IOSR Journal of Engineering (IOSRJEN) www.iosrjen.org
ISSN (e): 2250-3021, ISSN (p): 2278-8719
Vol. 12, Issue 12, December 2022, ||Series -I|| PP 22-29

Comparative Production of Biodiesel from waste cooking oil using CaO Nano-catalyst from Turkey, Duck and Guinea fowl egg shells

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Received 12 December 2022; Accepted 26 December 2022

Abstract
The role energy plays in our world today is immeasurable. Energy generated from petroleum reservoirs and other fossil sources has been of high demand which has resulted in environmental catastrophe such as depletion of ozone layer, emissions of trace and greenhouse gases, increased ultraviolet and infrared radiations from the sun to the earth etc. These hazards associated with the use of fossil fuels and the depletion of petroleum reservoirs has led to the search for alternative source of fuel that are environmentally friendly, re-useable and sustainable. Biodiesel produced from vegetable oil or animal fats is one of such alternative fuel. In this research, Calcium Oxide (CaO) nano-catalyst from duck, guinea fowl and turkey eggshell were investigated for the production of biodiesel from waste cooking oil (WCO) under the same operating conditions. The CaOnano-catalyst was obtained by calcining the egg shell powder which contains $CaCO_3$ in a furnace at 900°C for 3 hours. Xray florescence (XRF) analysis showed that the egg shells contain more of CaO with guinea fowl, duck and turkey shell having 92.396%, 89.82%, and 88.43% respectively. But the turkey had more silicon dioxide (SiO_2) and aluminum oxide (Al_2O_3) followed by duck and less in guinea fowl eggshells. The surface morphology of the CaOnano-catalyst using scanning electron microscopy (SEM) showed dense rod-like, porous aggregated shapes mainly made up of calcium oxide with wide surface area for all shells. 0.70 grams CaOnano-catalyst loading from duck, guinea fowl and turkey eggshells respectively, methanol to oil molar ratio of 12:1, and temperature 60℃, was found to be optimal for biodiesel production. The CaOnano-catalyst from turkey eggshell gave the highest biodiesel yield of 95.6 % followed by CaOnano-catalyst from duck (92%) and least in guinea fowl eggshells despite having the highest percentage of CaO. This can be attributed to the presence of more SiO_2 in turkey and duck eggshells that also acts as catalyst in the production of biodiesel compared to using only CaOnanocatalyst.
Keywords: **Biodiesel, waste cooking oil, transeterification, Turkey CaOnano-catalyst, Duck CaOnano-catalyst, Guinea fowl CaOnano-catalyst**

I. Introduction

Energy is inevitable in our world today. Every country needs energy in one way or the other to meet up with their daily activities such as cooking, heating, fueling engines etc. and it is a major source of income for most countries that generates energy. The demand for energy worldwide through the use of fossil fuels has resulted in environmental pollution and global warming through the emission of greenhouse gases, trace gases and also depletion of petroleum reservoirs. These have resulted in researchers looking for alternative fuels that are environmentally friendly, economical, renewable and sustainable. Fuels such as biodiesels are good replacement for petroleum based fuels.

Biodiesel is a biodegradable, renewable energy produced from edible oils and fats from animals. It is a non-toxic fuel with low particulate, low hydrocarbon, low carbon monoxide emissions, and high combustion efficiency fuel with high octane number and flash point [1] [2]. These properties makes biodiesel a good alternative for replacing petroleum based fuels and reducing environmental pollution and climate changes caused by the emission of greenhouse gases and trace gases to the environment [3].

Biodiesel is produce through transesterification reaction where vegetable oil or fat from animals are converted to biodiesel or monoalkylesters [4]. One way of producing biodiesel is through the use of calcium oxide (CaO) as catalyst from poultry eggshells with waste cooking oil (WCO) through transesterification process. Although other heterogeneous and homogeneous catalysts have been applied as catalyst in the transesterification process, CaO is readily available and cost effective [5]. The alcohol often used in transesterification process for biodiesel is methanol and ethanol. Several alcohols have also been studied for biodiesel production of which methanol and ethanol are the two most frequently used.

This research is focused on comparative use of CaOnano-catalyst obtained from turkey, duck and guinea fowl eggshells to produce biodiesel with WCO using methanol/ethanol in the transesterification process.

II. Material And Methods

The materials and equipment used for this research work are; Turkey, duck, and guinea fowl waste eggshells, methanol (CH_3OH), ethanol (C_2H_5OH), beaker, conical flask, measuring cylinder, magnetic stirrer, weighing balance, electric heater, oven, thermometer, separating funnel.

2.1 Preparation of waste cooking oil

Waste Cooking Oil was collected in a restaurant in Amassoma town, Bayelsa State, Nigeria. Food particles in the oil were removed through filtration using a filter paper. The oil was then heated to 110°C for thirty minutes to vapourize water present in the oil

2.2 Preparation of CaOnano-catalyst

Turkey, duck and guinea fowl eggshells were obtained in a poultry in Yenagoa in Bayelsa State, The eggshells were washed and placed in boiled water for about ten minutes. This is to allow for the removal of gelatinous material attached to the inner part of the eggshells. The eggshells were then washed with distilled water severally to remove impurities. The shells were then oven dried at 105°C for 24 hours. The eggshells were then grinded and sieved to obtain fine powder which was placed in a crucible and calcined at 900°C in a furnace for three hours to obtain calcium oxide nano-particle.

2.3Transesterifcation process for Waste Cooking Oil Measured quantity of waste oil was placed in a 250 ml conical flask containing a mixture of the desired CaO catalyst loading in methanol/ethanol and preheated to 60°C for an hour. This process was repeated using 25 milliliters of waste oil with different catalyst loading (0.15, 0.35, 0.7 and 1.00 gram) keeping temperature constant and time 1 hour with oil to methanol/ethanol ratio of 1:12. Oil to methanol/ethanol ratio of 1:12 was chosen based on previous research carried out by Erchamo et al [6]. Where they showed that biodiesel yield decreases beyond this ratio due to increase molar ratio of oil to alcohol which increased glycerin solubility in excess alcohol, thus reducing the yield of esters and decreasing the production of biodiesel. This same process was repeated a gain but this time temperature was varied (50, 60, 70, 80, 90 and 100°C) and optimum catalyst loading was kept constant at 1 hour reaction time. After the transesterification process, and the mixtures allowed to stand overnight, the mixture was then separated using separating funnels and the biodiesel extracted from the mixture containing catalyst, glycerol and biodiesel also known as methyl ester. The biodiesel produced was determined by applying equation 1.

$$\text{Biodiesel yield} = \frac{\text{Volume of biodiesel produced}}{\text{Volume of waste oil used}} \qquad 1$$

2.4 Density determination

The density of the biodiesel produced was calculated using equation 2

$$\text{Density} = \frac{\text{Mass of Biodiesel measured}}{\text{Volume of Biodiesel obtained}} \qquad 2$$

2.5 Viscosity Determination (at 40°C)

The viscosity of the biodiesel was carried out using a Jinotech rotational viscometer and a thermo cup for temperature investigation. 23 milliliters of the oil was heated to 40°C in a thermo cup with a thermometer. Then the viscometer was used to determine the viscosity of the oil. The kinematic viscosity of the oil was obtained by applying equation 3.

$$\text{Kinematic Viscosity } (mm^2/s) = \frac{\text{Dynamic Viscosity } (mPa.s)}{\text{Density } (g/cm^3)} \qquad 3$$

2.6 Flash point measurement

The flash point of the biodiesel was determined following similar procedure adopted by Gunstone [7]. 20 milliliters of produced biodiesel was poured into a round bottom flask and corked. The cork had an opening where thermometer was inserted to touch the biodiesel. The flask was heated and fumes forms and the temperature the fumes ignites is taken as the flash point of the biodiesel.

2.7Cloud Point Measurement

The cloud point of the biodiesel was measured following similar method by Gunstone [7] with few modifications. 5 milliliters of biodiesel was placed in a test tube with thermometer inserted. The test tube was placed in a 100 milliliters beaker partly filled with ice. The temperature at which the biodiesel start forming cloud is recorded as its cloud point.

2.8 **Acid value**

Applying similar method adopted by David and Matton [8] the acid value of the biodiesel was determined by mixing small quantity of the biodiesel with 30 milliliters of ethyl alcohol and boiled in a bath for 1.5 minute. The boiled mixture was titrated using 0.1 N potassium hydroxide and phenolphthalein indicator. Equation 4 was applied in calculating the acid value of the biodiesel. Where W is biodiesel weight (grams), V is the potassium hydroxide volume (milliliters) and N its normality.

$$\text{Acid value} = \frac{56.1 \times V \times N}{W} \qquad 4$$

III. Result and Discussion

Figure 1 shows the raw waste cooking oil obtained and table 1 shows the physiochemical properties of the oil measured before it was used for analysis.

Figure 1: Waste cooking oil

Table 1: Physiochemical properties for Waste cooking oil used for this research

Properties	Value
Colour	Dark
Density (Kg/m^3) at 25 °C	920
Kinematic Viscosity (mm^2/s) at 40 °C	30.20
Acid value (mg KOH/gm)	4.5

Figure 2 a, 2b and 2c respectively shows the raw eggshells for turkey, duck, Guinea fowl. And figure 3a, 3b and 3c shows the pulverized turkey eggshells, duck eggshells and guinea fowl egg CaOnano-catalyst obtained from the shells respectively used for biodiesel production.

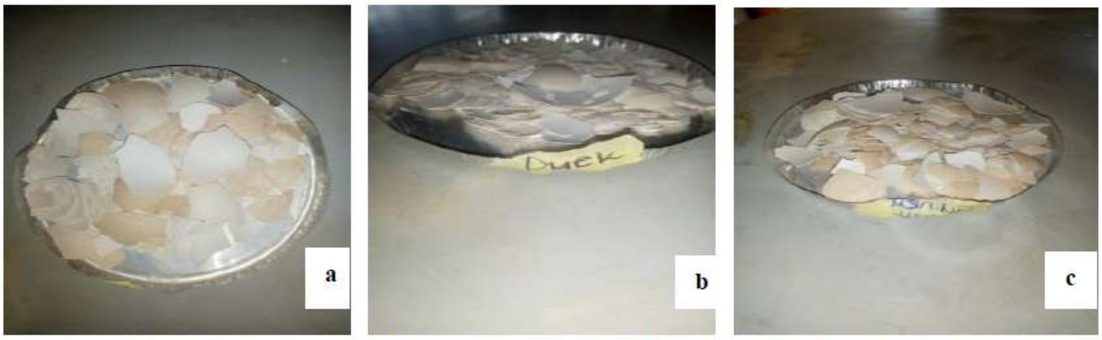

Figure 2: Raw egg shells (a) Turkey eggshell, (b) Duck fowl eggshell, (c) guinea fowl shell

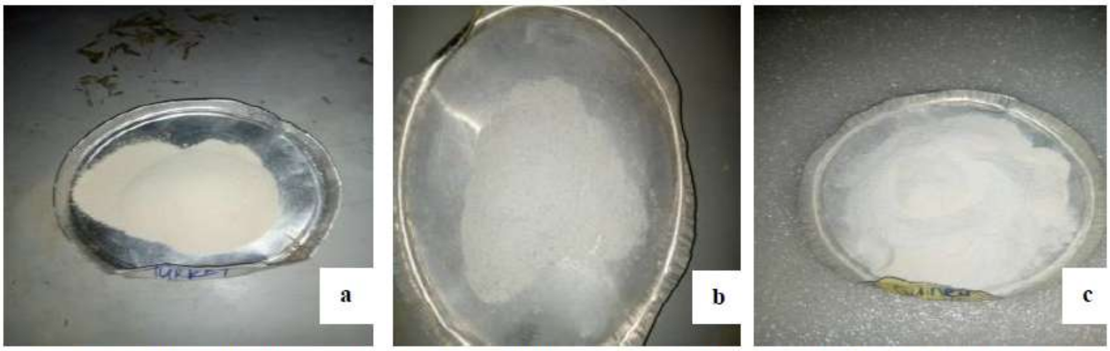

Figure 3 Calcined/pulverized eggshells (a) Turkey eggshell, (b) Duck eggshell, (c) Guinea fowl eggshell.

Figure 4 shows the transesterification process for the biodiesel production using CaOnanocatalyst from turkey eggshell. Figure 4a and 4b shows the methanol/ethanol mixture and heated WCO respectively. Figure 4c, 4d and 4f shows the transesterification processes. Figure 4c shows the WCO mixed with CaOnano-catalyst from turkey shell and the mixture turns cloudy. Figure 4d shows the mixture after overnight reaction and Figure 4e shows biodiesel produced after filtration process has been carried out. These processes were repeated for CaOnano-catalyst from duck eggshells and guinea fowl eggshells for comparism with turkey eggshell.

Figure 4: (a) methanol and ethanol mixture, (b) heated WCO, (c) transesterification process, (d) mixture after overnight, (e) Biodiesel after separation

Figure 5 (a), (b) and (c) shows the SEM image for turkey, guinea fowl and duck CaOnano-catalyst respectively, the figure shows a dense rod-like, porous aggregated shapes mainly made up of calcium oxide with wide surface area. The nano-catalyst have similar structures with turkey CaOnano-catalyst being the most aggregated and dense structure followed by guinea fowl. This is might be due to the presence of aluminum oxide, Al_2O_3 and silicon dioxide, SiO_2 in the egg shells.

The SEM analysis is corroborated with the x-ray fluorescence (XRF) result shown in table 2 which showed the elemental composition of the egg shells. From the XRF analysis, guinea fowl had the highest CaO value followed by duck shell and turkey shell. But the turkey had more aluminum oxide and silicon dioxide.

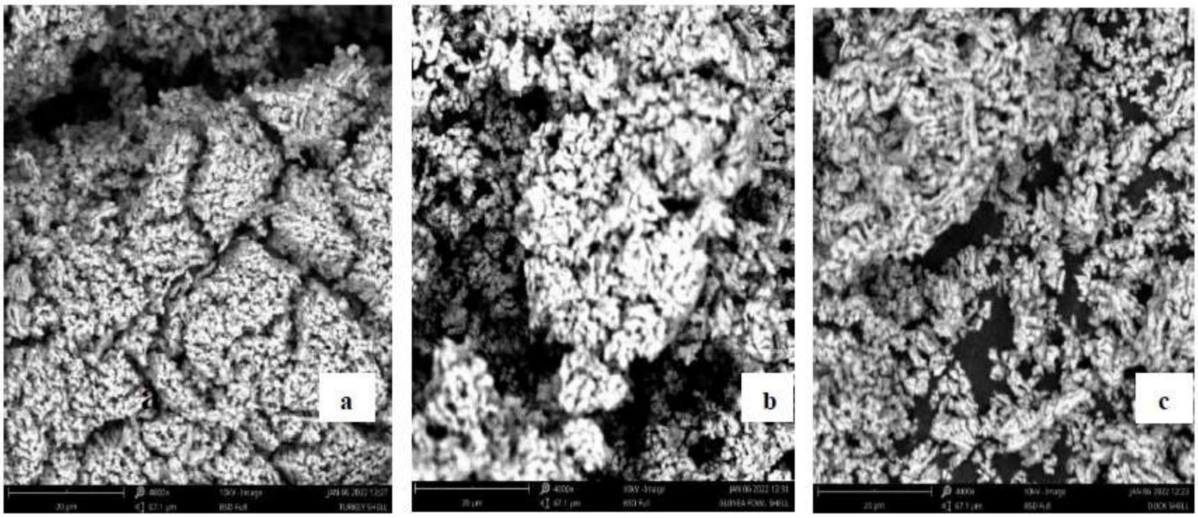

Figure 5: SEM images for (a) turkey, (b) guinea fowl and (c) duck egg shells

Table 2: XRF analysis of the pulverized egg shells

Compound	Composition (%)		
	Turkey	Guinea fowl	Duck
CaO	88.433	92.396	89.816
SiO_2	6.668	2.011	4.408
Al2O3	3.116	2.981	2.965

Table 3 shows the biodiesel produced using CaOnano-catalyst from the different eggshells by altering the catalyst loading from 0.15 – 1.00 gram. Turkey eggshell gave the highest yield of biodiesel despite guinea fowl and duck shell having higher CaO values. This is because researches have shown that CaO and silicon dioxide composite acts as good catalyst and effective in biodiesel production compared to using only CaO [9] [10]. Aluminum oxide also has catalytic properties too in biodiesel production [11]. Thus the presence of SiO_2 and Al_2O_3 in turkey shell CaOnano-catalyst acted as catalyst also to esterify the free fatty acid (FFA) hence; the presence of water did not have significant effect on the performance of the turkey eggshell. The presence of silicon dioxide and aluminum oxide also minimized the leaching of Calcium Oxide due to a higher surface area and stability, thereby producing higher quantity of biodiesel.

Table 3: Effect of varied catalyst loading on biodiesel produced

Catalyst Loading	Biodiesel Yield (%)		
	Turkey	Guinea fowl	Duck
0.15	83.40	80.1	83.7
0.35	88.80	83.20	89.20
0.70	95.60	89.00	92.00
1.00	88.00	85.20	86.80

The amount of biodiesel produced increased as catalyst loading increased from 0.15 grams to 0.70 grams and reduced when the catalyst amount was raised further to 1.00 grams. This might be due to more available surface area for reaction as catalyst loading increases gradually. However catalyst above 0.70 grams results in a slight decrease of biodiesel yield. This might be due to saturation of available surface area for reaction due to excess catalyst loading beyond optimum quantity. Thus, the optimum CaOnanocatalyst concentration from the different eggshells required for this experiment is 0.70 gram. Since 0.70 gram gave maximum yield of 92%, 89% and 95.6% for duck, guinea fowl and turkey CaOnano-catalyst respectively. This is corroborated with the plot in figure 6 which shows biodiesel production with varying catalyst loading. The figure showed low biodiesel production for guinea fowl at 0.15 grams and much higher production for duck and turkey shells with an increase peak production of biodiesel for turkey at 0.7 grams catalyst loading before declining as catalyst loading increased.

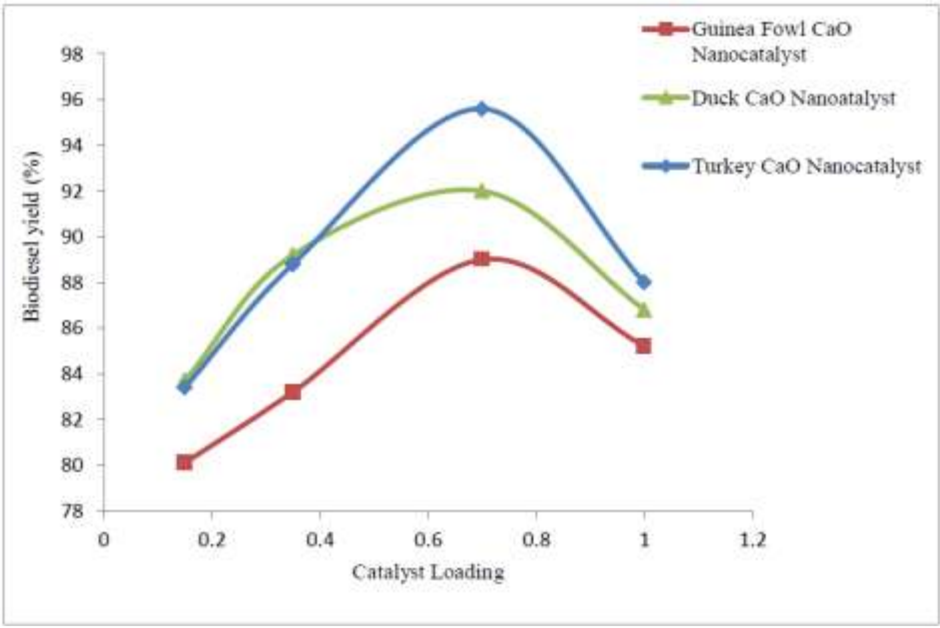

Figure 6: Biodiesel yield against Catalyst loading

Figure 7 shows the effect of varying temperature on the biodiesel production using 0.7 grams and oil to methanol/ethanol ratio of 1:12 for duck, guinea fowl and turkey CaOnano-catalyst loading respectively. The biodiesel yield increases from 50°C to maximum point at 60°C for all CaOnanocatalyst. At 60°C the biodiesel yields are 91.80%, 88.57% and 94.90 % for duck, guinea fowl and turkey CaOnano-catalyst respectively. Above 60°C the biodiesel produced start decreasing with least yield at 100°C. This is as a result of higher amount of glycerol as previously reported by Sivakumar and co-researchers [12] who observed that biodiesel obtained using CaO catalyst beyond 65°C reduced in quantity due to methanol-ethanol mixture vapourization. This research recorded 60°C as the maximum temperature for biodiesel production using CaOnano-catalyst from duck, guinea fowl and turkey eggshells respectively.

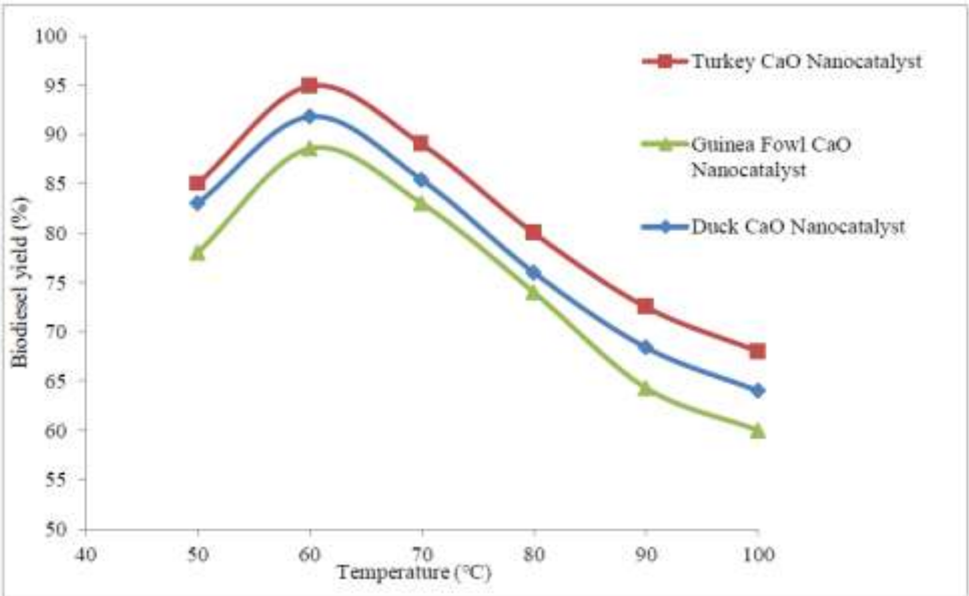

Figure 7: Biodiesel yield against temperature

Table 4 shows the comparism of the biodiesel produced using turkey, guinea fowl and duck CaOnanocatalyst to the America Society for Testing and Materials standard (ASTM-D6751) and the European standard for biodiesel (EN-14214) [13] [14]. These showed that the biodiesels produced using turkey, guinea fowl and duck CaOnanocatalyst falls within the ASTM and EN standard specifications. Biodiesel produced using turkey CaO had lower flash point, lower acid value and kinematic viscosity compared to duck and guinea fowl produced biodiesel. This indicates that the biodiesel from turkey CaO will ignite easily due to the low flash point, it contains less free fatty acid and less corrosive due to its reduced acid value and will improve the performance of the engine due to its lower kinematic viscosity compared to duck and guinea fowl produced biodiesels.

Table 4: Turkey, duck and guinea fowl biodiesel properties compared with ASTM-D6751 standards and EN-14217 for biodiesel

S/N	Property	Biodiesel			Biodiesel	
		Turkey	Guinea Fowl	Duck	ASTM-D6751 Standard	EN-14217 Standard
1	Density (kg/m^3) at 25°C	869	872	870	850-900	860-900
2	Kinematic viscosity (mm^2/s) at 40°C	3.89	4.12	3.94	1.9-6.0	3.5-5.0
3	Flash point (°C)	151	156	153	>130	>120
4	Cloud point (°C)	4.1	4.5	4.3	-3-12	-
5	Acid Value	0.21	0.30	0.26	<0.8	<0.5

IV. Conclusion

This research work has shown that biodiesel can be produced from CaO derived nano-catalyst from duck, guinea fowl and turkey eggshells. Methanol/ethanol to oil molar ratio of 12:1, temperature 60℃, and 0.70 grams CaOnano-catalyst loading from duck, guinea fowl and turkey eggshells respectively was optimal for biodiesel production. The CaOnano-catalyst from turkey egg shell gave the highest biodiesel yield of 95.6 % followed by CaOnano-catalyst from duck (92%) at the optimum catalyst loading and temperature. These increases in biodiesel yield is partly attributed to the presence of silicon dioxide and aluminum oxide present in turkey and duck shells that also acts as catalyst in the transesterification process. Biodiesel from turkey CaOnano-catalyst had lower flash point, acid value and kinematic viscosity compared to biodiesel from duck and guinea fowl. These parameters indicate that biodiesel produced using CaOnano-catalyst from turkey eggshell will perform better when applied in engines.

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Orlando Ketebu, et. al. "Comparative Production of Biodiesel from waste cooking oil using CaO Nano-catalyst from Turkey, Duck and Guinea fowl egg shells." *IOSR Journal of Engineering (IOSRJEN)*, 12(12), 2022, pp. 22-29.