International Journal of Research Publication and Reviews

Heterogeneous Catalyzed Biodiesel Production from Sesame Oil (Sesamumindicum*L.*) Using Calcined Chicken Eggshell

[1]Sani Saminu Bala, [2]Sabiu Shafiu, [3]Abdu Muhammad Bello, [4]Hauwa Ibrahim Muhammad

[1,2,3,4] Department of Chemistry, Faculty of Science, Kano University of Science and Technology, Wudil, PMB 3244, Kano State, Nigeria.

ABSTRACT

At present, the world faces severe issues on energy crises and environmental deterioration. Fuel is inevitable for the industrial development and growth of any country. However, fossil fuel resources have always been terrifying. Biofuel energy, a renewable source, seems to be an ideal solution for global energy and environmental concern. Furthermore, the problem associated with homogeneous catalysts of non-reusability resulting in higher production costs prompted the search for heterogeneous catalysts. In this study, the synthesis of heterogeneous CaO catalysts from waste chicken eggshells is reported, ensuing in a process that is economically viable and environmentally friendly. The work focuses on an optimized protocol for the production of biodiesel from a feasible source, sesame oil (*Sesamum Indicum L.*) through base-catalyzed transesterification. The eggshell was calcined at 900 °C for 3 hours. Upon calcination, the eggshell was transformed to CaO from the initial $CaCO_3$ structure, as can be observed from the FTIR spectrum that depicts a peak at 881 cm^{-1} corresponding to the Ca-O bond. The catalyst also has high basic sites of 2.933 mmol/g. When applied for the transesterification reaction, the optimal reaction conditions were found to be 1 wt. % catalyst amount (based on oil weight) and 15:1 methanol to oil molar ratio, with over 97.9% methyl esters conversion in 2 hours reaction period at a temperature of 60 °C.

Keywords: Sesame oil, Biodiesel, Calcined eggshell, CaO, Catalyst

INTRODUCTION

During the past decades, worldwide petroleum consumption has permanently increased due to the growth of the human population and industrialization, which has caused depleting fossil fuel reserves and increasing petroleum prices. On the other hand, the combustion of fossil fuels contributes most to emissions of greenhouse gases, which lead to atmospheric pollution and global warming. The transport section is almost utterly dependent on petroleum-derived fuels. The increase in the number of transport vehicles could affect the stability of the environment and climate on the whole planet (Balat, 2011). Therefore, there is a great need for a diesel fuel substitution with a clean, renewable fuel such as biodiesel. Biodiesel has a lot of technical advantages over fossil fuels such as lower overall exhaust emission and toxicity, biodegradability, derivation from a renewable and domestic feedstock, negligible sulfur content, superior flashpoint, and higher combustion efficiency. The biodiesel could be used as a pure fuel or as a blend with petro-diesel, which is stable in all ratios. Biodiesel production is expected to encourage employment and economic development in rural areas, to develop long-term replacement of fossil fuels, to reduce national dependency on petroleum import, and to increase the security of energy supply (Moser, 2009).

Transesterification, also known as alcoholysis, is a multistep reversible reaction in which triglycerides are converted to diglycerides and then to mono-glycerides which finally get converted to biodiesel and glycerol (by-product). Theoretically, 1 mole of triglyceride requires 3 moles of alcohol, Scheme 1. Nevertheless, generally higher amounts of alcohol are used to obtain high ester outputs, dependent on the type of oil used as feedstock, type and amount of catalyst, temperature, etc (Sharma and Singh, 2009; Jose *et al.,* 2011; Rashid *et al.,* 2016). When the alcohol used is methanol, the process is referred to as methanolysis. Methanol is the most preferred due to its low cost, polar structure, most available, and being the shortest chain alcohol. On the other hand, if ethanol is used, the process is termed as ethanolysis. Ethanol has the advantage of being renewable as it is produced from the fermentation of glucose and also has a low cost. Propanol, butanol, and octanol can also be used but their cost is higher as compared to methanol and ethanol (Demirbas, 2007; Balat, 2011; Shahid and Jamal, 2011).
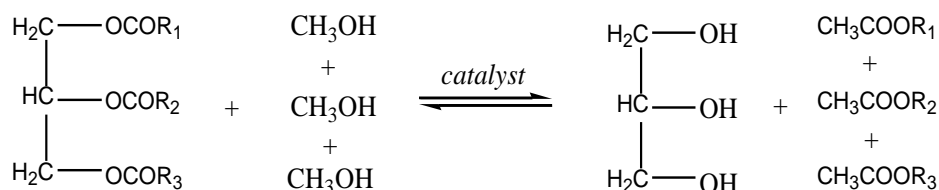
| Triglyceride | Methanol | | Glycerol | Methyl esters |

Scheme 1: Overall transesterification of a triglyceride.

Heterogeneous catalysis is widely used in industrial applications because of its catalyst re-usability, production purification, less energy, no water consumption, and facile separation, which often results in lower operating costs. On the other hand, homogeneous catalysis has limited industrial applications due to the difficult and costly catalyst separation and recovery (Hagen, 2006).

MATERIALS AND METHOD

Materials

The sesame oil used for this study was purchased from the Kurmi market in Kano State, Nigeria. Hydrochloric acid (HCl) with 37% purity, sodium hydroxide (NaOH), and methanol purity > 99% were supplied by QRëC^{TM}. All chemicals were of analytical grade and used without further purification.

METHODOLOGY

Catalyst Synthesis

Waste chicken eggshell was used as a precursor of calcium oxide (CaO) in this study. The eggshells were washed thoroughly with tap water and rinsed several times with de-ionized water to remove particles adhering to the surface, and dried in an oven at a temperature of 110 °C for 24 hours. The dry eggshells were crushed and sieved through a 63 mesh sieve. The dried powder was calcined in a muffle furnace at 900 °C for 3 hours. It was then cooled in a desiccator and stored in an air-tight glass bottle.

Basic Back Titration

Basic back titration was used to determine the basic sites of the prepared catalyst. Exactly 0.15 g of the catalyst was weighed into a centrifuge tube, and then 10 mL of distilled water was added and left for 24 hours. The mixture was then centrifuged, and the supernatant liquid was transferred into a conical flask. To this solution, 10 mL of 0.05 M HCl and 3 drops of methyl orange indicator were added and titrated against 0.02 M of NaOH solution to the endpoint.

FTIR (Fourier-Transform Infrared Spectroscopy)

Horizontal attenuated total reflectance Fourier transformation spectroscopy (FTIR-HATR) Cary 630 was used for the analysis of the catalyst sample in the range of 4000 cm^{-1} to 400 cm^{-1}. The sample was prepared by grinding and placing it in the sample window for analysis.

Free Fatty Acid Determination

To determine the free fatty acid content of the oil, a standard solution of 0.1 M KOH was prepared as a titrant. About 1.5 g of the oil sample was weighed and transferred to a conical flask with the exact measure being recorded (w) to which 50 cm^3 of propan-2-ol was added and stirred until dissolution, then 4 to 5 drops of phenolphthalein indicator was added to the mixture. The mixture was titrated against potassium hydroxide (KOH) solution to the first permanent purple colour and the volume of the titrant (v) was recorded. The same procedure was employed for the determination of FFA in biodiesel. The acid value (AV) of the sample was then calculated as in Equation 1, while the free fatty acid (FFA) content was determined using Equation 2.

$$ACID\ VALUE = \frac{MOLARITY\ OF\ KOH * VOLUME * MOLAR\ MASS}{WEIGHT\ OF\ OIL} \dots \dots 1$$

$$FREE\ FATTY\ ACID = \frac{ACID\ VALUE}{2} \dots \dots 2$$

Esterification

Exactly 40 mL of sesame oil was poured into a flask and preheated to 60 °C, followed by the addition of 51 mL of methanol to the preheated oil and stirred for a few minutes, and then 0.5% of H_2SO_4 was added to the mixture. Heating and stirring continued for 1 hour at atmospheric pressure. On completion of this reaction, the product was poured into a separating funnel. The excess alcohol and sulphuric acid used moved to the top of the surface and removed. The lower layer was separated for further processing (alkaline transesterification) (Anbumani*et al.,*2010).

Biodiesel Production

Precisely 10 mL of oil was measured and poured into a 250 mL two neck round-bottomed flask. The oil was preheated to 60 °C using an oil bath with a temperature regulator. A specific amount of calcium oxide catalyst (0.5%) was weighed and mixed with 13cm³ of methanol, to arrive at a 1:9 oil to methanol molar ratio. The mixture was then added to the preheated oil and the reaction continued at 60 °C. The product was separated from glycerol using a separating funnel after settling for 24 hours, while the excess methanol was distilled up. The biodiesel production was then optimized using the same procedure, but varying methanol to oil molar ratio: 12:1, 15:1, and 18:1; catalyst loading: 1%, 1.5%, and 2%; and reaction time: 1.5 hours, 2 hours, 2.5 hours and 3 hours, respectively. The percentage conversion was determined by the formula in Equation 3 (Ejeh and Aderemi, 2014).

$$\% \; Conversion = 1 - \frac{AV_{Biodiesel}}{AV_{Oil}} \; \dots \dots 3$$

Where, AV_{oil} and $AV_{biodiesel}$ are the acid values of oil and biodiesel, respectively.

DENSITY

The density of the biodiesel was measured with the help of a density bottle. The weight and volume of the oil were recorded and the density calculated.

RESULTS AND DISCUSSION

Catalyst Characterization

FTIR Analysis

The spectra of uncalcined and calcined eggshells are presented in Figures 1 and 2. From the spectra, it is clear that some peaks disappear in the spectrum of the raw eggshell and new peaks originate in the spectrum of the calcined eggshell. The peak at 881 cm⁻¹ corresponds to the Ca-O bond. The absorption peaks at 1417 cm⁻¹ and 877 cm⁻¹ are ascribed to the C-O bond. The absorption peak at 3640 cm⁻¹ is due to the O-H bond. The peaks at 2884 cm⁻¹, 2136 cm⁻¹, 1704 cm⁻¹, and 1689 cm⁻¹ were due to amines and amides present in the calcined eggshell membrane. The characteristics peaks of eggshell derived CaO and commercial CaO show nearly the same trend of the FTIR results. Hence, commercial CaO can be substituted by CaO derived from waste eggshells as a catalyst in biodiesel production to minimize the cost of production.
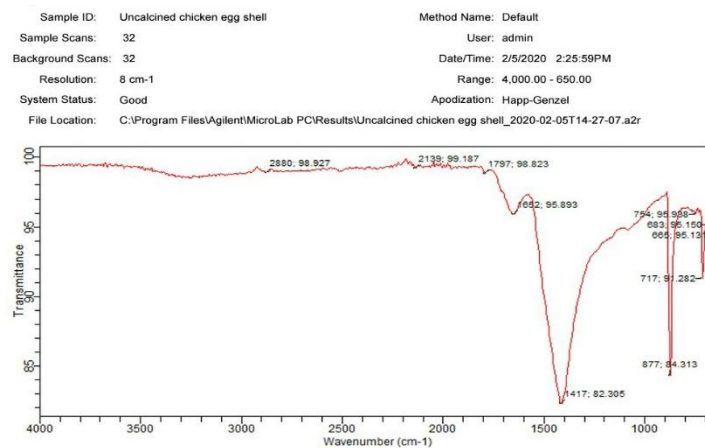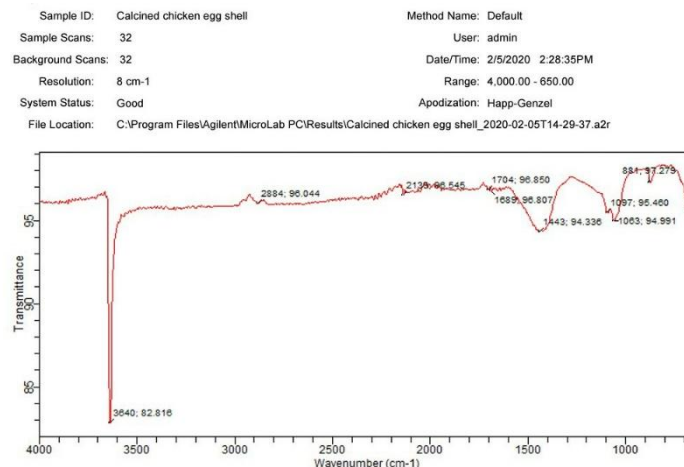

Figure 1: FTIR Spectrum ofUncalcined Chicken Egg Shell

Figure 2: FTIR Spectrum of Calcined Chicken Egg Shell

Basic Back Titration

From the result of the basic back titration, a value of 2.933 mmol/g was obtained as the basic site for the catalyst, which can be considered as high. Hence, the catalyst is expected to have high catalytic activity in the methanolysis reaction.

Biodiesel Analysis

Acid Esterification

For any biodiesel production to have a good yield, the acid value and the % FFA must be considered. A very high acid value leads to poor yield and increases production costs. The acid value (AV) and free fatty acid value (FFA) of the sesame oil before esterification were 9.724 and 4.862, respectively, which decreased to 2.36 and 1.18, respectively, after the esterification. These values resulted in biodiesel conversion of 94.6%, with a corresponding free fatty acid value and an acid value of 0.05 and 0.025. This conversion is very high and acceptable. Shashikant *et al.,* (2006) also prepared biodiesel from high acid value content mahua oil using a two-step transesterification process. The optimized process for the esterification process was 0.3 methanol/oil molar ratio, 1% H_2SO_4 at 60 ^{o}C for 1 hour. Zhang *et al.,* (2003) produced biodiesel from waste cooking oil and established that the acid-catalyzed process was better than the alkali-catalyzed process. The amount of acid catalyst variation affects the product. A higher amount of H_2SO_4 makes the product color blackish. The lower amount of acid addition affects the final product yield.

Alkali Transesterification

Effect of Catalyst Concentration and Methanol to oil ratio

Different amounts of catalysts; 0.5, 1.0, 1.5, and 2 wt% and oil to methanol molar ratio; 1:9, 1:12, 1:15, and 1:18, on the biodiesel production were investigated at 60°Cand 1 hour reaction time, the results are displayed in Table 3.1. For the 1:9 oil: methanol molar ratio, the biodiesel conversion was found to increase up to 78.9% with increasing catalyst amount from 0.5 to 1 wt%. However, when the catalyst concentration was increased from 1 to 2 wt%, the amount of biodiesel production was decreased to 77%. A similar trend follows for the 1:15 ratio, with the highest conversion of 94.6%. In the case of 1:12 and 1:18 ratios the highest conversion of 80.2% and 92.1%, were respectively obtained both with 0.5% catalyst amount. This implies the high catalytic activity of the synthesized catalyst since a very high conversion was obtained with a low amount. The decrease in the conversion with a high amount of catalyst may be attributed to the congestion of the reaction mixture by the catalyst, thereby avoiding mass transfer action. The result is also following the fact that the oil to alcohol mole ratio is a significant parameter that must be taken into account in the transesterification process.

In a similar study, Taufiq-yap *et al.,* (2011) studied transesterification of jatropha curcas oil using calcium-based mixed oxides catalyst. The optimum conversion of 80% was obtained at; molar ratio of 15, reaction time 6 hours, and catalyst amount 4% by wt. They found that CaZnO and CaMgO can be recycled up to 3 to 4 times. While, Nabi*et al.,* (2009) prepared biodiesel from high free fatty acid content Karanja oil. Due to high FFA, they pretreated the oil with H_2SO_4 and then used the alkali-catalyzed transesterification process. From GC studies up to 97% methyl ester conversion was obtained and the B100 mainly contained ester compared to alkanes and alkenes in diesel fuel.

Table 3.1: Catalyst Concentration and Methanol to oil ratio

CATALYST LOADING (%)	BIODIESEL YIELD (%)			
	1:9	1:12	1:15	1:18
0.5	73.6	80.2	82.5	92.1
1	78.9	70.3	94.6	80.2
1.5	68.0	64.0	91.5	48.0
2	77.0	72.0	93.0	80.2

Reaction Time Optimization

Based on the optimization of the methanol to oil molar ratio and catalyst loading, where the highest conversion of 94.6% was observed at 1% catalyst loading under 1:15 methanol to oil ratio, at 60 ^{o}C and 1-hour reaction. The reaction time was further optimized, and the results obtained were presented in Table 3.2. The conversion rate was observed to increase with the increase in reaction time. The effect of reaction time variation on the conversion efficiency slightly increased up to 120 minutes reaction with a maximum conversion of 97.9% and after that yield was observed to decrease slightly. This is because the transesterification reaction between oil and alcohol is a reversible process. Thus with an increase in reaction time, the reaction approaches equilibrium, after attainment of equilibrium the process reverse, leading to a decrease in conversion. This further buttresses the high activity of the catalyst, as the high conversion was obtained even at a low reaction time.

Table 3.2: Reaction Time Optimization

REACTION TIME (minutes)	YIELD (%)
60	94.6
90	95.3
120	97.9
150	96.8
180	93.9

Density

From the density results in Table 3.3, the density is observed to decreases as the conversion increases. For instance, the high conversion of 78.9% with 1:9 oil: methanol has a corresponding low density of $0.04 g/dm^3$. Whereas, the low conversion of 68% corresponds with a high density of $1.0 g/dm^3$. Similarly, a very low density of $0.03 g/dm^3$ was obtained when the conversion is highest, 94%. It is clear from this result that the higher the conversion, the lower the density. Hence, the essence of the transesterification reaction is achieved.

Table 3.3: Density of Biodiesel under Different Reaction Conditions

CATALYST LOADING (%)	OIL: METHANOL MOLAR RATIO			
	1:9	1:12	1:15	1:18
0.5	0.82	0.04	1.0	0.78
1	0.04	0.80	0.03	0.80
1.5	1.00	1.00	0.4	1.00
2	0.4	0.78	0.04	0.80

Comparison of Biodiesel Properties with ASTM Standards

The comparison of some biodiesel properties such as density, acid value, free fatty acid, and the percentage conversion with those of ASTM D6751 standards for biodiesel fuel, ASTM D975 standards for diesel fuel, and previous studies are presented in Table 3.4. The values for density were 0.88, 0.85, 0.03, and 0.866 respectively, for biodiesel fuel, diesel fuel, this study, and previous studies. The acid value was 0.05 and 2.70 for this study and the previous study, respectively. Free fatty acid and percentage yields were 0.025 and 94.60% for this study and 1.35 and 84.80% for the previous study.

Table 3.4 Comparison with Biodiesel Properties

PROPERTIES	ASTM D6751 STANDARDS FOR BIODIESEL FUEL	ASTM D975 STANDARDS FOR DIESEL FUEL	THIS STUDY	PREVIOUS STUDIES (Oseni*et al.,* 2012)
DENSITY	0.88	0.85	0.03	0.866
ACID VALUE ($65^{O}C$, g/dm^3)	0.5	-	0.05	2.70
FREE FATTY ACID (%)	-	-	0.025	1.35
PERCENTAGE YIELD (%)	-	-	94.60	84.80

CONCLUSIONS

In this study CaO catalyst was derived from waste chicken eggshell, the result from the FTIR analysis of the catalyst proved that catalyst synthesis was successful. Furthermore, the basic back titration result implied high basic sites for the catalyst, indicating the possibility of high catalytic activity. The sesame oil was found to have a high FFA of 4.86, making the direct transesterification process impossible, since, feedstock with high FFA couldn't be trans-esterified with alkaline catalyst due to soap formation. So two step processes were developed to convert FFA to its methyl ester. The first step is acid treatment, which reduces the FFA content of oil to 1.2 using 0.5% v/v H_2SO_4 catalyst, with methanol to oil ratio of 1:9 at 60 °C and 1 hour reaction time. After acid esterification, an alkaline transesterification reaction was carried out using different CaO amounts, oil: methanol molar ratio, and reaction time at 60 °C. The maximum yield of 97.9% was obtained with 1% catalyst, under 1:15 and 2 hours reaction time.

References

Balat M. (2011). Potential alternatives to edible oils for biodiesel production – a review. Energy Convers Manage; 52:1479–92.

Demirbas A. (2007).Biodiesel from sun flower oil in supercritical methanol with calcium oxide. Energy Conversion and Management 2007; 48:937-941.

Ejeh, J. and Aderemi, B. (2014).Production of Biodiesel from Shea Butter Oil using Homogeneous Catalysts. Leonardo Journal of Sciences, 24:39-48.

Jose D.M., Raj R.E., Prasad B.D., Kennedy Z.R., Ibrahim A.M., (2011). A multi-variant approach to optimize process parameters for biodiesel extraction from rubber seed oil. Appl. Energ. 88: 20562-2063.

Moser BR. Biodiesel production, properties, and feedstocks. In Vitro Cell Dev Pl 2009;45:229e–66.

Nabi M.N., Hoque S.M.N., Akhter M.S., (2009). Karanja, (PongamiaPinnata) Biodiesel production in Bangladesh, characterization of karanja biodiesel and its effect on diesel emissions.Fuel Processing Technology 2009; 90:1080-1086.

Oseni, M. I.; Obetta, S. E.; Orukotan, F. V. American Journal of Scientific and Industrial Research 2012, 3(2),62−68.

Rashid U., Ibrahim M., Nehdi I.A., Al-Resayes S.U., Ullah S., Mehmood M.A., Shahzadi S., (2016). Synthesis and characterization of poppy seed oil methyl esters. Chinese Journal   of Chemical Engineering. 24: 1087-1096.

Shahid EM, Jamal Y., (2011). Production of biodiesel: a technical review. Renew Sustain Energy Rev ;15:4732–45.

Sharma Y., and Singh B., (2009). Development of biodiesel: current scenario. Renew. Sustain. Energ.Rev. 13:1646-1651.

Taufiq-yap Y.H., Lee H.V., Hussein MZ, Yunus R. (2011). Calcium-based mixed oxide catalysts for methanolysis of Jatrophacurcas oil to biodiesel. Biomass Bioenergy; 35:827-34.

Zhang Y., Dube M.A., McLean D.D., Kates M. (2003). Biodiesel production from waste cooking oil: 1. Process design and Technological assessment. Bioresource Technology; 89:1-16.