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Synthesis of biodiesel from waste recycled oil employing animal bone ash

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Abstract

In this work, physiochemical properties of the waste used oil (WUO) were carried out for its aptness for biodiesel production. Calcined Animal Bone was used as a bio-base catalyst for the biodiesel production. The produced biodiesel was characterized and the optimum biodiesel produced was determined via statistical analysis using regression analysis. This was with a view to adding value to the waste used oil (WUO) and finding environmentally friendly alternative to fossil fuel.

Waste used oil (WUO) was preheated and purified to clean oil via filtration, and the physiochemical and other parameters (cetane number, API, aniline point among others) the cleaned oil were determined using standard methods. The Calcined animal bone was characterized using FTIR, SEM, XRF, BET adsorption, and qualitative analysis. Biodiesel production was done via base catalyst trans- esterification while statistical analysis was done using Microsoft Excel 8.0. In order to ascertain the quality of the biodiesel, the physicochemical properties were determined and the qualities were compared with ASTM D6751 and EN 14214.

Results showed that the refined WUO properties were in line with property of oil require for biodiesel production. The physicochemical characteristics of the WUO showed physical state of the oil to be liquid/dark brownish at 28^{oc}, viscosity 6.58 cP at 28 ^{0}C, acid value, 0.96 (mg KOH/g oil), FFA (% oleic acid), 0.48, iodine value, 152.00 (g I_2/100 g oil), peroxide value, 5.1 milli-equivalent of peroxide/kg of oil among others. The derived catalyst showed high basic strength with Calcium oxide (87.63 wt.%) 0s the dominant element in the catalyst. Optimum biodiesel yield was obtained at run 5 with 98.52 (%wt./wt.) at reaction time of 30 min, catalyst amount of 2.0 (%wt.), reaction temperature of 100 ^{0}C, and ethanol-oil molar ratio of 4:1. The produced biodiesel properties conformed to the recommended standard ASTM D6751 and EN 14214.

The study concluded that WUO could serve as feedstock for biodiesel production that is environmentally friendly and the derived catalyst could be used as a bio-base in catalytic industries.

Keywords: Transesterification; Free fatty acid; Waste used oil; Biodiesel; Physiochemical parameters; Calcination; Waste animal Bones

1. Introduction

The world's energy needs is majorly supplied through petrochemical sources. Coal and natural gases, with the exception of hydroelectricity and nuclear energy are finite and at current usage rates will be consumed shortly. The high energy demand in the industrialized world as well as in the domestic sector and pollution problems caused due to the widespread usage of fossil fuels make it increasingly necessary to develop the renewable energy source of limitless duration and smaller environmental impact than the traditional one. This has stimulated recent interest in alternative

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sources for petroleum- based fuels. One possible alternative to fossil fuel is the use of oils of plant origin like vegetable oils and tree borne oil seeds. This alternative diesel fuel can be termed as biodiesel. The production of Biodiesel in recent time has been of great importance especially in the achievement of the environmental sustainability which is one of the fundamental millennium development goals. Production, development, and commercialization of biodiesel have been boosted due to the urgency of finding the best solution to the world energy crisis. We need not to continue rely heavily on fossil fuel as the primary source of transportation fuels and electricity. Although many alternative energies such as solar, wind, biomass, and geothermal exist, only biofuel or biodiesel can be used on a large scale, especially for transportation, due to its reliability and economic feasibility. Moreover, biodiesel presents several advantages such as non-toxicity and eco-friendly properties, compatibility with existing diesel engines without extensive engine modifications, and the huge amount of renewable sources currently available worldwide. The quality of biodiesel can be evaluated on the basis of two major guidelines, i.e., the U.S. Specification (ASTM Standard) and the European Specification (EN Standard). .The use of biodiesel significantly diminishes the emissions of harmful GHG, particulate matter, and hydrocarbons but slightly rises fuel consumption and reduces the engine power. Although NOx emissions are increased in some cases, this can be minimized using exhaust gas recirculation (EGR) or other additives. It was confirmed that biodiesel produced from natural and renewable resources is an excellent alternative for existing petro-diesel, especially for transportation. Biodiesel has superior properties to petro-diesel in many areas: for example, higher cetane number (a significant advantage regarding engine performance and emissions), low ash content, and low carbon residue, whereas the other properties can be improved by using blending processes (Khariu Azly Zahan and Manabu Kano, 2018).

The environmental nuisance and threat created by the use of fossil fuels in Nigeria are nothing to write home about as it has led to the emission of both air, land and water pollution. Replacing fossil fuels with biodiesels produced from renewable organic material such as waste used oil has the potential to reduce to the barest minimum the consequences of fossil fuel usage (Abedin *et al*., 2014), which include conventional and greenhouse gas pollutant emission that cause global warming and undesirable climatic changes, exhaustible resource depletion and dependence on unstable foreign supplies. Biodiesel provides 93 % more usable energy than the fossil energy, reduces greenhouse gases by 41% compared with fossils, reduces several major air pollutants and has minimal impact on human and environmental health. The Biodiesel can be produced from straight vegetable oil, animal oil/ fats, tallow and waste cooking oil. The process used to convert these oils to Biodiesel is called transesterification. One of the processes is alcoholysis or transesterification in the presence of a suitable catalyst. Most biodiesel produced at present is from waste vegetable oil, though oil straight from the agricultural industry represents the greatest potential source. However, Biodiesel is not being produced commercially from the source simply because the raw oil is too expensive and will add to the cost of the biodiesel production compared with fossil diesel. Corn, wheat, sugar, vegetable oils grains are sources of first generation biofuels. First generation biofuels makes up the majority of the biofuels used today. Biologically fuels such as ethanol, propanol, and butanol are produced by the action of microorganisms and enzymes through the fermentation of sugars or starches, or cellulose. First generation biofuel processes are useful but there is a threshold above which they cannot produce enough biofuel without threatening food supplies and biodiversity. First generation biodiesel and ethanol biofuels produced today also can use vegetable oils (e.g., corn oil) and animal fats as their source feedstock. Many of such first generation biofuels are dependent on subsidies and are not cost-competitive with existing fossil fuels. There is need to move away from relying on first generation biofuel because their feedstock would otherwise be human food. With the growth population, it is more reasonable to use human food feedstock byproducts, known as second-generation feedstock, to produce second- generation biofuel (Sharma Y.C and Singh B.2010).Waste used oil (WUO) can often be sourced for free or sourced already treated for a small price but waste oil must be treated before conversion to biodiesel to remove impurities

Animal, plant, fats and oils are composed of triglycerides, which are esters formed by the reaction of three free fatty acids and the trihydric alcohol, glycerol. In this reaction, any strong base capable of deprotonating the alcohol will do (e g NaOH, KOH, sodium methoxide, etc).but the sodium and potassium hydroxides are often chosen for their cost. The presence of water causes undesirable base hydrolysis, so the reaction must be kept dry. The alcohol reacts with the fatty acids to form the mono-alkyl ester, or biodiesel and crude glycerol. In most production methanol or ethanol is the alcohol used (methanol produces methyl ester, ethanol produces ethyl esters) and is base catalyzed by either potassium or sodium hydroxide. In the transesterification mechanism, the carbonyl carbon of the starting ester ($RCOOR^1$) undergoes nucleophilic attack by the incoming alkoxide (R_2O) to give a tetrahedral intermediate, which either reverts to the starting material, or proceeds to the transesterified product ($RCOOR^2$)'. Potassium hydroxide has been found to be more suitable for the ethyl ester biodiesel production, either base can be used for the methyl ester (Jacob et al., 2020)

Biodiesel is produced using the transesterification or alcoholysis process, which is usually facilitated by acids, bases, enzymes, and other type and form of catalysts (Ong *et al*., 2013, Adepoju *et al*., 2022). The catalysts can be either in a homogeneous or in a heterogeneous phase as of the reactants. If the catalyst is in a different phase (usually non- liquid)

to the reactants, then that is the heterogeneous catalyst (Crucianelli *et al*, 2019). The appropriate catalyst selection depends on several factors, namely, the amount of free fatty acid (FFAs) in the oil, the water content, etc. This path has lower reaction times and catalyst cost than those posed by acid catalysis. However, alkaline catalyst has the disadvantage of its high sensitivity to both water and free fatty acids present in the oils. Base-catalyzed transesterification reacts lipids (fats and oils) with alcohol (typically methanol or ethanol) to produce biodiesel and an impure byproduct, glycerol. If the feedstock oil is used or has a high acid content, acid -catalyzed esterification can be used to react fatty acids with alcohol to produce biodiesel (Jacob *et al*., 2020, Yingying 2012).

Billions of kilograms of animal bone wastes are generated each year which are either rendered or disposed to avoid environmental concerns. These bone wastes can be potentially employed as catalyst for biodiesel production in a sustainable way (Adepoju, 2021).

Bones are rigid organ that constitutes part of the skeleton in most vertebrate animals. Bone is a non-uniformly solid, but consists of flexible matrix (about 30 %) and bound minerals (about 70 %) which are difficultly woven and endlessly remodeled by a group of specialized bone cells. Their distinctive composition and design allows bones to be relatively stiff and strong, while remaining lightweight. Bone matrix is about 90 to 95 % composed of elastic collagen fibers, also known as ossein, and the remainder is ground substance. The matrix is incurred by the blinding of inorganic mineral salt, calcium phosphate in a chemical arrangement known as bone mineral, a form of calcium hydroxylapatite.

Bone which is a waste materials are extensively available in the world and contains calcium, the transformation of waste into valuable materials is the best practice for waste management. These calcium rich waste materials involve waste animal bones, mollusk, and eggshells, industry wastes, and furthermore based on their origin which can be potentially used as catalysts for biodiesel production (Zang, 2011). The Ca rich wastes which act as a heterogeneous catalyst have a substantial potential for biodiesel production. Effective method for controlling waste is to transform it into useful and valuable substances through ecofriendly processes. Waste animal bones which cause land pollution can be potently transformed into valuable materials such as catalysts. These bones generally contain alkaline metal oxides and other non-metals. The major ingredients in bones are calcium and phosphate which can be transformed into hydroxylapatite and beta tri calcium phosphate upon thermal calcination, indicating considerable catalytic activity

There are different unit operations involved in catalyst synthesis such as calcination, precipitation, foaming operation, gelation, Hydrothermal transformation, decantation, impregnation, crushing, filtration, grinding, washing, mixing, drying and activation, (Perego and Villa 1997). This is basically a heat treatment of material without air in order to decompose a compound into smaller compounds .It leads to elimination of chemically bonded H_2O or CO_2, texture alteration through sintering, active phase generation, structure modification, and stabilization of mechanical properties (Perego and Villa, 1997).

2. Material and methods

2.1. Materials

Waste used oil (WUO) was obtained from University restaurant, Federal University Otuoke, Bayelsa State, Nigeria. The oil was preheated and filtered to remove the impurities present in the used oil. The clean oil after filtering was subjected to quality determination such as density, viscosity, acid value, saponification value, iodine value and other properties with the aim to determine its suitability for biofuel production. All chemicals used were of analytical grades, supply by Isolak Chemical Nig. Ltd., and need no further purification.

Waste Animal Bone (WAB) was collected from the dumping site in Abattoirs location in Swali Market, Bayelsa State, Nigeria. The bone was cleaned by boiling in a hot water to remove the adherent fleshy part, scrapped and sun-dried for four days. The dried bone was manually brake into smaller pieces and the bone marrow was removed, the smaller pieces of bones full of marrow fluid were washed with dilute ethanol (0.5 M ethanol) to make free of clean bone. The clean bones (pieces free of marrow fluid) were oven dried at 75 ^{0}C, and was calcined in a furnace at temperature 850-900 ^{0}C for 5 h. The Calcined bone ash (CBA) powder was allowed to cool to room temperature and was stored in a dry container for further processing.

2.2. Characterization of the Calcined bone ash (CBA)

The calcined bone ash (CBA) was characterized using the method earlier reported by Akhabue *et al*. (2023), the procedures are as follows:

2.2.1. BET procedure for catalysts analysis

The specific surface area and the pore size distributions of calcined bone ash were determined using Brunauer – Emmett Teller (BET) analysis .The technique is based on the physical adsorption of inert gases such as Nitrogen on the calcined bone ash. The adsorbed gases, remaining moisture and other surface impurities were first removed by warming the CBA at 150 ^{0}C for 45 min under helium gas flow which was allowed for 40 min at the pressure range of 0.04 to 0.2.The Nitrogen gas molecules were passed between the particles of calcined bone ash at 77 k and the volume of gas adsorbed on the surface was analyzed to determine the specific surface area and the pore size distribution of the calcined bone ash.

2.2.2. XRF procedure for catalysts analysis

The elemental composition of the calcined bone ash was determined using a dispersive X-ray fluorescence (XRF) spectrophotometer with a RH source and tube with a power of 2.2 k. The fine powdered calcined bone ash of grain size of<75 µm was mixed with a binding/ grinding aid (cellulose wax) and the mixture of grinding aid and the sample at 20 % to 30 % was pressed in a die at 20 to 30 T to produce a homogeneous sample pellet. The measured fluorescent emitted from the homogeneous sample pellet after being excited by primary X-ray generated in an X-ray tube which hits an inner shell electron of the atom to eject electron determines the elemental compositions of the CBA .

2.2.3. FTIR procedure for catalysts analysis

Fourier Transform Infrared Spectroscopy (FTIR) analysis was carried out on the prepared sample of calcined bone ash with a view to finding out the organic and inorganic compounds present in the sample. The procedure was carried out by adding 2 % of the sample, mixing and grinding to a very fine powder with the help of Potassium Bromide (KBr) in the range of 0.2 to 1 % to reduce the scattering losses and absorption band distortions and to ensure that the average particle size of the calcined bone ash is to a great extent less than the wavelength of the light particles are to transmit .About 5 to 10 mg of finely ground calcined bone ash (CBA) are then placed onto the face of a KBr plate, a small drop of mineral oil is added and the second window is placed on top. A gentle circular and back-and forth rubbing motion of the two windows will evenly distribute the mixture between the plates and finally the sandwiched plates are placed in the spectrometer where the infra-red radiation (IR) is applied to the sample and the sample absorbance of the infra-red light at various wavelengths is consequently measured to determine the calcined bone ash molecular structure which shows the organic and inorganic compounds present.

2.2.4. SEM procedure for catalysts analysis

The structure, morphology and the homogeneity of the bone ash obtained after calcinations at the temperature range of 850- 9000 ^{0}Cwere determined using scanning electron microscopy (SEM) .The calcined bone ash prior to the exercise underwent fixation with aldehydes and osmium tetraoxide which led to the dehydration of the sample by the ethanol. The sample was dried before mounting on the stub and sputter coated with conducive material to obtain the image on the SEM.

2.3. Biodiesel Synthesis

2.3.1. Experimental design

Major parameters affecting the synthesis of biodiesel using the designed catalyst were taken into consideration, and the findings were statistically analyzed. Table 1 displayed the variable range used in this study. These were done twice, and the outcomes were noted, recorded, and examined using the statistical program Microsoft Excel 8.0 to determine the regression parameters.

2.3.2. WUO biodiesel production

A 400 ml measuring cylinder was filled with well-prepared waste used oil (WUO) and subsequently transferred to one litre reactor, preheated at 60 ^{0}c for 2 h on a hot plate magnetic stirrer. A catalyst loading amount of 5 wt% was added to the mixture of ethanol and warmed oil at the ratio of 21:1. Three layers were observed; the oil layer, the whitish ethanol-oil-catalyst layer, and the clear ethanol layer. The generated mixtures were subjected to a chemical reaction at a specified temperature until the reaction time was reached. The products which comprises of immiscible liquids were transported to a separating funnel for separation and purification. Glycerol was removed from the bottom of the funnel, while green diesel with catalyst was separated by washing with methanolic-sodium hydroxide, filtering, and washing with distilled water. The recovered catalyst was purified and reused, while the wet green diesel was dried over calcium chloride and then filtered to produce biodiesel. The final product was the methyl ester known as biodiesel, and the yield was determined in terms of % (w/w) as specified in Eqn. (1).

$$Experimental\ yield\ \%\ (w/w) = \frac{Weight\ of\ oil\ biodiesel\ produced}{weight\ of\ oil\ sample} \times 100 \quad \ldots\ldots\ldots (1)$$

2.4. 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 (^oC)	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

2.5. Quality Characterization of biodiesel

The produced biodiesel was subjected to quality evaluation by observing the properties of the fuel and the results were compared with the recommended biodiesel standards (ASTM D6751, EN 14214 and SANS).

3. Results and discussion

3.1. Quality characterization of Waste Used Oil (WUO)

3.1.1. Physical properties of WUO

The content and compositions of the oil were subjected to physicochemical examination in order to assess the quality of the refined waste used oil (WUO) purchased from the restaurant.

Table 2 displays the outcomes. The obtained WUO had a dark-brownish color and a specific gravity of 0.92 at ambient temperature. Its moisture content was 0.002 %. The oil's color and refractive index were observed and corresponded with previously reported findings. According to Adepoju *et al.* (2014), the moisture content was 0.045 % and the specific gravity was 0.91. The viscosity, which is a gauge of oil's resistance to shearing, was 6.58 cP. This value is within the previously stated range (15.15 – 15.9 cP) for waste used oil (Cholapandian *et al*., 2022: Kirubakaran and Arul, 2020).

3.1.2. Chemical properties of WUO

Chemical qualities are one of the most crucial factors in figuring out the state and quality of oil samples right now. The findings regarding the WUO's chemical characteristics are presented in Table 2. The study's findings on WUO's low FFA level were suggestive of the oil's strong resistance to hydrolysis. A high value of 8.52 mg KOH/g oil was observed by Adepoju and Olawale (2014), compared to Ramos *et al* (2010) 0.67 for the FFA of WUO. It was demonstrated by the oil's low acid value of 0.96 mg KOH/g oil that it was not only ingestible but also had a potential for a lengthy shelf life.

The WUO showed a high saponification value of 186.40 (mg of KOH/g of oil), indicating a high concentration of triglycerides. This falls within the range (175-250 mg of KOH/g of oil) commonly observed in other seed oils such as corn, mustard, raspberry, sunflower, and safflower (Yong and Salimon, 2006). The WUO has a significant amount of unsaturation because to its high iodine value (152.00 g of I2/100 g of oil). The hydroperoxide content of the oil is measured by the peroxide value, and a low number denotes a high level of oxidation resistance. In this investigation, 5.1 milli-equivalents of peroxide/kg of oil was the figure for WUO, which is a low amount. High iodine content combined with low levels of peroxide value suggests that the WUO could be stored for a long period without deterioration.

Table 2 Physicochemical and Other Characteristics of WUO

Parameter	Mean values
Physical properties	
Physical state at 28°C	Brownish yellow
Moisture content (%)	0.002
Specific gravity	0.92
Viscosity (cP) at 40 °C	6.58
Chemical properties	
%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_2/100 g oil)	152.00
Peroxide value (meq O_2/kg oil)	5.10
Other properties	
Cetane number	41.38
API	22.30
Higher heating value (HHV)	39.51

3.1.3. Other properties of WUO

Additional fuel characteristics like the cetane number, HHV, and API of the WUO were identified (Table 2). The fuel's ignition delay and combustion quality are gauged by its cetane number. The delay interval is shorter and the combustibility is higher with a higher cetane number. Low cetane number fuels smoke because they are difficult to start. The minimum required cetane number for biodiesel is 40. (Ramos *et al.,* 2009). The WUO cetane number (41.38) found in this investigation demonstrated that it has a high fuel potential. The amount of heat released when one mole of a compound is totally burnt to CO_2 and H_2O at starting temperature and pressure is known as the Higher Heating Value (HHV) of oil. The latent heat of vaporization of water in the combustion products was taken into account when calculating the HHV for the WUO in this investigation, which was 39.51 MJ/kg. Additionally, the HHV obtained in this investigation fell within the previously reported range for vegetable oils (37.47 - 40.62 MJ/kg). Therefore, the WUO was a strong contender for utilization as an industrial feedstock or as edible oil based on its physicochemical properties. Although the transesterification of WUO might enhance its fuel characteristics, the API of WUO found in this study was relatively low at 22.30.

3.2. Catalytic Characterization and Analysis

3.2.1. BET analysis of catalyst

Utilizing several analyzers, the catalyst's characteristics were determined. Based on the result of the BET adsorption study carried out by data reduction acquisition using the DA method and nitrogen as adsorbate with mol. wt. 28.013 for catalyst mass of 0.12 g utilized for sampling, Fig. 1a shows the plot of different pore volumes acquired via sample diameter. At a best energy (E) of 0.807 kJ/mol, the maximum DA microspore volume was discovered to be 0.318 (cc/g), which equates to 2.80 nm in diameter pores. It was noted that the sample started to develop a large surface area with a high pore diameter as the plot approached its apex, increasing the reaction rate. Relationship between pore diameter, surface area, and the cumulative volume utilizing the BJ adsorption method are shown in Fig. 1b. The sample's nature as a catalytic basis for the generation of biodiesel was demonstrated by the maximum surface area, pore volume, and pore diameter measurements, which were attained at 442.708 m^2/g, 0.217 cc/g, and 2.132 nm, respectively.

3.2.2. XRS-FP analysis

The concentration method, the percentage mole, and the components discovered in the catalyst using the XRS-FP analyzer are as shown in Table 3 and are based on the XRS-FP analysis on the catalyst which demonstrated the intensity

method carried out by Gaussian. The catalyst contains a number of different elemental compounds, but the main one is Calcium oxide, which came from the full disintegration of the Calcium carbonate present in the Waste Animal Bone during burning. Calcium oxide's prominent role in the catalyst (89.50 weight percent) demonstrates its appropriateness as a viable catalyst for the production of biodiesel. Meanwhile, other elemental compounds were also identified in small concentrations, which also aids in the formation of biodiesel. The presence of SiO_2 (3.555 weight percent) however, demonstrated that the powder catalyst has some acidic strength, while SiO_2 also functions as a weak basic.

3.2.3. SEM analysis

Fig. 2(a, b, and c) show the semantic image of the structural outlook of the morphology displayed of the catalyst analysis via SEM at magnifications of 300x, 500x, and 1000x, respectively. Images revealed cracking structures of the catalytic sample with a shining but partially segregated trait, aggregated with a porous appearance indicating potential solubility in polar solvent. The presence of ZnO in the catalyst could explain the glittering appearance. However, the whiteness, brightness, and opacity of the sample may be attributed to the presence of SiO_2. The presence of K_2O and CaO, which indicate the base catalyst nature for the formation of biodiesel, could explain the beautiful glossy glaze, whitish pale appearance, caustic alkaline and crystalline solids at room temperature.

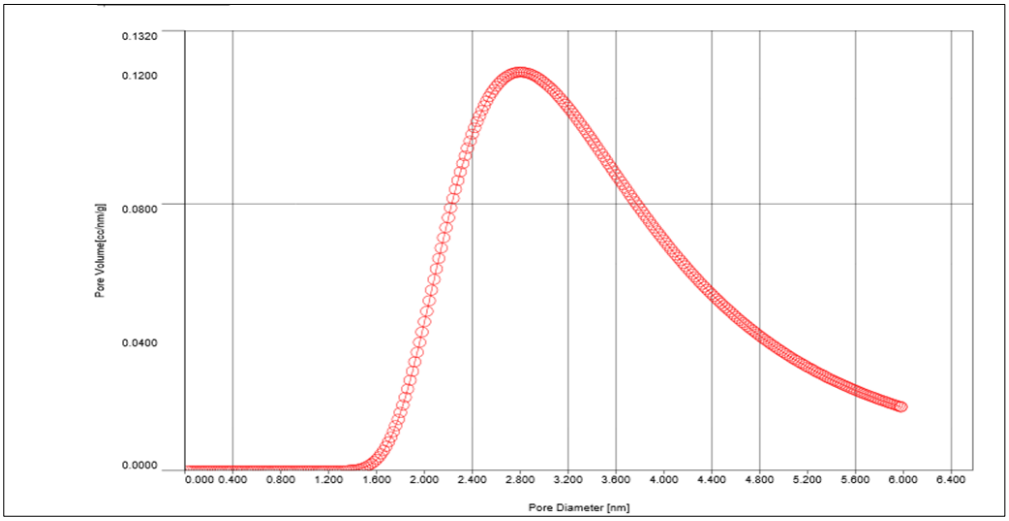


Figure 1a Micropore volume against pore diameter

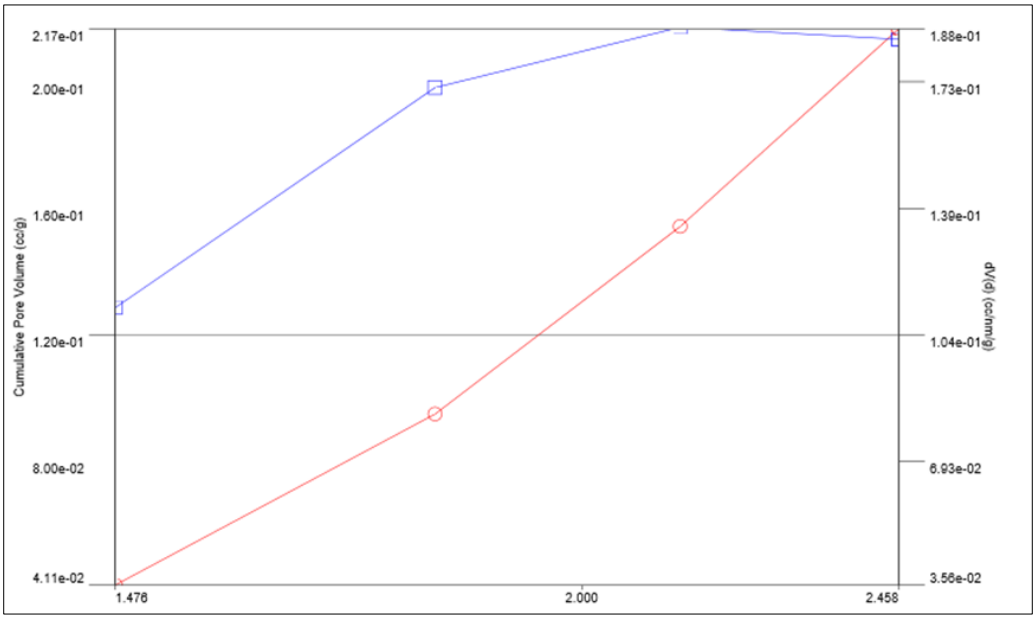


Figure 1b Cumulative pore volume, surface area against pore diameter

Table 3 XRS-FP Analysis Results on components against concentration

Component	Concentration (wt.%)
SiO_2	3.55
Fe_2O_3	1.074
CaO	89.457
Al_2O_3	3.950
Cl	0.549
SnO_2	0.515
Others	0.899
Total	100

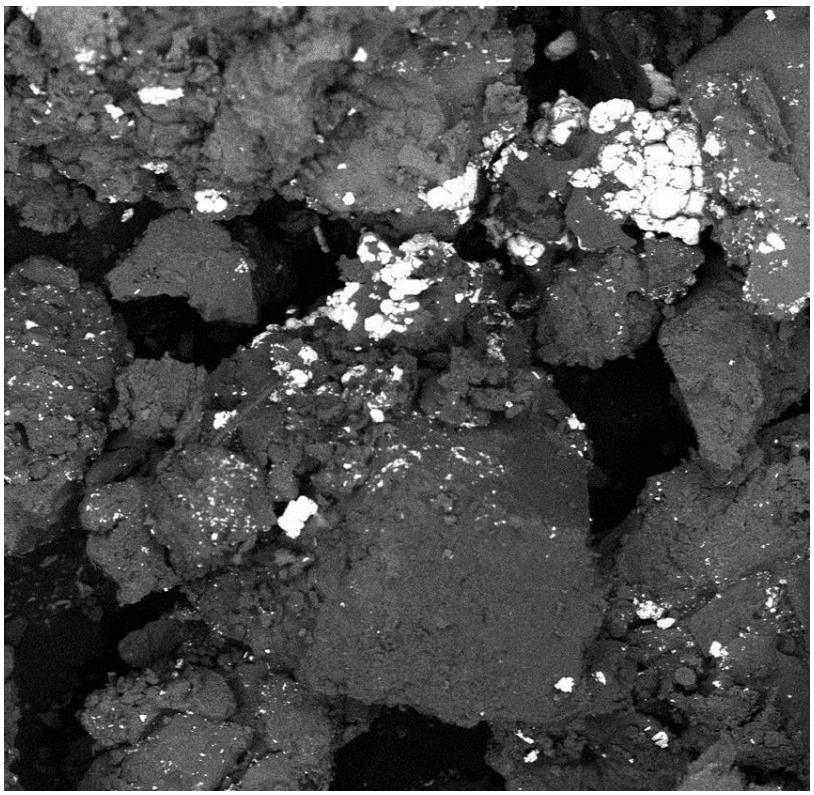


Figure 2a SEM image at magnification of 300x

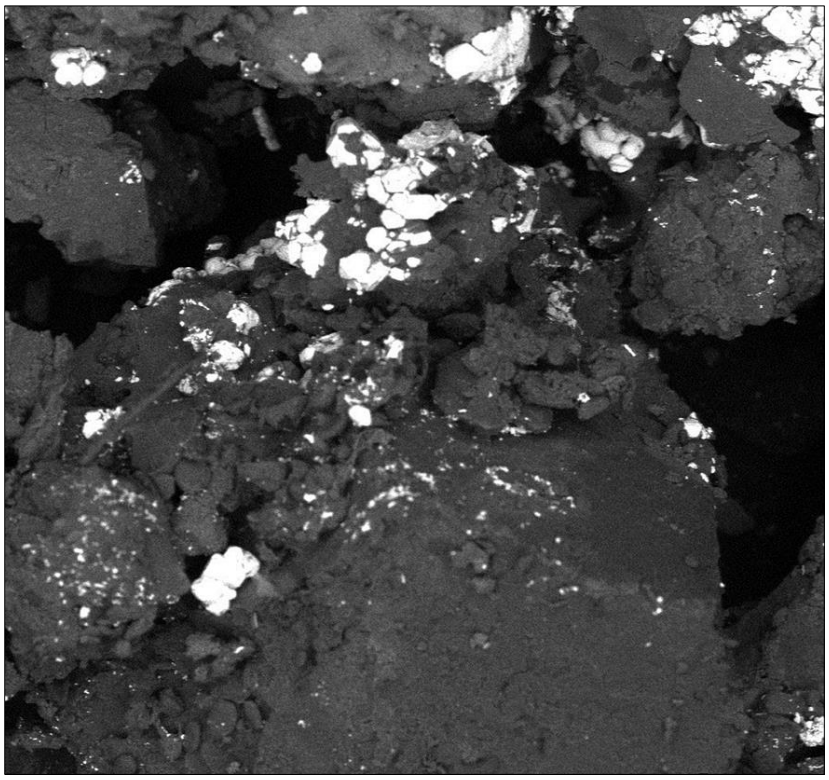


Figure 2b SEM image at magnification of 500x

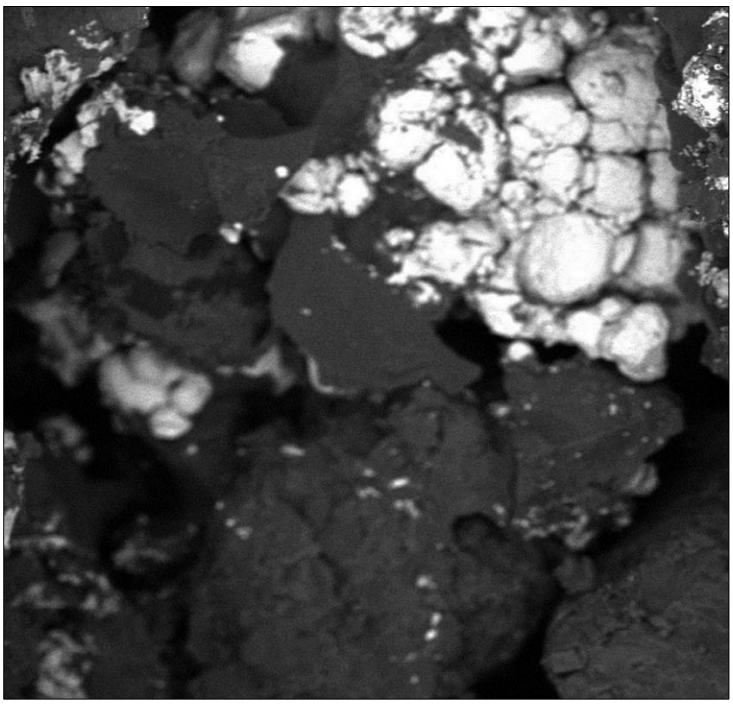


Figure 2c SEM image at magnification of 1000x

3.2.4. FTIR analysis

Fig. 3 shows the results of the FTIR examination of the burnt catalyst, including the scanning runs, peak, intensity, correlation intensity, base height, base length, area, and correlation area. At various wavelengths and angular phases,

several functional elements were identified. Normally, the mid-IR spectrum is separated into four regions: the single bond area (2500-4000 cm^{-1}), the triple bond region (2000-2500 cm^{-1}), the double bond region (2000-2500 cm^{-1}) and the triple bond region (2000-2500 cm^{-1}) (1500-2000 cm^{-1}), in addition to the fingerprint region (600-1500 cm^{-1}) (Nandiyanto and Ragadhita, 2019). The following functional groups can be recognized (Coates, 2000):

The following functional groups were found in the fingerprint region: I aliphatic organohalogen compounds such as C-F, C-Cl, C-I, and C-Br. (ii) the out-of-plane bend in Alcohol, OH (iii). Phenol, C-O stretch, (iv) primary, secondary, and tertiary alcohol, C-O stretch, (v) primary or secondary, OH in-plane bend, (vi) phenol or tertiary alcohol, OH bend, (vii) the peroxide, C-O-O-stretch, (viii) the Epoxy, oxirane rings, and Aromatic ethers, aryl-O stretch, (viii) the Alkyl-substituted ether, and Cyclic ethers with large rings, C-O stretch, (ix) the primary , secondary, and tertiary, both amine and aromatic CN stretch, (x) the carboxylate salt, the P-O-C, aromatic and aliphatic phosphates, the carbonate ion, sulfate, nitrate, calcium, silicate etc. were found.

The following functional group exists in the double bond region: I nitrogen-oxy compounds, open-chain imino -C = N- and open-chain azo -N = N- (ii) carbonyl compounds such as ketones, carboxylic acid, aldehydes, ester, amide, acid halide, and aryl carbonate. (iii) The N-H bend of the primary and secondary amines, (v) the olefinic (alkenes) such as Alkenyl C=C stretch, aryl substituted C=C, conjugated C=C (iv) aromatic ring (aryl) such as C=C-C aromatic ring stretch

The following functional groups were discovered in the triple bond region (2000-2500 cm-1): I Acetylenic (alkynes) compounds such as C-C terminal and medial alkynes, (ii) the transition metal carbonyl, (iii) the ester carbonyl, (iv) the nitrogen multiple and cumulated double bond compound such as Thiocyanate (-SCN), Isocynate (-N=C=O asym. stretch), Cyanate (-OCN and C-OCN stretch), aromatic (CH_3-O-).

There are functional groups such as I Alkynes C-H stretch, (ii) Olefinic (alkenes) such as terminal (vinyl) C-H stretch, pendant (vinylidene) C-H stretch, medial, cis-or trans-C-H stretch, (iii) Saturated aliphatic (alkenes/alkyl) such as methyl C-H asym./sym stretch, methylene C-H asym/ sym stretch, methyne C-H stretch, methoxy, methyl ether O-CH_3, C-H stretch, methylamino, N-CH_3, C-H stretch (iv) The Acetylenic (alkynes) such as alkynes C-H stretch (v) hydroxyl group, H-bonded OH stretch, typical polymeric OH stretch, Dimeric OH stretch, internally bonded and non-bonded hydroxyl group, OH stretch, primary, secondary, tertiary alcohol, OH stretch, phenols, OH stretch (vi) Methoxy ether and oxy compound, C-H stretch (CH_3-O-) (vii) Aliphatic and aromatic primary amine NHH stretch, secondary aliphatic and aromatic amine >N-H stretch, heterocyclic amine >N-H stretch, and imino compounds =N-H stretch (vii) S-H thiols stretch, (viii) common inorganic ions like ammonium ion. The wavelength peak discovered in this study is within the aforementioned ranges, hence the investigation of calcinated wood ash as a catalyst for biodiesel synthesis proved viable.

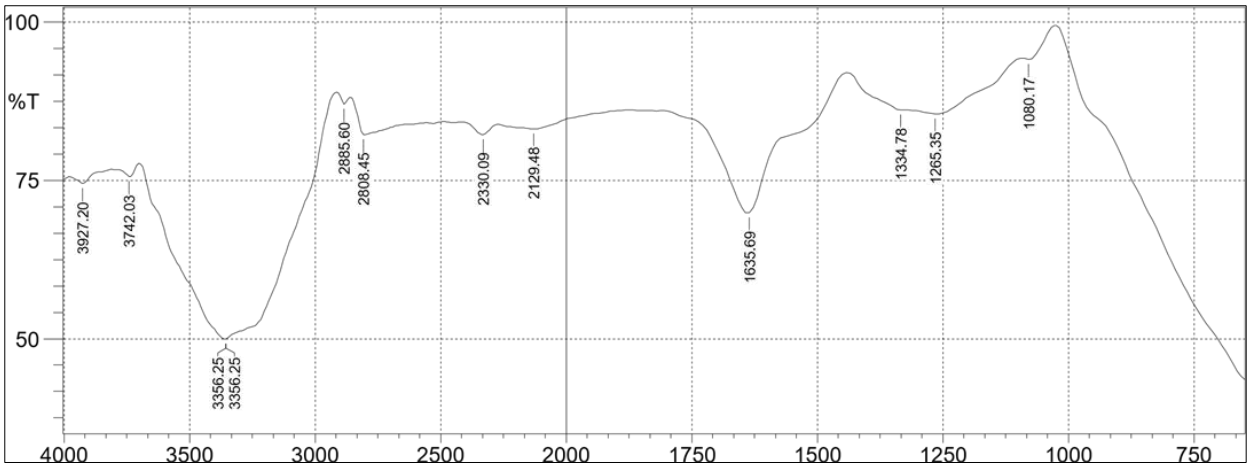
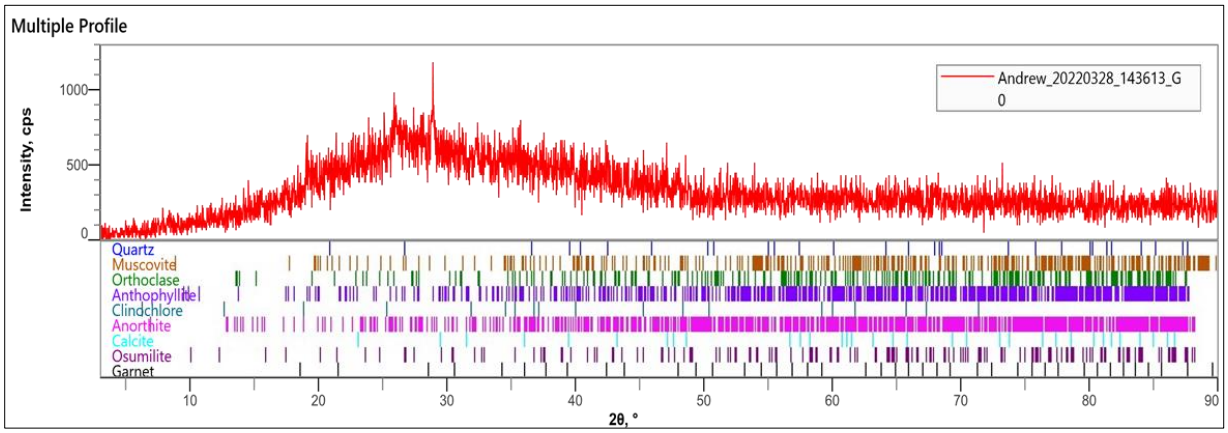


Figure 3 FTIR plot

The plot of intensity versus the angular phase diagram was reflected in further quantitative investigation on the catalyst utilized based on phase data view. The plot displayed a zig-zag pattern with quartz as the main compound and carbon as the main element. Other compounds having figures of merit based on weight fraction include Graphite, Adamite, Gahnite, Zinccite, and Willemite (Fig. 4). The presence of quartz in the catalyst represents the catalytic current, which aided in the rhythmic vibrating of the phases. The graphite in the catalyst is responsible for high tension lubrication and low viscosity product. The presence of adamite in the catalyst aided in the production of biodiesel color; adamite is

typically yellow in color and is responsible for light yellowish biodiesel synthesis in this work. Other substances also contribute in the generation of biodiesel



Dataset/ Weight Fraction	Quartz 42(3)	Muscovite 4.7(7)	Orthoclase 7.3(10)	Anthophyllite 3.0(4)	Clinochlore 3.8(11)	Anorthite 8(2)	Calcite 19(2)	Osumilite 1.5(5)	Garnet 10.3(12)

Figure 4 Results on the Quantitative investigation on the catalyst usability

3.3. Transesterification of WUO to Biodiesel

Table 4 displayed the findings of the biodiesel synthesized from WUO, which included the factor variables that varied in ranges as well as the biodiesel production. The maximum biodiesel production was produced at run 5 with 98.52 (%wt./wt.) at a reaction time of 65 minutes, a catalyst quantity of 5.0 (%wt.), a reaction temperature of 70 °C, and an ethanol-oil molar ratio of 7:1. This shown that the yield of biodiesel increases with increasing reaction conditions, but decreases at higher temperatures over 70 °C due to the catalytic character of the bio-base, which aggregates and clusters. As a result, the high FAME conversion burning temperature is the optimal burnt temperature for catalytic conversion of the powder to catalyst response for FAME conversion of 99%. (Wt.). Furthermore, ethanol boiling temperatures higher than the guideline temperature reduce biodiesel yield due to solvent loss during the reaction process.

3.4. Statistical Analysis

Table 4 Experimental findings of Biodiesel synthesis from waste used oil

SN	**Reaction Time(min)**	**Catalyst conc.(%wt)**	**Reaction temperature (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

The acquired results were statistically analyzed using Microsoft Excel 8.0. The plot in Fig. 5 demonstrated that variables considered in various ranges were remarkably significant, with a high coefficient of determination R-square (R^2) of 0.8164. Indicating a high degree of consistency between the experimental values and the factors taken into account R^2

values greater than 0.800 have been reported to be significant (Adepoju, 2020). The model equations indicating variables slope and intercept shown against yield.

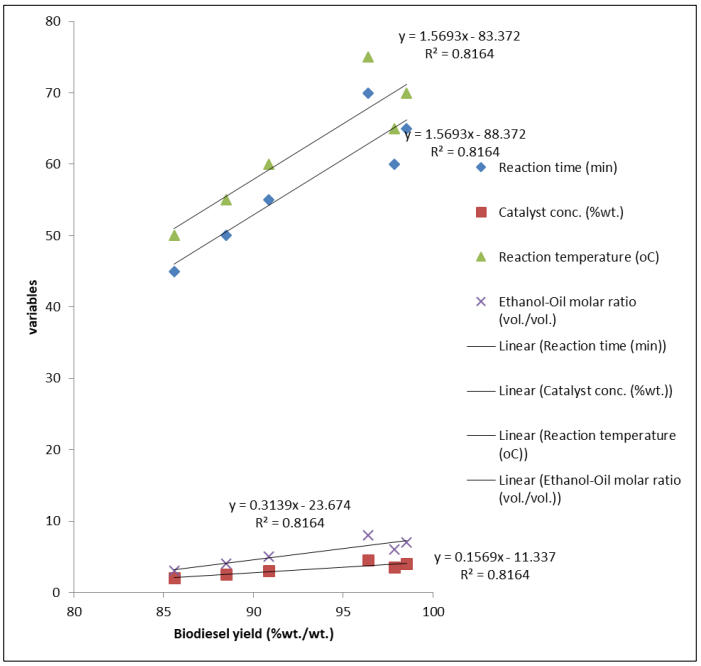


Figure 5 Excel plots of biodiesel yield against the variables

3.5. Physicochemical Properties of Biodiesel

To assess the acceptability of the biodiesel produced in this study, the physicochemical parameters of the biodiesel were determined using AOAC, 1997 techniques. The parameters of the produced biodiesel were displayed in Table 5. These results were compared to the recommended biodiesel standard. According to the table, the quality of the produced biodiesel was in accordance with the standards established by American and European biodiesel standards (ASTM D6751 and EN 14214). This means that the biodiesel produced in this study can be used in place of conventional diesel in industries and for commercial purpose

Table 5 Physicochemical Parameters and Characteristics of Biodiesel

Parameters	**Biodiesel**	**ASTM D6751**	**EN14214**
Physical properties			
Physical state at 28 °C	Light brown	-	-
Moisture content (%)	0.001	0.05max	0.08
Specific gravity	0.83	0.86 – 0.90	0.85
Viscosity (cP) at 40 °C	2.56	1.9 -6.0	3.5 – 5.0
Chemical properties			
%FFA (as oleic acid)	0.28	<0.40	0.25max
Acid value (mg KOH/g oil)	0.58	<0.80	0.50max
Saponification value (mg KOH/g oil)	182.32	-	-
Iodine value (gI_2/100 g oil)	116.00	-	140
Peroxide value (meq O_2/kg oil)	2.48	-	-
Other properties			

Cetane number	50.14	47	51max
Diesel index	50.40	-	-
API	36.95	-	-
Higher heating value (HHV)	36.15	-	-

4. Conclusion

From the result obtained in this study, the following conclusion can be drawn

- Calcine animal bone was found to be rich in calcium content (87 %)
- Optimum biodiesel yield of 98.52 (%wt./wt.) was obtained at reaction time of 30 min, catalyst amount of 2.0 (5%wt.), reaction temperature of 100 ℃, and the ethanol-oil ratio is 4:1 . A statistical analysis via Microsoft Excel proved that the constraint variable selected were remarkably significant with regression parameter R-square >0.8
- 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).
- The produce biodiesel in this study can replace conventional diesel that of economic standard and serve as IGR if other waste feedstock can be harnessed.

Compliance with ethical standards

Acknowledgments

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Disclosure of conflict of interest

No conflict of interest to be disclosed.

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