

## Preparation and Characterization of Calcium Oxide Heterogeneous Catalyst Derived from Guinea Fowl Egg Shell for Biodiesel Synthesis for a Sustainable Future

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### Abstract

Sustainable development turns out to be more and more central in the last few decades, in view of the fact that valiant steps are essential to guarantee the needs of future generations. The use of renewable sources for producing energy plays an important role to achieve sustainable development. There is a need to focus on non-edible oils for biodiesel production with a view of achieving sustainability. This research was conducted for the purpose of conversion of rubber seeds oil biodiesel via a transesterification with the use of guinea fowl eggshell wastes as raw materials for the preparation of heterogeneous catalyst in the biodiesel production. Proceeding to use, the calcium carbonate ( $\text{CaCO}_3$ ) content in the waste shell was converted to calcium oxide ( $\text{CaO}$ ) by calcining in a muffle furnace at high temperature of 900 for four hours. The catalytic activity of the catalyst in transesterification of RSO with methanol was evaluated, and the fuel properties of obtained biodiesel were measured. The effect of reaction time, reaction temperature, methanol/oil molar ratio, catalyst loading, agitation speed and reusability of catalyst was also investigated. The experimental result showed that 12:1 M ratio of methanol to oil, 1.5 wt.% catalyst, 64 reaction temperature, 2 hours' reaction time with speed of 250 rpm gave the best results. The  $\text{CaO}$  catalyst derived from waste calcined guinea fowl sustained a good catalytic activity even after being repeatedly used for 6 cycles with yield around 91%. The results reveal that both waste egg shell and rubber seed oil provides promising prospect for people to access cheap, reliable and clean energy in the future, which is one of the key elements to sustain healthy ecosystems and human life.

**Keywords:** *Biodiesel, Calcium oxide, Guinea fowl eggshell, Heterogeneous catalyst, Transesterification, Rubber seed oil*

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### **Background to the Study**

The continual rise in the world population, unsustainable extraction and consumption of fossil fuels has led to reduction in the underground carbon-based resources. This unsustainable consumption couple with the negative environmental effect has necessitated the search for alternative fuel from renewable sources. Despite the advances in exploration technologies, exploration is a business of diminishing return as less and less of oil is being found. In the last two to three decades, both society and governments have become aware of this issue and its effects on environment have led to quest for an alternative fuel which can replace or supplement fossil fuel. Biodiesel is considered as one of the most alternative fuel for diesel engines because they are nontoxic, renewable and biodegradable. One of the most effective ways to reduce the cost of biodiesel production is the use of non-edible oils, waste frying oil fish oil, and animal fats as raw materials. Chhetri et al, note that the price of edible plant and vegetable oils are usually higher than the conventional diesel. Edible vegetable oils like sunflower, soya bean, rapeseed, corn, and canola have been used for production of biodiesel. So far, above 95% of the global biodiesel production comes from the edible oil sources, in particular from the agricultural sector. This has led to the concern that the knock-on effect of this practice would be a global adverse food shortage. Abdalrahman et al., wrote that the fear resulted in instigating the research on biodiesel production to shift to non-edible seed oils and waste oils. The used oils which are cheap however, require a lot of effort and cost to refine them for good biodiesel production as they have high free fatty acid value which causes the formation of soap which affects the progress of the reaction and also the separation of the products.

Edible vegetable oils such as canola, corn, rapeseed, soybean and sunflower have been used for the production biodiesel. The non-edible vegetable oils like *Jathropha curcas*, calabash seed and others have also been found appropriate. Mustafa, [11] note that non-edible vegetable oils have been observed to be suitable for biodiesel production in developing countries. Besides, the world production and distribution of vegetable oils resources are dependent on climate, soil and socio-economic factors. There are two main issues that must be considered when selecting biodiesel as a substitute fuel; the costs of feedstock and the production process. These issues have led many researchers shifted to the non-edible seeds as potential biodiesel feedstock. Rubber fruits are hardly edible, but they contain viable seeds in which there is wasp. The rubber seeds which contain the oil that can be exploited for biodiesel production are by-products of processes from rubber plants. Rezaei et al., noted that in biodiesel production, it is preferable to use available local raw materials of the country where biodiesel plant will be installed, therefore, exploration of local renewable resource of energy such as rubber seed oil, available in Nigeria, is of great interest. There are various methods of producing biodiesel from oils and fats, these are enzymatic transesterification, acid-catalyzed transesterification, base-catalyzed transesterification, supercritical esterification and heterogeneous catalyst Acid catalysts simultaneously catalyze both esterification and transesterification, displaying a much higher tolerance to FFAs and water than basic homogeneous catalysts like sodium hydroxide and potassium hydroxide. Homogeneous acid-catalyzed reaction is about 4000 times slower than the homogeneous base-catalyzed reaction. Heterogeneous catalyst esterification process which is the aim of this work is expected to be an

effective method because of the process advantages compared with the existing processes such as process simplification, easier catalyst and product separation. Several studies were carried out to investigate the suitability of solid catalyst and their effect on operational variables such as feed temperature, molar ratio of alcohol to oil, reaction temperature, intensity of mixing, purity of reactant and the types of catalyst on reaction yield and residence time. Oxides alkaline earth metal with high basicity have been found suitable for biodiesel production and among which calcium oxide is one of the most promising heterogeneous base catalysts for biodiesel production. Waste shells of capiz, mussel, oyster, and white bivalve clam [2] were calcined to obtain calcium oxide and used effectively as a heterogeneous catalyst in biodiesel production.

The objective of this study is focused toward the development of a highly active CaO catalyst obtained from egg shells compare its activity with that of commercial CaO, with aim of achieving a sustainable developmental goal by using waste and helping eliminating some problems associated with disposal and environmental degradation.

## **Materials and Methods**

### **Experimental Procedure**

The rubber seeds were obtained from the farm in Benin-city, Nigeria and the fruits were broken and the seeds were sorted out, dehulled, ground into powder and the oil was extracted using soxhlet extraction method with n-hexane solvent. Guinea fowl egg shells were collected from fast food vendors in Kano, Nigeria. Anhydrous methanol of analytical grade and commercial CaO purchased from Ogbomoso, Nigeria were used in the transesterification reaction. Commercial CaO was treated in the muffle furnace at 600°C for 3 hours before use.

### **Catalyst Preparation**

Highly active CaO catalyst was prepared by the calcination, hydration, and dehydration treatment of egg shells. Egg shells were washed thoroughly to remove any unwanted material adhering on its surface, and rinsed twice with distilled water. The washed shells were then dried in hot air oven at 105°C for 24 hours. The dried shells were crushed to small pieces and calcined in a muffle furnace at 900°C for 2.5 hours under static air conditions so as to transform the calcium species in the shell into CaO particle. The CaO derived from the shell was then refluxed in water at 60°C for 6 hours and the solid particle was then filtered and dried in hot air oven at 120°C overnight [28]. The solid product was dehydrated by performing calcination at 600°C 3 hours to change the hydroxide form to oxide form. Thus the egg shells subjected to the calcination, hydration and dehydration treatment generated a highly active CaO. The solid powder was then crushed and sieved with 63 µm. The product was obtained as white powder. All calcined samples were stored in a desiccator to avoid the reaction with carbon dioxide and humidity in air before used.

### **Catalyst Characterization**

The surface areas of Egg shell and commercial CaO were determined by BET analysis using an ASAP 2020 surface area analyzer. Basic strength of the catalyst was measured using the Hammett Indicator Titration. In order to, determine the H range of basic sites in each catalyst

Hammett indicator titrations were conducted. 25 mg of each sample was shaken with 4 ml of a solution of Hammett indicator diluted in methanol and left to equilibrate for 2 hours. The Hammett indicators used are phenolphthalein (pKa = 9.8), indigo carmine (pKa = 12.2) and 2, 4-dinitroaniline (pKa = 15).

### **Transesterification Process**

Transesterification was carried out in laboratory scale in a round bottom flask with condenser on electric heater and magnetic stirrer. The reaction was performed to obtain the maximum yield and the best conditions of biodiesel by varying the operation variables such as methanol/oil ratio (3:1, 6:1, 9:1, 12:1 and 15:1), reaction temperature (40, 50, 60, 64 and 70°C), stir speed: (150, 200, 250 and 300 rpm), catalyst concentration (1, 1.5, 2 wt%) and reaction time (1, 2, 3, 4, and 5h). After the reaction was completed, the solid catalysts were separated by filtration. Then the solution was transferred into separatory funnel until two layers form which are the top layer is biodiesel product and the bottom layer is glycerol. The percentage yields of biodiesel were calculated.

### **Analytical Methods for Biodiesels**

#### **Determination of water sediment**

A centrifuge tube is used in determining the water sediment in a fuel. 100 mL sample of undiluted fuel is centrifuged at a relative centrifugal force of 800 for 10 minutes at 21 to 32°C. After the centrifugation the volume of the water and the sediment which has settled into the tip of the centrifuge tube is read to the nearest 0.005ml and reported as the volumetric % of water and sediment.

#### **Determination of density, specific gravity and API**

Specific gravity bottles were weighed on an electronic weighing scale and their weights recorded. The bottles were filled with different samples and weighed. An equal volume of water was also weighed and its weight recorded as the specific gravity of each sample. The API's gravity of the samples was also determined through the use of equation 1.

$$\text{API} = 141.5 / ((\text{SG}(15.5^\circ\text{C})) - 131.5) \quad (1)$$

#### **Determination of Acid Value**

The acid values of the produced rubber seed oil biodiesel was evaluated based on EN 14104 standard titration procedure. The acid value expressed as mgKOH/g is a measure of the amount of KOH required to neutralize the FFA present in 1 g of the biodiesel produced. About 2.5 g of the biodiesels produced was introduced into conical flasks. 25 mL of diethyl ether and was mixed with 25 mL ethanol and 1 mL phenolphthalein solution. And 0.1 mL KOH solution was titrated against this prepared mixture until a constant pink colour that persisted for 15 seconds was obtained. The acid value was determined by using equation 2.

$$\text{Acid value} = (\text{Titre value (ml)} \times 5.61) / (\text{Sample weight}) \quad (2)$$

### Determination of Kinematic Viscosity

The kinematic viscosity was measured with a u-tube viscometer immersed in a constant temperature (40°C) as stipulated in the European norm EN ISO 3104. 100 ml beaker was filled to three-quarter of its capacity with biodiesel sample, heated to 40°C and immediately placed on viscometer and a spindle of a viscometer was adjusted until it submerged into the sample. The viscometer was switched on after spinning; reading was taken from the scale.

### Determination of flash point and Fire point

The oil samples were separately introduced into an aluminium container and heated using a Bunsen burner at the rate of 10°C per minute. A thermometer was placed inside the oil and at every 5°C increase in temperature; a small flame was passed over the oil surface until a flash appeared. The temperature at which the flash occurred was recorded respectively for each sample as their flash points. The samples were subjected to further heating beyond the flash points, until a small flame passed over the oil surface and continuously burned for 5 seconds. The temperatures at which this occurred for each sample were recorded as their respective fire points.

### Determination of Heating Values

The heating value was obtained using the oxygen bomb calorimeter (Parr Instrument Company, US.) following the ASTM D240 method.

## Results and discussions

### BET Analysis

BET analysis was performed on Egg shell and commercial CaO to determine the specific surface area. Kumar and Ali [29] wrote that surface area of a solid catalyst has direct impact on its catalytic activity, and hence the higher surface area catalyst is expected to have higher catalytic activity. Hydration and dehydration treatments play a vital role in improving the surface area of a catalyst [28]. As shown in Table 2, the surface area of the commercial CaO was found to be 3.002 m<sup>2</sup>/g and guinea fowl egg shell was determined as 8.765 m<sup>2</sup>/g. The result shows similar trend with the findings of [28, 30]. The Hammett indicator experiment shows that the guinea fowl egg shell had the strongest basic strength and the results obtained presented in Table 1.

**Table 1:** Specific surface area and basic strength of catalysts

Catalyst	Surface area (m <sup>2</sup> /g)	Basic strength (H)
Commercial CaO	3.002	9.8<H<12.2
Egg shell	8.765	12.2<H<15.0

Comparison of the biodiesel production activity for guinea fowl egg shell and commercial CaO based catalysts

Guinea fowl egg shell and commercial CaO were employed for biodiesel production via transesterification of rubber seed oil. The reaction was performed with a 1.5 wt% catalyst

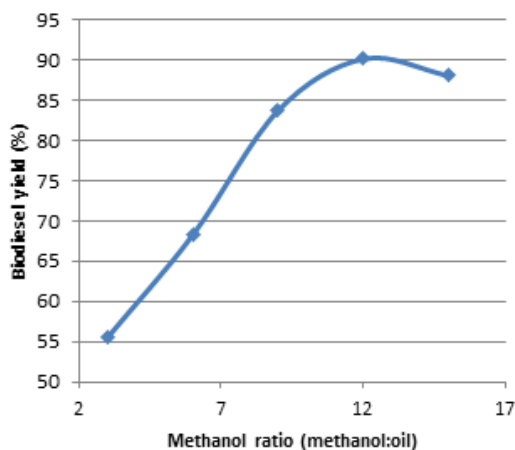
which is based on oil weight, methanol/oil ratio of 12:1, reaction temperature of 64°C, speed of 250 rpm and a reaction time of 2 hours. Commercial CaO produced a biodiesel conversion of 68.34% and guinea fowl egg shell exhibited the greatest catalytic activity producing a high biodiesel conversion of 95.08%.

### Effect of Variables on Transesterification Process

Five parameters plays important roles in this transesterification process namely methanol to oil molar ratio, reaction time, influence of temperature, reaction time and catalyst loading. The methanol/oil ratio is one of the most important factors affecting the yield of biodiesel. Although stoichiometric ratio requires three moles of methanol for each mole of oil, the transesterification is commonly carried out with an extra amount of methanol in order to shift the equilibrium towards the direction of methyl ester formation. For the studies on effect of methanol to oil molar ratio, catalyst amount, reaction temperature and time the speed of the stirring was kept at 200 rpm after a trial study.

### Effect of Methanol to oil Molar Ratio

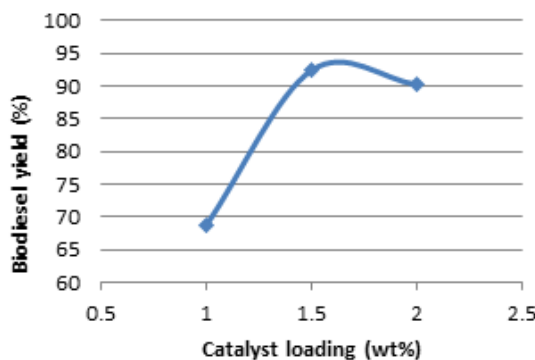
Figure 1 shows the effect of methanol to oil molar ratio on the yield conversion over the calcined guinea fowl egg shell catalyst. As shown in this figure, the yield conversion was increased from 68.35% at 6:1 molar ratio to 90.17% at 12:1 molar ratio. The results obtained is in agreement with findings of Ngamcharussrivichai et al., (2007) whom wrote that the amount of molar ratio of methanol to oil at the ratio of 10 or lower than that is not sufficient enough to dissolve the oil and catalyst phase. However, a further increased in methanol to oil molar ratio up to 15:1 result in decreased of biodiesel yield conversion which is due to the reversible transesterification process.



**Figure 1.** Effect of methanol to oil molar ratio on the biodiesel yield. Reaction conditions: catalyst loading, 2 wt%, reaction time, 3h and reaction temperature  $\pm 64$  0C.

### Effect of Catalyst Amount

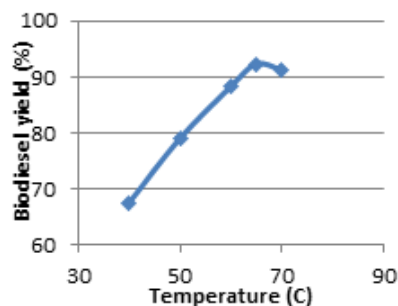
Figure 2 presented the effect of catalyst amount on the yield conversion over the calcined guinea fowl egg shell catalyst. The figure shows that the conversion of rubber seed oil to biodiesel increases when the amount of catalyst increased from 0.5 to 1.5 wt.% with the methanol to oil ratio of 12:1, but decreased when the amount of catalyst exceeded 1.5 wt.%. This is due to reversible nature of the transesterification process where the catalyst concentration levels greater than 1.5% may have favoured the backward reaction. The results suggest that optimum catalyst loading for rubber seed oil with guinea fowl egg shell transesterification is 1.5 wt.% with conversion of 92.35%. As shown in the Figure 2, the yield conversion was decreased to 90.17% after amount of the catalyst loading was increased to 2.0 wt%. Roschat et al., highlighted the effect of high surface area of calcined waste cockle catalyst which required higher catalyst loading. A huge excess of catalyst contributed to the formation of soap that will lead to emulsion that increase the difficulty in separation process. Apart from that, the formation of soap will drive the losses of triglyceride molecules that can be used to produce biodiesel.



**Figure 2** Effect of catalyst concentration on the biodiesel yield. Reaction conditions: methanol to oil molar ratio, 12:1, reaction time, 3h and reaction temperature  $\pm 64^{\circ}\text{C}$ .

### Effect of Reaction Temperature

The reaction and yield of biodiesel are greatly affected by the reaction temperature used. The effect of varying the temperature normally, as the reaction temperature increases, the rate of reaction increases as they are affected by temperature through the Arrhenius equation.

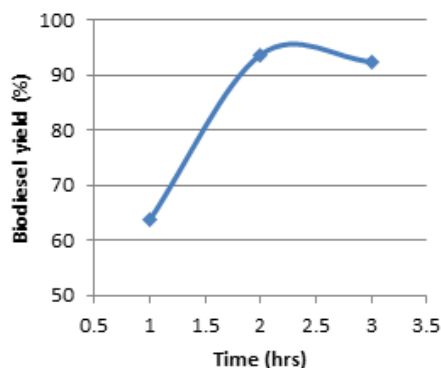


**Figure 3** Effect of temperature on the biodiesel yield. Reaction conditions: methanol to oil molar ratio, 12:1, reaction time, 3h and reaction temperature  $\pm 64^{\circ}\text{C}$ .

Figure 3 show that conversion increases from 67.55% to 92.35% when the temperature increased from 40°C to 65°C. Higher temperature improves the efficiency of transesterification, which in turn enhances the conversion. However, by increasing the temperature beyond the methanol boiling point, it may burn the methanol and may influence the saponification reaction of triglycerides. From the figure increasing the temperature above 64°C conversion reduces slightly to 91.33% when temperature increases to 70°C. This is due to methanol evaporation at temperature higher than methanol boiling point and hence oil to methanol ratio cannot be maintained to achieve a desirable reaction.

### Effect of Reaction Time

Other than the effect of methanol to oil ratio and the effect of reaction temperature, the effect of reaction time also influenced the production of biodiesel. The result of this effect is shown in Figure 4 by varying the reaction time from 1 to 3 hours and fixing the methanol to oil ratio, catalyst amount and reaction temperature at 12:1, 1.5 wt% and 64°C. As shown in Figure 4, the maximum yield of 95.06% was obtained in 2 hours. In the early stage of transesterification reaction, the production of methyl esters gradually increased and the rate diminished and finally started to decrease after about 2 hours. This is because transesterification reaction between oil and alcohol will form soap due to the reversible reaction when the reaction time increased. The extending of the reaction time in the transesterification process may contribute to the decreased of biodiesel yield and accelerate the ester formation. The reversible process between oil and alcohol during the long period of transesterification process may also contribute to these phenomena.

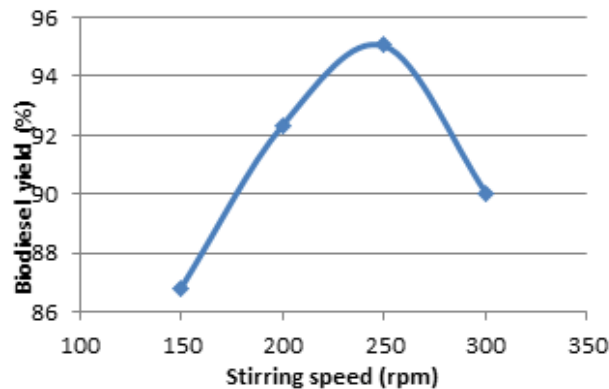


**Figure 4** Effect of reaction time on the biodiesel yield. Reaction conditions: methanol to oil molar ratio, 16:1, catalyst loading, 1.5 wt% and reaction temperature  $\pm 64$  0C.

### Effect of Stirring Speed

Stirring is very important in the transesterification process, as oils or fats are immiscible with methanol solution. The effect of stirring on yield is shown in Figure 5. The experiments were conducted with different rates of stirring at 150, 200, 250 and 300 rpm. The optimum yield of 95.06% was achieved at 250 rpm a further increased in the speed resulted in lower yield of 91.14%.





**Figure 5** Effect of stirring speed on the biodiesel yield.

### The Properties of Produced Biodiesel

#### Water and Sediment level

One of the important indicators of cleanliness of a fuel is the water and sediment level test since water reacts with biodiesel to form free fatty acid and this might lead to severe corrosion of fuel system components and reduction in the heat of combustion can result due to higher level of water content. It could also lead to microbial growth in storage tank and may contribute to filter plugging and fuel injection system wear. Water and sediment was found to be 0.02% which concurs with the ASTM standard of 0.05% maximum volume. The result shows that ethyl biodiesel produced is clean and may not form free fatty acid due to hydrolysis and microbial growth can be reduce during storage.

#### Densities, Specific and API Gravities

Densities, specific and API gravities were found to be  $0.82\text{g/cm}^3$ ,  $0.82\text{g/cm}^3$  and  $26.87\text{g/cm}^3$  respectively and all the values are within the ASTM limits of biodiesel. These values are within tolerable limits to allow optimum air to fuel ratio for complete combustion because high density biodiesel or its blends can leads to incomplete combustion and particulate matter emission. The results is an indication that biodiesel produced from rubber seed oil using guinea fowl egg shell as catalyst may undergo complete combustion and produce less particulate matter. The density of the biodiesel was found to be consistent with the values of  $0.885\text{g/cm}^3$  reported by Awulu et al. The specific gravity of the biodiesel also compared favourably with those reported by Phan and Phan, for waste cooked oil of 0.88.

#### Acid Number

The acid number being an important fuel property, it is a measure of free fatty acids in a given product. [39]. The acid number of the produced biodiesel is  $0.444\text{mgKOH/g}$ , this result satisfied the maximum acid value set in ASTM D6751 and EN 14214 standards. The results is compares with  $0.459\text{mgKOH/g}$  reported by Samuel et al., for water cooking oil and  $0.43\text{mgKOH/g}$  reported by Phan and Phan. This result indicates that ethyl ester biodiesel produced from rubber seed oil using guinea fowl egg shell as catalyst may not cause severe corrosion in internal combustion engine and fuel system.

### Flash Point and Fire Point

Flash point is also an essential fuel property and is the temperature at which fuel will ignite when exposed to flame. In this work 136<sup>o</sup>C was obtained for the flash point while the fire point is 168<sup>o</sup>C. Biodiesel usually have higher flash point compared to petroleum diesel. Flash point is not directly related to engine performance but is inversely related to fuel volatility. It is used to control the safety requirement for fuel handling, storage and transportation. The 119<sup>o</sup>C value obtained is in agreement with ASTM biodiesel standard which puts it at 130 °C minimum. The result obtained is in agreement with the result of 145 °C obtained by Awulu et al..

**Table 2:** Characterization of Biodiesel produce from rubber seed oil with egg shell as catalyst

Property	Value	ASTM limit
Water sediment (V %)	0.02	
Density (g/cm <sup>3</sup> )	0.83	
Specific gravity (g/cm <sup>3</sup> )	0.81	0.82 – 0.9
API (g/cm <sup>3</sup> )	27.36	
Calorific value (MJ/Kg)	40.12	
Flash point (°C)	119	
Fire point (°C)	137	>130
Cloud point (°C)	70	
Pour point (°C)	-4	
Kinematic Viscosity (cSt)	5.4	1.9 -6.0
Acid Value (mgKOH/g)	0.44	<0.50
Odour	Mild	
Colour	Brown	

### The kinematic viscosity

The kinematic viscosity measured at 40<sup>o</sup>C was found to be 5.41cts. The results is in compliance with the biodiesel standards; ASTM D6751 -02 and EN 14214. The viscosity of biodiesel is usually higher compared to fossil diesel the inference is that biodiesel will have more lubricating effect in engines which will be an added advantage to the users, since it will reduce wear and tear in the engine.

### Colour and Odour

The colour of the produced biodiesel is brown with mild odour.

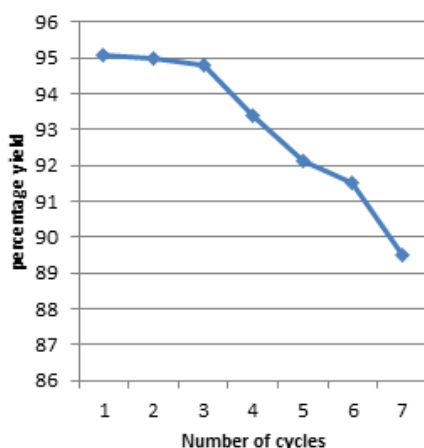
### Results of Heating Value

Heating value is the enthalpy released after the complete combustion reaction of fuel at a constant pressure or volume. Fuels possessing higher heating values would require lower fuel flow rate than the fuel with lower heating value for the same engine power output. The calorific value of 40.12 MJ/kg was obtained.

### Reusability of the Guinea Fowl Egg Shell Catalysts

Figure 6 shows yields after reuse of the catalyst. The results show that the catalyst can be repeatedly used for 6 times without apparent loss of activity. The yield after 6 cycles of

transesterification, was still 91%. One of the essential attributes for a heterogeneous catalyst is the ability to be recycled. Reusability of the guinea fowl egg shell catalyst obtained by the calcination–hydration–dehydration treatment of egg shells was examined for 6 cycles with 1.5 wt% catalyst (based on oil weight), a methanol to oil ratio of 12:1, reaction temperature of 65°C and a reaction time of 2 hours. After each cycle, the solid catalysts was separated from the reaction mixture by filtration and wash with methanol to remove the adsorbed stains and recalined at 600°C for further use. The results indicate that a high biodiesel conversion of above 90% was achieved for all the 6 tested runs.



**Figure 6** Effect of Reusability of the Catalyst

### Conclusion

This work revealed that the calcination–hydration–dehydration treatment is an appropriate method which increases the catalytic activity of waste shells possessing calcium carbonate as their main constituent. The experimental results showed that the methyl ester conversion for commercial CaO was 68.34% whereas it was found to be 95.05% for the CaO obtained from the calcination–hydration–dehydration treatment of guinea fowl egg shell at a 1.5 wt% catalyst (based on oil weight), a methanol to oil ratio of 12:1, a reaction temperature of 65°C, 250 rpm stirring speed and a reaction time of 2 hours. The yields after reuse of the catalyst show that the catalyst can be repeatedly used 6 times without apparent loss of activity. The produced biodiesel was compared with the ASTM standards of biodiesel and the properties water sediment, density, kinematic viscosity and flash point conformed to the ASTM D6751 specifications. The results obtained proved that CaO derived from guinea fowl egg shell waste can be used as catalyst in the production of biodiesel. The results reveal that both waste egg shell and rubber seed oil provides promising prospect for people to access cheap, reliable and clean energy in the future, which is one of the key elements to sustain healthy ecosystems and human life. The popularity of renewable energy technologies will definitely continue, if potential investors are encouraged to invest in renewable energy technologies. Therefore, studies for determining sustainability indicators play a significant role.

## References

- Abdalrahman, B., Fadhil, M. M., Dheyab, K., Ahmed, & Marwa, M. H. Y. (2012). Biodiesel Production from Spent Fish Frying Oil through Acid-Base Catalyzed Transesterification, *Pak. J. Anal. Environ. Chem.* 13(1), 09-15.
- Achanai, B., Nattawut, C., Vorrada, L., Chaiwat Wongweang, U. & Khamsrisuk, S. (2013). Application of Eggshell Wastes as a Heterogeneous Catalyst for biodiesel Production. *Sustainable Energy*. 1(2), 7-13.
- Atabani, A. E., Siltonga, A. S., Ong, H. C., Mahila, T. M. I. & Masjuki, H. H. (2013). Non-edible vegetable oils: a critical evaluation of oil extraction, fatty acid compositions, biodiesel production, characteristics, engine performance and emissions production, *Renewable and sustainable energy review*, 18, 211—245.
- Awulu, J. O., Ogbeh, G.O. & Asawa, N. D. (2015). Comparative analysis of biodiesel from calabash and rubber seed oil. *Int. Journal of Renewable Energy Development*, 4 (2), 131-136, doi.org/10.14710/ijred.4.2.131-136
- Boey, P. L., Maniam, G. P. & Hamid, S. A. (2011). Performance of calcium oxide as a heterogeneous catalyst in biodiesel production: a review, *Chem. Eng. J.*, 168, 15–22.
- Chhetri, A. B., Watts, K. C., & Islam, M. R. (2008). Waste cooking oil as an alternate feedstock for biodiesel production, *Energies*, 1 (3)–18.
- Darnoko, D. (1999). Continuous production of methyl esters from oil palm and recovery of beta-carotene by membrane technology, PhD thesis, University of Illinois, Urbana.
- Feng, G. & Zhen, F. (2004). Biodiesel production with solid catalysts, *biodiesel - Feedstocks and Processing Technologies*, Dr. Margarita Stoytcheva (Ed.), In Tech, Available from: <http://www.intechopen.com/books/biodiesel-feedstocks-and-processing-technologies/biodiesel-production-with-solid-catalysts> assessed 20/11/2017
- Gerpen, V. J. Tat, M. E. (2003). Fuel property effect in biodiesel, ASABE Paper No. 036034: *American Society of Agricultural Engineering Annual Meeting*, Las Vegas, USA.,
- Girish, N., Niju, S., Meera, K. M., S. Begum, & Anantharaman, N. (2013). Utilization of a cost effective solid catalyst derived from natural white bivalve clam shell for transesterification of waste frying oil, *Fuel*.111, 653–658,
- Glisic, S., & Skala, D. (2009). The problems in design and detailed analyses of energy consumption for biodiesel synthesis at supercritical conditions, *The J. Supercritical Fluids*, 49 (2), 293-301,

- Gryglewicz, S. (2000). Alkaline-earth metal compounds as alcoholysis catalysts for ester oils synthesis, *Applied Catalysis A: General*, 192 (1), 23-28,
- Hoekmana, S. K., Broch, A., Robbins, C. Ceniceros, E. & Natarajan, M. (2012). Review of biodiesel composition, properties and specifications, *Renewable and Sustainable Energy Reviews*, 16, 143-169.
- Heydarzadeh, J. K., Amini, G., Khalizadeh, M. A., Pazouki, M., Ghoreyshi, A. A. Rabeai, M., & Najafpour, G. D. (2010). Esterification of Free Fatty Acids by Heterogeneous  $\gamma$ -Alumina-Zirconia Catalysts for Biodiesel Synthesis, *World Appl. Sci. Journal*, 9 (11) 1306-1312.
- Javidialesaadi, A. & Raeissi, S. (2013). Biodiesel production from higher free fatty acid content oils: experimental investigation of the pretreatment step”, *APCBEE procedia*, 5, pp. 474-478.
- Kirn, A. Kang, H. B. Kirn, M. Park, Y. Kim, D., Lee, J. & Lee, K. (2004). Transesterification of vegetable oil to biodiesel using heterogeneous base catalyst, *Catalysis Today*, 93, 315-320.
- Koh, M.Y., Idaty, T. & Ghazi, M. A. (2014). Review of biodiesel production from *Jatropha curcas* L. oil, *Renewable and Sustainable Energy Reviews*, 15, 2240–2251.
- Kumar, D. & Ali, A. (2012). Nanocrystalline KeCaO for the transesterification of a variety of feedstocks: structure, kinetics and catalytic properties, *Biomass Bioenergy*, 46, 459–68.
- Mathiarasi, R., Mugesha kanna, C., & Partha, N. (2013). Transesterification of soap nut oil using novel Catalyst, *J. Saud. Chem. Soc.*, <http://dx.doi.org/10.1016/j.jscs.2013.07.006>.
- Mukhtar, M., Dangoggo, S. M. & Ross, A. B. (2012). Low temperature/pressure hydrothermal microwave as a potential alternative method of processing microalgae, *Proceeding of the 35th Chemical Society of Nigeria, Annual and International Conference*, 510-515
- Mustafa, B., (2011). Potential alternatives to edible oils for biodiesel production: A review of current work. *Energy Conversion Management*, 52, 1479–92.
- Nakatani, N., Takamori, H., Takeda, & Sakugawa, K. H. (2009). Transesterification of soybean oil using combusted oyster shell waste as a catalyst, *Bioresour. Technol.*, 100, 1510–1513.
- Ngamcharussrivichai, C., Wiwatnimit, W. & Wangnoi, S. (2007). Modified dolomites as catalysts for palm kernel oil transesterification. *Journal of Molecular Catalysis A: Chemical*, 276 (1-2), 24-33.

- Niju,S., Meera, K. M., S. Begum, & Anantharaman, N. (2014). Preparation of biodiesel from waste frying oil using A green and renewable solid catalyst derived from egg shell, *Environmental Progress and Sustainable Energy*.
- Otera, J. (1993). Transesterification, *Chemical Reviews*, 93 (4), 1449-1470.
- Oyelaran, O. A. (2014). Development of a Motorized Biomass Briquetting Machine, PhD Thesis, Dept of Mech. Eng., Fed. Univ. of Agric., Abeokuta, Nigeria.
- Phan, A. N. & Phan, T. M. (2008). Biodiesel production from waste cooking oils, *Fuel*, 87, 3490–3496.
- PremKumar, S. & Chetty, S. V. (2010). Technologies for biodiesel production from used cooking oil a review, *Energy Sustainable Dev.* 14,339–345.
- Ramirez-Verduzeo, A. R., Rodriguez-Rodriguez, J. E. & Jaramillo-Jacob, J. (2012). Predicting cetene number, kinematic viscosity, density and higher heating value of biodiesel from its fatty acid methyl ester composition, *Fuel*, 91, 102-111.
- Rezaei, R., Mohadesi, M., & Moradi, G. R. (2013). Optimization of biodiesel production using waste mussel shell catalyst, *Fuel*, 109, 534–541,
- Samart, C., Sreetongkittikul, P., & Sookman, C. (2009). Hetero-geneous catalysis of transesterification of soybeanoil using KI/mesoporous silica. *Fuel Processing Technology*, 90 (7-8), 922-925.
- Samuel, O. D., Waheed, M. A., Bolaji, B.O. & Dairo, O. U. (2013). Production of biodiesel from Nigerian restaurant, *Int. Jour.of Renew. Energy Res.*,3(4), 976 – 979,
- Sivaramakrishnan, K. & Ravikumar, P. (2011). Determination of higher heating value of biodiesels, *Int. Journal of Eng. Sci. and Techn.*, 3 (11), 7981- 7987,
- Sharma, Y. C., Madhu, B. D.,Liu, Y., & Yaakob, Z.(2014). Fast Synthesis of High Quality Biodiesel from 'Waste Fish Oil' by Single Step transesterification, *Biofuel Research Journal*.3, 78-80.
- Sharma, Y. C., & Singh, B. (2008). Development of Biodieselfrom karanja, a tree found in rural India. *Fuels*. 87(8-9), 1740-1742.
- Srilataha, K. P., Devi, B. L. A., Lingaiah, N., Prasad, R. B. N., & Sai, P. S. (2012). Biodiesel production from used cooking oil by two-step heterogeneous catalyzed process, *Bioresource Technology*, 119, 306-11.

- Suryaputra, W., Winata, I., Indraswati, N. & Ismadji, S. (2013). Waste capiz (*Amusium cristatum*) shell as a new heterogeneous catalyst for biodiesel production, *Renewable Energy*, 50, 795–799.
- Vyas, A. P, Verma, P. & Subrahmanyam, N. (2010). A review on FAME production processes, *Fuel*, 89, 1–9.
- Xie, W. & Li, H. (2006). Alumim-supported potassium iodide as a heterogeneous catalyst for biodiesel production from soybean oil, *J. Molecular Catalysis A: Chemica*, (1-2), 1-9,
- Yan, Y., Li, X., Wang, G., Gui, X., Li, G., Su, F., Wang, S., & Liu, T. (2014). Biotechnological Preparation of Biodiesel and Its High-Valued Derivatives: A Review. *Applied Energy*, 113, 1614-1631.
- Yoosuk, B., Udomsap, P., Puttasawat, B. & Krasae, P. (2010). Improving transesterification activity of CaO with hydration technique, *Bioresour. Technol.*, 101, 3784–3786.
- Zabeti, M., Daud, W. M. A. W., & Aroua, M. K. (2009). Optimization of the activity of CaO/Al<sub>2</sub>O<sub>3</sub> catalyst for biodiesel production using response surface methodology, *Appl. Catal. A Gen.*, 366, 154–159,
- Zhang, Y., Dube, M. A. McLean, D. D. & Kates, M. (2003). Biodiesel production from waste cooking oil: Process design and technological assessment, *Bioresour. Technol.*, 89, 1–16.