Yield Response of Biodiesel Production from Heterogeneous and Homogeneous Catalysis of Milk Bush Seed (Thevetia peruviana) Oil

O. Ogunkunle, O. O. Oniya, and A. O. Adebayo

Department of Agricultural Engineering, Ladoke Akintola University of Technology, Ogbomoso, Nigeria

ABSTRACT

Conventional production of biodiesel employs the use of alkaline catalysts because they are cheaper and less corrosive, and they use minimal energy when compared to other acidic catalysts. Heterogeneous catalysts have also shown significant effects on biodiesel production with its ease of recovery and reusability. Three reaction variables—temperature, time, and molar ratio of alcohol to oil—were optimized for biodiesel production from milk bush oil using snail shell as a catalyst. The catalyst was prepared by calcinating waste giant African land snail in an electric oven for 3.5 hours at 900°C. Also, a control transesterification experiment was carried out using potassium hydroxide (KOH) as a catalyst. Catalyst concentrations of 3.0 wt % of calcined snail shell (CSS) and KOH were used for the transesterification of the oil. A response surface analysis of biodiesel production using CSS as a catalyst showed that all reaction variables were significant. Biodiesel yield of 81% was recorded experimentally as the highest yield when temperature, reaction time, and alcohol-to-oil ratio were 65°C, 2 hours, and 9:1, respectively. An average yield of 94.33% was obtained at these same reaction conditions when KOH was used as a catalyst.

1. Introduction

Biodiesel produced from seed oils via transesterification reaction has turned out to be an increasingly possible proposal as a substitute for automotive gas oil (AGO) due to features such as high flash point, excellent lubricity, and high cetane number, in addition to economic and environmental advantages.1 Transesterification is a chemical reaction between triglyceride and alcohol in the presence of a catalyst. It consists of a sequence of three consecutive reversible reactions where triglycerides are converted to diglycerides and diglycerides are converted to monoglycerides followed by the conversion of monoglycerides to glycerol.2 The transesterification process requires the presence of catalysts. The catalyst is used to expedite the reaction rate and to get better-quality biodiesel.3 The transesterification reaction can be homogeneously or heterogeneously catalyzed depending on the solubility of the chemical catalyst in the reaction mixture.4 Homogeneous catalysts, such as bases, acids, and enzymes, are those that exist in the same phase (gas or liquid) where the reaction occurs.5 Most often, homogeneous catalysis involves the introduction of an aqueous phase catalyst into an aqueous solution of reactants. In such cases, acids and bases are often very effective catalysts, as they can speed up reactions by affecting bond polarization. Commonly used homogeneous catalysts include potassium hydroxide (KOH), sodium hydroxide (NaOH), sodium methoxide (NaOCH₃), and potassium methoxide (CH₃OK). Heterogeneous catalysts are catalysts that operate in a different phase from the reactants. Typically, heterogeneous catalysis involves the use of solid catalysts placed in a liquid reaction mixture.5 Commonly used solid base catalysts are alkaline earth metal oxides, zeolite, KNO₃ loaded on Al₂O₃, KNO₃/Al₂O₃, BaO, SrO, CaO, MgO, etc.6

A major problem associated with the use of homogeneous catalysts is the difficulty in their removal from biodiesel.6 A lot of energy, water, and time are consumed; moreover, these catalysts cannot be reused. In contrast, the heterogeneous (solid) base catalysts, being insoluble, are separated simply with filtration and can be reused many times. Heterogeneous catalysts are cheap and thermally stable, and they can be recovered and reused. It is therefore necessary to make use of heterogeneous catalysts derived from cheap waste materials, which could eliminate the additional running costs associated with the aforementioned purification stage in biodiesel production.

Biodiesel, which is an environmentally viable fuel, seems to be an alternative for diesel fuel as a result of increasing demand for fossil fuel across the country. The fossil fuel resources are dwindling day by day, and there is a need to develop an alternative source of economical fuel (biodiesel) that can be made from renewable resources such as organic oils, fats, and tallow. Basically, milk bush seeds and snail shell are presently of little economic importance as they are being treated as waste by people who have them. In order to prevent this improper disposition, there is a need to maximize their usage for production of biodiesel. The seed oil of milk bush is a reliable feedstock for biodiesel production, and snail shell comprises calcium-based oxide, which can be used as a catalyst for transesterification of milk bush oil.
Biodiesel production from milk bush oil has been carried out using ethanol and methanol as alcohol by a few researchers.\textsuperscript{7,8,9} For the most part, the catalysts that were used are homogeneous catalysts such as potassium hydroxide and sodium hydroxide. The work left undone is the utilization of calcium-based heterogeneous catalysts, which can be obtained from natural wastes, for biodiesel production from milk bush oil. Also, optimization of the transesterification process of milk bush oil using a heterogeneous catalyst derived from snail shell has not been carried out. This research work, which focused on biodiesel production from milk bush (\textit{Thevetia peruviana}) oil using different catalysts, was used to study the effects of process parameters such as reaction temperature, reaction time, and alcohol-to-oil ratio on biodiesel yield in order to establish the optimal reaction conditions for biodiesel production from milk bush oil.

2. Materials and Methods

2.1 Experimental Materials

All chemical reagents used were of analytical grades and were obtained from the Chemical Engineering Department Laboratory, LAUTECH, Ogbomoso. The milk bush fruits used in this research work were harvested from Idi Araba Baptist Church Mission House, Ogbomoso, Oyo State, Nigeria. The heterogeneous catalyst that was used in the transesterification reaction of biodiesel production from milk bush oil is snail shell. Snail shells of giant African snail (\textit{Achatina fulica}) were obtained from local antiques sellers at Oja Igbio, Ogbomoso. Calcined snail shells contain a calcium-based oxide (CaO), a heterogeneous catalyst that is suitable for catalysis of seed oil. The alcohol that was used for the transesterification process is methanol. Methanol is the simplest alcohol, and it is a light, volatile, colorless, flammable liquid with a distinctive odor very similar to that of ethanol (drinking alcohol).

2.2 Experimental Procedures

2.2.1 Mechanical extraction of milk bush oil

Oil was extracted from milk bush seeds mechanically. A mechanical screw press was used for expressing the oil. Milk bush seeds were crushed using a mortar and a pestle. The paste was spread on flat trays and put inside an electric oven and preheated to a temperature of 40°C. The crushed paste was left for 25 minutes inside the oven to a temperature of 75°C until oil started pressing out of it.

The warm material was taken in three handfuls, wrapped in muslin cloth, and placed between the pressing plates of the mechanical screw press to express the oil. The oil was collected and filtered to remove dissolved debris. It was further preheated on an electric plate at 100°C for 20 minutes to remove water molecules present in it.

The oil yield was determined by using the equation (1).

\[
OY = \frac{M_o}{M_c} \times 100
\]  

where

\(OY\) = oil yield(%)  
\(M_o\) = mass of extracted oil(g)  
\(M_c\) = mass of the crushed milk bush seed(g)

2.2.2 Catalyst characterization

The determination of chemical composition of calcined snail shell was done using X-ray fluorescence (XRF). A scanning electron microscope was used to determine the BET (Brunauer-Emmett-Teller) surface area (\(S_{\text{BET}}\)). The synthesized CSS was characterized solely on the chemical composition to determine the percentage composition of calcium oxide (CaO) composition in the catalyst. Researchers such as Wei et al.,\textsuperscript{10} Deka and Basumatary,\textsuperscript{11} and Hu et al.,\textsuperscript{12} have all established that mollusks’ shells are calcium-based catalysts that can be utilized for transesterification catalysis. They also reported that there is formation of CaO upon calcination of the shells at temperatures above 500°C.

2.2.3 The production of biodiesel fuel

The transesterification was conducted using methanol as alcohol. The standard transesterification mechanism employed was the same as that of Makama.\textsuperscript{13} CSS and KOH were used separately as catalysts. The experiments were conducted at temperatures (60°C C–70°C) below and above the boiling point of methanol in order to study the influence of reaction temperature on transesterification of milk bush oil. The reaction time ranged between 1 hour and 3 hours. Alcohol-to-oil ratio ranged between 6:1 and 12:1. The transesterification reactions were performed in a batch process. A 250-ml cylindrical tin flask equipped with a shaker was used as a reactor.

The catalyst concentration that was used in this work was 3 wt % for both catalysts. For catalysis of milk bush using calcined snail shell as a catalyst, reaction temperatures were 60°C for low level and 70°C for high level. Reaction time for low level was 1 hour, with 3 hours for high level. The ratio of alcohol to oil for this work was 6:1 and 12:1 for low and high level, respectively. For optimized conditions of milk bush transesterification using KOH as a catalyst, the reactions were carried out at low, medium, and high levels of reaction temperatures, time, and alcohol-to-oil molar ratio. The low, medium, and high values chosen for reaction parameters of transesterification of milk bush oil using potassium hydroxide as a catalyst are 50, 1, 6:1; 55, 2, 9:1, and 60, 3, 12:1 for reaction temperature, reaction time, and molar ratio for alcohol to oil, respectively.\textsuperscript{14}

It is important to note that the reaction parameters for this study were chosen from related research from the literature and subjected to preliminary experiments in the laboratory to practically determine the level of biodiesel production from milk bush oil.

Summarily, the following four operations were performed in the production of the biodiesel fuel:

a. Transesterification  
b. Phase separation  
c. Washing  
d. Drying

A schematic diagram showing the various components of the transesterification experiment is shown in Figure 1.
2.2.4 Production of biodiesel from milk bush oils using CSS as catalyst

The biodiesel production process was carried out using the Birla et al. transesterification mechanism. A measured quantity of CSS was dissolved in methanol and heated on a hot plate until it began to boil. The mixture was then transferred to the cylindrical reactor and stirred for 20 minutes. Milk bush oil (50 ml) was measured, placed in a beaker, and heated to a desired temperature. The warmed oil was then added to the stirred alcohol/CSS mixture and stirred for the desired duration of time (in respect with the experimental design) until a homogenous mixture was formed. Distilled water about 10% of the oil was added after the residence time, and continuous stirring was done for more 20 minutes to enhance easy settling and phase separation of the reaction products. The mixture was then transferred into a separating funnel and allowed to stand for 24 hours. After this period, biodiesel, unreacted oil and alcohol, and snail shell separated into three separate layers.

2.2.5 Production of biodiesel from milk bush oils using KOH as catalyst

The transesterification of milk bush oil using KOH as a catalyst was done according to the reaction mechanism of Abowei et al. The 6:1 alcohol-to-oil molar ratio was found to be optimum at a low reaction temperature of around 50°C. At a high reaction temperature between 50°C and 60°C, a 12:1 alcohol-to-oil molar ratio was recommended. Following this recommendation, transesterification of milk bush oil was carried out at low, medium, and high levels of reaction temperatures, time, and alcohol-to-oil molar ratio.

2.3 Comparison of transesterification reactions using CSS and KOH as catalysts

The reaction parameters that performed better when CSS was used as a catalyst were chosen from the experimental results. Transesterification reactions using KOH as a catalyst were carried out on milk bush oil using these reaction parameters three times. The average biodiesel production was determined and compared with the yield obtained when CSS was used as a catalyst. The aim of the comparison is to discuss the performance of each catalyst as it affects biodiesel yield and to establish optimal reaction conditions for biodiesel production from milk bush oil when CSS and KOH were used as catalysts.

2.4 Analysis of Fatty Acid Methyl Ester (FAME)

The analysis and determination of the fatty acid methyl ester (FAME) in the biodiesel was performed using the procedures and calculations outlined in the EN14103:0211 method. The FAME determination is a measure of the methyl nonadecanoate (C19:0) contained in the biodiesel. A Thermo Scientific TRACE GC Ultra was configured according to the requirements of the method. The operating conditions were set according to the requirements of the method.

A mixture of 150 mg of biodiesel sample and 5 mL of internal standard solution methyl nonadecanoate (C19:0) was mixed together in a vial. Each sample plus the internal standard solution was then dissolved in 10 mL toluene. Duplicates of the biodiesel samples were prepared to measure the reproducibility of the analysis. The analysis was done by injecting 1 µL of each sample into the GC at the temperature of 140°C and held for 5 minutes. The GC’s oven was heated to 250°C, and the resulting chromatogram was recorded. The total ester contents were then calculated using the integrated peak areas of the FAMES identified in the samples.

2.5 Physicochemical properties of milk bush oil and methyl ester

The physicochemical properties of milk bush oil sample and biodiesel were determined using standard methods. Standard test methods were used for determining the physical and chemical properties of milk bush oil biodiesel. Some selected physicochemical properties (kinematic viscosity, specific gravity, pour point, acid value, pH, cloud point, cetane number, and flash point) of milk bush biodiesel were determined according to the American Society of Testing and Materials (ASTM) and compared with ASTM standards for biodiesel fuel.

2.6 Statistical design and analysis

The study type used for the experimental design for the production of biodiesel production from milk bush oil using CSS as a catalyst was response surface methodology. Design Expert 6.0.8 software was used. The factors considered were temperature (a), time (b), and alcohol-to-oil ratio (C), while the response was biodiesel yield (Y1). The design generated 17 experimental runs. The highest responses were then compared with the yields from...
transesterification of bush milk oil using KOH as a catalyst at the same reaction variables. The column sheet that represents the design layout for biodiesel production is shown in Table 1.

3. Results and discussion

The experimental results obtained in this work include oil yield obtained from extraction of milk bush oil; yield of milk bush methyl esters after transesterification with two catalysts; comparison of methyl esters yield from transesterification of milk bush oil under the same reaction conditions using CSS and KOH as catalysts; and the fuel properties of milk bush oil and methyl esters.

3.1 Extracted Oil from milk bush seeds

An average result of the mechanical extraction of oil from 400 g of milk bush seeds is given in Table 2. The total oil yield from milk bush was 41.2%. A total of 1400 g of oil was expressed from 3400 g of milk bush seeds. The oil yield of 41.2% obtained from the seeds of milk bush is considered promising and falls within the same range reported by Sahoo et al. and Ibiyemi et al. This implies that milk bush seed is a good source of oil. The physicochemical properties of milk bush oil are presented in Table 3. Oil yield was low because a mechanical oil-expeller was used. *Thevetia peruviana* generally contains approximately 75% of oil in the seed kernel. This can be achieved through solvent extraction (using standard Soxhlet extraction method).

3.2 Catalyst characterization

The result of chemical compositions of catalyst is shown in Table 4. The result shows that the majority composition of the catalyst was calcium oxide (CaO). A percentage weight of 98.4% CaO was obtained at 900°C. Percentage weight fractions of elemental compositions of the CSS are also shown. The BET surface area was also determined to be 0.78 m²/g in size.

3.3 Biodiesel Yield from milk bush oil using CSS as a catalyst

The result of biodiesel yield obtained after the transesterification process under different temperature, time, and alcohol-to-oil ratio conditions using snail shell as a catalyst for various experimental runs is presented in Table 5. The minimum biodiesel yield was obtained at a temperature of 70°C, 3 hours reaction time, and alcohol-to-oil ratio 9:1, while the maximum was obtained when temperature, reaction time, and alcohol-to-oil ratio were 65°C, 2 hours, and 9:1, respectively (Table 5).

Almost the same reaction conditions were obtained from research carried out by Li et al. They derived a CaO-based catalyst from waste shells to produce biodiesel from *Jatropha curcas* oil. A high biodiesel yield of about 99.0% was obtained

| Table 1. Box Behnken design layout for biodiesel production. |
| --- |
| Std. order | Factor A | Factor B | Factor 3 | Response 1 |
| No. | Temperature (°C) | Time (Hour) | Alcohol to oil ratio (Mol) | Biodiesel yield (%) |
| 17 | 65.0 | 2.0 | 9:1 | 91.19 |
| 7 | 60.0 | 2.0 | 12:1 |
| 3 | 60.0 | 3.0 | 9:1 |
| 6 | 70.0 | 2.0 | 6:1 |
| 12 | 65.0 | 3.0 | 12:1 |
| 2 | 70.0 | 1.0 | 9:1 |
| 11 | 70.0 | 1.0 | 12:1 |
| 1 | 60.0 | 1.0 | 9:1 |
| 5 | 60.0 | 2.0 | 6:1 |
| 10 | 65.0 | 3.0 | 6:1 |
| 8 | 70.0 | 2.0 | 12:1 |
| 15 | 65.0 | 2.0 | 9:1 |
| 9 | 65.0 | 1.0 | 6:1 |
| 4 | 70.0 | 3.0 | 9:1 |
| 14 | 65.0 | 2.0 | 9:1 |
| 13 | 65.0 | 2.0 | 9:1 |
| 16 | 65.0 | 2.0 | 9:1 |
| 17 | 65.0 | 2.0 | 9:1 |

| Table 2. Average result of mechanical extraction of milk bush oil. |
| --- |
| Extraction No. | Weight of heated cake (g) | Applied pressure (kN) | Expressed oil (ml) | Expressed oil (g) |
| 1 | 400 | 330 | 136 | 122 |
| 2 | 400 | 350 | 146 | 131 |
| 3 | 400 | 350 | 152 | 137 |
| Average | 400 | 343.33 | 144.67 | 130 |

| Table 3. The physicochemical properties of milk bush oil. |
| --- |
| Parameters | Values |
| Specific gravity (40°C) | 0.9119 |
| Viscosity | 51.69 (mm²/s) |
| Pour point | 4.5 (°C) |
| Acid value | 2.156 (mgKOH/g) |
| pH | 6.07 |
| Cloud point | 4.43 (°C) |
| Refractive Index (20°C) | 1.4822 |

| Table 4. Percentage weight fraction of chemical composition of CSS. |
| --- |
| Composition | Weight fraction (wt. %) |
| CaO | 98.4 |
| K₂O | 330 |
| Fe₂O₃ | 0.023 |
| Cl₂ | 0.115 |
| SO₃ | −0.04 |

| Table 5. Biodiesel yield from milk bush oil using calcined snail shell as a catalyst. |
| --- |
| Runs | Temperature (°C) | Time (Hour(s)) | Alcohol to oil ratio (Mol) | Response (Biodiesel yield (%)) |
| 1 | 65.0 | 2.0 | 9:1 | 81.00 |
| 2 | 60.0 | 2.0 | 12:1 | 77.00 |
| 3 | 60.0 | 3.0 | 9:1 | 65.00 |
| 4 | 70.0 | 2.0 | 6:1 | 61.00 |
| 5 | 65.0 | 3.0 | 12:1 | 68.00 |
| 6 | 70.0 | 1.0 | 9:1 | 66.00 |
| 7 | 65.0 | 1.0 | 12:1 | 74.00 |
| 8 | 60.0 | 1.0 | 9:1 | 65.00 |
| 9 | 60.0 | 2.0 | 6:1 | 58.00 |
| 10 | 65.0 | 3.0 | 6:1 | 55.00 |
| 11 | 70.0 | 2.0 | 12:1 | 60.00 |
| 12 | 65.0 | 2.0 | 9:1 | 79.00 |
| 13 | 65.0 | 1.0 | 6:1 | 69.00 |
| 14 | 70.0 | 3.0 | 9:1 | 54.00 |
| 15 | 65.0 | 2.0 | 9:1 | 81.00 |
| 16 | 65.0 | 2.0 | 9:1 | 78.00 |
| 17 | 65.0 | 2.0 | 9:1 | 80.00 |
under the best reaction conditions (temperature 65°C, methanol/oil molar ratio 9:1, reaction time 3 h, and catalyst loading 3 wt% of oil). The catalyst was reused for seven times, and a yield of 75% of the fatty acid methyl esters was obtained. They also concluded that the activity of the used catalysts could be revived absolutely after recalcination.

The maximum biodiesel yield of 81% was obtained for milk bush transesterification as the yield ranged from 54% to 81%. This high biodiesel yield obtained was a result of moderate reaction variables, which were enough to cause production of biodiesel. Higher reaction variables actually led to reduction in biodiesel yield as a result of evaporation of the methanol and reversibility of the transesterification reaction. A similar result was obtained by Birla et al. in the transesterification of waste frying oil using calcined snail shell as a catalyst. They obtained a biodiesel yield of 87.28%. This also indicated that a reaction temperature of 65°C was adequate for complete transesterification of milk bush oil in 2 hours average reaction time. An alcohol-to-oil molar ratio of 9:1 was also sufficient for the transesterification reactions.

Reaction time higher than 2 hours showed signs of reduced biodiesel yields. This is related to the unstable (reversibility) nature of transesterification reaction at both reaction and product sides. Higher alcohol-to-oil molar ratio could also reduce the contact of triglycerides molecules on the active sites of the catalyst and thus decrease the catalyst activity. This actually generated more production of glycerol and favored backward reactions, which led to reduction of biodiesel yield. The varying biodiesel yield values presented in Table 5 are indications that milk bush transesterification reaction parameters considerably affect the biodiesel yield. Figures 2, 3, and 4 show the effect of reaction parameters on biodiesel production using CSS as a catalyst.

A few researchers have also worked on the optimization of biodiesel production from vegetable oil using heterogeneous catalysts. El-Gendy et al. used a response surface methodology based on central composite face centered design to statistically evaluate and optimize the conditions for maximum production of biodiesel and to study the significance and interaction of methanol to oil (M:O) molar ratio, catalyst concentration, and reaction time on biodiesel yield. This study was performed to optimize a base heterogeneous CaO catalyzed transesterification process for biodiesel production from waste frying sunflower oil. The optimum combination for transesterification was determined to be 7.05:1 M:O, 8.21 CaO wt%, and 1.5 h at 60°C, and a mixing rate of 300 rpm. The maximum predicted and actual biodiesel yield was 92.2 and 93%, respectively.

The statistical analysis for biodiesel production from milk bush oil using CSS as catalyst was done using analysis of variance (ANOVA). Table 6 shows the ANOVA of biodiesel yield from milk bush oil transesterification using CSS as a catalyst. The model F-value of 64.40 obtained for biodiesel
yield implies the model is significant. Values of Prob > F less than 0.0500 indicate model terms are significant. In this case A, B, C, A^2, B^2, C^2, AB, and BC are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. The lack of fit F-value of 1.96 implies the lack of fit is not significant relative to pure error. The lack of fit of the model indicated whether the estimated response surface represents the actual shape of the surface.

Standard deviation of 1.55, mean of 68.88, C.V. of 2.25, PRESS of 170.63, R^2 of 0.9881, adj R^2 of 0.9727, pred R^2 of 0.8788, and adeq precision of 22.976 were obtained for biodiesel yield. The predicted R-square of 0.8788 is in reasonable agreement with the adjusted R-square of 0.9727. A ratio greater than 4 is desirable. In this case, a ratio of 22.976 indicates an adequate signal. This model can be used to navigate the design space. The final empirical model in terms of coded factors (reaction parameters) for the biodiesel yield is given in Equation 2; the model shows that all the reaction variables are significant upon biodiesel production from milk bush oil using calcined snail shell as catalyst:

Biodiesel yield = 79.80 – 3.00A – 4.00B + 4.50C
– 9.90A^2 – 7.40B^2 – 5.90C^2 – 3.00AB
– 5.00AC + 2.00BC

(2)

where A, B, and C were the coded values of the independent variables, i.e., temperature, time, and alcohol-to-oil molar ratio, respectively. Guan and Yao reported that an R^2 should be at 0.80 for the good fit of a model. In this case, the R^2 value of 0.9881 indicated that the sample variation of 98.81% for the biodiesel production is attributed to the independent factors (temperature, time, and alcohol-to-oil molar ratio), and only 1.19% of the total variations are not explained by the model.

The result of the diagnostic case studies for biodiesel yield is shown in Table 7. The actual value on the table represents the biodiesel yield when milk bush oil was transesterified using CSS as a catalyst and methanol as alcohol, and the predicted value represents the standard generated by the software (Design Expert) used. The residual shows the closeness of the actual values to the predicted value. Negative values of the residual indicates that the actual value is greater than the predicted value, while a positive value implies that predicted is greater than the actual value.

### 3.4 Biodiesel Yield from milk bush oil using koh as a catalyst

The methyl ester yield from methanolysis of milk bush seed oil using KOH as a catalyst at low, medium, and high reaction conditions is shown in Table 8. The biodiesel yield from milk bush oil using KOH as a catalyst yielded well compared with biodiesel production from a homogeneous catalyzed transesterification. This is also close to the range of report by Darmoko and Cheryman. After transesterification, the settling mixture was observed to have separated into two distinct phases: biodiesel, a pale yellowish liquid, was formed at the top, while glycerol, a dark liquid that is denser and more viscous, settled at the bottom part of the separating funnel. From the results obtained, it was observed that the methyl ester yield also increased as reaction temperature increased and produced significant difference in the yield. Methyl ester content also increased with increase in reaction time. It was observed that the methyl ester

### Table 6. ANOVA of biodiesel yield from milk bush oil transesterification using CSS as a catalyst.

| Source     | Sum of Squares | DF | Mean Square | F Value | Prob > F | Comment |
|------------|----------------|----|-------------|---------|----------|---------|
| Model      | 1390.96        | 9  | 154.55      | 64.40   | < 0.0001 | Significant |
| A          | 72.00          | 1  | 72.00       | 30.00   | 0.0009   | Significant |
| B          | 128.00         | 1  | 128.00      | 53.33   | 0.0002   | Significant |
| C          | 162.00         | 1  | 162.00      | 67.50   | < 0.0001 | Significant |
| A^2        | 412.67         | 1  | 412.67      | 171.95  | < 0.0001 | Significant |
| B^2        | 230.57         | 1  | 230.57      | 96.07   | < 0.0001 | Significant |
| C^2        | 146.57         | 1  | 146.57      | 61.07   | 0.0001   | Significant |
| AB         | 36.00          | 1  | 36.00       | 15.00   | 0.0061   | Significant |
| AC         | 100.00         | 1  | 100.00      | 41.67   | < 0.0001 | Significant |
| BC         | 16.00          | 1  | 16.00       | 6.67    | 0.0364   | Significant |
| Residual   | 16.80          | 7  | 2.40        |         |          | Significant |
| Lack of Fit| 10.00          | 3  | 3.33        | 1.96    | 0.2619   | not significant |
| Pure Error | 6.80           | 4  | 1.70        |         |          |         |
| Cor Total  | 1407.76        | 16 |            |         |          |         |
| Std. Dev.  | 1.55           |    | R-Squared   | 0.9881  |          |         |
| Mean       | 68.88          |    | Adj R-Squared | 0.9727 |          |         |
| C.V.       | 2.25           |    | Pred R-Squared | 0.8788 |          |         |
| PRESS      | 170.63         |    | Adeq Precision | 22.976 |          |         |

### Table 7. Diagnostic case studies for biodiesel yield.

| Standard Order | Actual Value | Predicted Value | Residual |
|----------------|--------------|-----------------|----------|
| 1              | 65.00        | 66.50           | -1.50    |
| 2              | 66.00        | 66.50           | -0.50    |
| 3              | 65.00        | 64.50           | 0.50     |
| 4              | 54.00        | 52.50           | 1.50     |
| 5              | 58.00        | 57.50           | 0.50     |
| 6              | 61.00        | 61.50           | -0.50    |
| 7              | 77.00        | 76.50           | 0.50     |
| 8              | 60.00        | 60.50           | -0.50    |
| 9              | 69.00        | 68.00           | 1.00     |
| 10             | 55.00        | 56.00           | -1.00    |
| 11             | 74.00        | 73.00           | 1.00     |
| 12             | 68.00        | 69.00           | -1.00    |
| 13             | 81.00        | 79.80           | 1.20     |
| 14             | 80.00        | 79.80           | 0.20     |
| 15             | 79.00        | 79.80           | -0.80    |
| 16             | 78.00        | 79.80           | -1.80    |
| 17             | 81.00        | 79.80           | 1.20     |

### Table 8. Result of biodiesel yield from methanolysis of milk bush oil using KOH as a catalyst.

| Temperature (Degree centigrade) | Time (Hour) | Alcohol to oil ratio (Mol) | Biodiesel yield (%) |
|---------------------------------|-------------|----------------------------|---------------------|
| 50                              | 1           | 6                         | 88                  |
| 55                              | 2           | 9                         | 93                  |
| 60                              | 3           | 12                        | 97                  |
content increased as the methanol content of the reaction mixture increased.

The yields are presented in Table 8. The reaction with 60°C reaction temperature, 3 hours reaction time, and alcohol-to-oil ratio of 12:1 gave the highest yield and can thus be taken in this case as the optimal reaction conditions for complete methanolysis of milk bush seed oil using KOH as a catalyst.

Biodiesel yield was noticed to increase as temperature increased from 50°C to 55°C, and further increased a little bit when the temperature was 60°C. The increase in biodiesel yield can be said to be inversely proportional to increase in temperature. However, the little change in increase when the temperature was 60°C indicated that biodiesel yield might likely decrease or show no noticeable yield as temperature approaches the boiling point of methanol. Similarly, there was an increase in biodiesel production as the reaction time increased. Also, the higher the molar ratio of alcohol to oil, the higher the biodiesel yield as observed from the results obtained.

### 3.5 Comparison of transesterification reactions using CSS and KOH as catalysts

The reaction parameters that performed better when using CSS were 65°C, 2 hours, and 9:1 for temperature, time, and alcohol-to-oil ratio, respectively. Biodiesel yield of 81% was obtained from these reaction parameters. An average of 94.33% was obtained from three transesterification reactions using KOH as a catalyst under optimal reaction conditions chosen from the experimental results of Table 5 (65°C reaction temperature, 2 hours reaction time, and 9:1 alcohol-to-oil molar ratio). Considering the obtained results, it was clear that the compared KOH catalyst was more effective than the CSS in obtaining a higher biodiesel yield. The effect of the KOH catalyst on the reactants at these reaction conditions favored more biodiesel production. From the comparison at the same reaction temperatures, reaction time, and alcohol-to-oil molar ratio, the KOH catalyst gave better yield than the CSS catalyst. The CSS catalyst resulted in higher soap formation than the KOH catalyst.

The volume of biodiesel produced when the CSS catalyst was used reduced in volume gradually during and after the settling process. This was envisaged to be as a result of increased saponification reaction occurring alongside transesterification reaction. Generally, the low temperatures that favored higher biodiesel yield when the KOH catalyst was used favored biodiesel production, and this is a comparative advantage over the transesterification of milk bush oil using CSS. A higher temperature above 60°C was required to initiate an interphase reaction between the reactants. The residence time also was seen to favor methyl ester yield as it increases while the KOH catalyst was used. The methyl ester yield while using CSS increased for some time as the residence time increased and decreased again at temperatures above the boiling point of methanol. There was reduction in the methyl ester yield as a result of evaporation of the methanol needed for complete transesterification of the oil, and there was thicker glycerol byproduct in the product mixtures.

For the KOH catalyst, biodiesel yield also increased more as alcohol-to-oil ratio increased because there was more methanol for transesterification of oil. A molar ratio of 12:1 of alcohol to oil yielded 97% of biodiesel at first, a sign that total conversion of the oil to methyl ester had nearly taken place. This also showed that there was a linear relationship between temperature, time, and alcohol-to-oil ratio on biodiesel yield from milk bush oil using KOH as catalyst.

A study of the result of responses of the experimental data when calcined snail shell was used as catalyst for transesterification of biodiesel showed that the relationship between the reaction variables are quadratic as the increase in one variable does not necessarily lead to an increase in another: a higher alcohol-to-oil ratio at a lower temperature led to the formation of more glycerol, which reduced biodiesel yield; higher reaction temperatures led to the burning of alcohol; and higher reaction time led to a decrease of methyl ester yield. Glycerol collected from the reaction products of milk bush oil transesterification using calcined snail shell is whitish in color and has a thick, soapy feel, while glycerol collected when KOH was used as a catalyst is dark in appearance with a thick, syrup-like nature.

It can be seen from the experimental results that biodiesel production can be catalyzed successfully with the use of heterogeneous catalysts. Higher biodiesel yields can be obtained by producing catalysts with high activity and stability. João et al. concluded that heterogeneous catalysts appear to be suitable for biodiesel production. They reported on the differences between the status of biodiesel production using heterogeneous alkaline and homogeneous catalysts. They worked on the development of new heterogeneous catalysts able to produce biodiesel from vegetable oils. The research resulted in the selection of CaO and CaO modified with alkaline and alkaline earth metal catalysts. They show very good catalytic performances with high activity and stability. Biodiesel (FAME) yields higher than 94% were observed in several consecutive reaction batches.

### 3.6 Analysis of Fatty Acid Methyl Ester (FAME)

Table 9 shows the total FAME content reported for each biodiesel sample duplicate. The results also show the repeatability statements for the total FAME content. The sample analysis meets the method’s repeatability specifications for the total FAME content and the methyl linolenate content.

### 3.7 Physicochemical properties of milk bush methyl ester

The results of physicochemical properties of milk bush oil methyl esters produced using calcined snail shell and KOH as catalysts are shown in Table 10. The properties of milk bush biodiesel were compared with standards provided by ASTM. It was seen that the flash point of biodiesel produced using calcined snail shell and KOH as catalysts are 158°C.

### Table 9. Total FAME content of milk bush biodiesel samples analyzed using the revised EN14103:2011 method.

| Run | Total FAME (wt %) | Repeatability (wt %) |
|-----|------------------|----------------------|
|     | Average          | r                     | r (Spec)*           |
| A   | 92.8             | 92.4                  | 92.6                | 0.4 | 1.01 |
| B   | 88.6             | 88.1                  | 88.35               | 0.5 | 1.01 |

* r (Spec) is the maximum repeatability specified by the EN14103:2011 method. 
  a: biodiesel sample from KOH catalyst. 
  b: biodiesel sample from CSS catalyst.
Table 10. Comparison of fuel properties of milk bush biodiesel with standards provided by ASTM.

| Fuel properties | Milk Bush Biodiesel<sup>a</sup> | Milk Bush Biodiesel<sup>b</sup> | ASTM D6751 |
|-----------------|-------------------------------|-------------------------------|------------|
| Specific gravity | 0.891                         | 0.857                         | 0.87 to 0.98 |
| (40°C) | | | |
| Viscosity | 4.89 (mm²/s) | 4.46 (mm²/s) | 1.90 to 6.0 |
| Pour point | 1.00 (°C) | –1.50 (°C) | –15 to 13 |
| Acid value | 0.65 (mgKOH/g) | 0.59 (mgKOH/g) | 0.80 (max) |
| pH | 7.76 | 7.92 | 7 to 9 |
| Cloud point | 4.85 (°C) | 3.62 (°C) | –3.15 to 11.85 |
| Flash point | 158 (°C) | 142 (°C) | >130 |
| Cetane number | 46.2 | 54.4 | >45 |

<sup>a</sup>catalyst = calcined snail shell.
<sup>b</sup>catalyst = KOH.

and 142°C, respectively, when that of petrol-diesel is between 52°C and 96°C. Kinematic viscosities of biodiesel at 40°C (4.89 mm²/s and 4.46 mm²/s) were higher than that of petrol-diesel, which is about 2.98 mm²/s. For better combustion in engines, milk bush biodiesel should be blended with petrol-diesel. The pour points fell within the range of the ASTM standard for biodiesel, while the cetane numbers are higher than that of ASTM. All the selected physicochemical properties that were determined from milk bush biodiesel fell within the specifications of ASTM D6751 standards.

4. Conclusion

The results obtained in this work have shown that heterogeneous catalyst derived from the shell of the giant African land snail (Achatina fulica) is highly active and cost-competitive for the catalysis of transesterification of milk bush oil to biodiesel. Higher biodiesel yields were also obtained from the transesterification of milk bush oil using KOH as a catalyst.

ORCID

O. Ogunkunle <http://orcid.org/0000-0003-2362-4943>

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