can be seen between 1500–900 cm<sup>-1</sup> spectral regions for the utilized feedstock (PSO) and the produced biodiesel, and this spectral region is known as the fingerprint region.<sup>43</sup> In Figure 16, the oscillating and the bending vibrations of –OCH<sub>3</sub> were identified at 1117 and 1476 cm<sup>-1</sup>, but not in the PSO spectrum shown in Figure 15. This is attributable to the fact that triacylglycerols belong to the –OCH<sub>2</sub> and O–CH functional groups. Consequently, the conversion of peak 884 cm<sup>-1</sup> in the PSO spectrum, which denotes the vibrational stretch of C–O linked to –CH<sub>2</sub>, is observed in Figure 16 as 1035 cm<sup>-1</sup>. The transformation of this peak from 884 to 1035 cm<sup>-1</sup> is because of the vibration stretch of C–O attached to –CH<sub>2</sub>.<sup>44</sup> Also, the stretching vibrations of the carbonyl functional group of esters are responsible for the 1744 and 1666 cm<sup>-1</sup> peak intensities noticed in Figures 14 and 15 for both parsley oil and biodiesel, respectively.<sup>45</sup> The peak located at 3324 indicates the presence of the hydroxyl (O–H) functional group, which can be as a result of little glycerol residue in the processed biodiesel.<sup>46,47</sup> Furthermore, the GC-MS and FT-IR findings revealed that the conversion of PSO was accomplished successfully under the reaction conditions utilized to obtain good biodiesel yield.

**3.5. Biodiesel Yield from PSO Produced with KOH.** The production of parsley biodiesel from PSO using potassium hydroxide as a catalyst under various reaction conditions (high, medium, and low) is shown in Table 7. The obtained results showed that as the factorial level is increased from low to medium, the biodiesel yield increases, but at high-level parametric conditions, the yield begins to decline. As the alcohol-to-oil ratio, temperature, and catalyst loading increase, the biodiesel yield increases, and as these factors are increased beyond 9:1 alcohol: oil molar ratio, the temperature of 60 °C, and 3 wt % catalyst loading, the biodiesel yield decreases. This is due to methanol volatilization as the reaction temperature exceeds 60 °C.<sup>48</sup> Also, an excess amount of catalyst generates



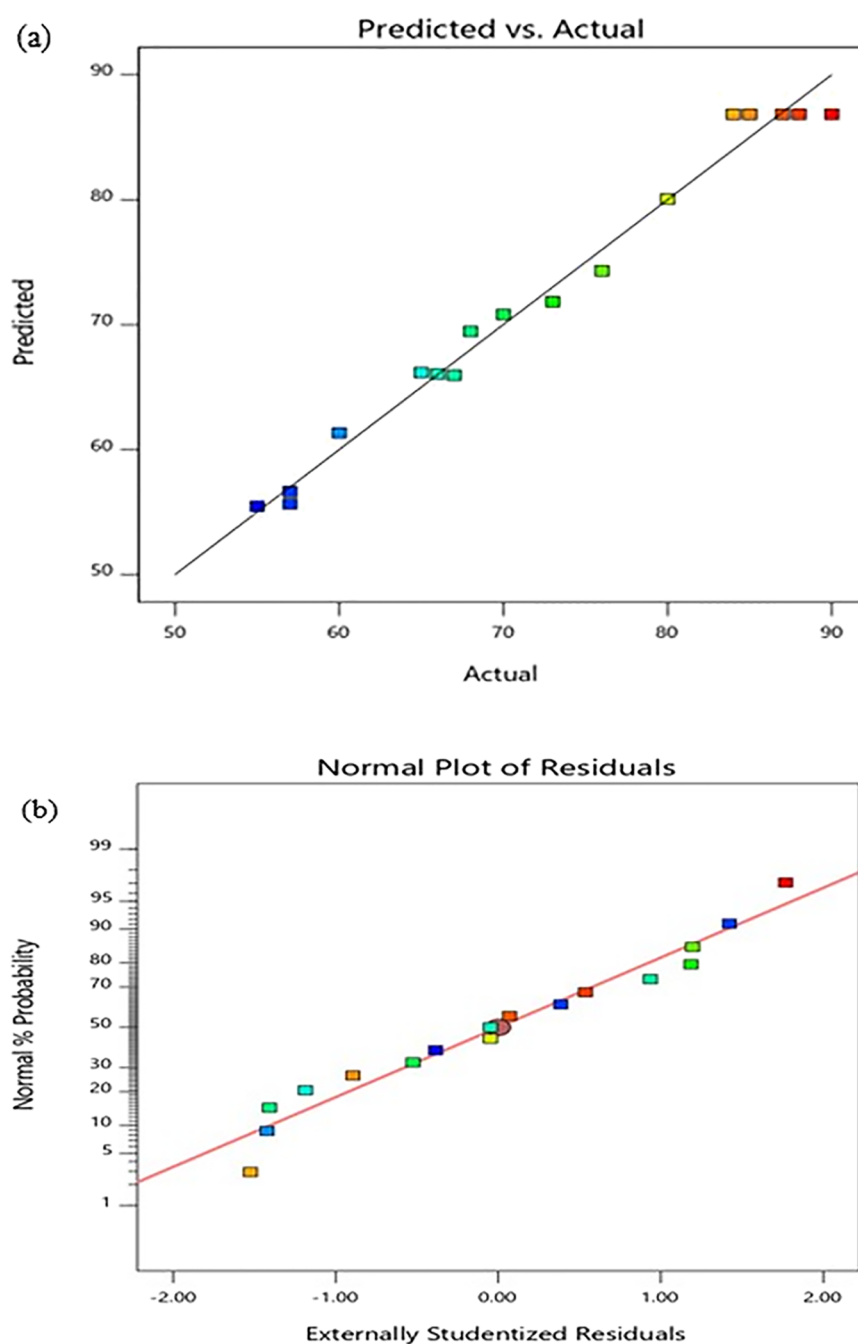


Figure 12. (a) Predicted and true values and (b) normal plot of residuals

excess soap over time, resulting in a decreased yield.<sup>49</sup> The decline in the biodiesel yield with respect to an increasing catalyst concentration can also be attributed to an increase in the viscosity of the reaction mixture. Moreover, increasing the viscosity of the reaction is liable to cause an increase in mass-transfer resistance and perturbation of the reactants, thereby decreasing the yield. Moreover, a catalyst concentration greater than 3 wt % may support a backward reaction, shifting the equilibrium to the left, resulting in glycerol production. Eevera and Pazhanicham observed similar results for cottonseed biodiesel using potassium hydroxide as the catalyst.<sup>50</sup> The authors reported that initially, as the catalyst amount was increased from 0.5 to 1.5%, the biodiesel yield increased and suddenly decreased as the catalyst amount was further increased. In this study, a maximum biodiesel yield of 98% was obtained at

a 9:1 alcohol-to-oil ratio, 60 °C, and 3 wt % catalyst loading. A decline in the biodiesel yield was observed above this parametric value. However, it was also observed that using too much methanol causes the byproduct (glycerol) to dissolve faster, making the separation of the biodiesel more difficult. As reported by Azcan and Danisman, a high amount of alcohol can boost the production of glycerol, which makes biodiesel recovery very difficult and in turn reduces the biodiesel yield.<sup>51</sup> Hence, it can be inferred that the high-level parametric reaction conditions (12:1, 70 °C, and 5 wt % for alcohol: oil ratio, temperature, and catalyst loading) are unfavorable for the generation of high percentage biodiesel yield.

**3.6. Comparison of Biodiesel Production from PSO Utilizing CCB and KOH Catalysts.** The maximum biodiesel yield obtained from the transesterification of PSO utilizing CCB

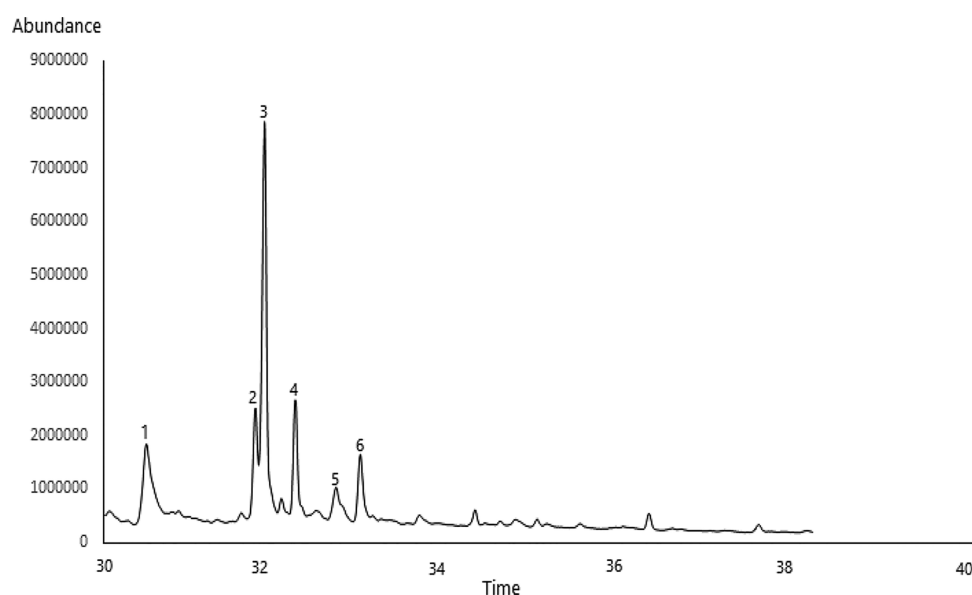


Figure 13. GC–MS Chromatogram of Parsley Biodiesel using CCB.

Table 6. The Fatty Acid Methyl Esters (FAME) Composition of the Biodiesel Produced with CCB

identified compounds	molecular formula	composition (%)	#peaks
hexadecanoic acid, methyl ester	C <sub>17</sub> H <sub>34</sub> O <sub>2</sub>	10.55	1
cis-13-octadecenoic acid, methyl ester	C <sub>19</sub> H <sub>36</sub> O <sub>2</sub>	12.10	2
11-octadecenoic acid, methyl ester	C <sub>19</sub> H <sub>36</sub> O <sub>2</sub>	32.00	3
9-octadecenoic acid, methyl ester	C <sub>18</sub> H <sub>34</sub> O <sub>2</sub>	20.11	4
heptadecanoic acid, 16-methyl-, methyl ester	C <sub>19</sub> H <sub>38</sub> O <sub>2</sub>	1.40	5
octadecenoic acid, methyl ester	C <sub>19</sub> H <sub>38</sub> O <sub>2</sub>	5.18	6

is 90% at optimum reaction conditions of 9:1, 60 °C, and 3 wt % for alcohol: oil ratio, temperature, and catalyst amount, respectively. However, the optimum reaction conditions (9:1, 60 °C, and 3 wt % for alcohol: oil ratio, temperature, and catalyst amount) that gave the highest biodiesel yield from the experimental results displayed in Table 4 were utilized to produce biodiesel using KOH as the catalyst. This was repeated three times, and the average biodiesel yield was 96.33%. This average biodiesel yield obtained revealed that the KOH catalyst is more efficient in achieving a higher biodiesel yield than the CCB catalyst. The reaction conditions adopted for both catalysts were the same, but the homogenous catalyst showed to be better than the heterogeneous catalyst. However, the lower biodiesel yield obtained from the heterogeneous catalyst (CCB) can be ascribed to the formation of a high amount of soap, which was observed after production during the settling stage (The mixture was allowed to stand for 24 h before separation). This can occur when transesterification is accompanied by an increased saponification, which in turn reduced the amount of biodiesel produced. In essence, for both catalysts, a moderate temperature (60 °C) favored higher biodiesel yield, while the increase in the alcohol: oil ratio made more methanol available for the transesterification reaction, which aided the increase in the biodiesel yield. The assessment of the experimental data showed that the reaction variables utilized had a quadratic relationship in which an increase in one variable does not immediately result in the increase in another. For instance, a

higher alcohol: oil ratio at a lower temperature resulted in a lower percentage yield of biodiesel because more glycerol was produced; a higher temperature resulted in methanol evaporation, and a much higher catalyst amount resulted in a lower yield. Also, the glycerol separated from the CCB catalyst and parsley biodiesel was soapy, thick, and whitish in color, which is in contrast to the black and soapy glycerol separated from the generated biodiesel when KOH was utilized as a catalyst. Nonetheless, the utilized homogenous and heterogeneous catalyst was suitable for parsley biodiesel production with a reasonable yield. However, the homogeneous catalyst was better than the heterogeneous catalyst with a higher biodiesel yield. However, the heterogeneous (CCB) catalyst can be modified to increase its catalytic activity to achieve a higher biodiesel yield. Nisar et al. modified waste animal bones with KOH and utilized it for the transesterification of *Jatropha* oil to obtain a high biodiesel yield of 96.1%.<sup>25</sup> Ghanei et al. also reported a higher biodiesel yield of 95.16% when sheep bone was impregnated with CaO to improve its catalytic activity for the processing of biodiesel from vegetable oil.<sup>52</sup> Furthermore, previous studies on the use of the bone-based catalyst for biodiesel production were compared to the parsley biodiesel prepared with the synthesized heterogeneous catalyst (CCB), as shown in Table 8. It was observed that the studies highlighted in Table 8 required high reaction conditions for high biodiesel yield; meanwhile, a high percentage yield of biodiesel was achieved using the CCB catalyst, with a lower alcohol-to-oil ratio, low catalyst amount, and within a short period of time. As a result, the eco-friendly CCB is very effective in the transesterification of PSO to produce biodiesel and is also cost efficient.

**3.7. Fuel Behavior of Parsley Biodiesel.** The result obtained from the assessment of the fuel properties of parsley biodiesel utilizing CCB and KOH catalysts is displayed in Table 9. The biodiesel produced with PSO and CCB catalysts possessed higher specific gravity than diesel fuel, as shown in Table 9. Biodiesel with a HHV increases the engine efficiency and performance during the course of combustion owing to the high oxygen levels, allowing for faster combustion rates and lower oxidation power.<sup>14</sup> The biodiesel obtained from this study possesses a HHV than petro-diesel, and it also met ASTM

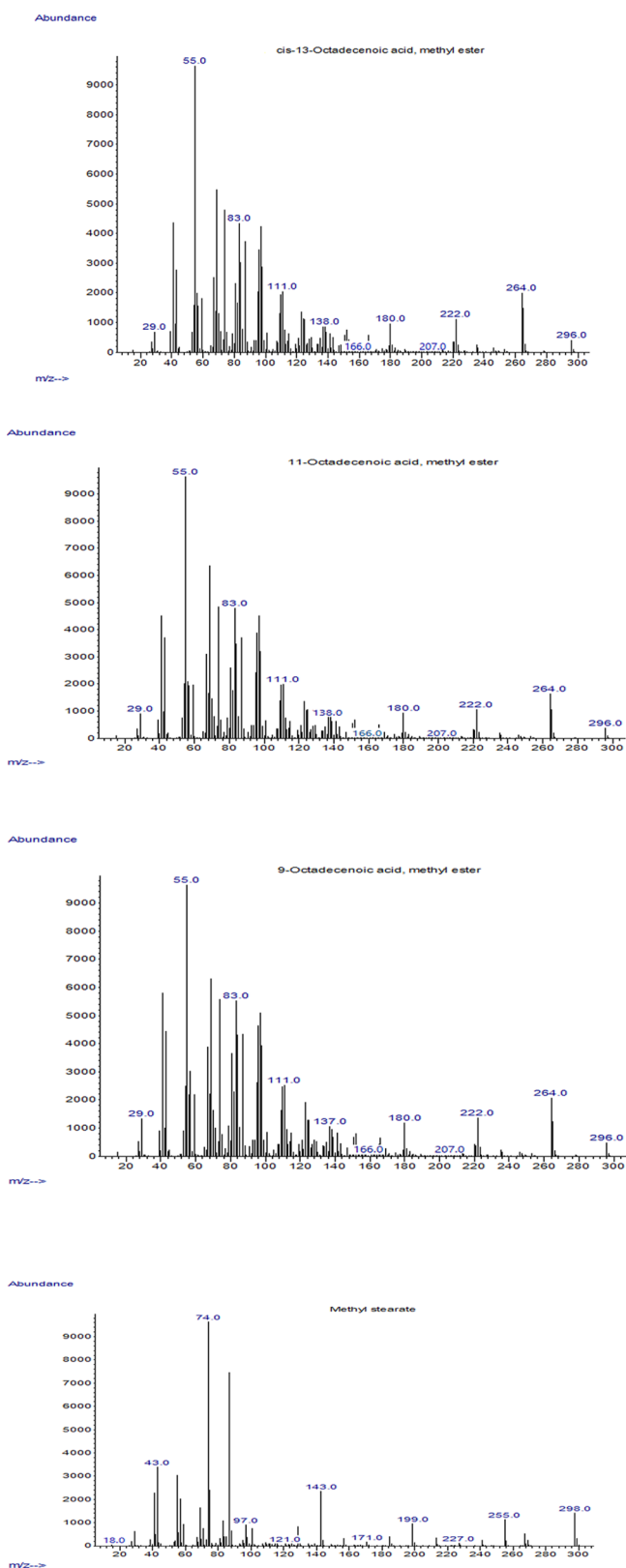


Figure 14. Mass spectrum of some identified fatty acid methyl ester.

standard specifications. However, PSO exhibited a viscosity of  $14.90 \text{ mm}^2/\text{s}$ , while the viscosities of the parsley biodiesel generated with CCB and KOH were  $4.86$  and  $4.77 \text{ mm}^2/\text{s}$ , respectively, as shown in Table 2. Apart from meeting the ASTM D6751 viscosity limit for biodiesel in both cases, the feedstock's

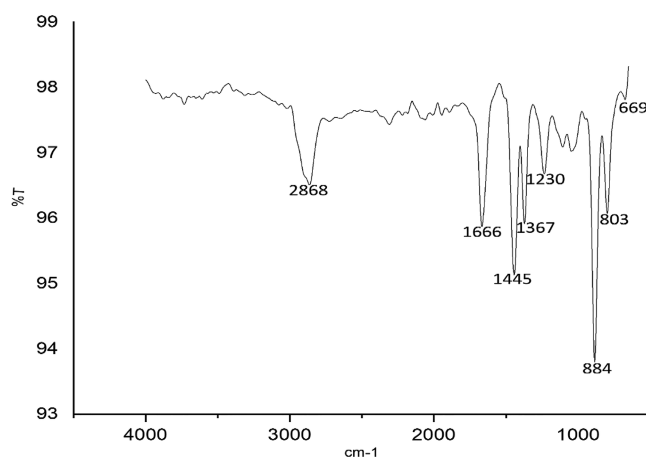


Figure 15. FT-IR spectrometry of PSO.

high viscosity was reduced during transesterification with the catalysts, indicating that transesterification occurred. Also, the biodiesel produced has a higher cetane number than diesel fuel, indicating a good and smoother combustion efficiency. Furthermore, biodiesel's high cetane number is due to its high oxygen levels that promote its combustion in a diesel engine with minimal noise.<sup>55</sup> The flashpoint was also employed to evaluate the durability, safety, and transportation of the fuel. However, for CCB ( $121.2 \text{ }^\circ\text{C}$ ) and KOH ( $110.7 \text{ }^\circ\text{C}$ ) catalysts, the flashpoint of the biodiesel is greater than that of conventional diesel. As a result, biodiesel produced in this manner is less flammable, safe to use, and risk-free.<sup>56</sup> In addition, the biodiesel's flash and fire point values met the ASTM standard values for biodiesel. Because of their effect on fuel usage in cold weather, the pour point and cloud point are employed to define the fuel's flow operability. The obtained low viscosity value of parsley biodiesel for cloud and pour points utilizing CCB and KOH as catalysts indicates low flow resistance and therefore means that the produced biodiesel can be adopted as a reliable fuel for diesel engine because it possesses similar properties as that of diesel fuel.<sup>57,58</sup>

#### 4. CONCLUSIONS

The following conclusions can be drawn based on the results of this study:

- i. The employed reaction parameters (alcohol to oil ratio, temperature, and catalyst loading) in this work showed a substantial effect on the percentage yield of the produced biodiesel, and the experimental values were similar to the predicted values.
- ii. The utilization of CCB in biodiesel production offered cost-effective reaction conditions for a high biodiesel yield. The maximum predicted reaction conditions for the production of high biodiesel yield of 88.51% were 9.2: 1, 61.3%, and 2.85 wt % for the alcohol: oil ratio, reaction temperature, and catalyst number, respectively.
- iii. In comparison with the homogenous catalyst (KOH) employed, the CCB catalyst can be reused for four cycles with good biodiesel yield, as revealed by the reusability test conducted while the homogeneous catalyst (KOH) cannot be reused.
- iv. For the production of parsley biodiesel using CCB, catalyst loading exhibited the most influence on the biodiesel yield.

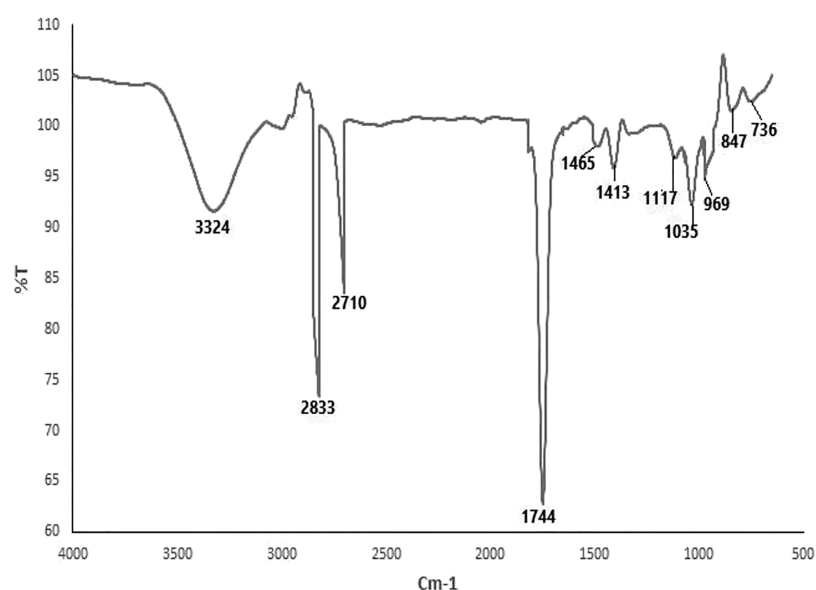


Figure 16. FT-IR spectrometry of parsley biodiesel using CCB.

Table 7. Yield of Biodiesel from PSO Utilizing KOH as the Catalyst

alcohol to oil ratio (mol)	factors temperature (°C)	catalyst loading (wt %)	response biodiesel yield (%)
6	50	1	73
9	60	3	98
12	70	5	57

- v. The homogenous catalyst (KOH) gave the highest biodiesel yield of 98% compared to the 90% biodiesel yield achieved with the heterogeneous catalyst (CCB).
- vi. Furthermore, the fuel properties of parsley biodiesel (for both catalysts) met the requirements for biodiesel as specified in the international standard ASTM D6751, indicating its potential as an alternative and renewable fuel.

Table 9. Comparison of Fuel Behaviors of Parsley Biodiesel with ASTM Standards

fuel behaviors	parsley biodiesel <sup>a</sup>	parsley biodiesel <sup>b</sup>	diesel	ASTM D6751
specific gravity (@ 40 °C)	0.891	0.887	0.85	0.87–0.98
viscosity (mm <sup>2</sup> /s) (@ 40 °C)	4.86	4.77	1.3–4.1	1.90–6.0
acid value (mg KOH/g)	0.69	0.56		0.80 (max)
pH	7.8	7.1		7–9
flashpoint (°C)	121.2	110.7	60–80	100–170
fire point (°C)	128.7	117.3		
pour point (°C)	–2.8	–2.9	(–35) – 15	–15 to 13
cloud point (°C)	2.4	1.4	–15 to 5	–3 to 12
HHV (kJ/kg)	46.04	40.43	42	
cetane number	46.87	46.81	40–50	>45

<sup>a</sup>Catalyst = CCB. <sup>b</sup>Catalyst = KOH.

Table 8. Comparison of the CCB Catalyst with the Bone-Based Catalyst from Previous Studies

catalyst employed	feedstock	reaction conditions with optimum yield				reference
		alcohol:oil molar ratio	temperature (°C)/time (hours)	catalyst loading (wt % or g)	yield/conversion of biodiesel (%)	
chicken bone	waste cooking oil	15:1	65/4	5	89.33	Farooq et al. <sup>16</sup>
waste pig bone supported K <sub>2</sub> CO <sub>3</sub>	palm oil	9:1	65/1.5	8.0	96.4	Chen et al. <sup>29</sup>
fish bone waste + KOH	jatropha oil	9:1	70 ± 3/3	6.0	96.1	Nisar et al. <sup>25</sup>
fish bone waste	palm oil	18:1	65/4	10.0	90	Sulaiman et al. <sup>53</sup>
waste ostrich bones	waste cooking oil	15:1	60/4	5.0	90.56	Khan et al. <sup>24</sup>
fish bone	waste frying oil	15:1	65/4	6.0	84	Raut et al. <sup>54</sup>
fish bone waste	karanja oil	10:1	65/1.5	2.5	97	Madhu et al. <sup>32</sup>
waste animal bones	palm oil	18:1	65/4	20.0	96.78	Obadiyah et al. <sup>12</sup>
chicken bone	PSO	9:1	60/3	3.0	90	this study

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## REFERENCES

- (1) Al-Muhtaseb, A. H.; Jamil, F.; Myint, M. T. Z.; Baawain, M.; Al-Abri, M.; Dung, T. N. B.; Kumar, G.; Ahmad, M. N. M. Cleaner fuel production from waste Phoenix dactylifera L. kernel oil in the presence of a bimetallic catalyst: Optimization and kinetics study. *Energy Convers. Manage.* **2017**, *146*, 195–204.
- (2) Al-Muhtaseb, A. H.; Osman, A. I.; Kumar, P. S.; Jamil, F.; Al-Haj, L.; Nabhani, A.; Kyaw, H. H.; Myint, M. T. Z.; Mehta, N.; Rooney, D. W. Circular economy approach of enhanced bifunctional catalytic system of CaO/CeO<sub>2</sub> for biodiesel production from waste loquat seed oil with life cycle assessment study. *Energy Convers. Manage.* **2021**, *236*, No. 114040.
- (3) Inayata, A.; Ghenaia, C.; Hammada, D.; Almarzooqia, S.; Tariqb, T.; Jamil, F.; Bokharic, A.; Ayoubd, M. Optimization of Biodiesel Production from Neem Oil using KOH Supported with Activated Carbon. *Chem. Eng. Trans.* **2020**, *81*, 1051–1056.
- (4) Al-Muhtaseb, A. H.; Jamil, F.; Al-Haj, L.; Al-Hinai, M. A.; Baawain, M.; Myint, M. T. Z.; Rooney, D. Efficient utilization of waste date pits for the synthesis of green diesel and jet fuel fractions. *Energy Convers. Manage.* **2016**, *127*, 226–232.
- (5) Górnaś, P.; Rudzińska, M. Seeds recovered from industry by-products of nine fruit species with a high potential utility as a source of unconventional oil for biodiesel and cosmetic and pharmaceutical sectors. *Ind. Crops Prod.* **2016**, *83*, 329–338.
- (6) Nde, D. B.; Foncha, A. C. Optimization methods for the extraction of vegetable oils: A review. *Processes* **2020**, *8*, 209.
- (7) Rashid, U.; Ibrahim, M.; Yasin, S.; Yunus, R.; Taufiq-Yap, Y. H.; Knothe, G. Biodiesel from Citrus reticulata (mandarin orange) seed oil, a potential non-food feedstock. *Ind. Crops Prod.* **2013**, *45*, 335–359.
- (8) Al-Muhtaseb, A. H.; Osman, A. I.; Jamil, F.; Al-Riyami, M.; Al-Haj, A.; Allothman, A. A.; Kyaw, H. H.; Myint, M. T. Z.; Abu-Jrai, A.; Ponnusamy, V. K. Facile technique towards clean fuel production by upgrading waste cooking oil in the presence of a heterogeneous catalyst. *J. King Saud Univ. Sci.* **2020**, 3410–3416.
- (9) Mansir, N.; Taufiq-Yap, Y. H.; Rashid, U.; Lokman, I. M. Investigation of heterogeneous solid acid catalyst performance on low grade feedstocks for biodiesel production: A review. *Energy Convers. Manage.* **2017**, *141*, 171–182.
- (10) Jamil, F.; Kumar, P. S. M.; Al-Haj, L.; Myint, M. T. Z.; Al-Muhtaseb, A. H. Heterogeneous carbon-based catalyst modified by alkaline earth metal oxides for biodiesel production: Parametric and kinetic study. *Energy Convers. Manage.* **2021**, *10*, No. 100047.
- (11) Jazie, A. A.; Pramanik, H.; Sinha, A. S. K. Transesterification of peanut and rapeseed oils using waste of animal bone as cost effective catalyst. *Mater. Renew. Sustain. Energy* **2013**, *2*, 11.
- (12) Obadiah, A.; Swaroopa, G. A.; Kumar, S. V.; Jeganathan, K. R.; Ramasubbu, A. Biodiesel production from Palm oil using calcined waste animal bone as catalyst. *Bioresour. Technol.* **2012**, *116*, 512–516.
- (13) Mori, K.; Yamaguchi, K.; Hara, T.; Mizugaki, T.; Ebitani, K.; Kaneda, K. Controlled synthesis of hydroxyapatite-supported palladium complexes as highly efficient heterogeneous catalysts. *J. Am. Chem. Soc.* **2002**, *124*, 11572–11573.
- (14) Khan, M. H.; Iqbal, T.; Ali, C. H.; Javaid, A.; Cheema, I. I. Sustainable biodiesel production from waste cooking oil utilizing waste ostrich (*Struthio camelus*) bones derived heterogeneous catalyst. *Fuel* **2020**, *277*, No. 118091.
- (15) Singh, V.; Sharma, Y. C. Low cost guinea fowl bone derived recyclable heterogeneous catalyst for microwave assisted transesterification of Annona squamosa L. seed oil. *Energy Convers. Manage.* **2017**, *138*, 627–637.
- (16) Farooq, M.; Ramli, A. Biodiesel production from low FFA waste cooking oil using heterogeneous catalyst derived from chicken bones. *Renewable Energy* **2015**, *76*, 362–368.
- (17) Buasri, A.; Inkaew Kodephun, T. L.; Yenyong, W.; Loryuenyong, V. Natural hydroxyapatite (NHAp) derived from pork bone as a renewable catalyst for biodiesel production via microwave irradiation. *Key Eng. Mater.* **2015**, *659*, 216–220.
- (18) Bitire, S. O.; Jen, T. C.; Belaid, M. Transesterification of parsley seed oil using a green catalyst: considering the optimization process and modeling. *Int. J. Sustainable Energy* **2021**, 1–25.
- (19) Ogunkunle, O.; Ahmed, N. A. Exhaust emissions and engine performance analysis of a marine diesel engine fuelled with Parinari polyandra biodiesel–diesel blends. *Energy Rep.* **2020**, *6*, 2999–3007.
- (20) Stacy, C. J.; Melick, C. A.; Cairncross, R. A. Esterification of free fatty acids to fatty acid alkyl esters in a bubble column reactor for use as biodiesel. *Fuel Process. Technol.* **2014**, *124*, 70–77.
- (21) Ansari Samani, M.; Hosseinzadeh Samani, B.; Lotfalian, A.; Rostami, S.; Najafi, G.; Fayyazi, E.; Mamat, R. The feasibility and optimization of biodiesel production from Celtis australis L. oil using chicken bone catalyst and ultrasonic waves. *Biofuels* **2020**, *11*, 513–521.
- (22) Musa, I. A. The effects of alcohol to oil molar ratios and the type of alcohol on biodiesel production using transesterification process. *Egypt. J. Pet.* **2016**, *25*, 21–31.
- (23) Bouaid, A.; Vázquez, R.; Martínez, M.; Aracil, J. Effect of free fatty acids contents on biodiesel quality. Pilot plant studies. *Fuel* **2016**, *174*, 54–62.
- (24) Khan, H. M.; Iqbal, T.; Ali, C. H.; Yasin, S.; Jamil, F. Waste quail beaks as renewable source for synthesizing novel catalysts for biodiesel production. *Renewable Energy* **2020**, *154*, 1035–1043.
- (25) Nisar, J.; Razaq, R.; Farooq, M.; Iqbal, M.; Khan Ali, R.; Sayed, M.; Shah, A.; Rahman, I. U. Enhanced biodiesel production from Jatropha oil using calcined waste animal bones as catalyst. *Renewable Energy* **2017**, *101*, 111–119.
- (26) Bano, N.; Adzila, S.; Jikan, S. S. B.; Salwah, S.; Basri, H.; Kanasan, N. Extraction of Biological Apatite from Cow Bone at Different Calcination Temperatures: A Comparative Study. *Key Eng. Mater.* **2019**, *796*, 46–52.
- (27) Chakraborty, R.; Bepari, S.; Banerjee, A. Application of calcined waste fish (*Labeo rohita*) scale as low-cost heterogeneous catalyst for biodiesel synthesis. *Bioresour. Technol.* **2011**, *102*, 3610–3618.
- (28) Sobczak, A.; Kowalski, Z.; Wzorek, Z. Preparation of hydroxyapatite from animal bones. *Acta Bioeng. Biomech.* **2009**, *11*, 23–28.

- (29) Chen, G.; Shan, R.; Shi, J.; Yan, B. Ultrasonic-assisted production of biodiesel from transesterification of palm oil over ostrich eggshell-derived CaO catalysts. *Bioresour. Technol.* **2014**, *171*, 428–432.
- (30) Hart, A. Mini-review of waste shell-derived materials applications. *Waste Manage. Res.* **2020**, *38*, 514–527.
- (31) Chingakham, C.; Tiwary, C.; Sajith, V. Waste Animal Bone as a Novel Layered Heterogeneous Catalyst for the Transesterification of Biodiesel. *Catal. Lett.* **2019**, *149*, 1100–1110.
- (32) Madhu, D.; Sharma, Y. C. Synthesis of a reusable novel catalyst ( $\beta$ -tricalcium phosphate) for biodiesel production from a common Indian tribal feedstock. *Resour. Technol.* **2017**, *3*, 144–157.
- (33) Rajesh, R.; Hariharasubramanian, A.; Ravichandran Dominic, Y. Chicken Bone as a Bioresource for the Bioceramic (Hydroxyapatite). *Phosphorus, Sulfur Silicon Relat. Elem.* **2012**, *187*, 914–925.
- (34) Saharudin, S.H.; Shariffuddin, J.H.; Ismail, A. Synthesis of hydroxyapatite from cockle shell wastes. In *Proceedings Book: National Conference for Postgraduate Research*. 2018, 180–185.
- (35) Bee, S. L.; Hamid, Z. A. A. Characterization of chicken bone waste-derived hydroxyapatite and its functionality on chitosan membrane for guided bone regeneration. *Composites, Part B* **2019**, *163*, 562–573.
- (36) Lin, Y. C.; Yang, P. M.; Chen, S. C.; Lin, J. F. Improving biodiesel yields from waste cooking oil using ionic liquids as catalysts with a microwave heating system. *Fuel Process. Technol.* **2013**, *115*, 57–62.
- (37) Bitire, S. O.; Jen, T. C.; Belaid, M. Synthesis of Beta-tricalcium Phosphate Catalyst from Herring fishbone for the Transesterification of Parsley seed oil. *Environ. Technol.* **2021**, 1–13.
- (38) Bitire, S. O.; Jen, T. C.; Belaid, M. The Potential for a Sustainable Biodiesel Production by Modified Biobased Catalyst-A review. *IOP Conf. Ser.: Mater. Sci. Eng.* **2021**, *1107*, No. 012206.
- (39) Chen, G. Y.; Shan, J. F.; Shi Yan, B. B. Transesterification of palm oil to biodiesel using rice husk ash-based catalysts. *Fuel Process. Technol.* **2015**, *133*, 8–13.
- (40) Essamlali, Y.; Amadine, O.; Larzek, M.; Len, C.; Zahouily, M. Sodium modified hydroxyapatite: Highly efficient and stable solid-base catalyst for biodiesel production. *Energy Convers. Manage.* **2017**, *149*, 355–367.
- (41) Suwannasom, P.; Tansupo, P.; Ruangviriyachai, C. A bone-based catalyst for biodiesel production from waste cooking oil. *Energy Sources, Part A* **2016**, *38*, 3167–3173.
- (42) Sai Bharadwaj, A. V. S. L.; Subramaniapillai, N.; Mohamed, K.; Begum, M. S.; Narayanan, A. Optimization of Continuous Biodiesel Production from Rubber Seed Oil (RSO) using Calcined Eggshells as Heterogeneous Catalyst. *J. Environ. Chem. Eng.* **2019**, No. 103603.
- (43) Ali, C.H.; Asif, A.H.; Iqbal, T.; Qureshi, A.S.; Kazmi, M.A.; Yasin, S.; Danish, M.; Mu, B.Z. Improved transesterification of waste cooking oil into biodiesel using calcined goat bone as a catalyst. *Energy Sources, Part A* **2018**, *40*, 1076–1083.
- (44) Rafati, A.; Tahvildari, K.; Nozari, M. Production of biodiesel by electrolysis method from waste cooking oil using heterogeneous MgO-NaOH nano catalyst. *Energy Sources, Part A* **2019**, 1–13.
- (45) Kudre, T. G.; Bhaskar, N.; Sakhare, P. Z. Optimization and characterization of biodiesel production from rohu (*Labeo rohita*) processing waste. *Renewable Energy* **2017**, *133*, 1408–1418.
- (46) Heikal, E. K.; Elmelawy, M. S.; Khalil, S. A.; Elbasuny, N. M. Manufacturing of environment friendly biolubricants from vegetable oils. *Egypt. J. Pet.* **2017**, *26*, 3–59.
- (47) Onukwuli, D. O.; Emembolu, L. N.; Ude, C. N.; Aliozo, S. O.; Menkiti, M. C. Optimization of biodiesel production from refined cotton seed oil and its characterization. *Egypt. J. Pet.* **2017**, *26*, 103–110.
- (48) Colucci, J. A.; Borrero, E. E.; Alape, F. Biodiesel from an alkaline transesterification reaction of soybean oil using ultrasonic mixing. *J. Am. Oil Chem. Soc.* **2005**, *82*, 525–530.
- (49) Baroi, C.; Yanful, E. K.; Bergougrou, M. A. Biodiesel production from oil using potassium carbonate as an unsupported catalyst. *Int. J. Chem. React. Eng.* **2009**, *7*, No. A72.
- (50) Eevera, T.; Pazhanichamy, K. Cotton seed oil: A feasible oil source for biodiesel production'. *Energy Sources, Part A* **2013**, *35*, 1118–1128.
- (51) Azcan, N.; Danisman, A. Alkali catalyzed transesterification of cottonseed oil by microwave irradiation. *Fuel* **2007**, *86*, 2639–2644.
- (52) Ghanei, R.; Khalili Dermani, R.; Salehi, Y.; Mohammadi, M. Waste Animal Bone as Support for CaO Impregnation in Catalytic Biodiesel Production from Vegetable Oil. *Waste Biomass Valorization* **2016**, *7*, 527–532.
- (53) Sulaiman, S.; Khairudin, N.; Jamal, P.; Alam, M. Z.; Zainudin, Z.; Azmi, S. Characterization of Fish Bone Catalyst for Biodiesel Production. *Int. J. Agric. Biol. Eng.* **2014**, *8*, 473–475.
- (54) Raut, S. N.; Jadhav, R.; Nimbalkar, P. Preparation of heterogeneous catalyst derived from natural resources for the transesterification of biofuel. *Int. Res. J. Eng. Technol.* **2016**, *3*, 2395–0056.
- (55) Ashok, B.; Nanthagopal, K. Eco friendly biofuels for CI engine applications. In *Advances in Eco-Fuels for a Sustainable Environment*. 2019, 407–440.
- (56) Purandaradas, A.; Silambarasan, T.; Murugan, K.; Babujanathanam, R. D.; Gandhi, V.; Dhandapani, K. V.; Anbumani, D.; Kavitha, P. Development and quantification of biodiesel production from chicken feather meal as a cost-effective feedstock by using green technology. *Biochem. Biophys. Reports* **2018**, *14*, 133–139.
- (57) Bitire, S. O.; Jen, T. C.; Belaid, M. Production and optimization of biodiesel from parsley seed oil using KOH as catalyst for automobiles technology. *Int. J. Adv. Manuf. Technol.* **2021**, DOI: 10.1007/s00170-021-07415-6.
- (58) Ayetor, G. K.; Sunnu, A.; Parbey, J. Effect of biodiesel production parameters on viscosity and yield of methyl esters: *Jatropha curcas*, *Elaeis guineensis* and *Cocos nucifera*. *Alexandria Eng. J.* **2015**, *54*, 1285–1290.