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Ethanolysis of Cao-Base Derived from Seashell for Conversion of Waste Used Oil for Biodiesel Production

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Abstract: *The physicochemical properties of the waste used oil (WUO) were carried out for biodiesel production. The heterogenous catalyst (CAO based) used in this work was derived from waste seashell. The produced biodiesel was characterized and the optimum biodiesel produced was determined through statistical analysis. This was with a view to add value to the WUO and finding the solution to reduction of the excess carbon release to the environment. According to the results obtained, it showed that the refined WUO properties were in line with oil property requirement for biodiesel production. The physicochemical characteristics of the WUO showed physical state of the oil to be liquid/dark brownish at 28 °C, viscosity 6.58 cP at 28 °C, acid value, 0.96 (mg KOH/g oil), FFA (% oleic acid), 0.48, iodine value, 152.00 (g I_2/100g oil), peroxide value, 5.1 milli-equivalent of peroxide/kg of oil among others. The derived catalyst showed high basic strength with potassium oxide (61.63 wt.%) as the dominant element in the catalyst. Optimum biodiesel yield was obtained at run 5 with 98.52 (%wt./wt.) at reaction time of 65 min, catalyst amount of 4.0 (%wt.), reaction temperature of 70 °C, and ethanol-oil molar ratio of 7:1. The produced biodiesel properties was compared with the recommended standard ASTM D6751 and EN 14214.*

Keywords: Biodiesel, Oil Kernel, Waste Used Oil, Waste Seashell, Characterization of Biodiesel, Renewable Energy

INTRODUCTION

Oil-kernel remain rare outside West Africa, and abundant in the southern part of Nigeria. There has been a record of oil-kernel production over the years by the USDA (United State

Department of Agriculture). According to this body, over 100 million tons of oil-kernel has been extracted as ranging from 2008 to date. USDA has recorded 11.75 million tons of oil-kernel produced as at 2008, 12. 22 million 2010, 12. 55 million tons 2011, 13.28 million tons 2012, 56.38 million metric tons 2013, 59.3 million metric tons 2014, 61.7 metric tons 2015, 58.92 million metric tons 2016, 65.17 million metric tons 2017, 70.42 million metric tons 2018, 74.05 million metric tons 2019, 73.23 million metric tons, and 2020, 75.45 million metric tons. These numbers have been recorded to be increasing because of the recent discoveries of the important of oil-kernel to the world (Shahbandeh 2022).

Oil-Kernel is an edible plant gotten from the kernel of palm oil, *Elaeis Guineesis* (Kukana *et al.*, 2021). This is entirely different from the two other edible oils derived from palm fruits which include; the palm oil, which is extracted from the pulp of the palm fruit and oil extracted from the kernel of the coconut, is called Coconut oil. Although oil-kernel, palm oil and coconut oil are three different derived species of oil, they collectively make up the 16-carbon saturated fatty acid (palmitic acid) that they contain. The extraction oil from the African palm (*Elaeis Guineesis*) has long been recognized in West Africa. Most neighboring countries trading with West Africa often purchase these palm oil for the use in their countries, using the Europeans as a case study (Pulse 2021).

Seashell was selected as the catalyst in this research work to reduce the cost of purchasing catalyst in the market, converting waste to wealth and also because of its abundant in the southern part of Nigeria. Most of these shells can easily be gotten from the river banks and in some market places especially in Bayelsa state Opolo market, where the market women obtain the snail and trash the shell at the road side causing Environmental pollution (Adepoju *et al.*, 2021).

Cao-base derived sea shell, has been reported to have higher percentage of calcium content which is a good catalyst for the conversion of waste oil-kernel and oil blend for the production of biodiesel through ethanolysis.

Experimental Procedures

Materials and Methods

Oil Kernel

The palm tree has been known to be one of the richest trees in the world, most especially in the southern part of Nigeria. The seeds, branches, leaves, roots, stems and other content of this tree is highly used for different purposes which makes the tree to contain 0% waste because every component from this tree is utilized.

Kernel oil is one of the constituents of the palm tree gotten from the kernel seed of the palm fruits. It is dark in color and has a unique strong interesting taste and smell. In the southern part

of Nigeria, oil derived from kernel has seen to offer most numerous health benefits that prevents and heal life-threatening sickness.

The extraction of oil from the African palm (*Elaeis Guineesis*) has long been recognized in West Africa. Most neighboring countries trading with West Africa often purchase these palm oil for the use in their countries, using the Europeans as a case study (Pulse 2021). Oil-kernel which is semi-solid at room temperature, is more saturated than palm oil and comparable to coconut oil. One of the most interesting characteristics of oil-kernel is that they do not contain cholesterol or trans fatty acids (Ogori 2020).
The oil palm has a single stem and reaches about 20 meters (66 feet) in height. It has many tiny flowers crowded on short branches that develop into a large cluster of oval fruits some 4 cm (1.6 inches) long. When ripe, the fruits are black with a red base and feature a single oily seed known as the kernel seed.

For commercial oil production, the outer fleshy portion of the fruit is steamed to destroy the lipolytic enzymes and then squeezed; the resulting palm oil is highly colored because of the presence of carotenes. The kernels of the fruit are pressed in mechanical screw presses to recover palm kernel oil, which is chemically quite different from the oil from the flesh of the fruit.

The commercial palm oil industry rapidly expanded in the late 20th century and led to the deforestation in Indonesia and Malaysia as well as large areas in Africa. Bornean and Sumatran orangutans are especially iconic species threatened by the expansion of oil palm farming in Indonesia. In addition to driving biodiversity loss, the burn-to-burn practices of oil palm cultivation have contributed significantly to poor seasonal air quality in parts of Southeast of Africa. Although attempts have been made to certify sustainably grown palm oil, corporate buyers have been slow to support those endeavors; some environmental groups have urged individuals to avoid products with palm oil altogether.

Figure 1: Palm fruits with kernel seed

Seashell

A seashell isn't an animal; it is a derived home for wide varieties of animals. The animal that lives in these homes are mollusks. Seashell (scientifically known as *carapace* or *peltidium*) is commonly found at the river banks, beaches and some nearby lakes. Not all mollusks use seashell, the cephalopod family use it as their defensive means to protect their selves from external attacks and environmental poison from other animals that comes after them. Seashell also serves as rigid back bones to these invertebrates since they do not have one. The clams and water snails use these shells as a means of defense against predators.

Figure 2: Different representation of a Seashell

Biodiesel

Biodiesel refers to a fuel made from biologically derived resources that has properties similar to those of petroleum-based diesel fuels. American Society for Testing and Materials (ASTM) defines biodiesel fuel as mono alkyl esters of long chain fatty acids derived from a renewable lipid feedstock such as vegetable oil, kernel oil or animal fat which is the must substitute to diesel.

Biodiesel was first used by Rudolph diesel in 1900 when he showed that engines could work with peanut oil (Betiku *et al.*, 2011). Concept of using vegetable oil as a fuel for the compression ignition engine. Biodiesel can also be used directly or blend with diesel, a blend

of 20% biodiesel with 80% diesel by volume, is termed *B20*, the most common blend (Degfie *et al.*, 2019).

Global climate change has become a threat to the ecosystem worldwide by temperature increase and climate swings. Report published by the Intergovernmental Panel on Climate Change (IPCC) highlighted that there is higher probability of about one million species' extinction if the average global temperature escalates the minimal margin of 1.5 °C Greenhouse gas emissions from series of activities such as burning of fossil fuel to meet the energy requirement are the major contributor to the temperature rise. It is further estimated that by 2050, minimum 40% reduction in GHG emissions is obligatory to sustain the average increase less than 1.5 °C (Malcolm 2021).

This phenomenon has led to the search for green alternatives both in energy resources and Chemical sustainability. One of the primary substitutes to conventional diesel is biodiesel, which received an ample attention.

Feedstock for Biodiesel

There are a lot of feedstock source for biodiesel production. The oil extracted from the feedstock include the vegetable oil, animal fat, waste cooking oil, coconut oil, Oil-kernel, palm oil, etc

Other sources of biodiesel

a) *Micro and Macro algae*: examples include the Scenedesmus dimorphs with 16-40% lipid content, Chlamydomonas with 21% lipid content, and chlorella vulgaris with 14-22% lipid content.
b) *Waste cooking oil:* left over oil after cooking can serve as feedstock source for biodiesel production. It is cheap because most of them are obtained easily from all the cooking enterprise around. It also reduces environmental pollution because when its recycled for biodiesel production, it will drastically reduce oil spillage.
c) *Waste frying oil:* just like the cooking oil, the frying oil such as the vegetable oils, margarine and palm oil can also serve the same purpose like the cooking oil.
d) *Waste oil kernel:* oil derived kernel used by most production firms who extracts oil and use the shaft to manufacture their products tend to deposit the extracted oil into as waste. Those waste can easily be converted into biodiesel thereby saving environmental pollution.

Experimental Procedure for the Waste Oil Conversion.

Collection

To convert waste oils to biodiesel, the waste oils were collected from different sources. The first step in collecting WO was establishing relationship with the providers. Because we have

fryers at or around the school, it made it easy enough to collect enough waste oils for the project work. providers typically return the fryer oil to its original vessel once it has cooled.

Filtration

The frying process often introduces food particles to the oil, and the oil must be filtered before undergoing the transesterification reaction. I typically pre-filtered the oil through a 100-micron sock filter. Old t-shirts make a good, quick substitute for sock filters. The filtration process was performed in advance of a transesterification reaction.

Heating and Settling

In addition to food particles, foods introduce water to the fryer oil. I pre-heated the WO to 70°C which allows water (and additional food particles) to settle to the bottom of the vessel. Excess water and solid material settled on the bottom of the oil container. Pre-heating was done a day before the transesterification reaction.

Titration

WUO (waste used oils) is typically more acidic than virgin oil. When foods containing water are fried in hot oil, some of the water reacts with triglyceride molecules to form free fatty acids (FFAs). FFAs are fatty acid molecules that are not bound to glycerin. These acids react with the base catalyst to form soap, effectively leaving less catalyst available for the transesterification of triglycerides to biodiesel. The result is a less complete transesterification reaction.

Catalyst preparation

The waste seashell collected from the community markets and river banks were washed thoroughly to remove the residual items like leaves, sand, and other chaffs in other to get a pure product. It was sun-dried for two weeks (because of the raining season which practically affects the weather) and also oven-dried at a temperature of 100°C to reduce the moisture content. It was later subjected to grinding into powdered form which was later calcined in a laboratory furnace.

Catalyst Characterization

The CaO based catalyst derived from waste seashell properties were characterized by X-ray diffraction (XRD) for identification of major components and for the determination of crystallite size. XRD analysis was performed with diffraction (XRD) system and Scanning electron microscope (SEM) was used to study the morphology of the synthesized catalyst. Porosity and the angular displacement would be characterized using BET and EDXRT or NHR.

Physiochemical Analysis of the Collected waste oils

The evaluation of physicochemical properties of the collected waste oil such as: moisture content, relative density, viscosity, acid value, saponification value, peroxide value, specific gravity, mean molecular mass, %FFA, higher heating value, cetane number and pH would be determined by AOAC. Iodine value would be obtained by Wij's method, while API Diesel index and Aniline point were obtained by methods reported by Dhawane *et al* (2016). While moisture content and peroxide value was determined by the method reported by (Adepoju *et al.*, 2022). The others physicochemical properties were determined using the methods reported by Ahmed *et al* (2014).

Moisture content (AOAC,1990)

Oil sample of 5g was carefully weighed into a pycnometer of 5cm diameter and 2cm deep with tight-fit-slip-over cover and was properly tighten with the cover. Then it was placed inside a vacuum oven with temperature of 120°C water boiling point (at working pressure) for 30mins interval and the weight of the sample was noted respectively until a constant weight was attained when there was no additional loss of 0.05%, The moisture content was calculated using

% Moisture content = x 100

Peroxide valve (AOAC, 1990)

Oil sample of 2g was weighed into a 250ml Pyrex flask; 20ml of the solvent mixture (2:1 glacial acetic acid / chloroform) and 2g KI powder was added. The mixture was boiled briskly in a water bath for 1 min at a temperature of 70^{o}C. To the flask containing 40 ml of 50% KI, boiled mixture would be washed twice with 25ml of distilled water into flask. The content of flask would then titrate with 0.004M sodium thiosulphate ($Na_2S_2O_3$) solution by using phenolphthalein as indicator. The peroxide value would be calculated as indicated in

Peroxide Value (meq0_2/ kg oil) =

Saponification value (AOAC, 1984)

Oil sample of 2g was weighed into a 250ml flask with 25ml of 0.1 Methanolic potassium hydroxide was added. The content was constantly stirred and will be allowed to boil gently for 60min. with reflux condenser placed on the flask containing the mixture to achieve uniform temperature. Two drops of phenolphthalein indicator were added to the warmed soap solution and then titrated with 0.5M of HCl to the end point until the pink color of the indicator disappeared. The saponification value was calculated in

S.V (mg KOH/g oil) = 28.05 X

Acid value (AOAC,1990)

The acid value would be determined by dissolving 5g of oil sample in a mixture of 25 ml (95%v/v) diethyl ether and 25 ml ethanol in a 250 ml flask. The solution was neutralized with 0.1 M potassium hydroxide solution using drops of phenolphthalein in as an indicator. The acid value would be calculated using

Acid value

Mean Molecular Mass

This was determined by the equation cited by Akintayo and Bayer (2002) which and described as

Mean molecular mass

% FFA – Free Fatty Acid (AOAC,1990)

The FFA would be obtained by

% FFA =

Iodine value (Wij's method)

Oil sample of 0.265g was dissolved in 5ml of cyclohexane 10ml of Wij's solution was added, the stopper flask was allowed to stand for 30 min in the dark at room temperature and 20ml of 10% potassium iodide solution was added. The resulting mixture was then titrated with 0.1M $Na_2S_2O_3$ using starch as indicator iodine value would be calculated using

Iodine value =

Where N = Concentration of sodium thiosulphate used

B= volume of sodium thiosulphate used for blank

S= volume of sodium thiosulphate used for determination.

Density

This would be calculated using:

Density

Specific gravity

This is the ratio of the weight in air of a given volume of the oil at a considerate temperature to that of the same volume of water at that same considerate temperature to determine the specific gravity of the oil, specific gravity bottle. It was cleaned and dried then weighed (W_0) and then filled with oil, stopper inserted and reweighed to give (W_1). The oil was substituted with water after washing and drying the bottle and weighed to give (W_2).

The expression for specific gravity (Sp.gr) is given as:

Sp.gr =

p-anisdine (AOAC,1990)

this would be determined by measuring the absorbance value at 350 nm of a mixture of solvent 20 ml isooctane and p-ansidine (1:1) with 1g of oil sample in UV- Spectrophotometer at room temperature. The p-anisdine value would be obtained using:

p- anisdine = 100 x Absorbency value obtained

Cetane number (ASTM D2015)

This would be calculated using:

Cetane no = 46.3 +

Higher Heating Value (HHV) – (ASTM D2015)

This would be calculated using:

HHV (MJ /kg) = 49.43 – [0.041(Sap. value) + 0.015(Iodine value 0]

Viscosity (AOAC,1990)

A viscometer glass tube which was held in vertical direction would be used. The sample of the palm kernel oil was drawn into a capillary tube via suction to a marked volume. The sample was then allowed to flow down into the lower bulb and the time taken to pass through the marks would be noted. The kinematic viscosity would be calculated using equation below

Kinematic viscosity = time taken x viscometer factor

API

API =

Diesel index

This would be determined by the equation citied by Dhawane *et al* (2016) as described below

Diesel index =

Totox number

Totox number = 2 x Peroxide value – p-Anisidine Value

Waste Used Oil biodiesel production

Oil basis was kept at 100 ml, transfer to 1 L reactor, preheated at 60 ^{o}C for 2 h on hot plate magnetic stirrer. A 2.00g of catalyst was measured and dissolved in a 37.5ml weight of ethanol and transferred to the preheated oil. Three layers were observed showing the oil layer, the whitish ethanol-oil-catalyst layer, and the clear layer of ethanol. The resulting mixtures were set to chemical reaction at 100 ^{o}C temperature until the reaction time was achieved. The product was transferred to a separating funnel for products separation and purification. The glycerol was removed from the bottom of funnel while the diesel with catalyst was separated by washing with methanolic-sodium hydroxide, filtered and also washed with distilled water. The recycled catalyst was refined and reused, while the wet diesel was dried over calcium chloride, and then filtered to obtained biodiesel. The final product was the methyl ester known as biodiesel and the yield was calculated in terms of % (w/w) as described below

Statistical Data Analysis

The results of biodiesel obtained along with variables constraint was analysed with Microsoft Excel 8.0 to determine the regression parameter and the level of significant of the variables.

Table 1: Experimental variables constraint

SN	Reaction time (min)	Catalyst conc. (%wt.)	Reaction temperature (^{o}C)	Ethanol-Oil molar ratio (vol./vol.)
1	45	2.0	50	3
2	50	2.5	55	4
3	55	3.0	60	5
4	60	3.5	65	6
5	65	4.0	70	7
6	70	4.5	75	8
7	75	5.0	80	9

RESULTS

Physiochemical Properties of the Waste Used Oil (WUO)

In table 2 below shows the result obtained while carrying out the physiochemical characteristics of the WUO. The waste oil obtained was dark-brownish in colour, with a moisture content and specific gravity of 0.002% and 0.92, respectively. From observations on the colour and the

refractive index of the oil, had almost same mean value with the report previously published. (Adepoju *et al.*, 2014) reported the moisture content of 0.045% with specific gravity of 0.91. The viscosity, which is a measure of the resistance of oil to shear, was 6.58 cP. (Cholapandian *et al.*, 2022; Kirubakaran *et al.*, 2020) also carried same analysis earlier reported for WUO which falls within the range (15.15 -15.9 cP).

Table 2 also contain the results obtained for the chemical properties of the waste used oil. Because of the low FFA content of WUO obtained in this study shows its usefulness as it serves as a good resistance oil to hydrolysis. (Adepoju *et al.*, 2014) obtained a high value of 8.52 mg KOH/g oil, while (Kirubakaran *et al.*, 2020) obtained 0.67 for the FFA of WUO in their work. Because of the low acid value 0.96 mg KOH/g oil of this oil makes it inedible but could also have a long shelf life.

Table 2: physiochemical properties of WUO

Parameters	Mean values
Moisture content (%)	0.002
Viscosity (cP) at 40 ^{o}C	6.58
Specific gravity	0.92
Physical state at 28^{o}C	Brownish yellow
%FFA (as oleic acid)	0.46
Acid value (mg KOH/g oil)	0.96
Saponification value (mg KOH/g oil)	186.40
Iodine value (g I_2/100g oil)	152.00
Peroxide value (meq O_2/kg oil)	5.10
Cetane number	41.38
API	22.30
Higher heating value (HHV)	39.51

A high saponification value of 186.40 (mg of KOH/g of oil) was obtained for the WUO, indicating high concentration of triglycerides. This is within the range (175–250 mg of KOH/g of oil) normally found in other seed oils such as mustard seed, raspberry seed, sunflower, safflower and corn. The iodine value of the WUO was high (152.00 g of I_2/100 g of oil), showing that the oil contained a substantial level of unsaturation. Peroxide value measures the content of hydroperoxides in the oil and its low value indicates high resistance to oxidation. The value obtained for WUO in this study was 5.1 milli-equivalent of peroxide/kg of oil and this is a low value. The combination of high iodine value and low peroxide value suggests that the WUO could be stored for a long period without deterioration.

Other fuel properties such as cetane number, HHV, and API of the WUO were determined and is shown in Table 2 Cetane number is a measure of the fuel's ignition delay and combustion

quality. The higher the cetane number the shorter the delay interval and the greater the combustibility. The reason why fuels smokes is because of its low cetane number and it makes it difficult to start. According to (Lee *et al.*, 2017) Standard specification of cetane number for biodiesel is minimum of 40. The WUO cetane number (41.38) obtained in this study showed that it had high fuel potential. The Higher Heating Value (HHV) of oil is the quantity of heat evolved when one mole of a compound is completely burned to CO_2 and H_2O at initial temperature and pressure. The HHV determined for the WUO in this study was 39.51 MJ/kg, which considers the latent heat of vaporization of water in the combustion products.

The API of WUO obtained in this study was 22.30 which is very low, but the transesterification of the WUO could improve its fuel properties. The HHV obtained in this study also was within the range earlier reported for vegetable oils (37.47 – 40.62 MJ/kg). Hence, the physicochemical characteristics of the oil showed that the WUO was a good candidate for use as edible oil or as an industrial feedstock.

Catalytic Characterization and Analysis

SEM analysis

The sematic image of structural outlook of the morphology displayed of the catalyst analysis via SEM are presented in Figure 3, and 4 respectively at the magnification of 500x, and 300x, respectively. The appearance of images showed cracking structures of the catalytic sample with a shining but partially segregated trait, aggregated with porous look showing potential solubility in polar solvent. The glittering like outlook could be attributed to the presence of ZnO found in the catalyst. However, the whiteness, brightness and opacity appearance could be due to the presence of SiO_2 found in the sample. The brilliant glossy glaze, whitish scarcely appearance, caustic alkaline, and crystalline solids at room temperature could be attributed to the presence of CaO, which justifies the base catalyst nature for the production of biodiesel.

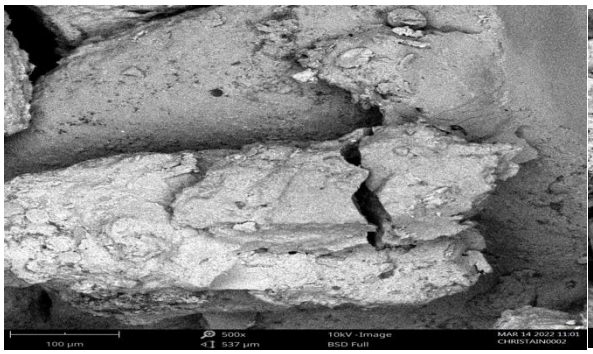

***Figure 3**: SEM analysis Mag. 500x*

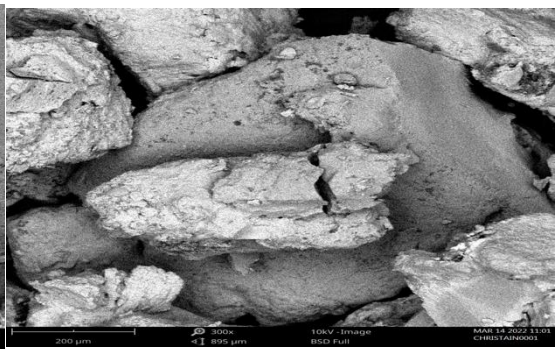

***Figure 4**: SEM analysis Mag. 300x*

XRS-FP analysis

Based on XRS-FP analysis on the catalyst which showed the intensity method carried out by Gaussian, the concentration method, the percentage mole, and the components found in the catalyst using XRS-FP analyzer are as presented in Table 2 Various elemental compounds are found in the catalyst, but the major element is calcium oxide which resulted from complete decomposition of the calcium carbonate present in the waste seashell. The dominant effect of calcium oxide (82.29 wt.%) in the catalyst shows its suitability as potential catalyst for biodiesel synthesis. Meanwhile, other elemental compounds were also identified in small concentrations, which also aids in the formation of biodiesel. However, the presence of SiO_2 (7.52 wt.%) showed that the powder catalyst holds some acidic strength, but SiO_2 also acts as weak base.

XRS-FP Analysis Report

Table 3: XRS-FP Analysis Report

Component	Concentration (wt. %)	Mole (%)
SiO_2	7.519	7.364
Fe_2O_3	1.786	0.658
CaO	82.294	86.358
SnO_2	0.305	0.119
Al_2O_3	4.750	2.741
K_2O	1.254	0.784
Others	2.092	1.976
Total	**100**	**100**

FTIR analysis

Displayed in figure 5 are the outcomes of the FTIR 8400S analysis of the waste seashell catalyst which indicated the scanning runs, the peak, the intensity, correlation intensity, the base height, the base length, the area and correlation area. Various functional elements are found at different wavelengths and angular phases. Normally, the mid-IR spectrum is divided into four regions: the single bond region (2500-4000 cm^{-1}), the triple bond region (2000-2500 cm^{-1}), the double bond region (1500-2000 cm^{-1}), and the fingerprint region (600-1500 cm^{-1}). The wavelength peak found in this study are within the aforementioned regions, therefore, it can be concluded that the analysis of the calcinated grinded waste seashell as catalyst for biodiesel synthesis was possible.

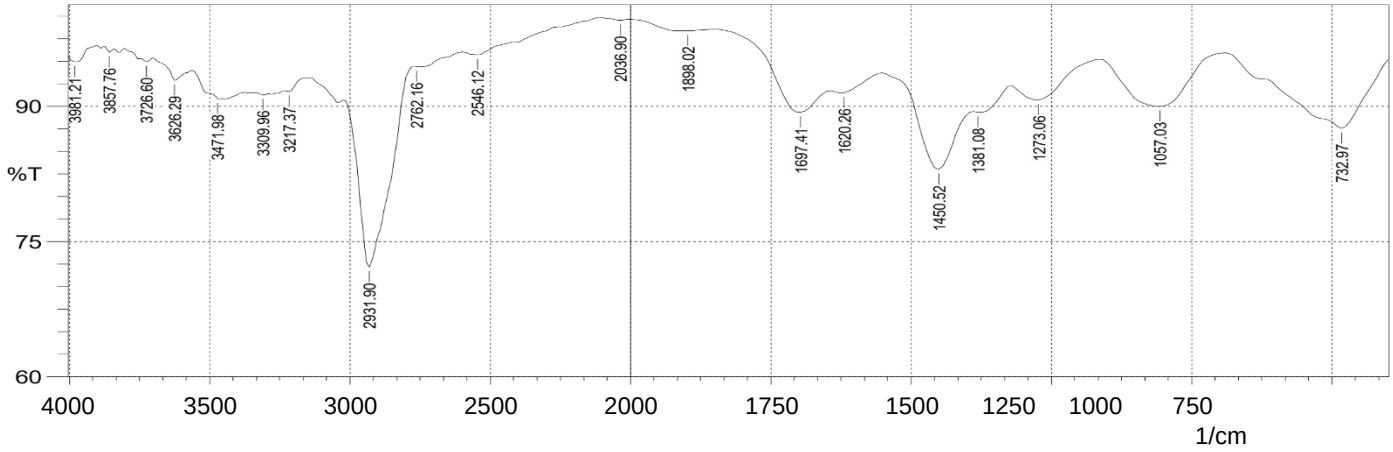

Figure 5: FTIR analysis of the waste seashell

Quantitative analysis

Further analysis via quantitative analysis on the catalyst used based on phase data view reflected the plot of intensity against the angular phase diagram. The plot showed a zig-zag plot with Quartz as the major compound containing carbon as the major element. Other compound such as Graphite, Adamite, Gahnite, Zincite, and Willemite are present with figure of merit based on weight fraction (Figure 6). The presences of quartz identify in the catalyst represent the catalytic current which helped in oscillatory vibration of the phases. The graphite discovered in the catalyst is responsible for high tension lubrication and also responsible for low viscous product. The presence of adamite in the catalyst helped in formation of biodiesel color, usually adamite always yellow in color which responsible for light yellowish biodiesel produced in this work. Other compounds also aid in biodiesel formation during production.

Plot

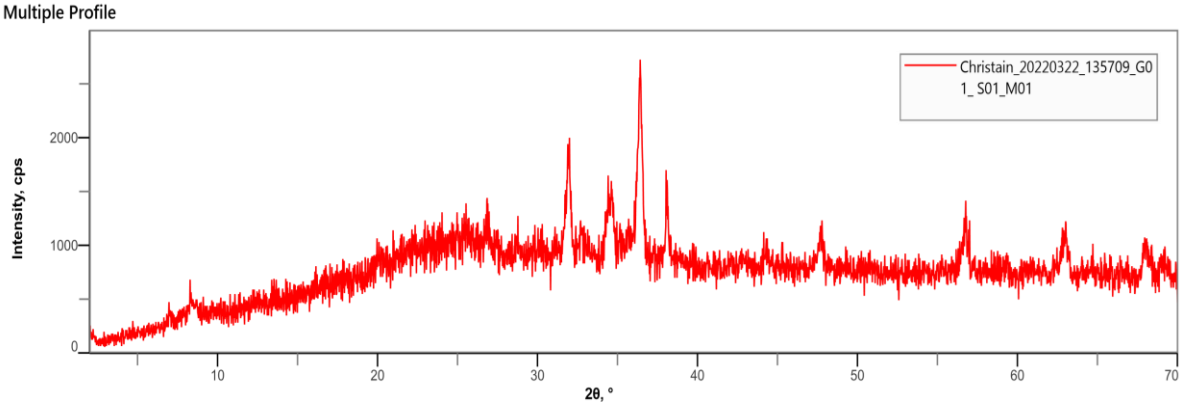

Figure 6: Quantitative analysis plot

Plot of the results

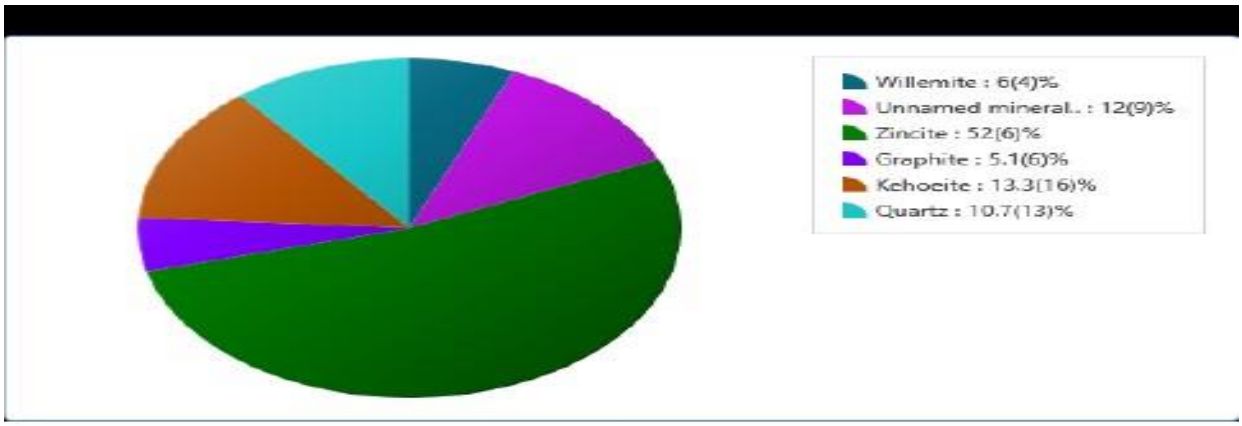

Figure 7: Pie chart plot of the results

Table of results

Table 4: Data set weight fraction

Dataset	*Value, Unit*	*Willemite*	*Unnamed minerals*	*Zincite*	*Graphite*	*Kehoite*	*Quartz*
Weight fraction	*0*	*6(4)*	*12(9)*	*52(6)*	*5.1(6)*	*13.3(16)*	*10.7(13)*

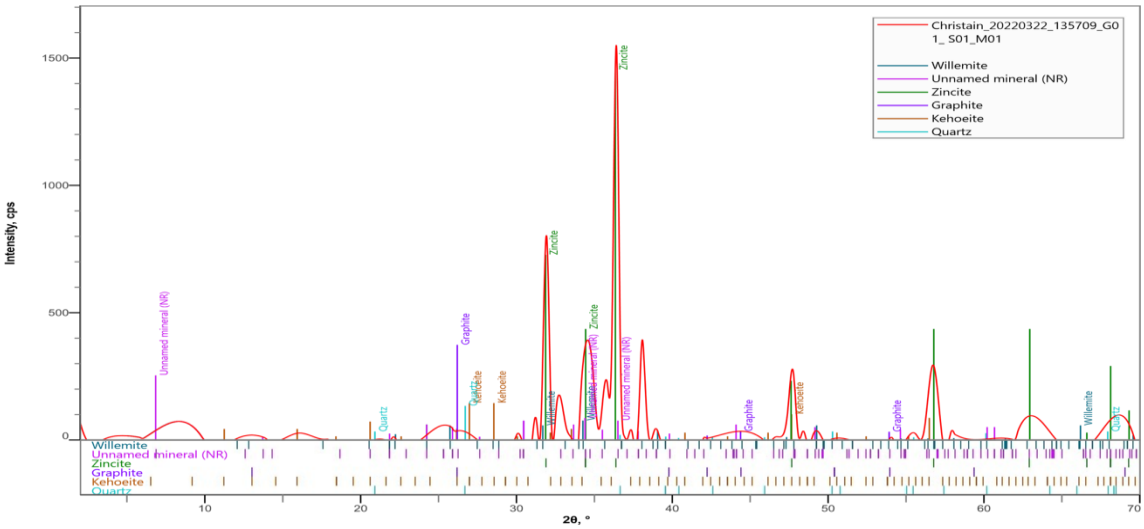

Figure 8: phase data view of the quantitative analysis

Transesterification of WUO to Biodiesel

The results of the biodiesel synthesized from WUO was shown in table 5, it comprises of the factor variables varied in ranges and the yield of the biodiesel. It was observed that the

maximum yield of biodiesel was obtained at run 5 with 98.52 (%wt./wt.) at reaction time of 65 min, catalyst amount of 4.0 (%wt.), reaction temperature of 70 ^{o}C, and ethanol-oil molar ratio of 7:1. This showed that the yield of biodiesel increases with increase in reaction conditions, but decreased at higher temperature above 70 ^{o}C owing to the catalytic nature of the bio-base which aggregate and cluster., the ethanol boiling temperatures above the reference temperature reduce the yield of biodiesel due to escape of solvent during reaction process.

Statistical Analysis

Statistical analysis was carried out with the result obtained using Microsoft Excel 8.0. The results displayed by plot in Figure 9 showed that variables considered in different ranges were remarkably significant with high coefficient of determination R-square (R^2) of 0.8164. Indicating a high consistency between the experimental values and the factors considered. R^2 above 0.800 have been reportedly significant (*Betiku et al.,* 2011). The model equations that indicated the slope and the intercept of variables plotted against the yield.

Biodiesel yield and constraint variables

Table 5: Biodiesel yield and constraint variables

SN	Reaction time (min)	Catalyst conc. (%wt.)	Reaction temperature (^{o}C)	Ethanol-Oil molar ratio (vol./vol.)	Biodiesel yield (% wt/wt.)
1	45	2.0	50	3	85.60
2	50	2.5	55	4	88.50
3	55	3.0	60	5	90.86
4	60	3.5	65	6	97.84
5	65	4.0	70	7	98.52
6	70	4.5	75	8	96.40
7	75	5.0	80	9	92.70

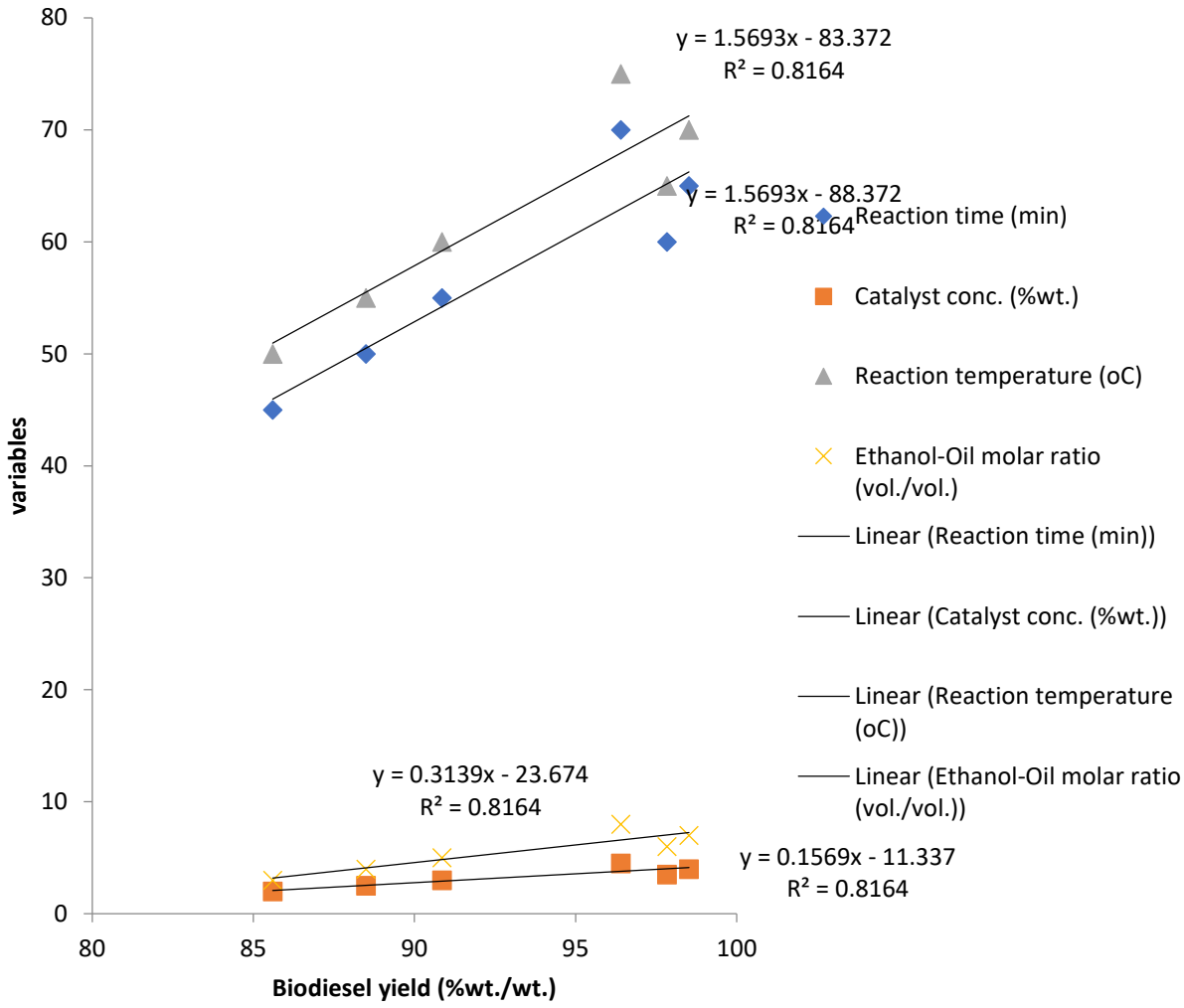

Figure 9: Excel plots of biodiesel yield against the variables

Physicochemical Properties of Biodiesel

The content and composition of the biodiesel obtained from this work were subjected to determination of its physicochemical properties using AOAC, 1997 procedures. Table 5 showed the results of the properties of the produced biodiesel. These results were compared with biodiesel recommended standard. From the table, it was observed that the quality of the produced biodiesel was in line with the standard laid down by American and European standard for biodiesel (ASTM D6751 and EN 14214). This implies that the produced biodiesel in this work can replace conventional diesel use in Industries and for commercial purposes.

Table 5: Physicochemical and Other Characteristics of Biodiesel

Parameters	Biodiesel	ASTM D6751	EN 14214
Physical properties			
Physical state at 28^{o}C	Light brown	-	-
Moisture content (%)	0.001	0.05 max	0.02
Specific gravity	0.83	0.86-0.90	0.85
Viscosity (cP) at 40^{o}C	2.56	1.9-6.0	3.5-5.0
Chemical properties			
%FFA (as oleic acid)	0.28	<0.40	0.25 max
Acid value (mg KOH/g oil)	0.58	<0.80	0.50 max
Saponification value (mg KOH/g oil)	182.32	-	-
Iodine value (g I_2/100g oil)	116.00	-	120 max
Peroxide value (meq O_2/kg oil)	2.48	-	-
Other properties			
Cetane number	50.14	47 min	51 min
Diesel index	55.75	50.40	-
API	38.98	36.95	-
Higher heating value (HHV)	36.15	-	-

CONCLUSIONS

Waste used oil was found to possess the characteristic of oil that can be used for biodiesel production. CaO derived from waste seashell was found to be rich in calcium content (82.294% wt.) which act as bio-base for biodiesel synthesis**.** Optimum biodiesel yield of 98.52 (%wt./wt.) was obtained at reaction time of 65 min, catalyst amount of 4.0 (%wt.), reaction temperature of 70 ^{o}C, and ethanol-oil molar ratio of 7:1. The statistical analysis through Microsoft Excel proved that the constraint variables selected were remarkably significant with regression parameter R-square >0.8**.** Therefore, the quality of the produced biodiesel was in line with the standard of American and European standard for biodiesel (ASTM D6751 and EN 14214). The produce biodiesel in this study can replace conventional diesel and can contribute in reduction of greenhouse gases which leads to environmental pollution.

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