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Optimization of Biodiesel Production from Milk Bush (*Thevetia peruviana*) Oil Using Snail Shell as Catalyst

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ABSTRACT

Heterogeneous catalysts are poised to play an important role in the problem of catalyst recovery during biodiesel production. The experimental parameters (temperature, time and molar ratio of alcohol to oil ratio) for biodiesel production from milk bush seed oil and methanol using calcined snail shell as catalyst were optimized statistically. The catalyst was synthesized by calcinating waste giant African land snail in an electric oven for 3.5 hours at 900^{o}C. A catalyst concentration of 3.0 wt % of oil was used throughout the transesterification reactions. The effect of varying the experimental parameters on biodiesel yield was investigated using a 2^{k} factorial design. The optimal conditions to maximize the biodiesel yield, obtained from the response surface analysis using a Box-Behnken design, was a ratio of 10.18:1 of alcohol to oil, 1.89 hours of time and a 63.67^{o}C temperature. Under these conditions a methyl ester (biodiesel) yield of 81.45% was predicted which clearly indicated the effectiveness of process variables optimization in biodiesel production, but an 81 % biodiesel yield was experimentally recorded as the highest methyl ester production from milk bush seed oil transesterification when temperature, reaction time and alcohol to oil ratio were 65^{o}C, 2 hours and 9:1 respectively has been the optimal parameters for biodiesel production from milk bush oil using snail shell as catalyst.

Keywords: Milk bush seed oil, Biodiesel, Calcined snail shell, 2^{k} factorial design, Box-Behnken design.

Aims Research Journal Reference Format:
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1. INTRODUCTION

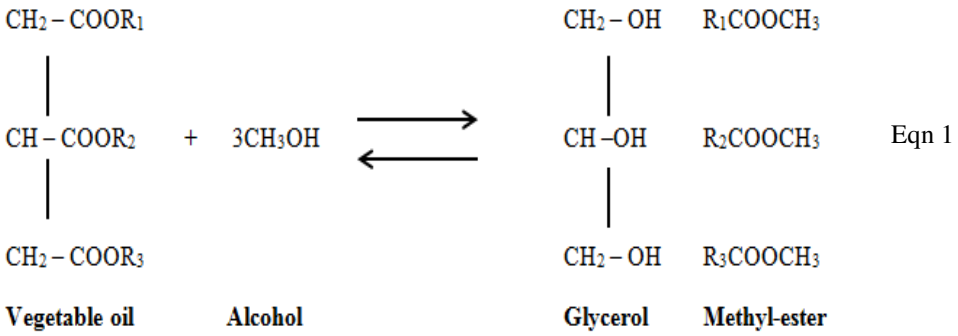
Biodiesel typically refers to renewable, non-toxic, biodegradable and environment friendly fuel for compression ignition engines which can be obtained by chemical processes from vegetable oils and animal fats. It can be used in all types of compression ignition engines directly or in the blended form (Victor *et al*., 2005). Biodiesel can be produced by chemically reacting a vegetable oil or animal fat with an alcohol such as ethanol. The reaction requires a catalyst, usually a strong base, such as sodium or potassium hydroxide (Van Garpen, 2004). Edible oils resources such as soybeans, palm oil, sunflower, safflower, rapeseed, coconut and peanut are considered as the first generation of biodiesel feedstock because they were the first crops to be used for biodiesel production (Chapagain *et al.,* 2009). However, their use in production of biodiesel raises many concerns such as food versus fuel crisis and is not feasible in the long term because of the growing gap between demand and supply of such oils in many countries (Chapagain *et al.,* 2009).

One of the possible solutions to reduce the utilization of the edible oil for biodiesel production is by exploiting non-edible oils (Kumar and Sharma, 2011). Virgin vegetable oil, waste vegetable oil and animal fats (tallow, lard, and yellow grease) are feedstocks that are used for biodiesel production (Demirbas, 2008). Alcohols that are commonly used in biodiesel production are those with short chains, including methanol, ethanol, butanol, and amylic alcohol (Van Gerpen *et al*., 2004). The most widely used alcohols are methanol (CH_3OH) and ethanol (C_2H_5OH) because of their low cost (Van Gerpen *et al*., 2004). Methanol is often preferred to ethanol in spite of its high toxicity because its use in biodiesel production requires simpler technology; excess alcohol may be recovered at a low cost and higher reaction speeds are reached (Meher *et al*., 2006).

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, diglycerides are converted to monoglycerides followed by the conversion of monoglycerides to glycerol. In each step, an ester is produced and thus three ester molecules are produced from one molecule of triglyceride (Sharma and Singh, 2008). It also gives glycerol as a by-product which has a commercial value.

Transesterification process requires the presence of catalysts. The catalyst is used to expedite the reaction rate and to get better quality biodiesel (Meher *et al*., 2006). Depending on the solubility of the chemical catalyst in the reaction mixture, transesterification reaction can be homogeneously or heterogeneously catalyzed (Ghadge and Raheman, 2005).

Stoichiometrically, three moles of alcohol are required for each mole of triglyceride, but in general, a higher molar ratio is often employed for maximum ester production depending upon the type of feedstock, amount of catalyst, temperature, etc. This reaction has been widely used to reduce the viscosity of vegetable oil and conversion of the triglycerides into ester. The transesterification reaction is shown in Equation 1. However, the yield of biodiesel is independent of the type of the alcohol used and the selection of one of these depends on cost and performance. Methanol is preferred over others due to its low cost (Ramadhas *et al*., 2005).



Eqn 1

Transesterification reaction of glycerides
Sources: Demirbas (2009); Singh and Singh (2009).

The conventional catalysts used are acid and alkali catalysts depending upon the nature of the oil used for biodiesel production. Homogeneous catalysts are those which exist in the same phase (gas or liquid) where the reaction occurs (Boundless, 2015). Acids, bases and enzymes are often very effective homogeneous catalysts, as they can speed up reactions by affecting bond polarization (Boundless, 2015). Heterogeneous catalysts are catalyst that operates respectively in a different phase from the reactants (Boundless, 2015). Homogenous catalysts are very effective catalysts which are frequently used but the major problem associated with the use of these catalysts is their removal from methyl ester which needs excessive washing (Xie *et al*., 2006). 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.

2. MATERIALS AND METHODS

2.1 Materials

The milk bush fruits used in this research work were harvested from Idi Araba Baptist Church Mission House, Ogbomoso, Oyo State, Nigeria. The fresh fruits were cut into halves to remove the pulps. The seeds were shelled to release the whitish coloured seed kernels. The kernels were sun dried at ambient temperature for about three weeks to prevent instant biodegradation. The kernels were crushed using a laboratory mortar and pestle prior to oil extraction. The fresh fruits and dried kernels of milk bush oil seeds are shown in Plate 1.

The heterogeneous catalyst that was used in the transesterification reaction of biodiesel production from milk bush oil was calcined snail shell. Snail shells of giant African snail (*Achatina fulica*) were obtained from local antiques sellers at Oja Igbo, Ogbomoso. Calcined snail shell contains a calcium based oxide (CaO), a heterogeneous catalyst which is suitable for catalysis of seed oil. The snail shells were washed with clean water first to remove any impurity present in them. The shells were sun dried under ambient temperature until they were dry. The shells were then ground into smaller particles using a mortar and calcined at 900 ^{o}C for 3.5 hours in an electric oven according to Birla *et al.* (2012). After 3.5 hours, the ground material was found to have turned into a whitish powder. There was a change in the physical state of the catalyst after heating; it totally turned into a smaller sized powdery particles. All chemical reagents used were of analytical grades.

Plate 1: Fresh fruits and dried kernels of milk bush oil seeds

2.2 Methods

2.2.1 Mechanical extraction of milk bush oil

Oil was extracted from milk bush seeds by mechanical extraction. A mechanical screw press was used for expressing the oil. The mechanical screw press has specifications of 182 mm ram diameter and a load capacity of 1500 KN. Milk bush seeds were crushed in a mortar into a semi-paste material. The crushed seeds were spread on flat trays and put inside an electric oven. The electric oven was preheated to a temperature of 40 ^{o}C before the crushed seeds were placed in it. The crushed paste was left for 25 minutes inside the oven until a noticeable change in the colour of the crushed seeds from white to brownish-white occurred, with oil seeming out of it. The oven was switched off at this stage at temperature 75 ^{o}C.

The warm brownish-white material was taken in handfuls and wrapped in muslin cloth. It was placed between the pressing plates of a mechanical screw press while the pressure lever was jerked continuously to press down the upper plate upon the lower plate. Oil seeped out of the milk bush cake unto the collecting plate and flowed into the outlet pipe. This action was repeated until the milk bush cake was exhausted. The average of the first three screw–pressings was taken in terms of applied pressure taken to express the oil and the quantity of the expressed oil in volume and weight.

The oil yield was determined by using the equation 2.

$$OY = \frac{M_o}{M_s} \times 100$$

…….Eqn .2

Where

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

2.2.2 Experimental design

The experiment was designed using Design-Expert version 6.0.8. (Stat-Ease Inc, Minneapolis, U.S.A.). The experimental design was based on a two level, three factor Box-Behnken Design with one response factor was generated using the parameters presented in Table 1. Temperature, time and alcohol to oil ratio were the numeric factors coded as A, B, C respectively. The response factor was coded as biodiesel yield.

Table 1: Box Behnken design layout for biodiesel optimization

Study Type	Response Surface			**Experiments**	17	
Initial Design	Box Behnken		**Blocks**	No Blocks		
Design Model	Quadratic					
Response	**Name**	**Units**	**Obs**	**Minimum**	**Maximum**	**Trans**
Factor	**Name**	**Units**		**Type**	**Low Actual**	**High Actual**
A	Temperature	Degree Centigrade		Numeric	60.00	70.00
B	Time	Hour(s)		Numeric	1.00	3.00
C	Alcohol to oil ratio Mol			Numeric	6:1	12:1

2.2.3 The kinetics of transesterification experiment

The transesterification process that was used was developed by Chindo *et al.* (2013). Methanol was measured based on volumetric calculations from its molar mass. As a result of the reversibility of transesterification reaction, a stoichiometric excess of 65% was used to facilitate complete reaction between methanol and catalyst. Warmed milk bush oil was poured into already stirred methanol – catalyst mixture and the following transesterification reactions (a hypothetical formula for plant oil suggested by Berchmans and Hirata (2008)), which is presented in equation 3 was used.

1 mol of triglyceride (plant oil) + 3 moles of methanol $\longrightarrow$ 3 moles of methyl ester + 1 mol of glycerol Eqn 3

According to Olatunji (2010), the molecular weight of milk bush oil was taken as 903.8 g/mol.

1mole of triglycerides = 903.8 g
6 moles of methanol (CH_3OH) = 32.04 × 6 moles = 192.24 g Eqn 4
903.8 g of oil will react with 192.24 g of methanol
45.6 g of plant oil will react

$$\frac{192.24 \times 45.6}{903.8} \; of\ methanol = 9.699\ g\ (0.009699\ kg) \qquad \text{Eqn 5}$$

Density of methanol = 792 kg/m^3

Volume of methanol used was

$$= \frac{mass}{volume} = \frac{0.009699}{792} \qquad \text{Eqn 6}$$

$$= 0.000012246\ m^3$$

= 0.012246 L = 12.246 *ml* = 12.25 *ml*

If 6 moles of methanol = 12.25 ml,
9 moles of methanol =

$$\frac{9 \times 12.25}{6} = 18.37 \qquad \text{Eqn 7}$$

= 18.37 *ml*

12 moles of methanol =

$$\frac{12 \times 12.25}{6} = 24.5 \quad \text{Eqn 8}$$

$= 24.5\ ml$

The stoichiometric excesses (65 % more) made the volume of methanol to be measured become:
6 moles of methanol = $1.65 \times 12.25 = 20.21\ ml$
9 moles of methanol = $1.65 \times 18.37 = 30.31\ ml$
12 moles of methanol = $1.65 \times 24.5 = 40.42\ ml$
The yield of the methyl esters, Y produced was calculated thus:

$$Y = \left(\frac{V_e}{V_r}\right) \times 100\ \% \quad \text{Eqn 9}$$

Where:
Y = Yield of the ethyl esters, %
V_e = Volume of methyl esters produced, ml.
V_r = Volume of raw oil used, ml.

2.2.4 The production of biodiesel fuel from milk bush oil

Summarily, the following four operations were performed in the production of the biodiesel fuel. These are transesterification, phase separation, washing and drying. The transesterification reactions were performed in a batch process. 250 ml cylindrical tin flask equipped with a shaker was used as the reactor. 3% by weight of oil of calcined snail shell was dissolved in methanol and heated on a hot plate until it began to boil. This was immediately removed to prevent evaporation of the methanol. 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 the experimental temperature. The warmed oil was then added to the stirred alcohol/snail shell mixture and stirred for the desired experimental time until a homogenous mixture is formed. Distilled water 10% of the oil was added after the residence time and was continuously stirred 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. Thereafter, the mixture of biodiesel formed and the unreacted oil, alcohol and snail shell was separated as two separate layers were formed. Biodiesel produced was at the topmost part, followed by unreacted oil, alcohol and snail shell at the bottom part of the separating funnel. Unreacted snail shell and alcohol were drained out while biodiesel was collected in dry clean sample bottle for measurement. The biodiesel was later washed with distilled water to remove dissolved alcohol and catalyst, and also heated on hot plate at 100 °C for 20 minutes to remove the water present in the product (biodiesel). Finally the dried biodiesel fuel was saved for further analysis.

2.3 Fuel Properties of Milk Bush Oil and Methyl Ester

The fuel properties of milk bush oil sample and biodiesel were determined using American Society for Testing and Materials (ASTM D6751) standard test methods. Some selected physicochemical properties (kinematic viscosity, specific gravity, pour point, acid value, pH, cloud point, cetane number and flash point) of milk bush oil and biodiesel were determined.

3. RESULTS AND DISCUSSION

The experimental results obtained in this work include the yield obtained for extraction of milk bush oil; yield of milk bush methyl esters after transesterification with two catalysts; effect of reaction parameters on biodiesel production from milk bush oil using snail shell as catalyst and the fuel properties of milk bush oil and methyl esters.

3.1 Extracted Oil from Milk Bush Seeds

The average 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 agrees within the same range with that reported by Sahoo *et al.* (2012) and Ibiyemi *et al.* (2002) and exceeded the value for Jatropha curcas seed oil as reported by Berchman and Hirata (2007). This implies that the percentage of milk bush oil is very high, making it a good source of oil for biodiesel production. An average result of the mechanical extraction of oil from 400 g of milk bush seeds is given below in Table 2.

Table 2: Result of mechanical extraction of milk bush oil

Extraction No.	Weight of heated cake (g)	Applied Force (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

3.2 Biodiesel Yield from Milk Bush Oil using Calcined Snail Shell as Catalyst

The results of biodiesel yield obtained after the transesterification process under different temperatures, time and alcohol to oil ratio conditions using snail shell as catalyst for various experimental runs are presented in Table 3. The lowest biodiesel yield was obtained when temperature was 70 ^{o}C, reaction time was 3 hours and alcohol to oil ratio was 9:1 and the maximum biodiesel yield was obtained when temperature, reaction time and alcohol to oil ratio were 65 ^{o}C, 2 hours and 9:1 respectively. A maximum biodiesel yield of 81% was obtained for milk bush transesterification. High biodiesel yields were obtained at medium reaction parameters with a yield of 78% upward. A similar result was obtained by Birla *et al*. (2012) in the transesterification of waste frying oil using calcined snail shell as catalyst. They obtained biodiesel yield of 87.28%. A reaction temperature of 65 ^{o}C was adequate for complete transesterification of milk bush oil in an average of 2 hours reaction time. An alcohol to oil molar ratio of 9:1 was also sufficient for the transesterification reactions. Even though ratios higher than this provided enough methanol for complete transesterification of milk bush oil, the yields were hampered by higher reaction temperatures greater than 65 ^{o}C (more than the boiling point of methanol) due to evaporation and drying of methanol.

Reaction time higher than 2 hours showed signs of reduced biodiesel yields. This is related to the unstable nature of transesterification reaction which is not in equilibrium 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 (Aworanti *et al*., 2013). This actually generated more production of glycerol and favoured backward reactions which led to reduction of biodiesel yield. The varying biodiesel yield values presented in Table 3 are indications that milk bush transesterification reaction parameters considerably affect the biodiesel yield. 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 temperature, time, alcohol to oil molar ratio and the interactive effects are significant model terms. The "Lack of Fit F-value" of 1.96 implies the lack of fit is not significant relative to pure error.

Table 3: Biodiesel yield from milk bush oil using calcined snail shell as catalyst

Runs	Factors			Response
	Temperature (Degree centigrade)	Time (Hour(s))	Alcohol to oil ratio (Mol)	Biodiesel yield (%)
1	65.00	2.00	9.00	81.00
2	60.00	2.00	12.00	77.00
3	60.00	3.00	9.00	65.00
4	70.00	2.00	6.00	61.00
5	65.00	3.00	12.00	68.00
6	70.00	1.00	9.00	66.00
7	65.00	1.00	12.00	74.00
8	60.00	1.00	9.00	65.00
9	60.00	2.00	6.00	58.00
10	65.00	3.00	6.00	55.00
11	70.00	2.00	12.00	60.00
12	65.00	2.00	9.00	79.00
13	65.00	1.00	6.00	69.00
14	70.00	3.00	9.00	54.00
15	65.00	2.00	9.00	81.00
16	65.00	2.00	9.00	78.00
17	65.00	2.00	9.00	80.00

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 "Pred R-Squared" of 0.8788 is in reasonable agreement with the "Adj R-Squared" of 0.9727. "Adeq Precision" measures the signal to noise ratio. 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 10; the model shows that all the reaction variables are significant upon biodiesel production from milk bush oil using calcined snail shell as catalyst.

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

Eqn 10

Where A, B, C were the coded values of the independent variables i.e. temperature, time and alcohol to oil molar ratio respectively. Guan and Yao (2008) reported that an R^2 should be at least 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.

3.2.1 Effect of reaction temperature on biodiesel yield

From Table 3, it can be inferred that biodiesel yield from milk bush oil using snail shell as catalyst increased as temperature increased from 60 ^oC to 65 ^oC and began to decrease drastically at temperatures beyond this. The decrease in the yield can be related to the burning or evaporation of methanol (boiling point of methanol is 64.7 ^oC) which resulted into lesser transesterification of the oil at higher temperatures. The same thing was observed by Boey *et al.* (2009) who reported an optimum temperature of 65 ^oC for methanolysis of palm oil using activated calcium oxide as catalyst. As shown in Figure 1, the maximum yield was obtained at a temperature of 65 ^oC. A decrease in yield was observed when the reaction temperatures were above 65 ^oC. Transesterification at temperatures above 65 ^oC caused excessive methanol loss due to evaporation and significantly reduced the overall biodiesel yield.

3.2.2 Effect of reaction time on biodiesel yield

As shown in Figure 2, biodiesel yield was high for the low level reaction time; it increased and started to decrease after the average reaction time chosen for the low and high level factors of the transesterification reaction. The decrease of methyl ester yield at higher reaction time can be attributed to the reversible nature of transesterification reaction: higher time residence of the reaction tends to allow for backward reaction which reduces the biodiesel yield. Results obtained revealed that 2 hours was sufficient for the complete transesterification of milk bush oil. This is comparable with the works of Boey *et al.* (2009) who reported an optimum reaction time of 2.5 hours for methanolysis of palm oil using activated calcium oxide as catalyst.

3.2.3 Effect of alcohol to oil ratio on biodiesel yield

Biodiesel yield increased more as alcohol to oil ratio increased because it helped increase the reactants concentration that drove the reaction equilibrium forward. This was made possible as there was more methanol for more transesterification of oil to methyl ester. A reduction in biodiesel yield at higher alcohol to oil ratio close to 12:1. The reduction can be attributed to the minimization of the contact between triglycerides molecules and the catalyst's active sites, thereby reducing the catalyst activity on the transesterification reaction (Aworanti *et al*., 2013). The maximum ester yield for milk bush oil were found to be 81% at the methanol to oil molar ratio of 9:1. This agreed with the findings of Gryglewicz (2000) who reported the highest biodiesel yield of 87.45% at methanol to oil ratio of 9:1 in the transesterification of rapeseed oil using carbonized shrimp shell as catalyst and methanol as alcohol. The effect of alcohol to oil molar ratio on the conversion of oil obtained in the transesterification of milk bush oil using calcined snail shell as catalyst can be seen in Figure 3. With further increase in methanol to oil molar ratio there was only little improvement in the product yield.

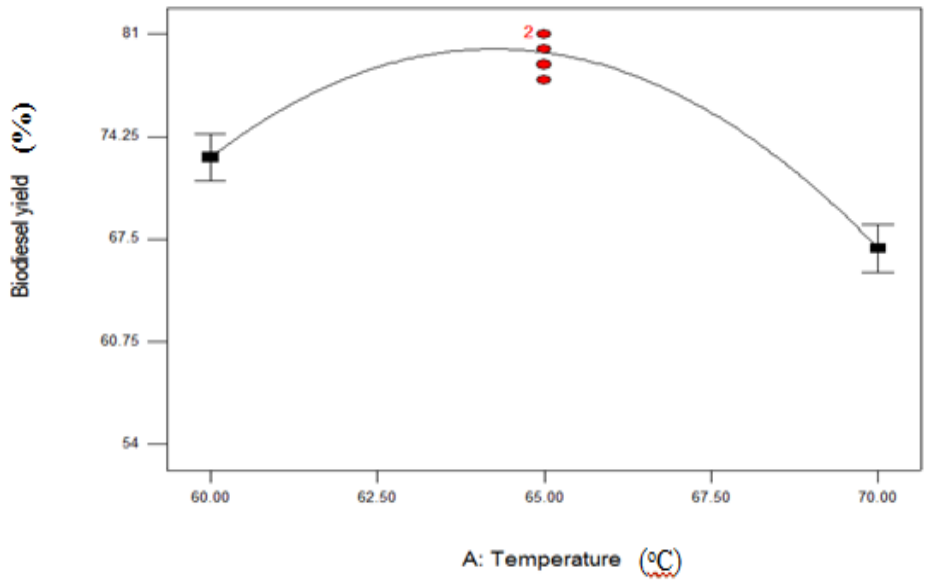


Figure 1: Effect of temperature on biodiesel yield using calcined snail shell as catalyst

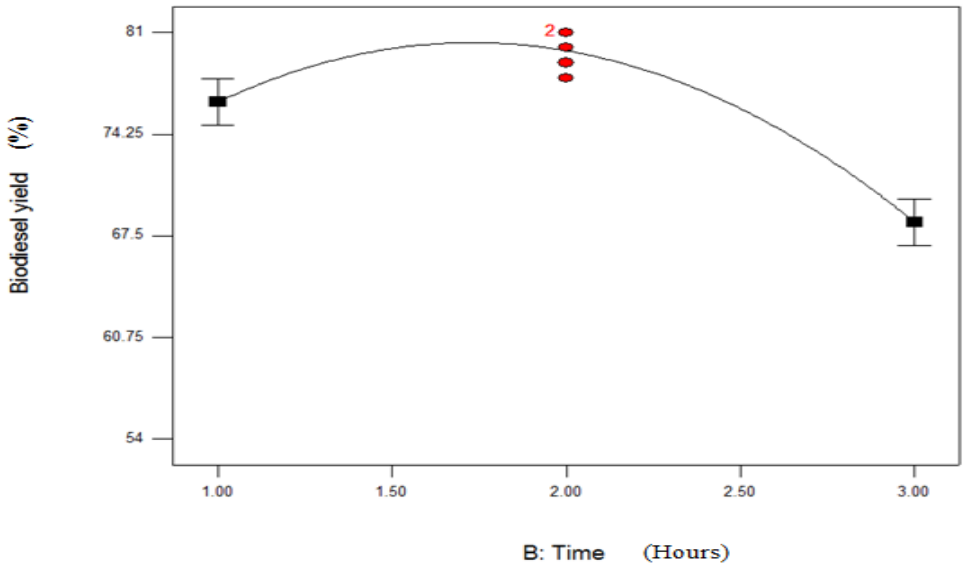


Figure 2: Effect of time on biodiesel yield using calcined snail shell as catalyst

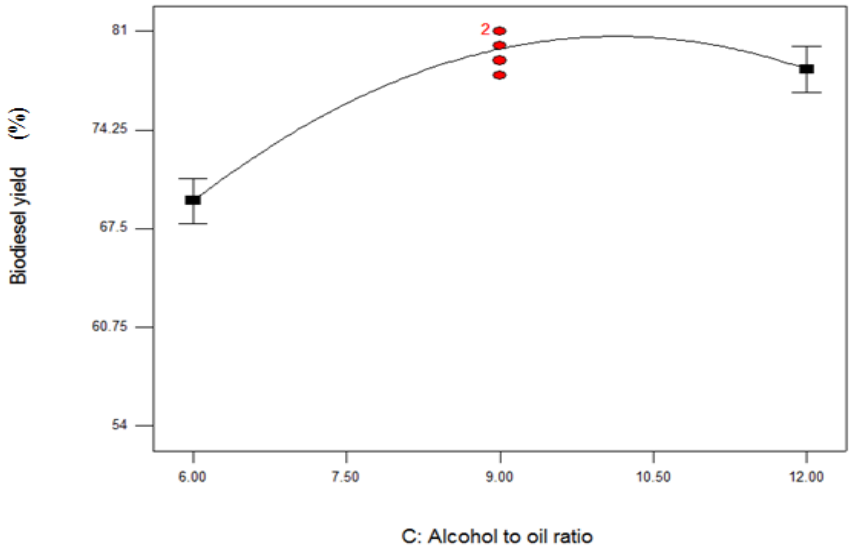


Figure 3: Effect of alcohol to oil ratio on biodiesel yield using calcined snail shell as catalyst

3.3 Effect of Interaction between Process Variables on Biodiesel Yield from Milk Bush Oil using Snail Shell as Catalyst

Three-dimensional response surfaces were plotted on the basis of the model equation to investigate the interaction among the reaction variables and to determine the optimum condition of each factor for transesterification for biodiesel production. The elliptical nature of the contour plots indicated that interaction between these reaction variables had a positive significant effect on the yield of biodiesel. This is supported by the work of Aworanti *et al*. (2013) who studied Statistical Optimization of Process Variables for Biodiesel Production from Waste Cooking Oil Using Heterogeneous Base Catalyst.

The effect of interaction of temperature and time on biodiesel yield can be seen in the 3D response surface plots (Figure 4). The biodiesel yield increased with increase in temperature and time and then decreased with further increase in time and temperature. The interaction between temperature and time is significant as indicated already by ANOVA results. The 3D response surface plot effect of temperature and alcohol to oil ratio and their interactive effect on biodiesel yield is presented in Figures 5. The biodiesel yield increased with increase in temperature and alcohol and then decreased with further increase in time and alcohol to oil ratio. A noticeable decline in biodiesel production was noticed when alcohol to oil ratio was increased at higher temperatures. The interaction between temperature and alcohol to oil is significant as indicated already by ANOVA results. The interactive effect of time and alcohol to oil ratio on biodiesel yield is presented in the 3D response surface plots as shown in Figures 6. The biodiesel yield increased with increase in time and alcohol and then decreased with further increase in time and alcohol. A continuous decline in biodiesel production was noticed when reaction time increased the more. This effect was observed to be more pronounced compared to increasing alcohol to oil ratio. The interaction between time and alcohol to oil is significant as indicated already by ANOVA results.

3.4 Optimization of the Transesterification of Milk Bush Oil Process Parameters using Calcined snail Shell as Catalyst

Optimum reaction conditions for maximizing biodiesel yield was determined by statistically analyzing the experimental data. In order to provide an ideal case for biodiesel production, the reaction temperature, reaction time and for methanol-to-oil molar ratio were set in range based upon the requirements of the reaction parameters and biodiesel yield was set on maximum level. The predicted optimum values of reaction temperature, reaction time and methanol-to-oil molar ratio were found to be 63.67 ^{o}C, 1.89 hours and 10.18:1 respectively, to achieve 81.45 % maximum milk bush biodiesel yield; while desirability was 1.00 for the experiment. This optimal solution chosen for biodiesel yield are favourable predicted optimum levels based on economic considerations (reduced temperature and reaction time and moderate alcohol to oil ratio which corresponds to reduced operating costs of the transesterification process for biodiesel yields) and not necessarily the highest biodiesel yield value. The optimal biodiesel yield chosen for transesterification of milk bush oil using snail shell as catalyst and the corresponding conditions are given in Table 4.

Further validation experiments conducted at the predicted optimal conditions yielded 80% of biodiesel. This value is in reasonable agreement with the predicted optimal yield. The value also compares well with literature value (Birla *et al.*, 2012).

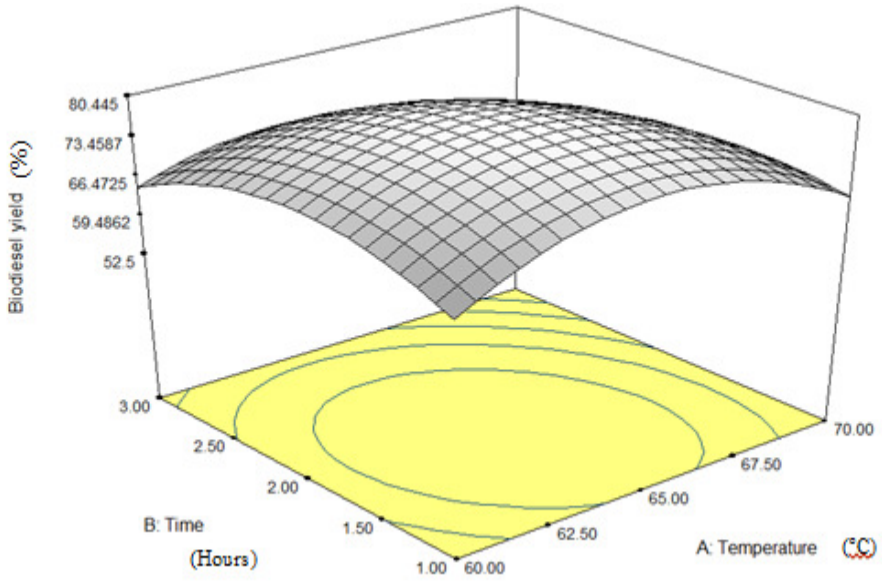


Figure 4: 3D response surface plots showing the effect of temperature, time and their interactive effect on biodiesel yield

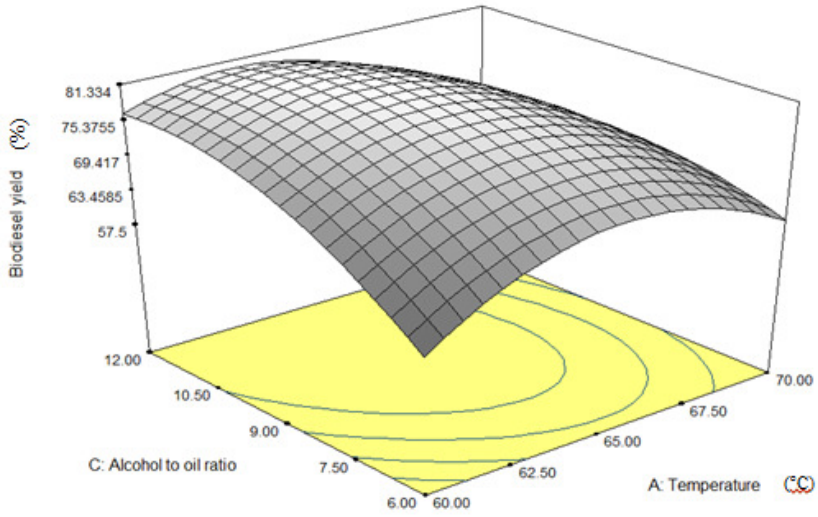


Figure 5: 3D response surface plots showing the effect of temperature, alcohol to oil ratio and their interactive effect on biodiesel yield

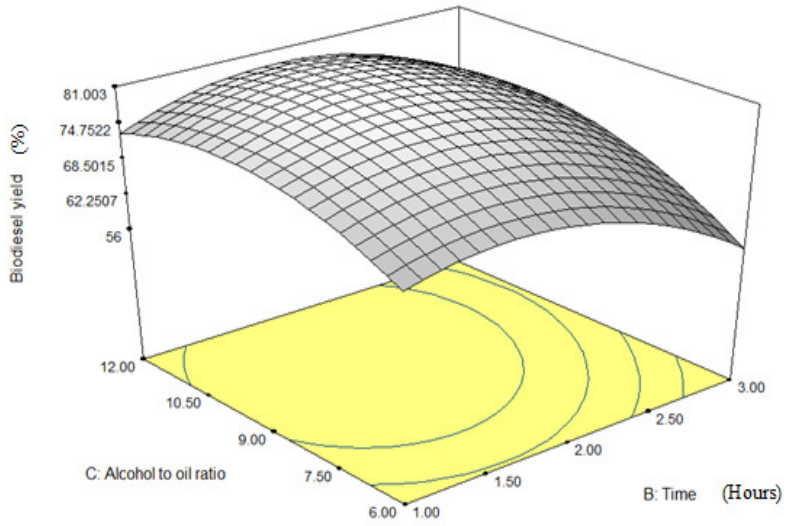


Figure 6: 3D response surface plots showing the effect of time, alcohol to oil ratio and their interactive effect on biodiesel yield

Table 4: Optimum values for Biodiesel production from milk bush oil using snail shell as catalyst

Process parameters	Optimum values
Temperature	63.67 ^{o}C
Time	1.89 hours
Alcohol to oil ratio	10.18:1
Biodiesel yield	81.4521%

As can be seen in Table 4, the biodiesel yield in the optimized conditions was 81.45% while the highest biodiesel yield from experimental work was 81%. The results clearly indicated the effectiveness of process variables optimization in biodiesel production. A full factorial experimental design using Box-Behnken design (BBD) was performed by Zhang *et al.* (2010) and Charoenchaitrakool and Thienmethangkoon (2011) to assess the effects of three variables on biodiesel yield from *Zanthoxylum bungeanum* seed oil (ZSO) and waste frying oil, respectively. Zhang *et al*. (2010) obtained high conversion of ZSO to biodiesel in which the yield was around 96% and the determined optimum experimental conditions were methanol-to-oil ratio, 11.69:1, CaO catalyst amount, 2.52% and reaction time of 2.45 hours.

Wang *et al.* (2008) used a central composite design to investigate the optimal conditions for biodiesel production from trap grease with 50% free fatty acid. The highest methyl ester content of 89.67 % was obtained when methanol to oil molar ratio of 35:1, 11.27 wt % H_2SO_4, 95 ºC reaction temperature and reaction time of 4.59 hours were used. Also, Encinar *et al.* (2005) reported that for the biodiesel production from waste frying oil, 94.2% maximum FAME yield was achieved when a methanol to oil molar ratio of 6:1, 1 wt. % KOH, and 65 ºC with the reaction time of 2 hours were used as reaction conditions.

3.5 Physicochemical Properties of Milk Bush Oil and Methyl Ester

The physicochemical properties of milk bush oil and methyl ester are as presented in Tables 5 and 6 respectively. Two important properties of methyl esters processed from milk bush oil using calcined snail shell as catalyst, which are viscosity and flash point were found to be 4.89 mm^2/s and 158ºC respectively. Both properties met the specifications of ASTM D6751 standards. Milk bush oil has a high viscosity of 51.69 mm^2/s which dropped down on transesterification to 4.89 mm^2/s when calcined snail shell was used as catalyst; a sign that transesterification indeed took place. Fuel properties of milk bush biodiesel were compared with standards provided by ASTM (Table 7).
All the selected physicochemical properties that were determined from milk bush biodiesel fell within the specifications of ASTM D6751 standards.

Table 5: The physicochemical properties of milk bush oil

Parameters	Values
Specific gravity (40 ^{o}C)	0.9119
Viscosity	51.69 (mm^2/s)
Pour point	4.5 (^{o}C)
Acid value	2.156 (mgKOH/g)
pH	6.07
Cloud point	4.43 (^{o}C)
Refractive Index (20 ^{o}C)	1.4822

Table 6: The physicochemical properties of milk bush methyl ester using calcined snail shell as catalyst

Parameters	Values
Specific gravity (40 ^{o}C)	0.891
Viscosity	4.89 (mm^2/s)
Pour point	1.00 (^{o}C)
Acid value	0.65 (mgKOH/g)
pH	7.76
Cloud point	4.85 (^{o}C)
Flash point	158 (^{o}C)
Cetane number	46.2

Table 7: Comparison of Fuel Properties of milk bush Biodiesel with ASTM Standards

Fuel properties	Milk Bush Biodiesel	ASTM D6751
Specific gravity (40 ^{o}C)	0.891	0.87 to 0.98
Viscosity	4.89 (mm^2/s)	1.90 to 6.0
Pour point	1.00 (^{o}C)	-15 to 13
Acid value	0.65 (mgKOH/g)	0.80 (max)
pH	7.76	7 to 9
Cloud point	4.85 (^{o}C)	-3.15 to 11.85
Flash point	158 (^{o}C)	>130
Cetane number	46.2	>45

4. CONCLUSION

The results from the study showed that low-cost heterogeneous catalyst derived from the shell of giant African land snail for catalysis of milk bush oil transesterification is possible. Reaction parameters such as temperature, time and alcohol to oil molar ratio affecting biodiesel yield from milk bush oil using snail shell as catalyst were investigated. The significance effects of reaction parameters on biodiesel yield at $p<0.05$ shows that reaction temperature, reaction time and molar ratio of alcohol to oil all have significant effects on biodiesel yield. The optimization of transesterification reaction using snail shell produced a solution of minimal economic parameters which are 63.67 ^{o}C temperature, 1.89 hours of reaction time and a molar ratio of 10.18:1 of alcohol to oil to yield 81.45% of biodiesel. The fuel properties of milk bush methyl ester further suggests its potential as an alternative fuel for diesel.

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