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The use of Waste Duck Eggshells for Sustainable Energy Production

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Abstract: In this study, waste duck eggshells were processed into high grade CaOheterogenous catalyst for the esterification-transesterification of palm kernel oil (PKO) to obtain biodiesel. The production processes involved are calcination of duck eggshells into CaO, XRD and XRF analysis of CaO produced, PKO fatty acid components determination, transesterification of the esterified PKO and the formulation of a suitable model. High biodiesel yield of 84% was obtained at catalyst concentration of 9 wt./wt. %, reaction time of 2 hours and methanol/oil mole ratio of 13, using CaO catalyst (derived from duck eggshell). The good quality of biodiesel produced was ascertained by its properties that fall within ASTM specifications (kinematic viscosity of 4.1 mm^2/s, flash point of 195^0C, density of $869kg/m^3$, water content of 0.045 v/v %).
Keywords: Biodiesel, calcination, CaO, catalyst, duck eggshell, transesterification

1. Introduction

The adoption of renewable forms of energy has been adjudged not only as an alternative to fossil fuels, but also a reliable approach to the attainment of sustainable energy across the globe. According to[1–2],energysustainability can be defined as havingaccess to sufficient and reliable supplies of environmentally and socially acceptable forms of energy at reasonable prices without jeopardizing the energy needs of future generations. One form of renewable energy that can be considered for energy sustainability is biodiesel [3–5].

In addition to the acceptance of biodiesel as a renewable and sustainable form of energy, it is also an eco-friendly source of energy with no sulphur emission and it can be used on diesel engine without any form of engine modification [3, 6]. Biodiesel,usually referred to as fatty acid methyl ester,can be obtained through transesterification process. This is a production process involvinga reversible reaction between the short chain alcohol (preferably methanol) and the triglycerides of vegetable oils, in the present of a suitable catalyst [7].

The mainprocess variables that affect the yield of biodiesel significantly are alcohol to oil mole ratio, reaction temperature, reaction time, agitation rate and catalyst concentration [6–7]. Thecatalystsinvolved in transesterification process can be grouped into two: homogenous and heterogenous catalysts. Homogenous catalysts are catalysts in same liquid state with all the reagents and materials involved in the transesterification reaction, while the heterogenous catalysts are solid state catalysts compare to the reactants which are in liquid forms. Without the introduction of catalyst, transesterification reaction would not take place [8–12]. Some of the advantages of theuse of

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heterogenous catalysts over homogenous catalysts during transesterification process include high purity level of the biodiesel produced, ease of catalyst recovery and catalyst reusability [5, 8, 12–14]. And examples of the heterogenous catalysts include MgO and CaO.

The conversion of certain waste materials (such as duck eggshells) that are rich in $CaCO_3$into catalysts for transesterification process is a laudable attempt that needs to be promoted, particular now that efforts are being intensified to reduce the pollution rate associated with the wrong disposal of such wastes. In this research, production of suitable CaO catalyst from duck eggshells (for transesterification) will be investigated, the quality of CaO obtained from duck eggshell will be establishedand model that shows correlation between biodiesel yield and process variables will be formulated.

2 Materials and methods

2.1 Materials, reagents and equipment

Waste duck eggshell was collected from a local poultry in Ota, Ogun state Nigeria. Palm kernel oil (PKO) was purchased from Oja-Ota market, Ota, Ogun state. Reagents used include Methanol, Benzene, Sodium hydroxide pellets, Hydrochloric acid, Tetraoxosulphate (VI) acid. The equipment used include X-ray fluorescence (XRF) spectrometer, X-ray diffraction spectrometer, Agilent Technologies 7890A (GC System/5975C), Digital Magnetic Stirring Hot Plate, Open cup Flash Point Tester, Pour Point Tester, Viscometer Bath with U tube calibrated glass.

2.2Methods

2.2.1 Design of experiment: Tagushi design method (with three variables) was used for the design of the experiment during biodiesel production. The three process variables considered were methanol to oil mole ratio of (10–16), (3–9) wt/wt%catalystconcentration and (1–3) hoursreaction time.

2.2.2 Preparation of the CaO (calcined duck eggshell catalyst): Waste duck eggshells obtained were carefully washed in warm water (to remove impurities) and then oven dried at 110^0C for 30 minutes. The white lining in the shells were removed, the shells were reduced to fine particles of 60 μm and then calcined at 800^0C for 4 hours, to obtain very fine white powder of CaO.

2.2.3 XRD and XRF Analysis of CaO: The elemental composition, quantification and the diffraction pattern of CaO produced were done using XRF and XRD spectrometers.The XRD analysis involved the use of macscience X-ray diffraction system with the incorporation of CuKα X-ray source (λ = 0.20nm and k = 1.5406 Âe), carried out at 40mA and 50 kV, with a step size of 0.05. The diffractogrampattern obtained were recorded in 2θ between the range of5–70.While X-ray fluorescencespectrometer was used to showthepercentage compositionofthecomponents of the calcinedduck eggshell.

2.2.4 Pre-treatment of Palm Kernel Oil: The pre-treatment of palm kernel oil (PKO),which entails sand, free fatty acid and water removal,was carried out before the transesterification process. It is essential to subject the oil to these pre-treatments to avoid low yield of biodiesel production (as well as the formation of any unwanted by-product) during transesterification[3].Filtration process (industrial sieve of 50 μm) was adopted for the impurities removal and the free fatty acid present in the oil was removed through esterification process.

2.2.5 Oil Fatty Acid Components determination: Oil triglycerides was determined by analysing the fatty acid components of the oil using GCMS equipment. The oil sample was auto-injected (with the aid of the attached syringe, at 70 °C) into round the column, with the aid of carrier gas (99.9%

Helium). Detectors identified the various fatty acids in the oil, at exit of the column. Electrical signal that corresponded to each acid detected was quantified through the attached data analysis system (a computer system connected to the device).

*2.2.6. Biodiesel Production:*Appropriate quantity of the calcined duck eggshell catalyst (CaO) was added to the required quantity of methanol and then mixed very well. The mixture was continuously stirred and then added to the hot esterified oil (60 ^{0}C), for transesterification reaction to take place.Considering the Tagushi experimental design, each of the experimental runs was maintained at the required reaction time, expected methanol/oil mole ratio, constant temperature of 60^{0}C and constant stirring rate of 600 rpm. After the reaction, biodiesel obtained was separated from the by-product (glycerol), CaO catalyst and the excess methanol (the separation was made easy by considering their different densities).

3. Results and discussion

3.1. GCMS Analysis

The results of the GCMS analysis on PKO are as shown in Figure 1 and Table 1. The results showed that PKO contains mainly saturated fatty acids.78.93% of the fatty acids were saturated fatty acids, monosaturatedacids (oleic and eicosenoic) were 17.06 while polysaturated fatty acids (linoleic and linolenic) were 4.01%. The result also showed that lauric acid (42.19%) was more than any other acid in PKO. This result was in conformity with the results obtained by some researchers [7, 14].

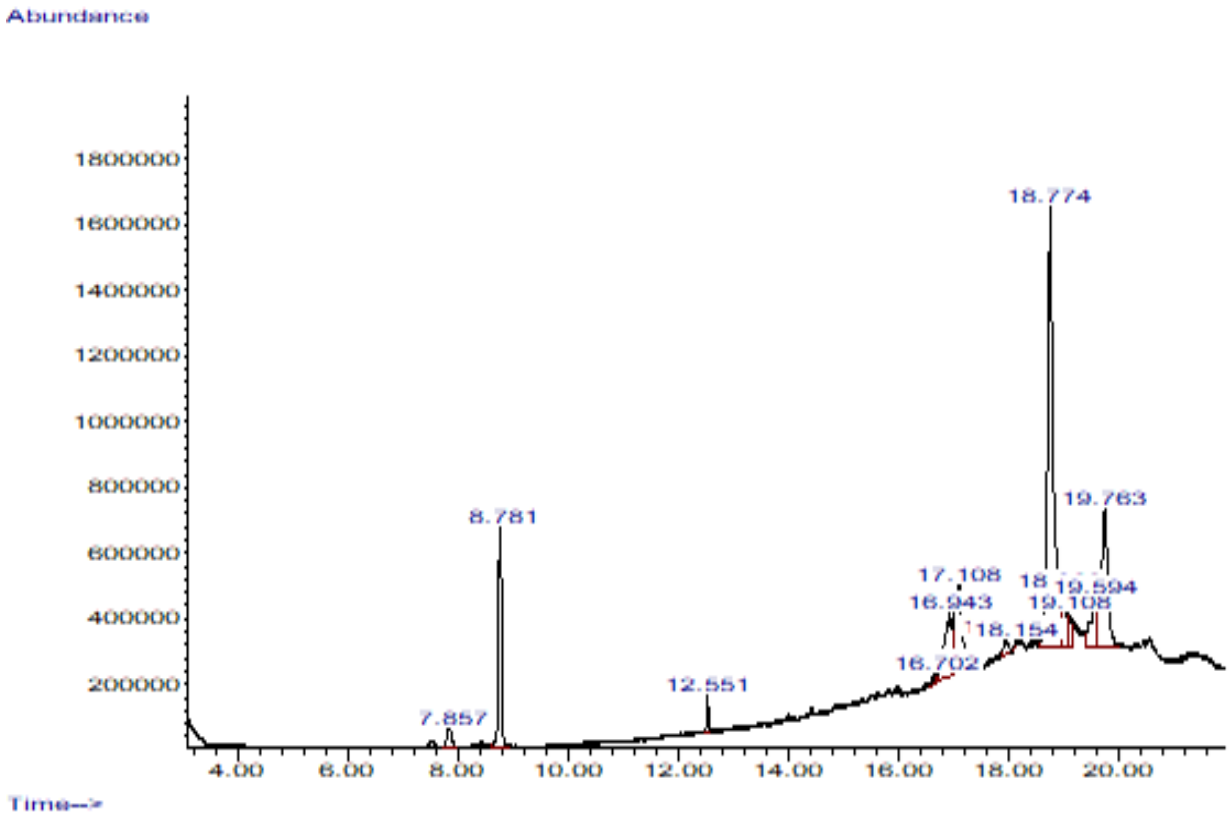

Figure1: GCMS analysis of PKO fatty acid compositions

Table 1: PKO fatty acid composition

Peak Number	Retention Time (min)	Component	Formula	Structure (C:n)*	Composition (%)
1	7.857	lauric	$C_{12}H_{24}O_2$	12:0	42.19
2	8.781	myristic	$C_{14}H_{28}O_2$	14:0	16.31
3	12.551	palmitic	$C_{16}H_{32}O_2$	16:0	9.03
4	16.702	capric	$C_{10}H_{20}O_2$	10:0	2.98
5	16.946	caprylic	$C_8H_{16}O_2$	8:0	3.22
6	17.108	stearic	$C_{18}H_{36}O_2$	18:0	2.04
7	18.154	oleic	$C_{18}H_{34}O_2$	18:1	15.67
8	18.215	linoleic	$C_{18}H_{32}O_2$	18:2	3.40
9	19.108	linolenic	$C_{18}H_{30}O_2$	18:3	0.61
10	19.594	arachidic	$C_{20}H_{40}O_2$	20:0	3.16
11	19.763	eicosenoic	$C_{20}H_{38}O_2$	20:1	1.39

*C = number of carbon present and n = number of double bonds

3.2 CaOCatalyst characterisation

Figure 2 showsthe XRD analysis of the CaO catalyst obtained from calcined duck eggshell. The diffratogram patterns revealed major peak values 2θ of 28.0, 30.0, 37.0, 54.5 and 64.5 and 67.0. These values correspond to the characteristic values of CaO, in conformity with the results reported in the literatures [5, 14].

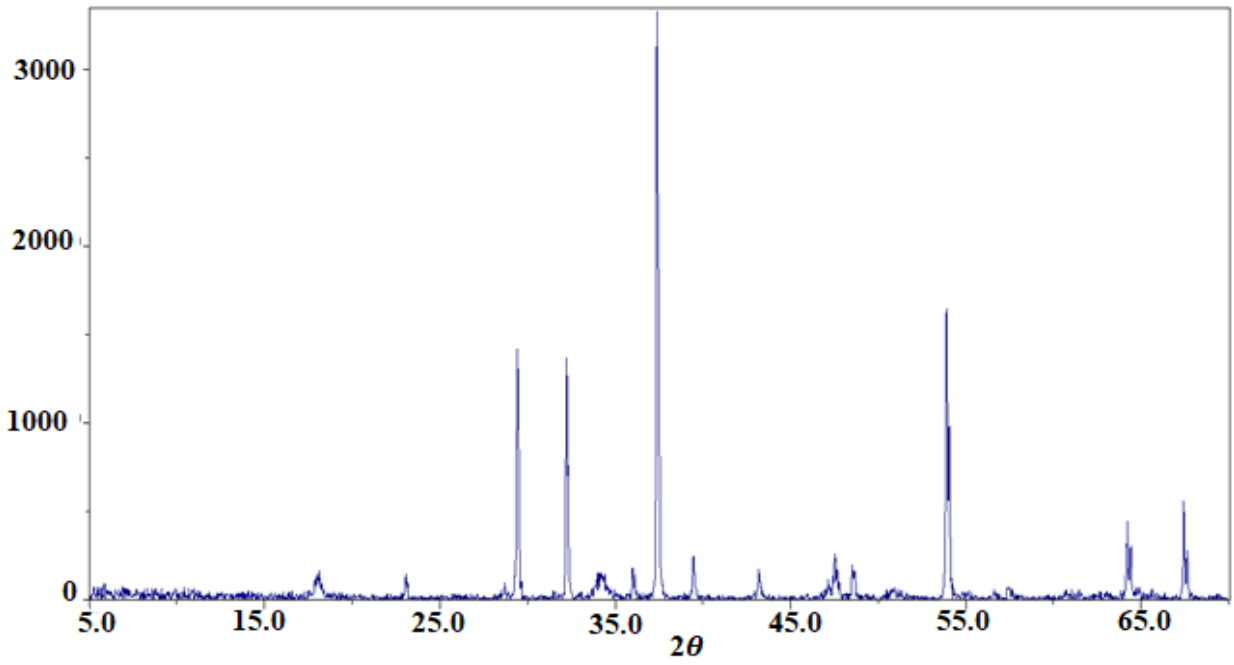

Figure 2: XRD analysis of the calcined duck eggshell (CaO) catalyst

Table 2 shows the results of XRF analysis of the CaO catalyst. The analysis revealed very high value (94.75%) of CaO composition in the calcined duck eggshell. This results justifies the fact that the CaO production process has high level of reliability.

Table 2: XRF and some properties of duck eggshell catalyst

Property	Value obtained (%)
CaO	94.75
P_2O_5	2.03
MgO	1.05
Al_2O_3	1.02
Na_2O	0.37
Mn_2O_3	0.46
K_2O	0.32

3.3The effects of the process variables on biodiesel yield

The biodiesel yields obtained from the experimental runs were shown in Table 3. The main interactive effects ofthe variation of catalyst concentration (3 – 9 wt./wt. %), reaction time (1 – 3 hrs) and methanol to oil mole ratio (10 – 16) on biodiesel yields, using calcined duck eggshell catalyst (CaO), were shown in Figures3.

The main effects plots showeda steady increase in biodiesel yield foran increase in CaO catalyst concentration between 3 and 9 wt./wt%. An indication that the catalytic behaviour of CaO improved with increased quantity. Also, it was observed that an increase in the reaction time up to 2 hours increased biodiesel yield. But further increase in reaction time resulted into lower biodiesel yield. This could be explained in term of the reversibility nature of the transesterification process. That is, increase in the reaction time beyond 2 hours led to backward reaction which is the conversion of biodiesel produced into the reactants, thereby reduced the biodiesel yield[7,13].

Methanol/oil mole ratio increased biodiesel yield up to 13, additional methanol quantity added only inhibited the reaction by not taking part in the reaction but later obtained as excess methanol (unwanted by-product). This finding is in agreement with the results obtained from the literatures. That is,13 mole ratio of methanol and oil is the appropriate mole ratio obtained using heterogenousCaOcatalyst [7,13].

Table 3: Tagushi design method and biodiesel yields obtained

Catalyst concentration (wt./wt. %)	Reaction Time (hr.)	Methanol/Oil mole ratio	Biodiesel Yield (%)
3	1	10	74
3	2	13	81
3	3	16	69
6	1	13	82
6	2	16	84
6	3	10	75
9	1	16	80
9	2	10	85
9	3	13	84

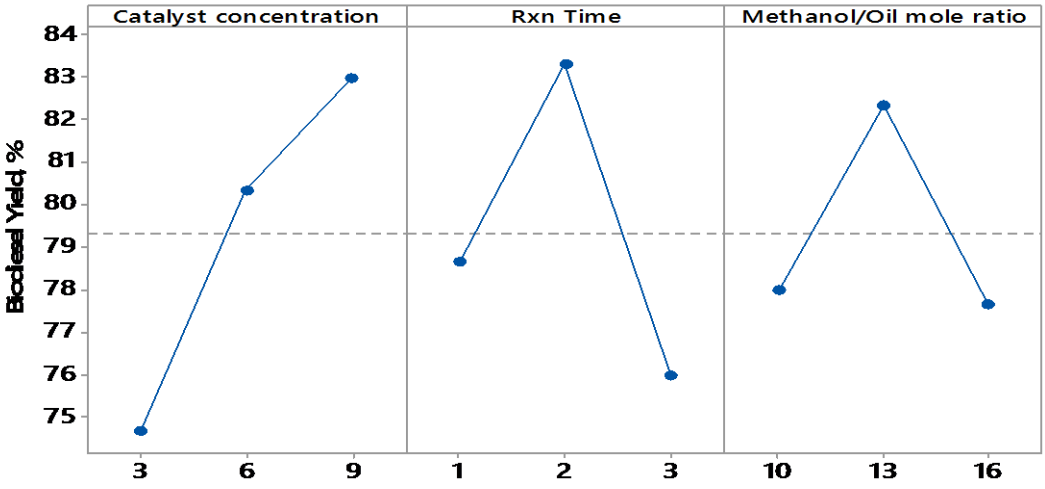

Figure3: The main effects of the three processing variables on biodiesel yields

The interactive effects of the processing variables, as expressed in contour plots, are shown in Figures4&5. In Figure4, the yield of biodiesel was highest (85%) when the catalyst concentration used was between (8 – 9) wt./wt. % at thereaction time of (2.0 – 2.5) hours.And the least yield of 70% was recorded at the CaOcatalyst concentration of (3.0 – 3.5) wt./wt. % and reaction time of 3 hours and beyond. These results further confirm the results obtained from main effect plots.

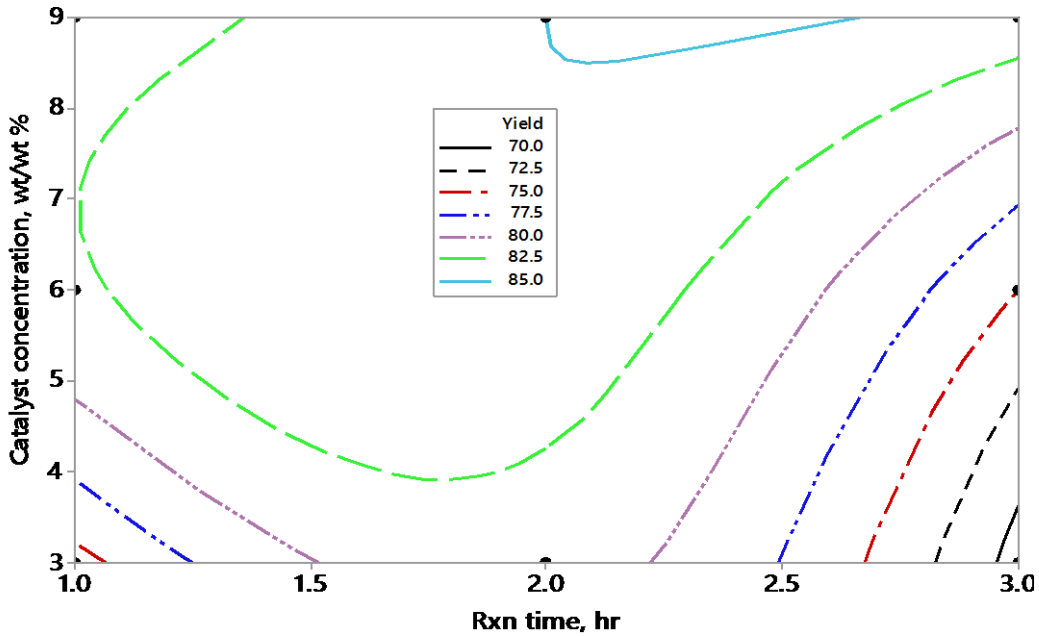

Figure 4: The interactive effects of the concentrations of the catalyst and time of reaction on yields

The combined effects of the catalyst concentration and methanol to oil mole ratio on the yield of biodiesel showed that the highest yield of biodiesel (82.5%) was obtained at methanol to oil mole ratio of 13 and (7 – 9) wt./wt/ %CaO catalyst concentration (Figure 6).

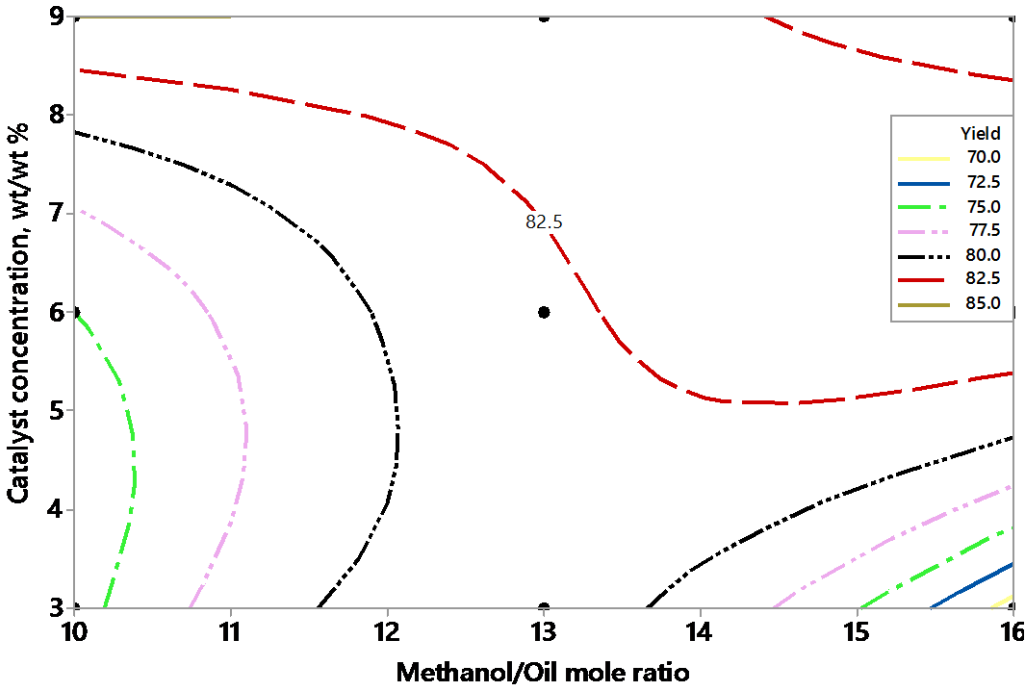

Figure 5: The interactive effects of the concentration of the catalyst and methanol to oil mole ratio on the yields

3.4 Regression model of the yield

Model that established the relationship between biodiesel yield (response) and the process variables (catalyst concentration, X1; reaction time, X2; and methanol to oil mole ratio, X3) was formulated (Equation 1). The accuracy of the model in the formulation and prediction of the relationship between the yield and the process variables was confirmed by the high value of **0.99** of the ***R-sq***(regression coefficient) and low value of percentage average absolute deviation of **(%ADD)** of **0.04%,** as shown in Table 4 and Equation 2. These results confirm a good correlation between the experimental data and the predicted data.

Biodiesel Yield = -18.11 + 1.667X1 + 17.50X2 + 10.78X3 + 0.2222X1X1 + 3.000X1X2
- 0.7778X1X3- 2.500X2X2 - 2.333X2X3***Equation1***
R- sq = 0.99

Table 4: Percentage Average Absolute Deviation of the model

X1	X2	X3	Exp. Yield (%)	Calc. Yield (%)	Deviation (d)
3	1	10	74	74.02	0.02
3	2	13	81	81.03	0.03
3	3	16	69	69.05	0.05
6	1	13	82	82.03	0.03
6	2	16	84	84.04	0.04
6	3	10	75	75.03	0.03
9	1	16	80	80.04	0.04
9	2	10	85	85.02	0.02
9	3	13	84	84.04	0.04
714	**714.30**		**0.30**		

X1 = Catalyst concentration, X2 = Reaction time and X3 = Methanol/Oil mole ratio

$$\text{Percentage Average Absolute Deviation (\% AAD)} = \frac{\sum(d)}{\sum(\text{Exp .Yield })} X\ 100$$

$$\% \text{ AAD} = \frac{0.30}{714} X\ 100 \quad = 0.04\ \%$$

3.5 Properties of biodiesel produced

Table 5 shows the properties of biodiesel produced, using ASTM specifications.The values of the properties obtained revealed that quality biodiesel was obtained. This is because the values obtained were within the ASTM standard values.

Table 5: Properties of biodiesel produced

Viscosity @40^{0}C	**Flash pointPour point**	**DensityWater @25^{0}C**	**content**
ASTM code	D445D935	D97D1298	D2709
ASTM std.value	(1.9 – 6.0)	≥ 93≤ -4	(0.860 – 0.890) ≤ 0.05
Value obtained	4.1 mm^2/s	195^{0}C	-7 0.869g/cm^3 0.045 v/v %

4. Conclusion

This research work reveals that the conversion of waste duck eggshellsinto a suitable CaOcatalyst for biodiesel production is not only feasible, but can also lead to high quantity and quality CaO catalyst production, as revealed by both XRD and XRF results. Also, at the prevailing experimental conditions, high quantity and quality PKO biodiesel were produced, as justified by both the yields and properties of the biodiesel produced. Also, high biodiesel yield of 84% can be obtained at catalyst concentration of 9 wt./wt. %, reaction time of 2 hours and methanol/oil mole ratio of 13, using CaO catalyst.

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