Waste shells of chicken and guinea fowl eggs as catalysts for the production biodiesel

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Abstract: Raw material costs are responsible for the greater percentage of biodiesel production cost**.** In this research, chicken and guinea fowl wastes eggshell were used as feedstock for the producing heterogeneous catalyst for the production of biodiesel. Preceeding their utilization, calcium oxide (CaO) was obtained by calcining the eggshells which contains calcium carbonate ($CaCO_3$) in a muffle furnace at of 1000℃ for four hours. The solid oxide catalysts produced were then characterized by the Brunauer-Emmett-Teller (BET) and XRF methods. The activity of the produced catalyst in transesterification of calabash seed oil with methanol was assessed, and the properties of biodiesel obtained were evaluated. The various effect of reaction time, reaction temperature, methanol/oil molar ratio, catalyst loading, agitation speed and their reusability of the produced catalyst were also evaluated. The experimental outcome showed that methanol to oil of 12:1 M ratio, 1.5 wt.% catalyst, 64℃ reaction temperature, two hours reaction time and speed of 250 rpm gave the ultimate results. The results also indicated that the guinea fowl egg shell derived CaO catalyst had higher surface area, basicity and smaller particle size. The guinea fowl egg shell also exhibited higher biodiesel yield of 96% compared to 95% for chicken egg shell. The CaO catalyst derived from waste calcined chicken and guinea fowl egg shell endured a good catalytic performance after being repetitively used for 8 cycles with yield of around 91%, which suggests possible saving and inexpensive biodiesel production potentials. Egg shell of chicken and guinea fowl are therefore potential bioresource for the production of heterogeneous catalyst that can be effectively exploited for the production of biodiesel.

Keywords: biodiesel, eggshell wastes, calcium oxide, transesterification, heterogeneous catalyst.

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1 Introduction

The world energy needs are increasing year by year and recent energy crisis has drawn exceptional attentions from researchers into a potential replacement fuel for current petroleum-based fossil fuel as a result of oil reserves depletion. One of the alternative fuels which can now be produced from renewable sources is biodiesel (Viraya-empikul etal., 2010). Biodiesel is made up of fatty acid methyl esters (FAME) which can be produced by transesterification of edible and non-edible oils, waste cooking oil and animal fat. Theansuwan and

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Triratanasirichai (2011) noted that Biodiesel burned cleaner, significantly decreased carbon monoxide, particulate matter, hydrocarbons, and eliminated sulfur dioxide emissions than conventional petroleum diesel. The biodiesel also possessed the following properties over petroleum diesel high cetane number, high flash point, and excellent lubricity and miscibility (Knothe, 2008). Manuel (2007) wrote that greenhouse gas emission was reduced by 41% compared with petroleum diesel when biodiesel is used. Acid, base, or enzymes are used to catalyze transesterification process (Birla et al., 2012). The advantage of using heterogeneous catalysts was its ease of separation and regeneration and cheapness (Sharma et al., 2008). Generally, for biodiesel production, the catalysts usually used for transesterification reaction are homogeneous and heterogeneous catalysts.

The homogenous catalysts have the advantage that the moderate process conditions are fast reactions (Asakuma et al., 2009). The homogenous catalyst however, possesses some disadvantages associated with its usage which comprised presence of water during the process which could forms soap and the inability to reuse the catalyst (Macleod et al., 2008). Soap formations are unwanted side-reactions, since soap formations consume the catalyst, which result in the reduction of biodiesel yield and also cause difficulty in separation and purification steps (Vicente et al., 2004). A heterogeneous catalyst such as calcium oxide has many advantages, for example, they are non-corrosive, environmentally friendly, and with less disposal difficulties. Heterogeneous catalysts are moreover far simpler to separate from the liquid products and are envisioned to possess better activity with a longer catalyst lifetime (Razali et al., 2006). Lee et al. (2009) wrote that recovery of solid catalysts was easy and were re-usable. Atadashi et al. (2013) noted that heterogeneous catalytic process decreased energy and water consumption which was made possible by eliminating the neutralization step of generating wastewater. Heterogeneous catalyst was obtained from a diverse of waste sources which included shells, bones, ashes and rocks with high capacity of production (Nakatani et al., 2009; Wei et al., 2009). Eggshells consist of calcium carbonate ($CaCO_3$), magnesium carbonate ($MgCO_3$), calcium phosphate ($Ca_3(PO_4)_2$), protein fibers, some organic substances and water. $CaCO_3$, is the main component of eggshell with calcite (Oliveira et al., 2013). Utilization of waste is an indispensable element of sustainability and since waste eggshells are seldom used to generate products and processes. Hence, using it as feedstock for catalyst synthesis might eradicate the wastes and concurrently manufactured catalysts with high cost effectiveness. Researches related to the use of eggshell waste as catalyst has carried out by many researchers (Boro et al., 2012; Sharma et al., 2010). Many researches on CaO produced from eggs shells particularly chicken egg shells had been reported in literatures, Wei et al. (2009), Viriya-empikul et al. (2010), Jazie et al. (2013), Cho and Seo (2010), Sharma et al. (2010), Niju et al. (2014), and Chen et al. (2014). Calcining of eggshell at temperature of 600℃ to 1000℃ have been reported with 92.96% biodiesel yield.

In this present study, CaO derived from of chicken and guinea fowl waste egg shell is been studied as heterogeneous catalyst for the production of biodiesel from calabash seed oil. Calabash seed oil was selected due its low cost and availability that can reduce the production costs of biodiesel. The objective of this research is to optimize the process for biodiesel production from calabash seed oil using CaO catalyst derived from waste egg. The physicochemical properties of the chicken and guinea fowl egg derived catalysts, prior and after calcination were investigated. Subsequently, the biodiesel yield via the catalysts were tested and compared under the same operating conditions, effects of reaction time, reaction temperature, methanol/oil molar ratio, catalyst loading, and reusability of catalyst were studied

2 Materials and Methods

2.1 Materials

The calabash (Lageneriasinceraria) seeds were obtained from the farm in Ogbomoso, 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. Egg shells were collected from fast food vendors also in Ogbomoso. Anhydrous methanol of analytical grade and commercial CaO purchased from Ibadan, Nigeria was used in the transesterification reaction. Commercial CaO was treated in the muffle furnace at 600 for 3 hours before use.

2.2 Preparation of eggshell waste-derived catalyst

The egg shells were first soaked in distilled water and then washed to remove all the impurities. The inner white membrane of the chicken and guinea fowl eggshells was then removed. They were then dried overnight at 100℃ in an oven to remove the excess water. The egg shells were later crushed into smaller pieces with mortar and pestle before grinding them mechanically to obtain the fine powder. The powder obtained was passed through 250 μm sieve mesh to obtain particles size less than 250 μm. After that, the powder was calcined at 1000℃ in a muffle furnace to convert calcium carbonate, ($CaCO_3$) into calcium oxide (CaO). The hot calcined samples were taken from of the muffle furnace before the temperature of the furnace reaches room temperature (Aworanti et al., 2013). The calcined and activated calcium oxide was then kept in in desiccators to prevent contamination with atmospheric water moisture and carbon dioxide (Sharma et al., 2010).

2.3 Catalyst characterization

The surface areas of chicken, guinea fowl egg shell, and commercial CaO were analyzed using BET analysis using ASAP 2020 surface area analyzer. The basic strength of the catalyst was also analyzed by the Hammett Indicator Titration. In order to, determine the H range of basic sites in each catalyst Hammett indicator titrations were conducted. Twenty-five 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).

2.4 Transesterification process

A batch reactor was used in carrying out the transesterification. 100 ml of calabash seed oil was placed in a 500 ml two necked flat bottom flask fitted with a reflux condenser and stirred at 600 rpm for each test runs. The oils were heated for 5 minutes at 105℃ in a heating metal to evaporate water and other volatile impurities that might be present. A magnetic stirrer at about 600 rpm was used to stir the mixture of the oil and catalyst. A predetermined amount of methanol was then added. The experiment continues at 64ºC. At the end of the reaction, the mixture was allowed to cool down and settle so as to separate the catalyst. The separated catalyst was washed with methanol for reuse. To remove the catalyst completely the mixture was filtered. After which, a separating funnel was used for 10 min so as to separate layers visibly. The Biodiesel was then dried by flash evaporation at 90ºC to remove residual methanol. Distillation process was used to recover excessive amount of methanol before analysis of fatty acid methyl esters.

2.5 Testing of biodiesel (methyl esters)

In this research work, FTIR (Thermo-Nicolet 5700 model) was used to analyze the calabash seed oil biodiesel. The spectra obtained were in the region of 500 – 4000 cm^{-1}, having a resolution of 4 cm^{-1}. In the Average 32 scans using a multi bounce ATR were recorded. The technique used by Giuliano et al. (2004) was applied for quantitative analysis. To calculate the concentration of ester in the biodiesel layer, absorbance band at wave number 1741 cm^{-1} height was used. As a result of measuring the height of the 1741 cm^{-1} bands of ester and oil samples of known compositions calibration plots were obtained. For the purpose of calibration purpose, methyl ester and triolein were used as examples of ester and oil respectively. The biodiesel yield was calculated using equation 1 below.

$$\text{Yield}=\frac{E_1}{W_0}\times E_c \quad (1)$$

Where:E_1, E_c and W_0 are the biodiesel volume in (mL), ester concentration in (g mL^{-1}), and weight of oil used in (g) respectively.

2.6 Reaction method

Transesterification of the oil was performed in

laboratory scale in a round bottom flask which has a condenser on electric heater with magnetic stirrer. The experiment was carried out with a view of obtaining the maximum yield and with best conditions of the biodiesel by adjusting the process variables such as catalyst concentration (1.0%, 1.5%, 2.0%, 2.5% and 3.0% (w/v); methanol/oil ratio (3:1, 6:1, 9:1, 12:1 and 15:1), the process temperature (30ºC, 35ºC, 40ºC, 45ºC, 50ºC, 55ºC, 60ºC, 65ºC, 70ºC,75ºC and 80ºC) for 2 hours; reaction time (1, 2, 3, 4, and 5 hours). After the complexion of the reaction, filtration was used to separate the solid catalysts. After which the solution was pour in separatory funnel and allow to settle till two layers are formed upper layer been biodiesel product and t glycerol been the lower layer. The biodiesel yield in percentage was then calculated. Each experiment was carried 3 times with the standard deviation not greater than 6% for any point.

3 Results and discussion

3.1 BET analysis

BET surface area analysis was used to evaluate the surface area and pore volume of the produced catalyst, as shown in Table 1. The BET divulged that the area of the calcined chicken (CCES) and guinea fowl egg shells (CGFES) catalysts were greater than that of non-calcined chicken egg shell (NCES), non-calcined guinea fowl egg shell (NGFES) and the pure commercial calcium oxide (CCO). It can be established that calcination has a better effect on the performance of the catalysts as a result of the increasing of BET surface area. Kumar and Ali (2012) stated that solid catalyst surface area had direct influence on its catalytic performance and therefore the greater the surface area of a catalyst the higher the catalytic activity. The analysis results in Table 1 showed that the calcined guinea fowl egg shell possessed the highest BET surface area of 71.42 m^2 g^{-1} and total pore volume of 0.0216 cm^3 g^{-1} while calcined chicken egg shell were found to be 54.63 m^2 g^{-1} and 0.0149 cm^3 g^{-1} respectively. Consequently, the values show that the active site is exist at the peripheral surface of the catalyst which could increase diffusion problems as a result of bigger pore size hence better flow channels. Owing to the intrinsic pore structure of eggshell surface and its abundance, eggshell is a promising raw material for production of fine powder, which paves its way for its utilization as porous solid catalyst.

Table 1 BET surface area of calcined and uncalcined egg shell catalyst

Physical property	Material				
	CGFES	CCES	UGFES	UCES	CCO
Bet surface area (m^3 g^{-1})	71.42	54.62	4.11	1.91	36.82
Pore volume (cm^3/g)	0.0216	0.0149	0.0009	0.0006	0.0126
Average pore radius (A)	6.13	5.44	4.44	4.37	6.83

3.2 The composition of waste eggshells

The composition of eggshells is shown in Table 2. The calcined guinea fowl eggshell contains 98.50% CaO while the calcined chicken eggshell has 98.01% by XRF analysis. Other chemical compositions contain in the calcined eggshell were MgO (0.500%), Al_2O3 (0.100%), CuO, (0.045%), SrO (0.062%) for guinea fowl egg shell while chicken egg shell has MgO (0.512%), Al_2O_3 (0.102%), CuO, (0.046%) and SrO (0.060%). The finding is in agreement with Wei et al. (2009) whom wrote that eggshell calcined above 800°C were found to be the most active with a biodiesel yield range of 97%-99%. The results showed that CaO was the most abundant element in the eggshells. Small content of other compositions in the eggshell suggest that waste eggshell could be natural carbonate-based materials. The findings are in agreement Syazwani et al. (2015) whom wrote that calcium oxide (CaO) was a promising alkaline earth metal oxide with high basicity, suitable for biodiesel production. Gole and Gogate (2012) and Rezaei et al. (2013) also wrote that shells could be calcined to produce CaO which could be used as a heterogeneous catalyst in biodiesel production.

Table 2 Chemical compositions of waste egg shells

Chemical Composition	CGFES	CCES
MgO [%]	0.500∓0.03	0.512∓0.02
CaO [%]	98.500∓0.31	98.010∓0.22
Al_2O_3 [%]	0.100∓0.01	0.102∓0.01
CuO [%]	0.045	0.046
SrO [%]	0.062	0.060
Others[%]	0.793∓0.02	1.270∓0.02

3.3 Effect of parameters on biodiesel production

3.3.1 Effect of methanol to oil molar ratio

The methanol to oil molar ratio is also an important factor that highly has impact on transesterification process. Figure 1 shows methanol/oil mole ratio on biodiesel content. The yield of biodiesel increased with the increase of methanol/oil molar ratio from 6 to 12. The reaction equilibrium will shift to the forward direction with an optimum methanol to oil molar ratio which helps in achieving maximum yield. However, further addition in methanol/oil ratio beyond the optimum ratio will not promote the reaction. As can be observed from Figure 2, the most preferable methanol oil ratio on the transesterification for derived CaO from chicken, guinea fowl egg shell waste and commercial calcium oxide is 12:1 because it gave the maximum yield of biodiesel of 95.3% and 96.3% respectively and 96.5 for commercial calcium oxide. The percentage biodiesel yield is directly proportional to the methanol to oil molar ratio for all catalysts. However, there is a slight reduction in yield as methanol to oil molar ratio increased. Customarily, to achieve higher yield of biodiesel excessive alcohol is favor to shift the equilibrium.

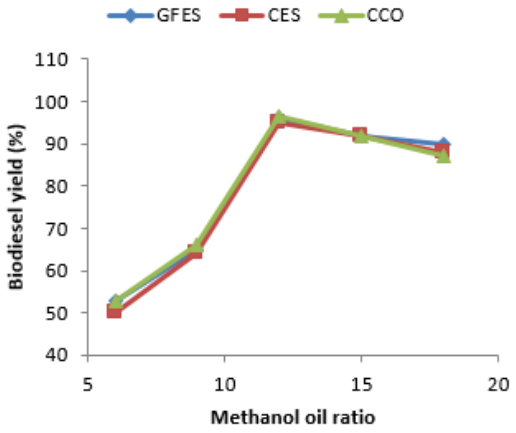

Figure 1 Effect of methanol oil ratio

In order to enhance the contact between the alcohol and oil higher molar ratio was used. However, too high ratio of oil to alcohol will give contrary effect on the biodiesel yield. Ghoreishi and Moein (2013) reported that addition of large quantity of alcohol, methanol could slow down the separation of esters and glycerol phases, thereby having effect on the final biodiesel yield. Anwar et al. (2010), Kafuku and Mbarawa (2010) and Cao and Zhang (2015) who used Hibiscus esculentus, Moringaoleifera and Hodgsoniamacrocarpa as feedstock, respectively, also reported the same results. Therefore, methanol to oil molar ratio of 12:1 was used as an optimum ratio for chicken and guinea fowl egg shell derived CaO catalysts.

3.3.2 Effect of catalyst amount

The catalyst concentration (%w/v) effect on the transesterification was studied by varying the amount of catalyst from 1% to 3% which is on the basis of weight of catalyst to the volume of the calabash seed oil. shown in Figure 2, the derived CaO from chicken and guinea fowl egg shell can be successfully used to catalyze the transesterification reaction. The conversion reaction increased with an increase in catalyst concentration from 1 to 1.5 wt.%. A close observation reveals that the most preferable catalyst concentration on the transesterification for derived CaO from chicken, guinea fowl egg shell waste and commercial calcium oxide is 1.5% (w/v) since it gives the maximum biodiesel yield of 95.5%, 96.0% and 96.2% respectively. This result reveals that increasing the amount of catalyst increases the contact between the reactants and catalyst. Nevertheless, higher amount of catalyst (>1.5 wt.%), results in slightly decrease of biodiesel yield. The existence of moisture and remaining fatty acid in the raw material leads to side reaction that is saponification reaction, which produces soap and emulsion. This leads to increase in viscosity, formation of foams consequently increases the difficulties in separation process, leading to reduction in the biodiesel yield. Cao and Zhang (2015) and Kafuku and Mbarawa (2010) reported similar results. Ghoreishi and Moein (2013) reported that yield is not increase when catalyst amount increased in biodiesel significantly but will rather increase the overall production costs. An amount of 1.5 wt.% catalyst is adequate in order to obtain high biodiesel yield. This result implies that the transesterification is strongly dependent on the number of basic sites (Ngamcharussrivichai et al. 2008). From this study, it can be concluded that the most suitable amount of

CaO required for the transesterification of calabash seed oil with methanol is 1.5 wt%.

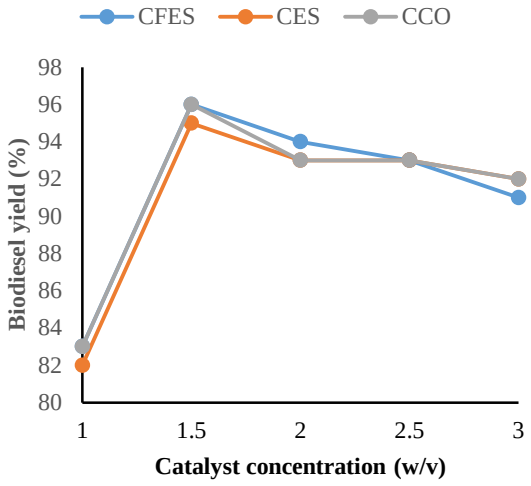

Figure 2 Effect of catalyst concentration

3.3.3 Effect of reaction temperature

The reaction temperature greatly has impact on reaction and biodiesel yield. The effect of reaction temperature on the yield of biodiesel is shown in Figure 3. In the same reaction conditions, there is an increase in yield when the reaction temperature is increased from 50℃ to 64℃, and subsequently the yield decreased. As can be observed from Figure 3, the most preferable temperature for the transesterification for derived CaO from chicken, guinea fowl egg shell and commercial calcium oxide is 64℃ since it produces the maximum yield of biodiesel of 95.1%, 95.3% and 95.5% respectively. At 64℃ methanol begins to boil and which increases the likelihood of collisions between molecules and promoting complete reaction. However, with higher temperature beyond 64℃, higher glycerol and lower biodiesel yields are obtained. Sivakumar et al. (2014) wrote that the alcohol would burn when the reaction temperature was higher than 65℃ hence, results reduction of biodiesel yield since the boiling point of methanol was at 65℃. Sivakumar et al. (2014) wrote that the yield obtained after 65℃ from catalysts would be reduced as a result of vaporization of methanol. Furthermore, the glycerol obtained beyond 65℃ will be more viscous than the normal. This is because the mono and diglycerides ester are believed to dissolve in the glycerol phase, which may be responsible for the very high glycerol volumes.

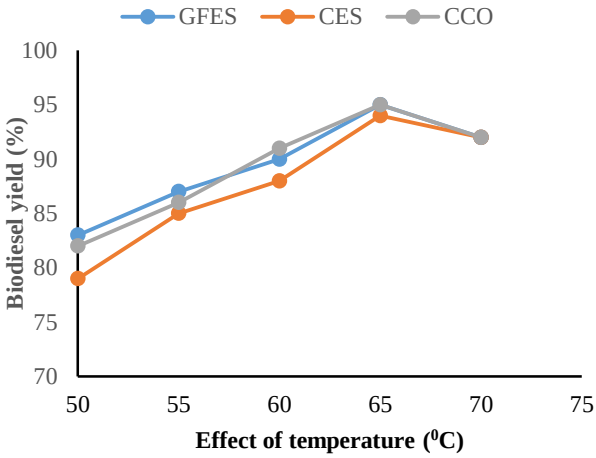

Figure 3 Effect of temperature

3.3.4 Effect of Reaction Time

One of the vital parameters during the transesterification process is the reaction time. Consequently, to compare the performance of the two CaO catalysts derived from chicken and guinea fowl egg shell, two runs were carried out in batches and the obtained results were compared. The catalyst amount of 1.5 wt.% was kept fixed, while the molar ratio of methanol to oil used is 12:1 and the reaction temperature of 64℃ was used. The obtained results for the two catalysts are shown in Figure 4. In the early stages of the transesterification reaction, biodiesel production was fast and eventually reached optimum in about 2 hours. However, as the time was prolonged, the yield was reduced. This is in agreement with Samart et al. (2009) whom explained that transesterification reaction between oil and alcohol was reversible, when the reaction time was long enough. As can be observed, the most preferable time for the transesterification for derived CaO from chicken, guinea fowl egg shell waste and commercial calcium oxide is 2 hours since it gives the maximum biodiesel yield of 95.1%, 96.2% and 96.3% respectively. Yin et al. (2012) reported that the conversion of biodiesel was highly dependable on the methanol to oil molar ratio and that greater methanol to oil molar ratio, results in shorter reaction time in reaching the equilibrium. Lu et al. (2010) wrote that since

transesterification reaction was reversible, there was decrease in the yield of biodiesel with longer reaction time. Consequently, optimum reaction time was considered to be 2 hours. The maximum yield of 95%, 96% and 96.2% were obtained in 2 hours at 64℃ for chicken, guinea fowl egg shell and commercial calcium oxide respectively.

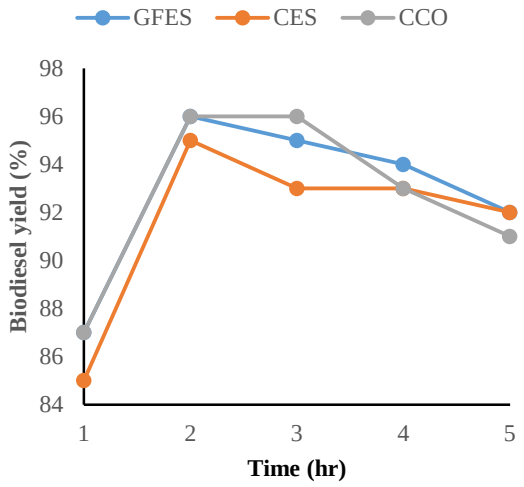

Figure 4 Effect of time

3.3.5 Effect of agitation speed

From the results shown in Figure 5, in the same reaction conditions, there was little variation in the biodiesel yield of the two catalysts. The yield increased when the speed increased from 200 to 250 rpm, and afterward kept practically constant as a result of a virtually reaction equilibrium.

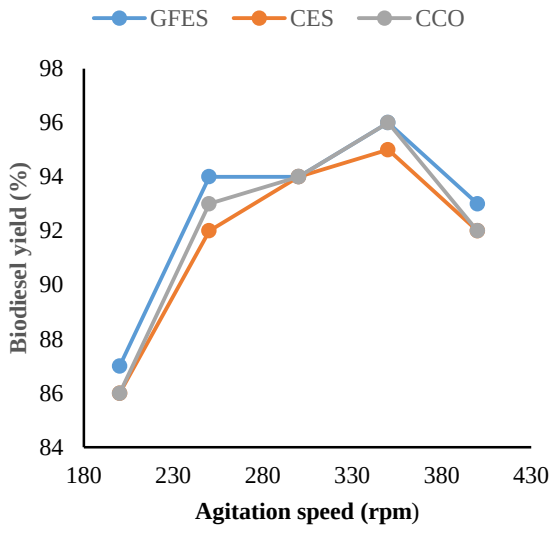

Figure 5 Effect of agitation speed

The result shows that the biodiesel yield increased with increasing speed of rotation. Mass transfer rate is improved with faster speed, which leads to increase in the contact rate among the reactants and hence increases the yield. However, continuously increasing the speed will nevertheless, also inhibit the effectiveness of the contact time of the reactants. As can be observed the most preferable agitation speed for the transesterification for derived CaO from chicken, guinea fowl egg shell waste and commercial calcium oxide is 250 rpm since it gives the highest biodiesel yield of 95.2%, 95.8% and 96.3% respectively.

3.4 Reusability of egg shell derived catalyst

Reusability is one of the important attributes of heterogeneous catalysts that is their ability to be reuse. The reusability of the catalyst derived from chicken and guinea fowl egg shell were examined for 10 cycles in the optimal condition: 1.5 wt.% catalyst (based on oil weight), a methanol to oil ratio of 12:1, a reaction temperature of 64℃, a reaction time of 2 hour and agitation speed of 250 rpm. At the end of each run, centrifugation method was used to separate the catalyst from the reaction mixture after which it was washed with n-hexane to remove the adsorbed stains, dried and recalcined at 700℃ for reutilization. The biodiesel yield was found to be about 91% for all the 8 tested runs. Thus, the biodiesel yield decreases when number of cycle increase. Nevertheless, CaO catalyst derived from chicken and guinea fowl eggshell demonstrated a high potential as catalyzing substance for biodiesel production as they show good stability and reusability in transesterification with little losses in its catalytic activity during reaction up to 8 cycles. The result obtained is in agreement with the findings of Tan et al. (2015) that CaO catalyst derived from waste calcined ostrich and chicken egg shell sustained good catalytic activity after being repeatedly used for 5 cycles. Jazie et al. (2012) also reported that the CaO catalyst derived from waste chicken egg shell was used repeatedly for 14 times without apparently losing its activity.

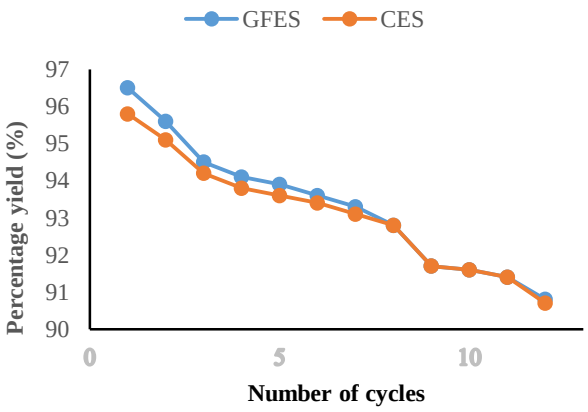

Figure 6 Effect of reusability of the catalyst

4 Conclusion

In this study, highly active catalysts were prepared from chicken and guinea fowl egg shells by using improved hydration method. The derived catalyst was found to be an efficient catalyst for the transesterification and significantly increase the conversion of biodiesel due to the presence of large surface area with good reusability off over eight cycles. 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 a speed of 250 rpm gave the best results. The results also show that the guinea fowl egg shell derived CaO catalyst exhibit higher surface area, higher basicity and smaller particle size. The guinea fowl egg shell also exhibits higher biodiesel yield of 96% compared to 95% for chicken egg shell as shown in Figure 6. The CaO catalyst derived from waste calcined guinea fowl and chicken egg shell sustained a good catalytic activity even after being repeatedly used for 12 cycles with yield around 91%, which indicates probable saving and cheaper biodiesel production possibilities. The calcined egg shell waste, is at a low cost, safe to handle material that can be used as catalyst for the transesterification of calabash seed oil to produce methyl ester. Egg shell is abundantly available, making it a potential raw material for a cheap, active catalyst for large scale biodiesel production. Only one calcination step is required to activate the material without any need for hazardous chemicals and its reusability.

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