

OPTIMIZATION OF BIODIESEL PRODUCTION CATALYSED BY CALCIUM OXIDE OBTAINED FROM WASTE EGG SHELL USING SURFACE RESPONSE METHODOLOGY

Bankole MT^{1,3}, *Tijani JO^{1,3}, Abdulkareem AS^{1,2} and Lawal MA¹

¹Department of Chemistry, Federal University of Technology Minna, P.M.B. 65, Niger State, Nigeria

²Department of Chemical Engineering, Federal University of Technology Minna, P.M.B. 65, Niger State, Nigeria

³Nanotechnology Research Group, Center for Genetic Engineering and Biotechnology, Federal University of Technology Minna, P.M.B. 65, Niger State, Nigeria

^{1,3} jimohtijani@futminna.edu.ng

* Corresponding author

Abstract

This study focused on the optimization of biodiesel production via the transesterification process of groundnut oil catalysed by CaO prepared from waste egg shells. The prepared solid calcium oxide catalyst was characterised for its morphologies, crystallinity and specific surface areas by High Resolution Scanning Electron Microscope (HRSEM), X-ray diffraction (XRD) and Brunauer–Emmett–Teller (BET). The effects of temperature, reaction time and stirring speed on the biodiesel yields using central composite designs were investigated. The XRD and HRSEM analysis revealed the formation of a highly crystalline CaO with agglomerated honey comb web morphology. The optimum applied experimental condition to obtain the highest biodiesel yield of 92.83% using highly active CaO catalyst were temperature (60 °C), reaction time (3 hrs) and stirring speed (600 rpm). The reaction time and temperature are inversely proportional and exerted greater influence on the yield of biodiesel than the stirring speed. It can be deduce from various analysis conducted that the waste egg shell can be utilized as a catalyst for biodiesel production.

Keywords: Biodiesel, calcium oxide, Egg shell, groundnut oil, optimisation

1. Introduction

There is a growing concerns for an alternative renewable energy sources to petroleum fuels across the globe as a result of increasing demand for fossil fuels characterized with high cost, inadequate supply, non-renewability and negative environmental impact on human and other ecological species (Leandro *et al.*, 2017). The issue of environmental pollution specifically land deterioration and degradation caused by the exploration and exploitation processes of fossil fuels has become worrisome (Leandro *et al.*, 2017; Niju *et al.*, 2014). In addition, high cost of conventional chemicals used as catalyst in the production of biodiesel remains a hurdle, which invariably contributed to high production cost of diesel engines (Bello and Daniel, 2015). Thus, the production of a cleaner-burning alternative fuel similar to petroleum diesel is considered necessary. Biodiesel is a biodegradable, environmental friendly, renewable and non-toxic fuel with low emission profile compared to petrol diesel mostly used for diesel engines (Ellabban *et al.*, 2014). Biodiesel production involving the use of edible or non-edible oils feedstock including animal fats, fish oil can be achieved using transesterification process catalysed by either homogeneous or heterogeneous catalysts. Homogenous catalysts include NaOH, KOH, while heterogeneous catalysts are CaO, MgO, and hydrotalcite amongst others (Abdulkareem *et al.*, 2012; Niju *et al.*, 2014; Renita *et al.*, 2016). Transesterification process involves the application of homogeneous alkali based catalyst which transformed the feedstock within shorter reaction time into high quality biodiesel at a relatively low temperature (Jazie *et al.*, 2013). Invariably, the homogeneous process mostly results to higher yields provided the content of free fatty acids (FFAs) in the used feedstock is less than 1 %, compared to the heterogeneous catalytic transesterification (Karmakar *et al.*, 2010). The homogeneous catalytic process has some inherent shortcomings such as the post-separation issues of the applied catalyst after reaction, non-reusability nature, purification problems,

generation of excessive wastewater, as well as high energy consumption (Niju *et al.*, 2014; Sharma and Singh, 2010). In order to solve the highlighted problems stated above, heterogeneous catalyst was discovered and researchers have utilised this catalyst type for biodiesel production (Alamu *et al.*, 2010). Heterogeneous catalyst are preferable to homogeneous due to the ease of catalyst recovery and purification, production of less wastewater, reusability potentials, and less consumption of energy (Ramezani *et al.*, 2010). In spite of the several benefits associated with the use of heterogeneous catalysts for biodiesel production, proper identification of a solid based catalyst that will enhance the transesterification process and obtain high yield biodiesel under mild reaction conditions constitutes a problem (Ojolo *et al.*, 2011).

Among the solid base catalyst, alkaline earth metal oxides such as calcium oxide (CaO) of high basicity are considered appropriate heterogeneous catalyst to catalyse feedstock conversion to biodiesel (Mohadi *et al.*, 2016; Navajas *et al.*, 2013; Renita *et al.*, 2016). For instance, Nakatani *et al.*, (2009) obtained 73.8% biodiesel yield during the transesterification of soybean oil catalysed by 25% weight CaO obtained from oyster shells over reaction time of 5 hrs. Niju *et al.*, (2014) employed 8% white bivalve clam shell as catalyst for the conversion waste frying oil of biodiesel and reported biodiesel yield of 95.84% within 3 hrs reaction time. In this study, Ground nut (*Arachis hypogea*, L.) which belongs to the leguminosae family was used as a feedstock to produce Biodiesel due to its availability and abundance in Nigeria. Groundnut oil is otherwise categorised as the oleic-linoleic acid oil containing a comparatively significant amount of unsaturated fatty acids namely the monounsaturated oleic acid as well as the polyunsaturated linoleic acid (Suleiman *et al.*, 2012). In addition, indiscriminate dumping of waste eggshell constitutes an environmental nuisance and conversion of the waste eggshells with catalytic activity can mediate transesterification reaction and aids in abatement of environmental pollution (Wei *et al.*, 2009).

In spite of several research work done on waste eggshell catalysts for biodiesel production, the survey of literature reveals that there is scanty information on the influence of process parameters such as stirring speed, stirring time and reaction temperature on the yield of biodiesel from groundnut oil catalysed by CaO prepared from waste egg shells. Therefore, this present study is focused on the application of surface response methodology in the optimisation of aforementioned process parameters on the yield of biodiesel from groundnut oil catalysed by CaO obtained from waste egg shells. The result obtained in this study was compared with commercially available NaOH, KOH, MgO and CaO for the transesterification of groundnut oil. The morphologies, mineralogical phases and surface areas of the prepared CaO were characterized by High Resolution Scanning Electron Microscopy (HRSEM), X-ray diffraction (XRD) and Brunauer–Emmett–Teller (BET).

2. Methodology

2.1 Materials

The groundnut oil was bought from Bosso market, Minna metropolis. Waste chicken eggs were randomly collected from different location in Kure market, Minna Niger state. All other chemicals were of analytical grade (AR), methanol (99.9%), alcoholic KOH (>85%) and potassium iodide (99.9%) supplied by Sigma-Aldrich. The reagents were used as supplied without further purification.

2.2. Sample Pre-treatment

The collected Ground nut oil was filtered using filter paper (0.7 μ m) to remove suspended particles and kept in the water bath at 110°C for 4 hrs to get rid of the moisture. The waste egg shells (70 g) were washed with distilled water to remove impurities and dried in an oven at 110 °C for about 8 hrs. The dried eggshells were ground to fine powder and sieved using a 200 μ m mesh sieve and were used as a raw material in the production of catalyst.

2.3. Physico-chemical characterisation of ground nut oil

The physico-chemical characterisation of the ground nut oil was carried out using standard methods to determine the following parameters: free fatty acid value, saponification value, viscosity and iodine value (Association of Official Analytical Chemists, 2012).

2.4. Catalyst preparation

The solid metal oxide catalyst (CaO) was prepared using calcination of the waste egg shells. The fine powdered dried egg shells of approximately 30 g placed in a quartz boat were calcined in a muffle furnace under static air conditions at 900 °C for 4 hrs decompose the calcium species in the egg shell into CaO particle as shown in equation 1.



The calcium based oxides from the egg shells were refluxed in distilled water at 50 °C for 6 h and thereafter filtered and then dried in oven at 120 °C for 6 hrs. Again, the solid particle was dehydrated by performing calcination at 600 °C for 3 hrs to transform the hydroxide material to oxide form. The calcium oxide obtained after decomposition was used as the catalyst for transesterification reaction.

2.4.1. Characterization of the prepared CaO

The mineralogical phase of synthesized solid metal oxide (CaO) was determined by powder X-ray diffraction (XRD; PW 1800 diffractometer, Philips, Netherlands) analysis performed on a Bruker AXS D8 Advance with Cu-K α radiation. A portion of the solid metal oxides were sprinkled on a de-greased glass slide and diffractograms were recorded between diffraction angles of 200 and 800. The morphology of the synthesised materials was examined using Zeiss Auriga HRSEM. A mass of 0.05 mg powdered sample was sprinkled on carbon adhesive tape and sputter coated with Au-Pd using Quorum T150T for 5 minutes prior to analysis. The microscope was operated with electron high tension (EHT) of 5 kV for imaging. For BET N₂ adsorption, about 100 mg of the dry powder sample in a sample tube was first degassed at 90° C for 4 hours to remove residual water and other volatile components that were likely to block the pores. The BET surface area and average pore volume distributions were obtained from the plot of volume adsorbed (cm³/g STP) versus relative pressure. The N₂ adsorption-desorption isotherms were collected at -196° C using Brunauer-Emmett-Teller (BET; NOVA 4200e, Quantachrome Instruments, USA).

2.4.2. Optimization of biodiesel yield using Response surface methodology

Surface response methodology was applied to optimise the biodiesel production and to check the influence of process parameters such as stirring speed, stirring time and temperature of the transesterification process on the yield of the biodiesel. A 2³ Central Composite Design (CCD) of experiment was used where three factors each at lower and upper levels) were chosen. The factors are temperature (°C), time (hours) and stirring speed (rpm). The range of temperature, reaction time and stirring speed were chosen as follows; 60 °C – 80 °C, 1hr - 3hrs and 200 rpm – 600 rpm. Six centre points were considered, plus four low points and four high points and six alpha points making a total of twenty experimental runs carried out. The details are presented in Table 1.

Table 1: Influence of process parameters on Biodiesel yield using surface response methodology

Run	Factor 1 Temperature (°C)	Factor 2 Time (hour)	Factor 3 Stirring speed(rpm)	Response yield (%)
1	70	3.68	400.00	15.35
2	80	1	600.00	25.20
3	70	2	400.00	50.12
4	70	2	63.64	25.20
5	60	1	600.00	69.03
6	70	0.32	400.00	30.45
7	70	2	736.36	55.35
8	70	2	400.00	50.52
9	60	3	200.00	90.12
10	53.18	2	400.00	85.04
11	80	3	600.00	14.78
12	80	1	200.00	31.95
13	86.82	2	400.00	10.75
14	70	2	400.00	50.43
15	60	1	200.00	64.85
16	70	2	400.00	50.32
17	60	2	400.00	85.75

18	80	3	200.00	18.98
19	70	2	400.00	50.82
20	60	3	600.00	92.83

2.4.3. Transesterification procedures

Approximately, 2 g of CaO (catalyst) was added to 19.2 ml of methanol in a conical flask and stirred vigorously separately at a speed of (200, 400 and 600 rpm) on a magnetic stirrer until the CaO dissolved. Furthermore, the transesterification reaction was carried out in a 250 ml conical flask equipped with a thermometer and magnetic stirrer. 80 ml of groundnut oil was put into the conical flask and heated to 70 °C. Thereafter, the catalyst solution was gently poured into the conical flask containing the oil. The temperature of the system was maintained individually at (60, 70 and 80 °C), stirring speed of (200, 400 and 600 rpm) and the reaction was monitored for (1hr, 2 and 3 hrs). After the completion of the reaction, the product settled for 24 hours and the catalyst and the transesterification product was separated using a separating funnel. The clear upper layer containing the Fatty Acid Methyl Esters (FAME) was biodiesel while the lower dense layer was the glycerol. The biodiesel was screened using filter paper (0.7µm) in order to remove suspended particles (catalyst) and further washed with warm distilled water to remove glycerol and impurities. Thereafter, the biodiesel was immersed in water bath at 110°C to evaporate the residual methanol. The quantity of biodiesel yield for each run was determined using the following formula

$$\text{Biodiesel yield} = \frac{\text{Volume of biodiesel produced}}{\text{Volume of Oil used}} \times 100\% \quad (3)$$

2.4.4. Characterisation of the biodiesel yields

The highest and lowest yield of biodiesel produced were characterised for its kinematic viscosity at 40°C, specific gravity, flash point, acid value, saponification value, iodine value pour point, cloud point and smoke point in accordance with the ASTM protocols. While the Cetane number was determined according to the equation 4 proposed by Alamu *et al.*, (2010).

$$\text{Cetane number (CN)} = \text{CI} - 1.5 \quad (4)$$

$$\text{Where Cetane index (CI)} = \frac{46.3 + 5458}{\text{SV}} - 0.225 \text{ IV} \quad (5)$$

Where SV= saponification value of the biodiesel and IV= Iodine value of biodiesel

3.0. Results and Discussion

3.1. Groundnut oil characterisation

The composition of groundnut oil was determined as explained in section 2.3 and the characterisation result is shown in Table 2.

Table 2: Physico-chemical properties of groundnut oil

S/No	Parameters	Obtained values
1	Saponification value (mgKOH/g)	193.2
2	Acid value(mgKOH/g)	4.58
3	Iodine value(mgI ₂ /g)	84.24

4	Specific gravity(g/cm ³)	0.94
5	Free fatty acid value (FFA) (%)	2.29
6	Kinematic viscosity @ 40°C	38.50
7	Pour point (°C)	6
8	Flash point (°C)	178

According to Table 2, the FFA of the groundnut oil was determined to be 2.29% and high FFA above 1% reduce the efficiency of homogeneous catalyst and affects the biodiesel yield (Wanodya and Budiman, 2013). On the contrary, studies have shown that heterogeneous catalysts could catalyse oil with FFA in the range of 6% - 15% without any pretreatment (Bello and Daniel, 2015). In the same vein, Bello and Agge, (2012) found that groundnut oil with FFA >3% produced more than 90% biodiesel under the following reaction conditions (temperature 60 °C, reaction time 3 hrs, catalyst weight of 2%). This shows the ground nut oil used in this study is a useful feedstock for biodiesel production. Furthermore, the specific gravity of the oil was determined to be 0.94, which shows that water is heavier than the oil. The iodine value of 84.24 mgI₂/g is an indication of low level of saturation. The saponification value indicates the ability of the oil to form soap during transesterification process. High saponification value suggests the presence of fatty acid that could be transformed into soap and hence low yield of biodiesel. The saponification value of the groundnut oil was 193.2 mg/KOH, which means the oil has a tendency of soap formation.

3.2. X-ray Diffraction analysis of the calcined eggshells

The XRD pattern of the calcined eggshell at 900°C for 4 hours is display in Figure 1. As shown in Figure 1, the presence of intense and sharp diffraction peak at $2\theta = 34.2^\circ, 47.4^\circ, 53.7^\circ, 55.6^\circ, 63.9^\circ,$ and 74.3° with a crystal plane of (200), with a corresponding crystal planes (200), (220), (311), (221), (222) and (210) were assigned to CaO. The diffraction peak of low intensity observed at $2\theta = 29.4^\circ$ in the XRD pattern indicates the formation of Ca(OH)₂. The presence of Ca(OH)₂ in the XRD spectra is an indication of interaction of CaO with water vapour on the air, which further show that the CaO is highly hydroscopic in nature. The observed peaks are similar with those reported by Wei *et al.*, (2009) and Sharma and Singh, (2010) under similar conditions although with different type of eggshells. This further demonstrates that the difference in the composition eggshell did not affect the mineralogical phase present in the calcined sample. Therefore, the same calcination process can be used to obtain CaO catalyst regardless of type of eggshell (Navajas *et al.*, 2013).

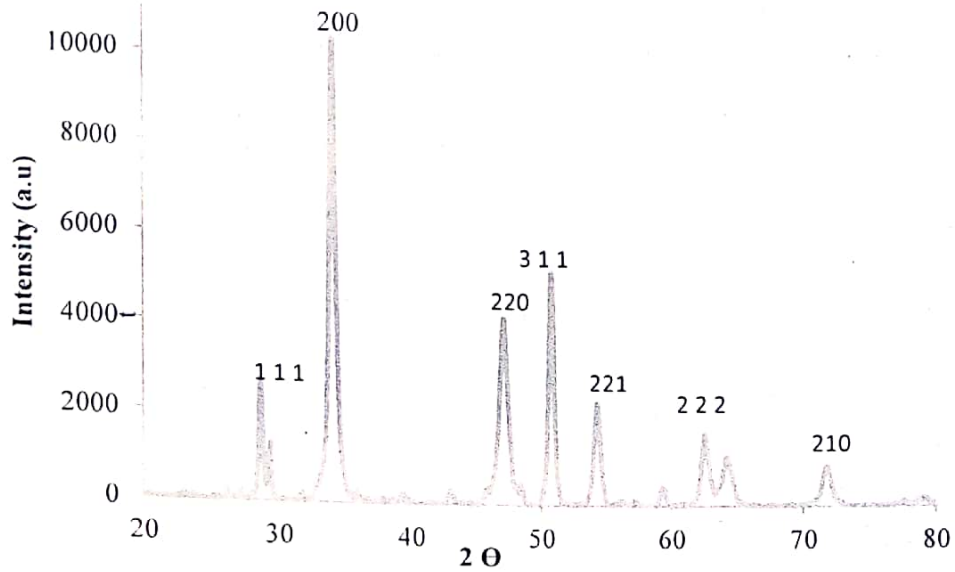


Figure 1: XRD spectrum of the calcined calcium oxide particles at 900 °C

3.3 HRSEM analysis of the prepared CaO

Figure 2 shows the low and high magnification images of the CaO catalyst obtained from the calcination of egg shells at 900 °C.

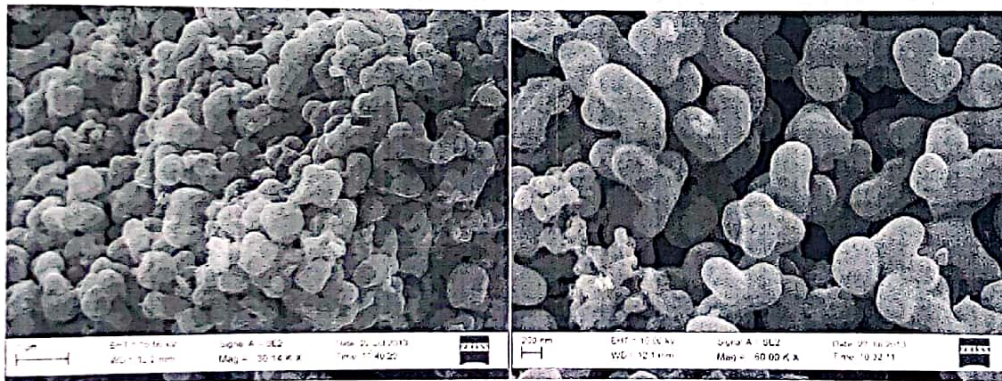


Figure 2: HRSEM micrographs of the calcined calcium oxide particles at (a) low magnification (b) high magnification

Figure 2 demonstrates the presence of agglomerated homogeneously distributed honey comb web- like morphology. The porous honey comb-like morphology is similar to the shape of CaO obtained from egg shells after calcination at 900 °C for 2.5 hrs (Niju et al., 2014).

3.4. BET surface area of the CaO obtained from waste egg shells

Table 3 shows the specific surface area of the prepared CaO in comparison with the commercial CaO.

Table 3. Specific surface area of the as-prepared CaO and commercial CaO

Parameters	As-prepared CaO	Commercial CaO
BET surface area (m ² g ⁻¹)	4.041	3.012
Pore volume (cm ³ g ⁻¹)	1.356	1.216

According to Table 3, it can be noticed that the surface area of as-prepared CaO in this study is slightly higher than that of commercial CaO. This implies that the catalytic activity of CaO prepared in this study will be higher than that of commercial CaO. The value obtained is closely related to what was reported by Niju et al., (2014).

3.5. Statistical analysis from RSM

The following parameters such as temperature, reaction time and stirring speed were chosen as independent variable in the production of biodiesel catalysed by CaO from waste egg shells with biodiesel yield as a dependent variable. A set of 20 experiments were carried out as shown in Table 1. The model was statistically significant with 95% confident level and all three independent variables exhibited positive effects on the biodiesel yield. The model was assessed with coefficient of determination ($R^2=0.9563$). Based on the CCD design and result of experiments (Table 1), regression analysis generated the following quadratic regression model data (based on the coded factors)

$$R_1 = 50.07 - 25.69X_1 + 0.021X_2 - 2.72X_3 - 9.06X_1X_2 - 2.23X_1X_3 + 0.14X_2X_3 + 0.42X_1^2 - 8.4X_2^2 + 6.53X_3^2 \quad (6)$$

Where R_1 indicates the yield of biodiesel (%); X_1 temperature (°C); X_2 reaction time (hour); and X_3 stirring speed (rpm). The equation was used to analyse the response yield by multiple regression through the least square method. Using the above results, different effects of the independent variables on the response were studied by plotting a three-dimensional response surface based on the model equation.

3.5.1. Interaction of time and temperature

The optimum biodiesel yield from groundnut oil catalysed by CaO obtained from waste eggshell was 92.53% at a temperature of 60 °C, for 3 hours and with stirring speed of 600 rpm as shown in Table 1. The interaction of reaction time and applied temperature is shown in figure 3. As shown in Table 1, it was observed that the highest yield of biodiesel was observed at reaction time of 3 hrs (92%) at optimum temperature of (60 °C). The value obtained is closely related to 96% yield reported under similar condition (3 hrs at 60 °C) by Jazie *et al.*, (2013), though with a rapeseed oil using eggshell as catalyst. In the same vein, Ramezani *et al.*, (2010) also reported 87.30% yield of biodiesel using homogeneous catalyst (KOH) under similar condition (2 hrs, at 65 °C) with castor oil. With continuous increase in reaction time (>3 hrs) (Figure 3), the yield decreases due to loss of solvent in the reaction medium. Conversely, increase in the applied temperature with other conditions constant; corresponded to decrease in biodiesel yield. Specifically, at temperature of 60 °C, a reasonable yield of biodiesel (50.12%) was obtained at time (2hrs), while 30% yield of biodiesel was obtained at temperature of 80 °C. This suggests that the biodiesel yield decrease with increasing temperature. Thus, the reaction time and temperature are inversely proportional and increase in one of the parameters beyond optimal value corresponds to decrease in the yield of biodiesel.

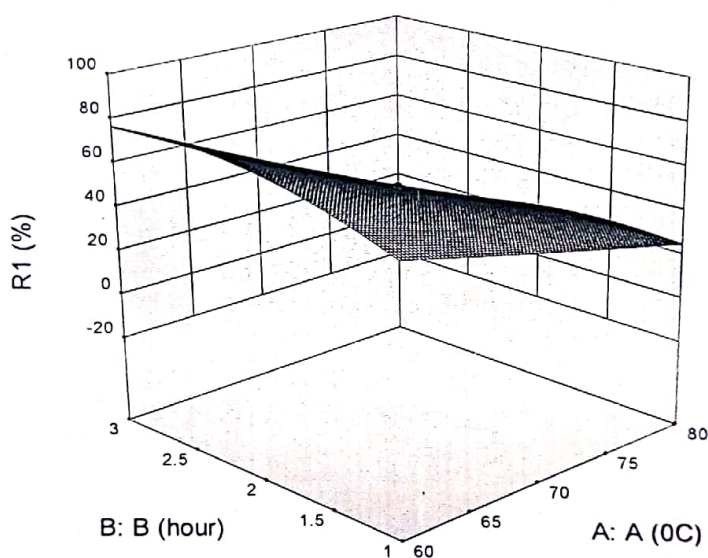


Figure 3: Interaction of time and temperature, where A-axis represents the temperature and B-axis depicts reaction time

3.5.2. Interaction of time and stirring speed

Figure 4 shows the influence of interaction of reaction time and stirring speed on the biodiesel yields. It can be observed that an increase in reaction time (1-3 hrs) is directly proportional to the biodiesel yield whereas an increase in the stirring speed (200 rpm-600 rpm) had little effect on the biodiesel yield. This implies that the stirring speed did not follow a specific trend and exert no significant effect on the yield of biodiesel. In figure 4, the optimal yield of biodiesel was obtained at 3 hrs with a corresponding stirring speed of 600 rpm. However, there is no much disparity in the biodiesel yield obtained using either a stirring speed of 400 rpm or 600 rpm. According to Table 1 and Figure 4, when the reaction time was 1 hour, temperature (60 °C) and stirring speed of 600 rpm (experimental runs 5), the yield of biodiesel was 69.03%, while at same

temperature and reaction time with stirring speed of 200 rpm (experimental runs 15), the yield of biodiesel was found to be 64.85%. The yield obtained at experimental runs 5 is slightly higher than that of experimental runs 15 due to difference in the stirring speed. This suggests effective interaction between the catalyst, oil and methanol at 600 rpm and slow diffusion reaction at 200 rpm. Furthermore, when the stirring speed was 200 rpm at constant reaction time of 3 hrs, (experimental runs 9 and 18) with different applied temperature of 60 °C and 80 °C, the yield of biodiesel was 90.12% and 18.98%. Similarly, when the stirring speed was 200 rpm, reaction time 1 hr, under the same temperature (experimental runs 9 and 18), and the biodiesel yields were 31.95% and 64.85%. This means under the same stirring speed, the biodiesel yields fluctuate possibly due to different in the applied temperature and reaction time.

Also, there were no much differences in the yield of biodiesel when the stirring speed was 400 rpm and even 600 rpm. When the stirring speed was 400 rpm irrespective of the temperature and reaction time, the yield of biodiesel were 15.35%(experimental runs 1), 50.12% (experimental runs 6), 50.52% (experimental runs 8), 85.04% (experimental run 10), 31.95%(experimental run 12), 10.75% (experimental run 13), 50.43% (experimental run 14). This again shows that the variation of stirring speed on the yield of biodiesel did not follow a specific pattern. It was found that the yield of biodiesel reported by Fadhil *et al.*, (2016) slight higher than what was obtained in this study. The possible reason may be ascribed to differences in the stirring speed and catalyst types.

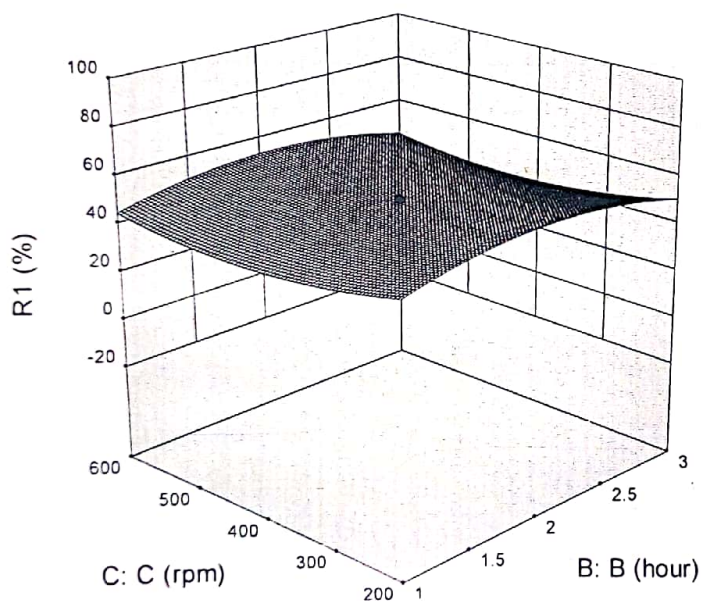


Figure 4: Effect of reaction time and stirring speed on the biodiesel yield, with C-axis stands for stirring speed while D-axis depicts

In summary, the highest biodiesel yield catalysed by CaO obtained from waste egg shells was 92.83% at runs 20 under the following reaction condition; temperature (60°C), reaction time (3 hrs) and stirring speed (600 rpm). While the least yield of 15.32% of was obtained at experimental runs 1 under the following condition of temperature (70°C), reaction time (3.68hrs) and stirring speed of 400 rpm. This implies that the optimal conditions to obtain greater yield of biodiesel are: stirring speed (200 rpm), reaction time (2 hrs) and temperature (60 °C). The statistical analysis of the experimental range revealed the order of significance of the independent variable as temperature > reaction time > stirring speed.

3.6. Characterisation of the prepared biodiesel properties

Table 4 shows basic properties of the prepared biodiesel in comparison with ASTM standards D6751

Table 4. Comparison of prepared biodiesel properties with ASTM standard

Properties	Values obtained Prepared biodiesel	ASTM D6751
Specific gravity (g/cm ³)	0.91	0.86 - 0.90
Kinematic viscosity @ 40°C	6.0	1.9 - 6.0
Flash point (°C)	135	100-170
Pour point (°C)	6.0	
Iodine value (mgI ₂ /g)	68.9	120
Cloud point (°C)	8.5	-3 to 12
Cetane number (min)	62.35	47

Key: ASTM= American Standard for Testing and Measurement

According to Table 4, the specific gravity of the biodiesel produced is 0.91 which fall within the ASTM standards range of 0.86 - 0.90. Also, the biodiesel flash point was 135 °C which is slightly higher than the ASTM limit of 130 °C. This signifies that the biodiesel could easily ignite into flame, though blending with conventional diesel is recommended to reduce the value. The biodiesel cloud point of 8.5°C which is less

than the ASTM value of 9 °C, implies that the biodiesel from groundnut oil could fit into regions with lower temperature. Kinematic viscosity is considered very important in the monitoring and performance evaluation of fuel injection system particularly at low temperatures. It can be observed that the viscosity of biodiesel fall within the range of ASTM and thus confirming the suitability of the prepared biodiesel as fuels in diesel engines. Cetane number is referring to the ignition delay time of a fuel when injected inside the combustion chamber or sometimes defined as the times it takes white smoke after start up, drivability before warm up and intensity of diesel knock at idle. The cetane number of the biodiesel was found to be 61.27, which fall within the ASTM limit of 47 min and hence compatible with diesel engines.

Table 5: Comparison of the biodiesel yield results of the previous and present study

Catalyst	Conditions of biodiesel production	Biodiesel yield (%)	Reference
NaOH	No optimization however catalyst dosage (0.7 g)	91.98	Ojolo <i>et al.</i> , 2011
NaOH	Reaction temperature (40°C), reaction time (1 hr 30 min), stirring speed (not studied), catalyst concentration (0.5wt %)	99	Abdulkareem <i>et al.</i> , 2012
NaOH	Reaction temperature (60°C), reaction time (1 hr), stirring speed (600 rpm), catalyst concentration (1 wt%)	68.7	Bello and Agge, 2012
KOH	Reaction temperature (60°C), reaction time (2 hrs), stirring speed (600 rpm), catalyst concentration (2.4 wt%)	75.22	Bello and Daniel, 2015

CaO from waste egg shells	Reaction temperature (60°C), reaction time (3 hrs), stirring speed (600 rpm), catalyst concentration (2.5wt %)	92.83	This study
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As shown in Table 5, it can be noticed that with the biodiesel yield obtained in this study based on surface response methodology competes favourably with the values reported in the literature. In some cases, the solid CaO catalyst exhibited higher catalytic activity than the commercial homogeneous catalysts such as KOH, NaOH. Conversely, the biodiesel yield reported by Abdulkareem *et al.*, (2012) and Muthu and Viruthagiri, (2015) is slightly greater than the observed yield in this study. The differences may be attributed to the longer reaction time used by Abdulkareem *et al.*, (2012) during the biodiesel production and higher catalyst concentration employed by Muthu and Viruthagiri, (2015) compared to reaction time of 3 hrs and 2.5 wt% catalyst concentration used in this study. Previous studies have shown that higher biodiesel yield is a function of reaction time and catalyst concentration.

4. Conclusion

In summary, CaO was obtained from waste egg shells via calcination process and subsequently utilised as a solid heterogeneous catalyst for the production of biodiesel from groundnut oil. Based on this study, the following conclusions were drawn. Groundnut oil served as a useful feedstock for biodiesel production. The XRD and HRSEM analysis demonstrated the formation of highly crystalline CaO resembling aggregated honey comb web. The optimum applied experimental conditioned to obtain high biodiesel yield of 92.83% using CaO of excellent catalytic activity were temperature (60 °C), reaction time (3 hrs) and stirring speed (600 rpm). The reaction time and temperature are inversely proportional to the yield of biodiesel and the order of contribution to biodiesel yield was as follows: temperature > reaction time > stirring speed. This study revealed CaO prepared from waste egg shells can serve as a substitute to commercially available homogeneous or heterogeneous solid catalyst. Finally, this study demonstrated for the first time that application of surface response methodology involving interactions of process parameters aids in the transformation of groundnut oil to biodiesel using CaO catalyst prepared from waste egg shell.

References

- Abdulkareem A.S, Jimoh A, Afolabi A.S, Odigire J.O and Odili O.C. (2012). Production and Characterization of Biofuel from Refined Groundnut Oil. Energy Conservation, Book Chapter Published by INTECH, Chapter 8, Pp. 197-220.
- Alamu, O.J. Waheed, M.A. and Jekayinfa, S.O. (2010). Biodiesel production from Nigerian palm kernel oil: effect of KOH concentration on yield. *Energy Sustainable Development*. Vol. 11 (3), 77-82.
- Bello E.I and Daniel, F (2015). Optimization of Groundnut Oil Biodiesel Production and Characterization. *Applied Science Reports*, Vol. 9 (3), 172-180
- Bello EI and Agge M. (2012). Biodiesel Production from Ground Nut Oil. *Journal of Emerging Trends in Engineering and Applied Sciences*, Vol.3 (2), 276-280.
- AOAC. (2012). Official Methods of Analysis of AOAC international. 19th edition. AOAC 54 International, Gaithersburg, Maryland, US
- Ellabban O, Haitham A and Blaaberg, F. (2014). Renewable energy resources:current status, future prospects and their enabling technology. *Reviews*, Vol. 39, 748-764.

- Fadhil, A.B., Aziz, A.M. and Al-Tamer, M.H (2016). Biodiesel production from silybum marianum L seed oil with high FFA content using sulphonated carbon catalyst for esterification and base catalyst for transesterification. *Energy Conversation Management*, Vol.108:255-65
- Jazie A., Pramanik H. and Sinha, S.S.K. (2013). Eggshell as Eco-Friendly Catalyst For Transesterification of Rapeseed Oil: Optimization for Biodiesel Production. *International Journal of Sustainable Development and Green Economics*, Vol. 2, 2315-4721.
- Karmakar A., Karmakar S. and Mukherje S. (2010). Properties of various plants and animals feedstocks for biodiesel production. *Bioresource Technology*, Vol.101, 7201-7210.
- Leandro MC, Juan AC, Enrique RC, Célio LC, I and Rodrigo SV (2017). Relevance of the Physicochemical Properties of Calcined Quail Eggshell (CaO) as a Catalyst for Biodiesel Production. *Journal of Chemistry*, Vol, Article ID 5679512, 12 pages
- Lee H.V., Yunus R., Juan J.C. and Taufiq-yap Y.H. (2011). Process optimization design for jatropha-based biodiesel production using response surface methodology. *Fuel Processing*, Vol.92, 2420-2428.
- Mohadi R, Anggraini K, Riyanti F, Lesbani A (2016). Preparation Calcium Oxide (CaO) from Chicken Eggshells. *Journal of Environment*, Vol.1(2): 32-35
- Muthu K and Viruthagiri T (2015). Optimization and production of biodiesel using calcium oxide as a heterogeneous catalyst. *Int. J. Chem. Sci*, Vol.13(3): 1357-1364
- Navajas A, Issariyakul T, Aramendi G, Gandia L.M, Dalai A.K. (2013). Development of egg shell derived catalyst for transesterification of used cooking oil for biodiesel production. *Asia-Pac. J. Chem. Eng.* Vol. 8, 742-748
- Nakatani N, Takamori H, Takeda K, Sakugawa H. (2009). Transesterification of soybean oil using combusted oyster shell waste as a catalyst. *Bioresources Technology*, Vol. 100,1510-1513.
- Niju S, Meera S, Begum KM, Anantharaman N. (2014). Modification of egg shell and its application in biodiesel production. *Journal of Saudi Chemical Society*, Vol. 5, 702-6.
- Ojolo SJ, Adelaja AO, Sobamowo GM (2011). Production of Bio-Diesel from Palm Kernel Oil and Groundnut Oil. *Advanced Materials Research*, Vol. 367, 501-506
- Ramezani K., Rowshanzamir S. and Eikani, M.H. (2010). Castor oil transesterification reaction: a kinetic study and optimization of parameters. *Energy*. Vol. 35, 4142-8
- Renita A, Chowdhury P.P, Sultana P, Phukan P, Hannan A (2016). Utilization of waste eggshells for production of renewable catalyst for transesterification. *International Journal of Pharmacy and Pharmaceutical Sciences*. Vol 8(7). 143-146
- Sharma Y.C. and Singh B. (2010). Development of biodiesel: current scenario. *Renewable and Sustainable Energy Reviews*, Vol.13, 1646-1651.
- Suleiman M.M, Bello A.U., Itumoh J.E, Bello K, Bello A.M and Arzika A.T. (2012). Physicochemical properties of some commercial groundnut oil products sold in Sokoto metropolis, Northwest Nigeria. *Journal of Biological Science and Bioconservation*, 4: 23-34