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Soybean Oil Biodiesel Production using Renewable Catalyst Synthesized from Guinea Fowl Eggshells.

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Abstract-
The need for a sustainable energy has given rise to the search for a renewable source of energy. This research study presents the production of soybean oil biodiesel using synthesized guinea fowl eggshell catalyst (renewable catalyst). The catalyst preparation involves calcination at 850 ^{0}C for 3 hours in a muffle furnace. It was characterized using X-Ray Flourescence (XRF) and Scanning Electron Microscopy (SEM). Biodiesel was produced using 3-8 wt % of calcined catalyst within a time range of 1-2 hour, methanol/oil ratio of 0.25-0.5 w/w%. The highest biodiesel yield was 87.6% at optimum conditions of 8 wt%, 1.5 hours and 0.25 w/w% for catalyst amount, reaction time and methanol/oil ratio respectively. The biodiesel produced validates the successful synthesis of the guinea fowl eggshell into CaO. Biodiesel was then characterized to determine the acid value, flash point, cetane number, specific gravity, density, iodine value and kinematic viscosity. The characterization result of the biodiesel synthesized by using the guinea fowl eggshell catalyst produced showed that the biodiesel produced compares favorably with ASTMD standards.

Keywords: Guinea fowl eggshells, calcination, biodiesel, Soybean oil, trans-esterification

1. Introduction

Due to the current energy demand and the crisis created by greenhouse gas, a need arises to adopt a new energy source known as the renewable source of energy. Generally, the awareness of energy challenges and environmental issues related to fossil fuels burning has inspired several researchers to examine the prospect of using renewable fuel sources of fuel [1]–[3]. One of these sources is biodiesel which appears to be viable enough due to its high biodegradability and minimal toxicity which makes it easier to substitute the conventional diesel fuel in various functions such as in internal combustion engines [4]. The use of biodiesel fuel in diesel engines requires no major modifications and only a little reduction in performance has been recorded so far. Another benefit in the use of biodiesel include no emission of sulfates, negligible emissions of aromatic compounds and other substances that are not environmentally friendly [5]–[7]. Biodiesel synthesis is carried out by several procedures but the frequently used procedure is the reaction in which the alkoxyl group present in an ester compound is exchanged by an alcohol in the presence of an acid or a base catalyst [8].

In biodiesel production, the feedstock includes different types of vegetable oil such as soybean oil, rapeseed oil, yellow oleander oil, sunflower oil and other vegetable oils. In this study, soybean oil was used for the production of biodiesel in an attempt to establish the use of the calcined guinea fowl eggshells as the CaO catalyst [9], [10].

Widely, the catalyst used is either homogeneous acid or base catalyst, but recently researchers have discovered a better type of catalyst called the heterogeneous which is advantageous in that it is mostly cheaper and easier to use compared to the widely used homogeneous catalyst [11]. The Guinea fowl eggshell catalyst used in this reaction is a heterogeneous catalyst and calcium oxide which is the end product of the synthesis of the guinea fowl eggshell is a naturally occurring chemical substance in animal bones, shells and mollusks [12], [13].

This study attempts to investigate and optimize the production of biodiesel from soybean oil using guinea fowl eggshells as a heterogeneous catalyst.

2. Methodology

2.1 Catalyst Synthesis

The waste guinea fowl eggshells and periwinkle shells were collected from a local market in Ota, Ogun state. The catalysts were prepared by calcination method adopted from Pedavoah, Badu, Boadi, & Awudza, (2018). The shells were washed under a flowing tap of water and rinsed of in warm water to minimize organic materials. The shells were then dried in an oven at 120 ^oC for 3 hours and then ground to 75 microns mesh size in a stainless steel grinder. The crushed sample was then calcined in a muffle furnace at 850 ^oC for 3 hours hold time. The calcined samples were stored in a desiccator.

2.2 Reaction Procedure

The trans-esterification reaction was carried out using a 250 ml spherical flat bottom flask with stopper placed on a hot plate with magnetic stirrer. 80 ml of esterified soybean oil was charged into a 250 ml spherical glass reactor and heated to 60 ^oC. A known amount of calcined guinea fowl egg shell was dissolved in a known volume of methanol and was quickly transferred into the preheated oil (Table 1). The reaction was allowed to run for a desired duration of time at 65 ^oC and stopped when the time was reached. The content of the reactor was transferred into a separating funnel and was allowed to settle overnight. The content of the separating funnel separated into three layers in which the first layer was biodiesel, the second layer was glycerol and the third layer was Calcined Guinea Fowl Eggshell (CGFES) catalyst. The second and third layer was carefully decanted leaving behind the Calcined Guinea Fowl Eggshell Biodiesel (CGFESB). The first layer containing CGFESB was washed with warm distilled water thrice to get rid of glycerol, soap and residual catalyst. The washed CGFESB was dried over the heating mantle to remove the untapped water after which it was stored in an air tight container. The CGFES Biodiesel yield was determined gravimetrically in terms of (%w/w) as described in Eq. 1.

$$\text{CGFESB Yield} = \frac{weight\ of\ biodiesel\ produced}{weight\ of\ oil\ used} \quad \text{(Eq. 1)}$$

Table 1: Design of experiment.

Variable	Symbol	Coded factor levels		
		-1	0	+1
Methanol/oil ratio (w/w)	A	0.250	0.375	0.500
Catalyst amount (w/w)%	B	3.0	5.5	8.0
Reaction time (hr)	C	1.0	1.5	2.0

2.3 Catalyst Characterization
Scanning electron microscopy analysis was done to analyze the surface morphology of the catalyst. X-Ray fluorescence (XRF) (Thermo Scientific Niton XL3t) is a compositional analysis to determine the elements present in the catalyst.

2.4 Biodiesel Characterization
The quality of the CGFES biodiesel produced was analyzed following the standard methods of ASTM D.

2.5 Statistical Analysis using Response Surface Methodology (RSM)
The study was carried out with RSM statistical tool to test the effect of methanol/oil ratio, reaction time and catalyst amount on the trans-esterification of soybean oil into biodiesel. Three factorial levels including twelve factorial points and three center points was generated from Box-Behnken to fit in the second order response surface equation as represented below in Eq. 2.

$$Y = \alpha_o + \alpha_1 A + \alpha_2 B - \alpha_3 C - \alpha_{11} A * A + \alpha_{22} B * B - \alpha_{33} C * C + \alpha_{12} A * B + \alpha_{13} A * C - \alpha_{23} B * C \quad \text{(Eq. 2)}$$

where Y is the predicted response (biodiesel yield), α_o is intercept term, α_1, α_2 , and α_3 are the linear coefficients, α_{12}, α_{13} and α_{23} are interactive coefficients, α_{11}, α_{22} and α_{33} are the quadratic coefficients and A, B and C are the coded factors. The Minitab® version 17.1.0 (LEAD Technologies, Inc.) software was applied.
Table 2 gives the Box-Behnken design for the 15 experimental runs that were generated from the statistical tool. These experimental runs were arranged randomly to reduce the effects of unforeseen variableness in the observed responses. The method used gives rise to the variety of the procedure by formulation of an equation of the second order. Furthermore, the biodiesel produced was analyzed through the least squares method to fit the second order equation above.

Table 2: Box-Behnken design of CGFESB trans-esterification process

Standard run	**A**	**B**	**C**	**Yield**
1	0	0	0	62.5
2	0	-1	1	83.5
3	-1	1	0	87.6
4	0	0	0	60.2
5	0	1	1	75.0
6	1	0	-1	78.7

7	-1	-1	0	80.8
8	0	0	0	65.6
9	-1	0	-1	79.1
10	-1	0	1	63.5
11	1	-1	0	63.5
12	0	-1	-1	79.3
13	1	1	0	60.8
14	1	0	1	65.6
15	0	1	-1	63.1

A: methanol/oil ratio; B: catalyst amount; C: reaction time

3. Result and Discussions

3.1. Elemental Composition and Morphological Structure of CGFES catalyst

Table 3 represents the elemental composition of CGFES catalyst synthesized at a temperature of 850 ºC for 3 hours by X-Ray Fluorescence (XRF). The amount of Ca in the catalyst can be attributed to the presence of $CaCO_3$ which decomposed to form CaO through calcination. Other elements that were present in the catalyst are as listed in the table with trace amounts compared to that of Ca.

Table 3: Elemental composition of CGFES by XRF analysis

Element	Fe	Mn	Ca	Al	Zn	Si
% Composition	0.05	0	68.735	0.718	0.001	0.993

The SEM analysis indicated the surface morphology of the calcined guinea fowl eggshell as shown in the Figure 1 below. The morphology displays a cone layer structure with a palisade layer of adjacent exospheric particles with magnification of 1000x and size range of 80 μm. The microstructures of the eggshells are changed from cone layered to porous structure due to calcination which in turn increases the surface area of the catalyst as it was also reported by Pedavoah *et al*., (2018). This porous structure gives the catalyst the ability to become more active in the trans-esterification reaction.

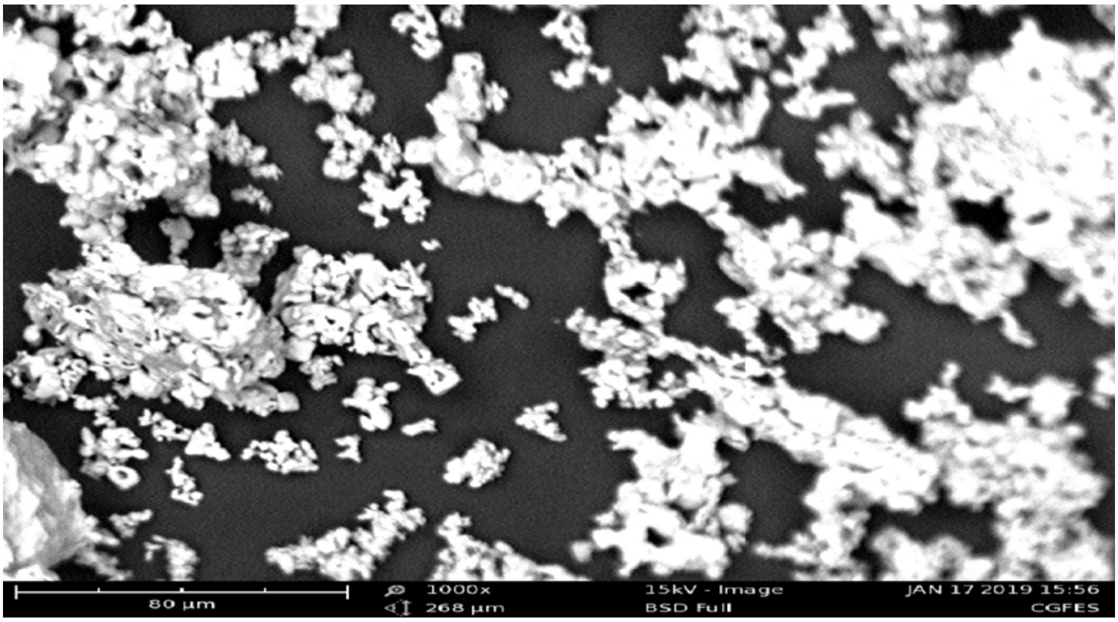

Figure 1: Morphological study of CGFES catalyst

3.2 Biodiesel Characterization

The biodiesel produced from guinea fowl eggshell catalyst with soybean oil was characterized for its fuel properties and fatty acid profile as seen in Tables 3 and 4 respectively. The fuel properties compared well with biodiesel standard specification of ASTMD. From the fuel properties table, it can be inferred that the flash point tested for the produced biodiesel makes it safe to use since the value is well above the minimum specification for operational use.

Table 4: Properties of CGFESB compared with biodiesel standard specification.

Properties	(CGFESB)	ASTMD Standard
Specific Gravity (@ 30°C)	0.992	0.86-0.9 (ASTM D6751)
Pour Point (°C)	-19.8	-35 to -15 (ASTM D975)
Acid Value (mg KOH/g)	0.711	<0.8 (ASTM D6751)
Cetane Number	59.93	47.0 min (ASTM D613)
Kinematic Viscosity (mm^2/sec) (@ 40°C)	6.9	1.9-6.0 (ASTM D6751)
Flash Point (°C)	128.2	93 min (ASTM D6751)

Min-minimum, max-maximum.

3.3 Quadratic Regression Model

In order to describe the most valid operating parameters for this study a factorial plan was used [14]. The regression model for soybean oil catalyzed by guinea fowl eggshell using Box-Behnken composite design is presented as independent variables in coded values is given by Eq. 3.

$$Y = 124.1 - 26.5\,A - 0.62\,B - 66.5\,C + 446.7\,A*A + 0.529\,B*B + 19.52\,C*C - 38.72\,A*B - 75.6\,A*C + 6.280\,B*C \qquad \text{(Eq. 3)}$$

where Y is the conversion of soybean oil to biodiesel (%), A the methanol-oil ratio, B the CGFES amount and C reaction time.

The ANOVA results are represented in Table 5. This regression model has an F-value of 31.15 and p-value of 0.001 indicating that this model is valid. The p-value indicates the probability error which is used to check the validity of the coefficients of regression. If p-value is less than 0.05, then it means that the model term is significant [10], [11]. In this study, A, B, C, AB, AC, BC, AA, BB and CC were all significant terms. The regression model equation and fitness of the model were evaluated. The R^2 value which is the coefficient of determination was used to obtain the goodness of fit of the model and was found to be 0.9825 and this indicates that this research model can illustrate 98.25% of the variability. The optimal conditions for the production of CGFES biodiesel was methanol-oil ratio 0.25 (w/w), reaction time 1.5 hours and catalyst amount 8 %(w/w). The average absolute deviation (AAD) which must be less than 2% was evaluated to be -0.1064 and this depicts that the regression model is accurate.

Table 5: Test of significance for the regression coefficients and ANOVA results

Source	**DF**	**Adj SS**	**Adj MS**	**F-Value**	**P-Value Prob > F**
A	1	40.05	40.051	9.05	0.030
B	1	0.50	0.500	0.11	0.750
C	1	6.30	6.301	1.42	0.286
A*A	1	179.85	179.848	40.64	0.001
B*B	1	40.31	40.311	9.11	0.029
C*C	1	87.90	87.900	19.86	0.007
A*B	1	585.64	585.640	132.32	0.000
A*C	1	89.30	89.303	20.18	0.006
B*C	1	246.49	246.490	55.69	0.001
ANOVA					
Model	9	1240.71	137.856	31.15	0.001
Lack-of-Fit	3	10.60	3.534	0.61	0.668
Pure Error	2	11.53	5.763		
R^2		98.25%			

DF = Degree of Freedom, Adj SS = Adjusted Sum of Square, Adj MS = Adjusted Mean Square, F = Fischer, p = Probability.

3.3.1 Effects of model variables on the yield of CGFES biodiesel

Three dimensional response plots are presented in Figure 2-4 and these plots illustrate the interactions between the model variables. Figure 2 depicts that at the highest catalyst amount considering a constant reaction time and at the lowest methanol/oil ratio, there was an increase in biodiesel yield. Figure 3 shows that of reaction time and methanol/oil ratio has an effect on the biodiesel produced. At lower methanol/oil ratio and increased time using a constant catalyst amount, no significant increase in the biodiesel yield was observed. Figure 4 also shows the effect of catalyst amount and reaction time on the yield of biodiesel produced. When reaction time is low and the catalyst amount is at the lowest, the biodiesel yield is reduced significantly compared with their respective highest values.

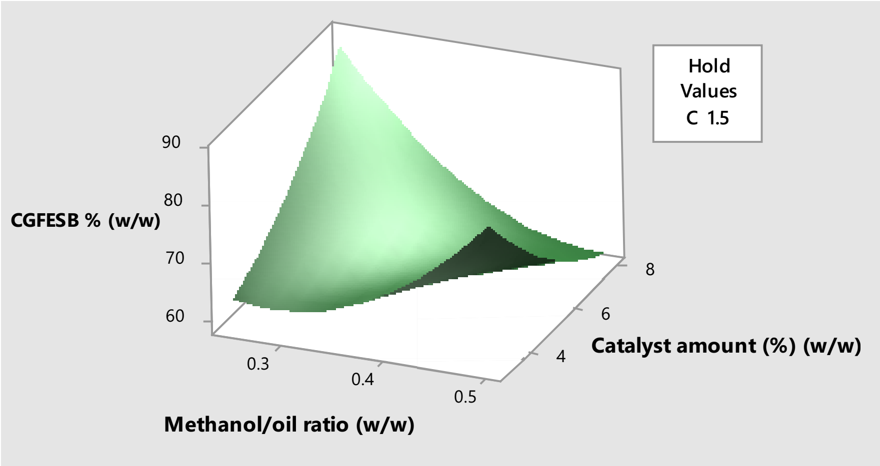

Figure 2: Three dimensional diagram of CGFESB vs Catalyst amount and Methanol/oil ratio

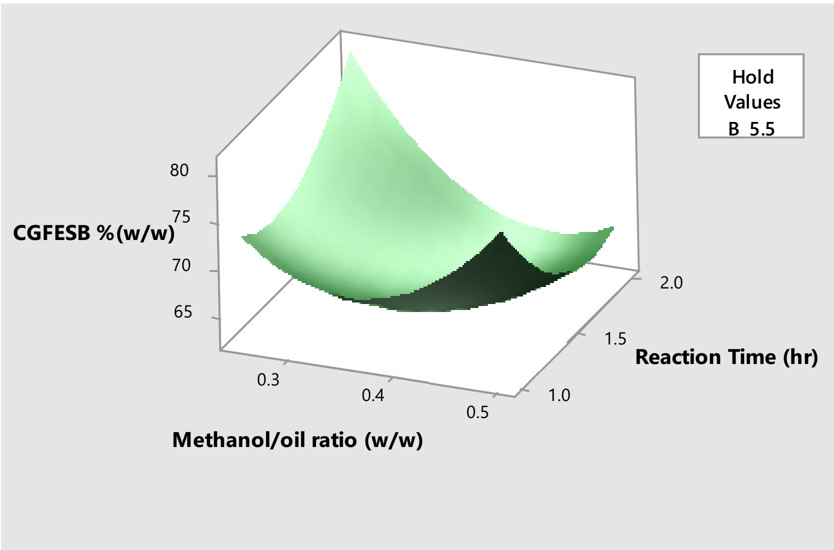

Figure 3: Three dimensional diagram of CGFESB vs Methanol/oil ratio and Reaction time

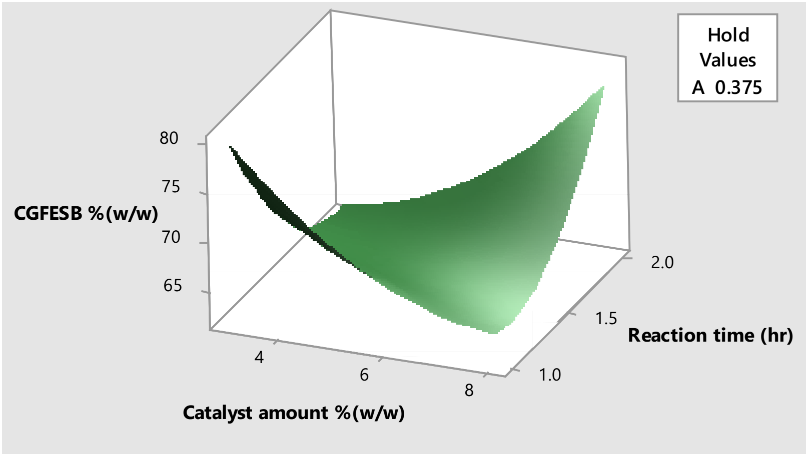

Figure 4: Three dimensional diagram of CGFESB vs Catalyst amount and Reaction time

4. Conclusion

The optimal reaction condition was evaluated to achieve the highest yield conversion for this study. The quality of the biodiesel produced was examined and characterized to evaluate the level of conversion of free fatty acids in relation to the amount of methyl ester biodiesel present [14]. According to the results obtained, it can be deduced that the synthesized guinea fowl eggshell catalyst has been produced and contributed to a high yield in biodiesel production as depicted by the statistical tool.

5. Recommendation

I would recommend that a further research on the kinetic study on the behavior of guinea fowl eggshell catalyst during the trans-esterification reaction.

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