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PRODUCTION OF BIODIESEL FROM WASTE OIL USING A CATALYST SYNTHESIZED FROM WASTE CLAM SHELL

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ABSTRACT

An investigation into biodiesel production from waste vegetable oil using a catalyst synthesized from waste clam (*Mercenaria mercenaria*) shells was carried out. The clam shells were thermally decomposed at 800 °C for 5 h and its properties were characterized with SEM and XRF. It is composed of 30.88 wt.% CaO and other basic oxides catalysts known to be active in transesterification; and a surface morphology indicating pores in the catalyst. The transesterification reaction was conducted and the effect of alcohol to oil molar ratio, catalyst concentration, reaction time and temperature on the yield of the biodiesel were determined. Maximum biodiesel yield of 76.18 wt. % was realized at 60 °C, 9:1 molar ratio of alcohol to oil, a catalyst concentration of 3 wt.% in a reaction time of 2 h. The FTIR studies of the biodiesel showed that it is composed of alkanes, aromatics, alcohols and the physiochemical properties, namely density, viscosity and flash point are 0.897 g/mL, 3.9 mm^2/s and 152.8 °C, respectively; falls within the biodiesel ASTM specifications.

Keywords: Clam shells, Calcium oxide, Waste vegetable oil, Transesterification, Biodiesel.

INTRODUCTION

The world suffers global warming owing to the depleting ozone layer and emission of greenhouse gases. These greenhouse gases are substantially released from the burning of fossil fuels. In addition, these fossil fuels are not renewable within the time scale of life; crude oils are formed over millions of years. Therefore, the world energy generation trends are moving away from fossil fuels in order to combat this twin problem of environmental degradation and energy sustainability (Wauton and Ogbeide, 2019a; Tshizanga *et al.*, 2017; Dalvand and Mahdavian, 2018; Sisca *et al.*, 2020; Fattah *et al.*, 2020).

Biodiesel has a great capability for development as an alternative to fossil fuels; it has the advantage of carbon dioxide neutrality in combustion as compared to fossil diesel. Molecular analysis reveals that the same quantity of carbon dioxide absorbed during photosynthesis in the growth of the plant is discharged on the combustion of fuel obtained from it. Essentially, the use of biomass energy is the reversal of photosynthesis (Dara, 2006; Bhetalu *et al.*, 2012; Atelge, 2022; Fattah *et al.*, 2020). Further, biodiesel has a better exhaust gas emissions and fuel properties, namely lubricity and flash point that makes it easier to handle (Glistic and Orlovic, 2014 Sisca *et al,* 2020).

Biodiesel is an ester produced from the reaction between a triglyceride and monohydric alcohol, known as esterification (Moser, 2009; Fattah *et al.*, 2020). The triglycerides used to produce the biodiesel can be gotten from a variety of lipids such as palm oils, palm kernel oil, coconut oils, waste frying and cooking oils from the canteens, jatropha oil, vegetable oil and animal fats (Meng *et al.*, 2009; Sahafi *et al.*, 2021).

Nigeria is considered as the third leading producer of oil palm in the world. It has a high potential for the production of biodiesel due to its favourable climatic condition for the cultivation of oil plants, namely coconut palm (*Cocus nucifera*), oil palm (*Elaeis guineesiss*), soybean (*Glycin max*), shear butter (*Sesomum indicum*) and groundnut (*Arachishypogea*) etc. (Olutoye *et al.*, 2016; Onanuga and Coker, 2013). However, an energy production should preferably not compete with food for substrate; hence, waste vegetable oil as an alternative source of energy is most desirable than many other sources of biodiesel production (Bhattacharya and Kumar, 2010; Asadullah *et al.*, 2007; Mckendry, 2002; Sahafi *et al.*, 2021; Singh *et al.*, 2021; Hosseinzadeh-Bandbafha *et al.*, 2022; Suzihaque *et al.*, 2022). The use of waste vegetable oil for the production of alternative energy mitigates environmental concerns occasioned by its improper management (Mohamed *et al.*, 2020;

Singh *et al.*, 2021).

Most researchers had concluded that animal fats and vegetable oils is a possible alternative for diesel engines, but it cannot be used raw owing to their low volatility and high viscosity, which can lead to several problems for the engine. Some of these problems include, injector coking, deposit formation in the engine and piston ring sticking (Asadullah *et al.*, 2007; Mckendry, 2002). However, these defects can be minimized or eliminated through a process called transesterification. In this process, reaction of triglyceride from vegetable oil with alcohol produces biodiesel and glycerin as a by-product (Balat and Balat, 2010).

Transesterification can occur with or without a catalyst. A catalyst, homogenous or heterogeneous increases the rate and yield of biodiesel. NaOH, CH_3ONa, and KOH are some homogeneous catalysts used to produce biodiesel (Demirbas, 2011; Atapour and Kariminia, 2011). The increase in the rate of reaction, yield and conversion to biodiesel using these catalysts at moderate pressure and temperature has been reported. However, the limitation to the use of these catalysts include the formation of emulsion, catalyst separation, generation of excess wastewater that can affect the yield and downstream purification of the biodiesel and high energy consumption (Talebian-Kiakalaieb *et al.*, 2013; Mohamed *et al.*, 2020; Fattah *et al.*, 2020). To eliminate these shortcomings of transesterification with homogeneous catalysts, researchers are concentrating on the use of heterogeneous catalyzed transesterification. Before the use of solid catalysts, proper investigation should be carried out to prevent deactivation processes. This investigation will show characteristics such as pore size, hydrophobic surfaces, high concentration of active site etc. of the solid catalyst (Ritro *et al.*, 2008; Lotero *et al.*, 2005; Dalai *et al.*, 2006; Miao and Shanks, 2009; Sisca *et al.*, 2020).

Heterogeneous catalyzed transesterifications are often time-consuming as a result of diffusion across the alcohol, oil and solid catalyst phases. Hence, it is expedient to determine a heterogeneous catalyst of high performance (Niju and Anantharaman, 2014). Thus, oxides of alkaline earth metal with high basicity are appropriate for transesterification and among these group of metal oxides, calcium oxide has proven to be the most effective solid catalyst for the production of biodiesel (Chen and Fang, 2011; Ilgen, 2011; Birla *et al.*, 2012).

Research on the utilization of calcium carbonate ($CaCO_3$) from seashells for the production of biodiesel and biosorption materials has been of recent interest (Boey *et al.*, 2011; Yan-jiao, 2013). Clam shell waste which is a product of the consumption of the sea food, is littered in most communities on the coastline, especially in Bayelsa State, Nigeria. The shells of these organisms are made up largely of calcium carbonate (Akhabue and Ogogo, 2018; Chojnacha, 2005). When calcium carbonate is heated at high temperature, it can be converted to calcium oxide, an effective solid catalyst for the reaction between triglyceride and monohydric alcohol to produce methyl ester (Tshizanga *et al.*, 2017).

There is a paucity of reports on the production of biodiesel from clam shells. Nair *et al.* (2012) produced biodiesel from low free fatty acid waste frying oil using calcium oxide synthesized from the clam (*Mereterix mereterix*) as a heterogeneous catalyst. Niju *et al.* (2016a; 2016b) subjected white bivalve clam shell to calcination, followed by hydration and dehydration to synthesize calcium oxide catalyst with high activity to produce biodiesel in batch transesterification of waste frying oil. They obtain 94.25 wt. % yield of methyl ester at 7 wt. % catalyst (based on oil weight), methanol to oil ratio of 12:1, reaction temperature of 65 $^{\circ}$C and reaction time of 1 h. The biodiesel yield was 26.68% higher than that produced from commercial calcium oxide. Their investigation was advanced with a continuous flow jacketed packed bed transesterification reactor. The packing material was the synthesized calcium oxide catalyst. The reboiler temperature was fixed at 65 $^{\circ}$C, the optimum obtained from their previous study. A maximum biodiesel yield of 94.41 % was realized at a reactant flow rate of 0.2 mL/min, methanol/oil ratio of 6:1 and catalyst bed height of 180 mm.

Our review does not reveal a catalyst synthesis from the clam (*Mercenaria mercenaria*) shell nor its

usage for biodiesel production. Hence, this investigation on the production of biodiesel from waste vegetable oil (WVO) using a catalyst synthesized from waste clam (*Mercenaria mercenaria*) shell is advanced.

MATERIALS AND METHODS

Collection of Materials

Waste vegetable oil was obtained from restaurants in Yenagoa, Bayelsa State, Nigeria. The methanol (99.05 wt. % pure; 64.54 °C boiling point) was purchased from Doubra Scientific Instruments Nig. Ltd., Yenagoa, Bayelsa State, Nigeria. Waste clam shells were collected from a food vendor at Ekowe, Bayelsa State, Nigeria. Other chemicals used include sulphuric acid, sodium hydroxide, ethanol and phenolphthalein indicator. The chemicals were all of analytical grade.

Waste Vegetable Oil Sample Preparation

WVO collected was allowed to settle at atmospheric temperature and pressure for 5 days and thereafter filtered by sieves of 100 nm diameter in order to remove entrained food particles; subsequently, it was heated at 105 °C for water removal.

Catalyst Preparation

The waste clam shells were washed thoroughly with tap water to remove dirt, then boiled for 15 min. and scrubbed with a brush to remove the surface coatings. The shells once again were washed using distilled water and then dried to a constant weight. Figures 1 and 2 present waste clam shells before and after washing and drying, respectively.

Figure 1: Waste clam shells before washing and drying.

Figure 2: Waste clam shells after washing and drying.

The clean dry shells were oven baked at 200 °C for 1.5 h to increase brittleness. Then they were crushed and ground into powder form. The powder obtained was then separated with sieves to obtain particle sizes (≥ 0.3 mm). Calcination was carried out in a muffle furnace (Model: VECSTAR LF3) at 800 °C for 5 h for complete conversion of calcium carbonate ($CaCO_3$) to calcium oxide (CaO) as in Equation 1 (Nair *et al.*, 2012; Tshizanga *et al.*, 2017)

$$CaCO_3 \rightarrow CaO + CO_2 \quad (1)$$

The hot calcined samples were immediately transferred from the muffle furnace into a desiccator and left to cool to room temperature. The cooled samples in the desiccator were stored in an air tight glass bottle until they are needed to prevent moisture.

Catalyst Characterization

Scanning electron microscope (SEM) (Model: F E I Quanta FEG 200) was used to determine the surface morphology of the CaO catalyst synthesized from the clam shell. Micrographs

were observed at 500 and 1000 magnifications. X-ray fluorescence (XRF) (Thermo Scientific ARL OP-TIM'X 166) was employed to determine the chemical composition of the synthesized catalyst.

Oil Pretreatment

Determination of Free Fatty Acid Concentration

The standard analytical methods of fats and oils of the American Oil Chemists' Society (AOCS) were adopted in the determination of the concentration of free fatty acids in the waste vegetable oil. 10 g of the waste vegetable oil was introduced into a 250 mL conical flask and 20 g of ethanol (99.5%v/v) added. The mixture was slightly heated to dissolve the oil. Three drops of phenolphthalein indicator were added and titrated with 0.1 M NaOH. The End point of the titration was indicated by the change in the colour of the WVO from light brown to deep purple. Triplicate titrations were carried out and an average value was obtained. The percentage free fatty acids concentration was calculated using equation 2 (Ayoola *et al.*, 2016; Viele *et al.*, 2016):

$$\% FFA = \frac{(V \times M \times W)100}{m} \qquad (2)$$

Where, FFA is the free fatty acid content of the waste vegetable oil, V is the volume (mL) of NaOH used, M is the molarity (mol/1000 mL) of the NaOH used, W is the average molecular weight (212.81 g/mol) of the fatty acid components in the WVO, m is the mass (g) of the waste vegetable oil sample.

The Waste Vegetable Oil Pretreatment

Pretreatment of the waste vegetable oil was carried out to reduce the percentage of free fatty acids to less than 1%. The pretreatment process was carried out in a 1 L round bottom flask using a 7:1 molar ratio of methanol to oil, sulphuric acid concentration of 1 wt. % and heated to 60 °C reaction temperature and stirred at 800 RPM using a temperature-controlled hotplate and magnetic stirrer (Model: JENWAY 1000) for 2 h. At the end of the time, the reaction product was transferred into a separating funnel and left to settle for 1 h. Two layers were observed. The ester at the top was separated from the excess methanol and water at the bottom and further heating of the ester was done to remove any water present. Thereafter, the free fatty acid concentration of the treated oil was determined to know if it is less than 1% (Akhabue and Ogogo, 2018; Akhabue *et al.*, 2022).

Biodiesel Production and Purification

Biodiesel was produced from the treated waste vegetable oil in a 250 mL conical flask using a temperature-controlled hotplate and magnetic stirrer. The effects of transesterification reaction parameters on biodiesel yield were determined as follows:

Effect of Reaction Time on Biodiesel yield

The transesterification process was run at a reaction time of 40, 60, 90, 120 and 150 min for a catalyst concentration, methanol to oil molar ratio and reaction temperature of 1 wt. %, 6:1, and 60 °C, respectively. The reaction time of maximum yield of biodiesel was determined. Triplicate experiments were conducted and an average value obtained.

Effect of Catalyst Weight Percent on Biodiesel yield

The reaction time for maximum biodiesel yield determined from the first run, 6:1 methanol to oil molar ratio and temperature of 60 °C were taken as constant for the second run and the transesterification process was repeated with catalyst concentrations of 1, 2, 3, 4 and 7 wt. % to determine the effect of catalyst concentration on biodiesel yield. The average value was obtained from triplicate experiments.

Effect of Alcohol to Oil Molar Ratio on Biodiesel Yield

The third run was conducted with an alcohol to oil ratios of 5:1, 6:1, 7:1, 9:1 and 12:1 using the catalyst concentration and reaction time that gave maximum biodiesel yield in the first and second run and reaction temperature of 60 °C was kept constant. The alcohol to oil ratio that furnished the maximum yield of biodiesel determined. The average value was obtained from triplicate experiments.

The Effect of Temperature on Biodiesel Yield

Lastly, the reaction was repeated with maximum biodiesel yield values of concentration of catalyst,

reaction time and alcohol to oil ratio in the 1st, 2nd and 3rd runs, while temperature of the reaction was varied as 45, 50, 55, 60 and 70 °C in order to determine the effect of reaction temperature on biodiesel yield. Triplicate experiments were carried out and the average value was obtained.

Biodiesel Purification

At the end of each reaction, the mixture was separated from the catalyst by decantation and then filtration. Thereafter, the filtrate was introduced into a separating funnel and allowed to settle overnight. The bottom layer composed of glycerol was separated from the biodiesel layer. The biodiesel produced was rinsed with approximately one-third its volume of warm water thrice inside the separating funnel. The washed biodiesel was later heated to a temperature of 105 °C in an oven in order to remove any entrained water in the biodiesel. The yield of the biodiesel was calculated using equation 3 (Akhabue and Ogogo, 2018; Ayoola *et al.*, 2016; Viele *et al.*, 2016):

$$yeild = \frac{mass\ of\ biodiesel}{mass\ of\ WVO} \times 100 \qquad (3)$$

Biodiesel Characterization

The biodiesel produced at maximum transesterification process parameters was characterized using the American Society of Testing and Materials methods (ASTM). The physical properties determined include: viscosity (ASTM D445), pour point (ASTM D97), flash point (ASTM D92), acid value (ASTM D664), moisture content (ASTM D1744) and density (ASTM D4052). The functional groups found in the biodiesel obtained were determined using FTIR (Model: WQF 510A).

RESULTS AND DISCUSSION

Catalyst Characterization

Scanning Electron Microscopy (SEM) Analysis

The surface morphology of the synthesized catalyst examined by the scanning electron microscope (SEM) at two different magnifications are shown in Figures 3 and 4. The SEM images indicated that the catalyst has a rough surface morphology with non-uniform small and large particle sizes ranging from 80 to 100 μm. The roughness could be attributed to the hard nature of clam shell and the presence of pores (Olutoye *et al.*, 2016).

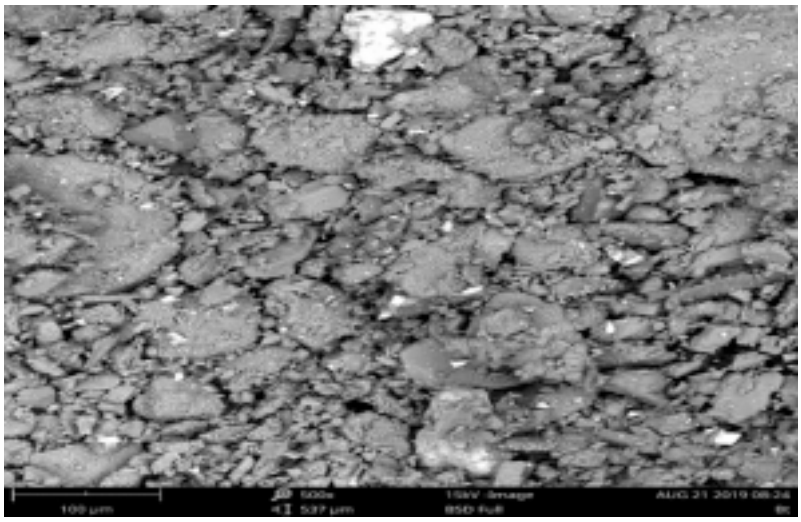

Figure 3: Scanning electron microscope images of calcined clamshells at magnification of 500.

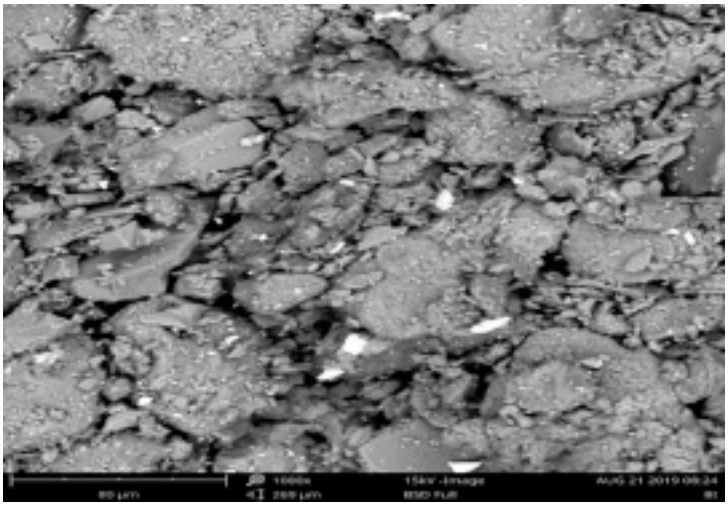

Figure 4: Scanning electron microscope images of calcined clamshells at magnification of 1000.

X-Ray Fluorescence

The catalyst composition prepared from clamshell was determined by X-Ray Fluorescence (XRF) as presented in Table 1. Table 1 shows that it contained a higher concentration of CaO (30.88%), which is a favorable base catalyst in the production of biodiesel with little toxicity and reacts easily with water (Zhang *et al.*, 2003), followed by K_2O (20.94%), SiO_2 (14.76%), Fe_2O_3 (9.67%), Ta_2O_5 (7.62%), TiO_2 (3.44%), Al_2O_3 (2.72%), WO_3 (2.14%). The residual is composed of different metals oxides such as MgO, BaO, ZnO, CeO, etc in trace amounts. These oxides have been known to be active materials for transesterification (Birla *et al.*, 2012). The basic oxides (MgO, K_2O, FeO_3) will enhance the catalyst's basic strength, while the acidic components such as SiO_2 and SO_3 have potential to mediate esterification of the feedstock's FFA content (Boey *et al.*, 2011).

Table 1: Chemical composition of clam shell catalyst.

Compound	Concentration (%)
CaO	30.88
K_2O	20.94
SiO_2	14.76
Fe_2O_3	09.67
Ta_2O_5	07.62
TiO_2	03.44
Al_2O_3	02.72
WO_3	02.14
ZrO_2	01.86
MnO	01.66
BaO	00.71
MgO	00.59
Others	00.64

Table 2: % FFA composition after pretreatment steps.

Experiment	% FFA
Before pretreatment	2.61
1st pretreatment	1.39
2nd pretreatment	0.91

Table 3: Physiochemical properties of waste vegetable oil (WVO) biodiesel.

Property	Unit	WVO biodiesel	ASTM biodiesel standard (Patil *et al*., 2012; Degfie *et al*., 2019)
Density @ 27 °C	g/mL	0.897	0.8 – 0.9
Viscosity @ 40 °C	(mm^2/s)	3.90	1.9 – 6
Moisture content	(%)	0.6	--
Pour point	(°C)	22.0	-15 – 16
Acid value	(%)	0.267	Max 0.80 *kg KOH/g*
Flash Point	°C	152.8	100 – 170

Percentage Composition of Free Fatty Acids in Oil

The result of pretreatment on the concentration of free fatty acids in the waste vegetable oil is as shown in Table 2. Before pretreatment, the composition of free fatty acids in the waste vegetable oil was determined as 2.61%. It reduced from 2.61% to 1.39% after the first pretreatment and from 1.39% to 0.91% after the second pretreatment to produce a feedstock of less than 1% free fatty acids, suitable for transesterification reaction (Viele *et al.*, 2016; Akhabue *et al.* 2022).

The average volume of NaOH used for determining the free fatty acid composition in the oil was seen to reduce from 12.5 mL to 4.35 mL during titration. This could be adduced to the reduction of free fatty acids concentration from the pretreatment. Similar observations were reported in literature (Akhabue and Ogogo, 2018; Viele *et al.*, 2016).

Effect of Reaction Time on Biodiesel Yield

The result of the effects of reaction time on biodiesel yield is as presented in Figure 5. It shows that as time of reaction increased from 40 to 120 min, the yield of biodiesel also increased from 51% to a maximum of 67.61% but further increase in reaction time to 150 min caused a decrease to 66.17% biodiesel yield. This reduction in biodiesel yield could be adduced to backward reaction in the transesterification process due to excess reaction time. This is in agreement with findings in literature that excess time of reaction does not favour the yield of biodiesel but rather favours the reverse reaction (Lakshmana *et al.*, 2015).

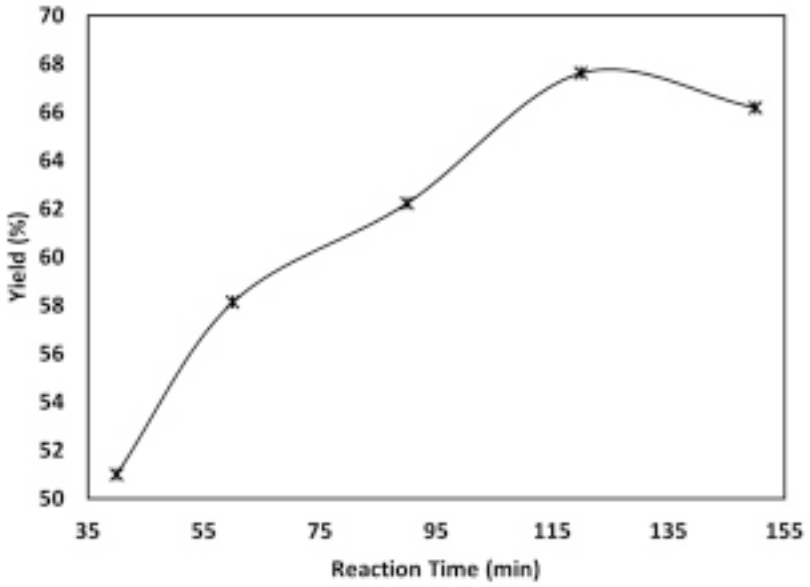

Figure 5: The effect of reaction time on biodiesel yield.

The Effect of Catalyst Weight Percent on Biodiesel Yield

Figure 6 presents the result of the effect of catalyst concentration on the yield of biodiesel. It showed that an increase in catalyst concentration from 1 to 3 wt. %, increased the yield of biodiesel from 54.57% to a maximum of 68.32% but increasing the catalyst concentration to 4 or 7 wt. % results into a significant decrease in biodiesel yield of 47.02% and 31.4%, respectively. This could be attributed to the formation of excess emulsions occasioned by very high catalyst concentration. A similar observation has been reported in literature; less amount of catalyst only slows the time required to reach complete conversion and increasing the catalyst weight percent beyond the optimum does not increase the conversion (Olutoye *et al.*, 2016).

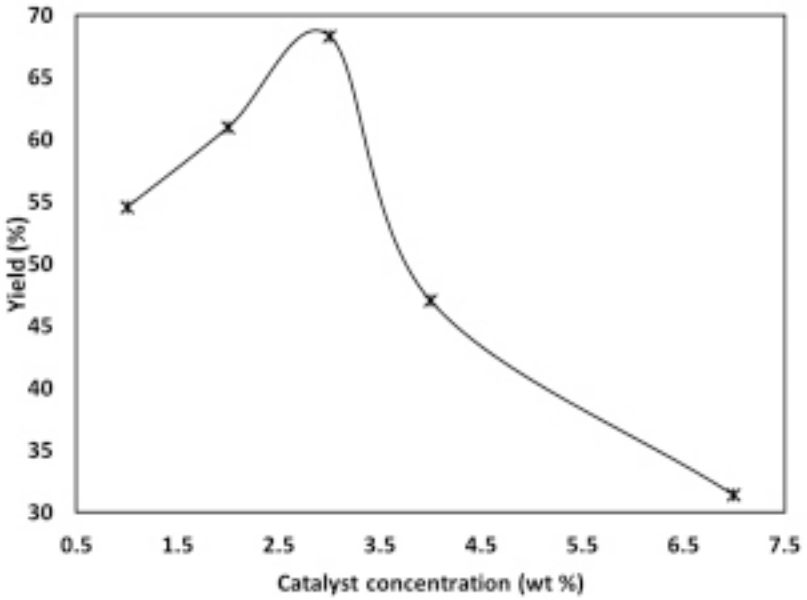

Figure 6: Effect of catalyst weight percent on the yield of biodiesel.

Effect of Methanol to Oil Molar Ratio on Biodiesel Yield

The effect of methanol to oil molar ratio on the yield of biodiesel is presented in Figure 7. It can be seen that as methanol to oil molar ratio increased from 5:1 to 9:1, biodiesel yield also increased from 47.77% to a maximum of 69.73%, further increase in the molar ratio of methanol to oil to 12:1 resulted in a decline in biodiesel yield to 54.93%. This could be adduced to the fact that excessively high methanol to oil ratios interferes with the separation of the glycerol from biodiesel produced due to an increase in solubility. Also, lower values of alcohol decreases biodiesel production (Lakshmana *et al.*, 2015).

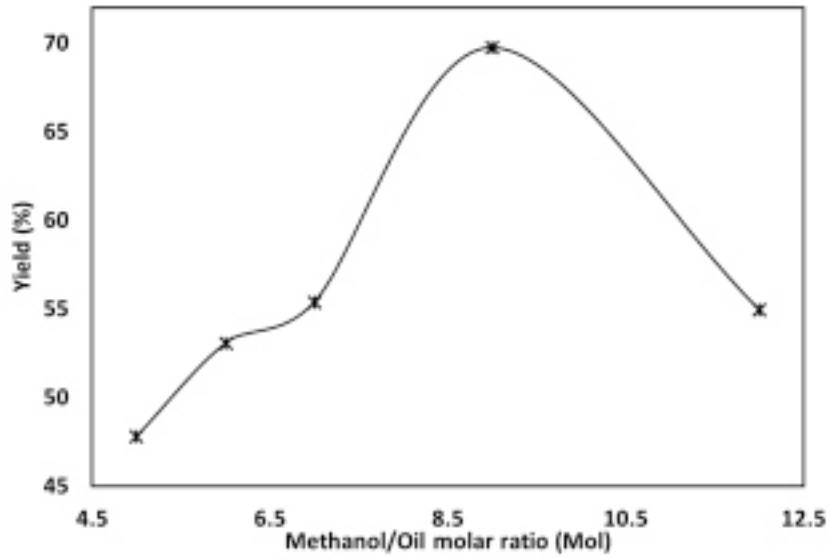

Figure 7: Effect of methanol to oil molar ratio on the yield of biodiesel.

Effect of Reaction Temperature on Biodiesel Yield

The effect of reaction temperature on the yield of biodiesel is as shown in Figure 8. It shows that increasing the reaction temperature from 45 to 60 °C, increased the yield of biodiesel from 50.88% to a maximum of 76.18%; thereafter, further increase in reaction temperature, decrease the biodiesel yield to 52.03% at 70 °C. This may be attributed to the formation of large bubbles as methanol vaporizes, which inhibits the transesterification process due to reaction temperature exceeding the boiling point of methanol (65 °C). A similar observation was reported in literature (Lakshmana *et al.*, 2016).

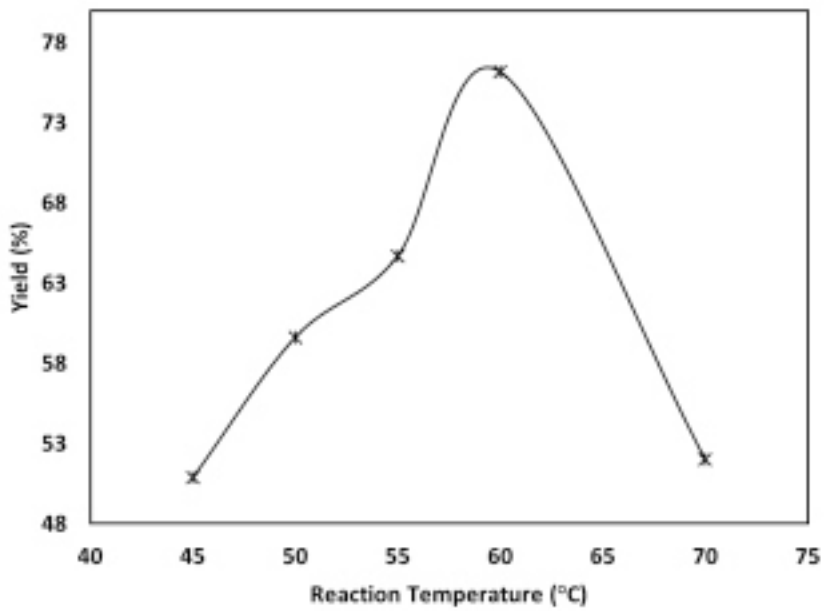

Figure 8: Effect of reaction temperature on the yield of biodiesel.

Physiochemical Properties of the Biodiesel

The physicochemical properties of the biodiesel produced under maximum esterification reaction conditions were analyzed and compared with the ASTM D6751 biodiesel standard as presented in Table 3. It can be seen from the Table that the fuel properties such as density, viscosity, acid value and flash point of the biodiesel produced are within the biodiesel standard.

Fourier Transform Infrared Radiation Spectroscopy (FTIR)

Figure 9 shows the infrared radiation spectra (FTIR) of the biodiesel produced from the waste vegetable oil. The absorption band between approximately 2850 and 3000 cm^{-1} can be attributed to the presence of C-H stretching of alkanes and alkyls. Also the absorption band between 1735–1750 cm^{-1} can be as a result of the stretching of the C=O bonds in the Esters group. The band between 1450 and 1600 cm^{-1} can be attributed to the ring C=C stretching of the aromatic compounds. The bands observed between 1000 and 1350 cm^{-1} is due to the C-F stretch of the Alkyl halides while the bands at around 1180–1260 cm^{-1} can be attributed to the C-O stretch of the alcohols. Absorption bands between 700 and 1000 cm^{-1} likely indicates the presence of alkyl halide and Aromatic compounds of C-Cl stretch and C-H bend, respectively. The presence of these functional groups indicates that the biodiesel produced from waste vegetable oil using waste clam shell as catalyst can be used as an alternative fuel to fossil fuel.

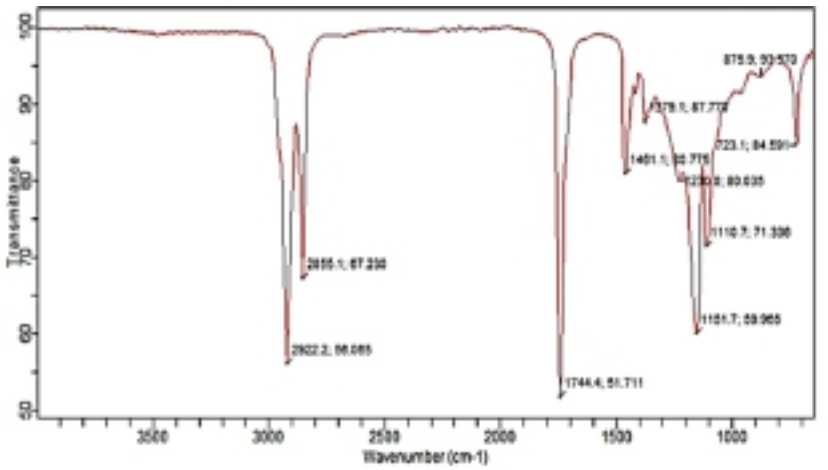

Figure 9: FTIR spectra for the produced biodiesel

CONCLUSION

An investigation was conducted on the production of biodiesel from waste vegetable oil using a catalyst synthesized from waste clam (*Mercenaria mercenaria*) shells. The catalyst was produced by the thermal decomposition of the clam shells. The composition of CaO in the synthesized catalyst is the highest, which was found to be 30.8787 wt. %. Other basic oxides known to be active catalysts in transesterification reactions were also present and a surface morphology indicating pores.

The composition of free fatty acids in the waste vegetable oil reduced from 2.61 to 0.91% after pretreatment, which is less than 1% as required for biodiesel production. The effect of esterification process parameters on the yield of biodiesel was investigated. A maximum biodiesel yield of 76.18% was observed at a reaction time of 120 min, 3 wt. % of catalyst, methanol to oil molar ratio of 9:1 and a temperature of 60 ºC. The characteristics or qualities of the biodiesel fall within the range of the ASTM standards.

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