Biodiesel Production from Waste Cooking Oil Using Highly Efficient Heterogeneous Catalyst Derived from Cow Bone

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Abstract- ***This study investigates the production of biodiesel from waste cooking oil using a catalyst derived from cow bone, and evaluate their potential as heterogeneous catalysts for the production of biodiesel. The use of cow bone as a catalyst support holds promise as a sustainable and cost-effective approach for biodiesel manufacturing. A series of nanocatalysts, incorporating magnesium (Mg), cobalt (Co), and zinc (Zn) dopants into calcium oxide (CaO), were synthesized and applied in the transesterification process of waste cooking oil. The materials were characterized using multiple techniques, including X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET) surface area analysis, scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDX). The reaction conditions were optimized to fine-tune various reaction parameters. These parameters, such as Mg, Co, and Zn doping levels, catalyst loading, methanol-to-oil molar ratio, and reaction time. Remarkably, the optimal conditions yielded a good biodiesel conversion rate of 96.74%. The optimal condition was determined as, methanol-to-oil molar ratio of 20:1, catalyst loading of 5wt.%, a reaction temperature of 65°C, and a reaction duration of 4 hours. Confirmation of biodiesel product was accomplished using Gas Chromatography-Mass Spectrometry (GC-MS) technique. The outcomes indicate that the cow bone-derived porous materials, doped with Mg, Co, and Zn exhibited high catalytic activity and stability. This suggests their potential suitability for large-scale industrial biodiesel production processes.***

Keywords: Biodiesel Production, Waste Cooking Oil, Heterogeneous Catalyst, Cow Bone, Transesterification.

I. INTRODUCTION

The increasing consumption of traditional fossil fuels and the escalating concerns about greenhouse gas emissions have redirected the focus of the scientific community towards renewable energy sources (Wan *et al*., 2014). It has become imperative to seek alternatives to fossil fuels to avert severe environmental consequences, should the exploration of alternative energy sources be neglected (Soudagar *et al*., 2021). The global shift towards biofuels has gained significant momentum in recent decades, with biodiesel emerging as a prominent substitute for conventional diesel in numerous countries. Biodiesel is favored for its renewable, sustainable, and non-toxic nature (Mujtaba *et al*., 2020).

In general, biodiesel production involves the transesterification of oils, fats, or greases with low carbon alcohols, often employing homogeneous basic or acidic catalysts (Shan *et al*., 2015). While homogeneous base catalysts are known for their high catalytic efficiency under mild conditions and are thus commonly used, they have drawbacks, including corrosion risks to reactors and difficulties in separation from the mixture. Furthermore, the need for water washing and purification steps to achieve the required fuel quality contributes to higher production costs (Luque *et al*., 2010). In contrast, the use of heterogeneous catalysts in biodiesel production offers advantages such as easy separation, non-corrosiveness, and eco-friendliness (Kumar and Sharma, 2016). Heterogeneous catalysts can be both acidic and basic, with the base-catalyzed transesterification process gaining prominence due to its potential to mitigate issues related to extended reaction times and high temperatures associated with acid-catalyzed transesterification (Kalam *et al*., 2020).

Among heterogeneous base catalysts, calcium oxide (CaO) is highly regarded for its properties, including strong basicity, mild reaction conditions, cost-effectiveness, high biodiesel yield, and minimal solubility in fuel (Nisar *et al*., 2017). Recent research efforts have focused on designing and developing catalytic materials from affordable and waste renewable sources to enhance the overall sustainability of the biodiesel production process. Waste materials rich in calcium, such as waste animal bones, mollusk and eggshells, and industrial byproducts, have been explored as potential catalysts for biodiesel production. This approach not only

transforms waste into valuable materials but also addresses ecological concerns associated with waste disposal (Bennett, Wilson, Lee, 2016).

The utilization of Ca-rich waste materials as heterogeneous catalysts holds significant promise for biodiesel production, as it avoids ecological damage and disposal issues, offers moderate catalytic activity, and reduces production costs, thus enhancing competitiveness (Boro *et al*.,2020) Transforming waste materials into valuable substances through environmentally friendly processes is a highly effective waste management strategy. Waste animal bones, which contribute to land pollution, can be converted into valuable catalysts. These bones contain alkaline metal oxides and other non-metals, with calcium and phosphorous being the major components that can be converted into hydroxyapatite and beta tricalcium phosphate upon thermal calcination, exhibiting substantial catalytic activity. Over the past decade, catalysts derived from waste animal bones have found effective application in various fields, including the synthesis of bioactive compounds, hydrogen and biodiesel production, organic synthesis, organic reduction reactions, oxidation of organic compounds, and treatment of environmental pollutants (Shan *et al*., 2016).

Additionally, waste bone-derived hydroxyapatite (HAp) has potential applications in drug delivery, adsorption, chemical sensing, bio-ceramics, chromatographic lighting materials, and powder carriers due to its rich elemental composition (Haider *et al*., 2017).

The aim of this study investigates the production of biodiesel from waste cooking oil using a catalyst derived from cow bone, and evaluate their potential as heterogeneous catalysts for the production of biodiesel.

The specific objectives are to;
(i) convert cow bone to CaO by manual grinding and calcination at 900^0C,
(ii) Characterize the material in (i) using FTIR, SEM, EDX, TGA, TEM, BET and PXRD,
(iii) Investigate the catalytic activity potential of material in (I) as heterogenous catalyst in transesterification reaction of waste cooking oil, and
(iv) characterized the biodiesel product obtained in (iii) using GC-MS and FTIR.

II. MATERIALS AND METHODS

Waste cow bones were collected from Abattoirs in Ajanaku Tanke town around Oke Odo area Ilorin, Zinc Nitrate dihydrate [Zn $(NO_3)_2 \cdot 6H_2O$], Cobaltous chloride ($CoCl_2.6H_2O$) and Magnesium oxide (MgO) and NaOH were commercially sourced from Sigma Aldrich. Methanol (94%) and deionized water were purchased from Central Research Lab, Ilorin. All reagent and solvent used in the synthesis process were of analytical grade and were used without further purification. Waste cooking oil was sourced from Cafeteria, located inside the University of Ilorin campus.

2.1 APPARATUS

Muffle furnace, measuring cylinder, filter paper, beaker, conical flask, 3-neck flask, water bath, sieve of mesh, oven, analytical weighing balance, thermometer, grinding machine, hot plate, mortar and pestle. All apparatus used were washed and rinsed before the commencement of the lab work.

2.2 Catalyst Synthesis

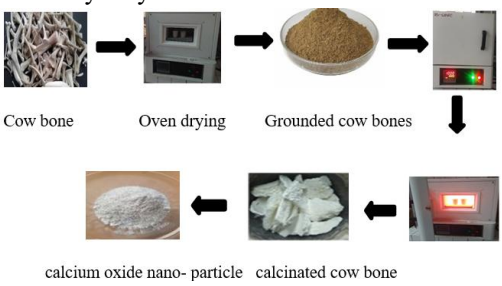


Fig1: step by step catalyst synthesis

2.3 SAMPLE PREPARATION

The collected waste animal bones were shaved by using knife to remove sticking organic parts like meat and cartilage and then boiled using de-ionized water for 20 minutes to remove dirt and any remaining meat. The bones were then washed repeatedly with tap water and rinsed with distilled water to remove other impurities and were sun dried for 72 h and oven-dried overnight at 105°C for 24 h. The dried waste cow bones were crushed with jaw crusher and milled by mortar and pestle then sieved using 63 µm sieve to obtain a powder form with this particle size.

2.3.1 CALCINATION OF WASTE COW BONES

The cow bone powder was analyzed to identify the calcination temperature range. The grounded cow bone powder was placed in ceramic crucibles and calcined in muffle furnace (MV106 model, USA) at 900°C for 3 h. Some portion of the calcinated cow

bone powder was refluxed in deionized water at 60°C for 6 h which was followed by oven dried at 105°C over-night. The powder was further dehydrated by calcination at 800°C for 3 h to convert the hydroxide form into a highly porous calcium oxide nano-particle. After calcination process the synthesized catalyst was allowed to cool and then stored in the desiccator for further process.

2.3.2 CATALYST CHARACTERIZATION

The solid catalyst was subjected to several physical and chemical characterizations using various techniques, such as elemental analysis by X-ray fluorescence (XRF). The surface porosity; pore volume and XRD of the catalyst were determined by Bruneur-Emmet-Teller. The weight loss as a measure of thermal stability of the catalyst was determined by Thermogravimetric Analysis and the surface morphological features of the catalyst was determined using Scanning Electron Microscope analysis. The EDX (Energy Dispersive Xray Analysis) analysis was carried out in TECNAI G2 20 S-TWIN (200 KV) at a Resolution: 2.4 A0. The analyses were performed at the Department of Chemistry, University of Connecticut Storrs, USA.

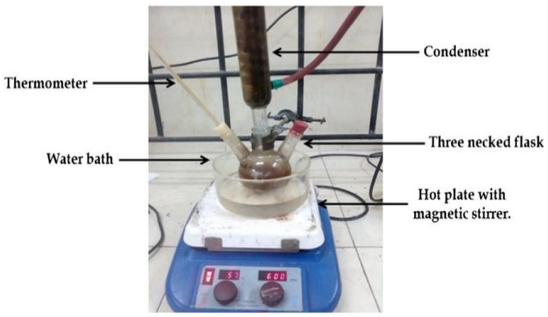
2.4. ZnO, MgO and Co doped CaO Nano Catalyst

The synthesis of MgO-doped CaO catalyst was carried out by using the parent CaO catalyst and analytical grade magnesium oxide by co-precipitation method. During the synthesis process, the required (9.477 g of CaO with 0.499 g of MgO) amount of calcium oxide and hexahydrate was mixed in deionized water separately and allowed to stir for 40 minutes. After the completion of 40 minutes, the solution with Magnesium oxide hexahydrate is added to calcium oxide solution dropwise so that MgO can fill the interstitial spaces of CaO. After 1 h of mixing of magnesium oxide and CaO,1M NaOH solution is added to the homogenous mixture so that white precipitate is developed in the solution. This white precipitate is stirred for another 30 min at room temperature and kept for 5 h without stirring. Subsequently the precipitate is washed four times with water and ethanol. Then the precipitate was dried at 120^{o}C for an hour after to get MgO-doped CaO sample (Lee *et al*., 2013; Cho and Seo,2010). This sample is then annealed at 250^{o}C for 4 h. The produced catalyst was then characterized using the following techniques: XRF, BET, XRD and TGA. The material gotten from the annealed MgO-doped CaO catalyst was also characterized using techniques such as Scanning Electron Microscopy (SEM), Energy Dispersive spectroscopy (EDX), Thermogravimetric Analysis (TGA), FTIR, and Brunauer Emmett-Teller surface area analysis (BET)

2.5 PRE-HEATING OF WASTE COOKING OIL

The waste cooking oil collected was filtered to remove all the impurities present followed by heating at 110 °C for 30 min to remove the moisture. The acid value of waste cooking oil was determined and found to be 1.67 mg KOH g^{-1}; hence direct transesterification can be performed to produce biodiesel.

2.6 Transesterification Reaction



Trans-esterification reaction set up

Transesterification reaction was used to test the performance of the synthesized catalyst. The reactions were performed in 500ml three-neck round bottom flask with a hot plated magnetic stirrer and fitted condenser with cool water to reduce evaporation of methanol. The reaction condition such as reaction time (3h,5h,2h,1h,40minutes), molar ratio (25:1,9:1,6:1,4:1,1:4 and 1:1), catalyst loading (3wt%, 6wt%, 1.4wt% and 0.4wt%), reaction temperature (120^{0}C,65^{0}C, 60^{0}C and 70^{0}C) and string speed (660rpm) was set based of the different reaction conditions reported on the literatures. Known amount of oil sample with 9:1 M ratio of methanol to oil was prepared and heated to 110^{0}C for 30 minutes to remove unbounded moisture if any and cooled to reaction temperature (60^{0}C). On the other separate flask known amount of methanol and catalyst (3wt%, 6wt%, 1.4wt%, 5wt% and 300mg) samples were mixed in the flask and an exothermic nature was observed which confirms the formation of methoxides. Then the methoxides and the cooled oil sample were added to the glass reactor for reaction. The reaction was carried out at 60^{0}C for 3 hours at a high speed of 660rpm. After the reaction completed, the reaction mixture was put in centrifuge (pro-

Analytical C2004 model) at 3000rpm for 30 minutes to separate catalyst then the rest solution was put in a 500ml separating funnel for overnight. The product obtained was heated to remove excess methanol and then allowed to settle in a separating funnel. The upper phase consists of fatty acid methyl esters (biodiesel) and the lower phase contains glycerol as the by-product. The amount of the obtained biodiesel was weighed and the yield of biodiesel with respect to the amount of waste cooking oil used during the reaction was estimated by Equation. Further, the purity of the obtained biodiesel in terms of mono FAME formation was determined using 1H NMR analysis (eq.1)

$$Yield\ wt\% = \frac{Weight\ of\ produced\ biodiesel}{Weight\ of\ waste\ cooking\ oil} \times 100$$

2.7. Characterization waste cooking oil fatty acid methyl esters (biodiesel)

Physico-chemical properties such as density, viscosity, acid value, free fatty acid, saponification value, calorific value, cetane number and iodine value the samples were estimated/determined as per American Society for Testing and Materials (ASTM) methods. Further, the conversion (purity of produced biodiesel) of the triglycerides of waste cooking oil was monitored quantitatively and qualitatively, then the sample was analyzed by gas chromatograph-mass spectrometer chromatograph-mass spectrometer (GC-MS) (GC-MS OP 5000series, Shimadzu Japan, 2010) to identify the fatty acid composition.

2.8 GC-MS Principle/Methodology

A Perkin Elmer Turbo Mass Spectrophotometer (Norwalk, CTO6859, and USA) with a Perkin Elmer Auto sampler XLGC was used for the GC-MS analysis. The column utilized was a Perkin Elmer Elite -5 capillary column measuring 30m 0.25mm and made of 95% Dimethyl polysiloxane. Helium was employed as the carrier gas, with a flow rate of 0.5ml/min. A sample injection volume of 11 cm^3 was used. The intake temperature was kept constant at 250°C.

The oven temperature was set to 110°C for 4 minutes, then increased to 240°C. The temperature was then programmed to rise to 280°C at a rate of 20°C per minute for 5 minutes. The whole run time was 90 minutes. The temperature of the MS transfer line was kept at 200°C. The source temperature was kept constant at 180°C. For compound identification and quantification, GC-MS was analysed using electron impact ionization at 70 eV and data was reviewed using total ion count (TIC). The component spectrums were compared to a database of known component spectrums kept in the GC-MS library. Turbo-Mass OCPTVS-Demo SPL software was used to measure peak areas and process data.

III. RESULTS AND DISCUSSION

3.0 Heterogeneous Catalyst Preparation

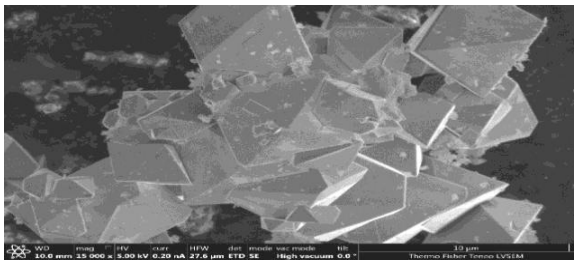
Heterogeneous catalyst preparation from waste cow bone was done by following the previous studies by Nisar *et al*., (2017). It was reported that calcination at 900°C is the best according to research conducted by Nisar *et al*., (2017), where the percentage of biodiesel produced reached 96.1%. Calcination aims to remove carbon dioxide (CO_2) compounds in the waste cow bone in order to form oxide so that the surface area of the material increases CaO results in calcination of cow bones at a temperature of 900^0C for 3 hours. It was observed that the colour changed from a brownish gray, to a clean white color. The discoloration is an indicator of the change in compounds found in cow bones that were once $CaCO_3$ now changed to CaO. This is in accordance with previous research conducted on Malau & Adinugraha research (2020). $CaCO_3$ compounds heated at 900^0C decay and turn into CaO. The decay event is caused by the provision of a high temperature enough to result in the release of carbon. The chemical reactions that occur are as follows.

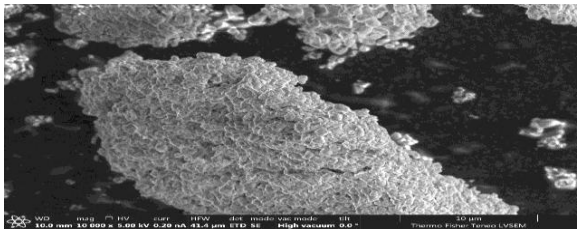
$$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)} \quad (1)$$

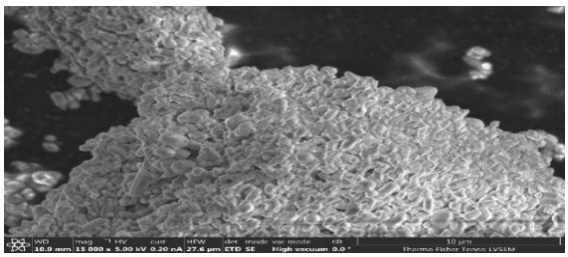
The material is ready to be tested for activity as a catalyst in the transesterification reaction of waste cooking oil to produce biodiese1. Before calcined cow bone particles have a rather coarse texture, but after calcined cow bone particles have a smooth texture with a lighter mass.

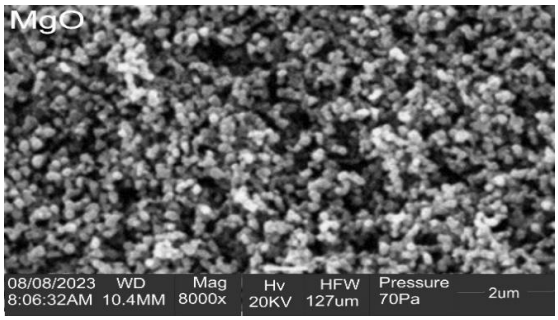
3.1 Characterization of the Catalyst.

3.1.0 Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) analysis

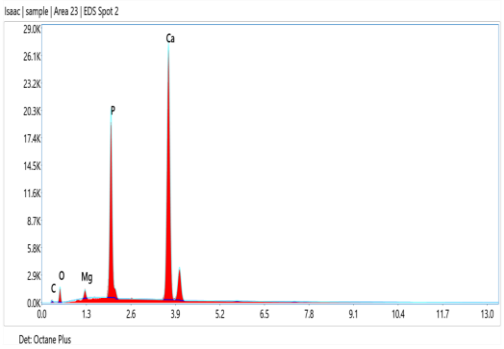




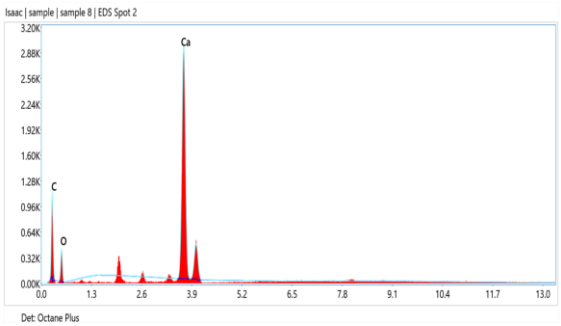




SEM micrograph of the powder shows that, the particles had irregular shapes, including small spheres, agglomerated together in some parts. It is may be happened due to the inter link up of HA particle each another.



Uncalcined cow bone



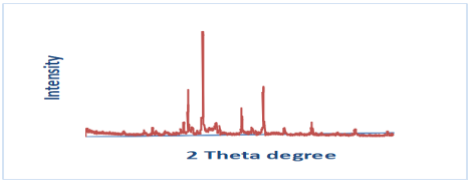
calcined cow bone

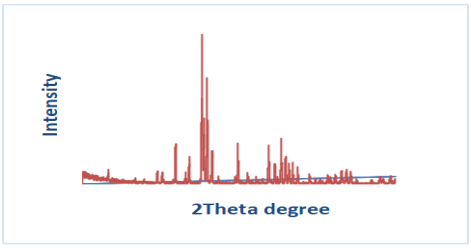
Element	Weight uncalcined cow bones (%)	Atomic uncalcined cow bones (%)	Weight calcined cow bones (%)	Atomic calcined cow bones (%)
C K	5.03	8.60	1.32	2.27
O K	41.16	52.82	51.55	66.63
Na K	26.60	23.76	9.92	8.92
Mg K	-	-	3.30	2.81
P K	2.08	1.38	12.35	8.25
Ca K	16.62	8.52	21.56	11.13
Cl K	8.50	4.92	-	-

Table 1. *EDS analysis of calcined cow bones and uncalcined cow bones*

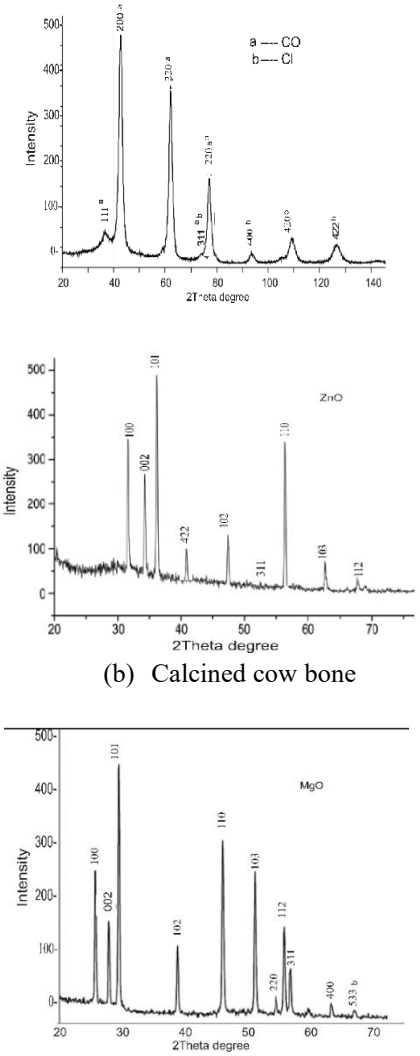
EDS testing aims to determine the percentage of elements and chemical compounds contained in the material. Table 1. showed that non-calcined material containing inorganic content consisted mainly of calcium (Ca) of 16.62%, sodium (Na) of 26.60% and oxygen (O) 41.16%, phosphorus (P) of 2.08%, and chlorine (Cl) of 8.5. However, on the calcined material the content of Ca, O and P increased to 21.56%, 51.55% and 12.35% which confirmed that the material was dominated by $((Ca)_5\ (PO_4)_3(OH)$ with an increase in composition in the element Ca, P and O and supported by XRD data that compounds formed in 900°C calcination material are $((Ca)_5(PO_4)_3(OH)$ as the main content based on XRD peak intensity which reaches 1000 rails. Increased elements of Ca, P and O in calcined materials, the calcination process was able to decompose organic compounds in the material, which was also evidenced by a decrease in the percentage of element C in calcined material from 5.03% to 1.32% so that a decrease in the percentage of organic elements inside material, there is an increase in inorganic elements in the material.

3.1.1 POWDER X-RAY DIFFRACTION





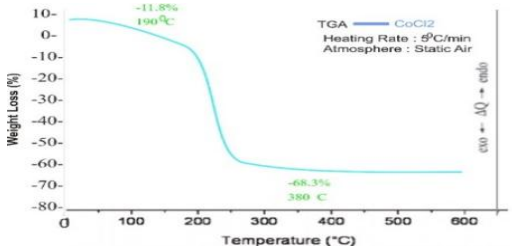
(a) Uncalcined cow bone

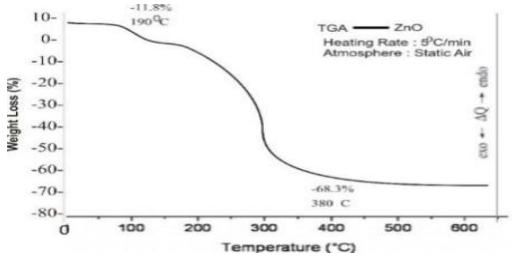


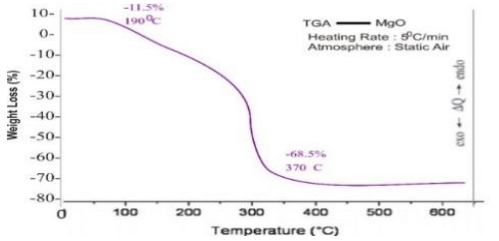
(b) Calcined cow bone

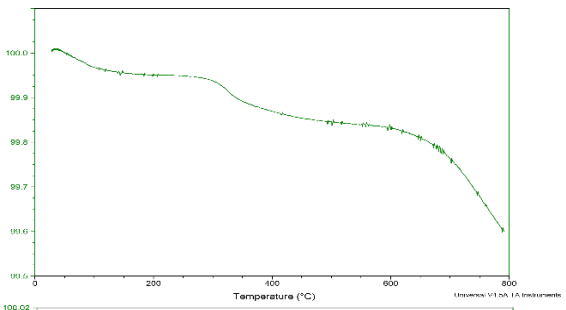
Based on adjustments to the JCPDS database, cow bone powder produces calcium carbonate ($CaCO_3$) with two phases, namely calcite and aragonite. The formation of calcite can be seen in diffraction peaks with an angle of 2θ: 25.9200°, 32.130° and 35.4700°. Aragonite can be seen at angles 2 23: 23.1050°, 28.8900° and 39.7800 °. In addition, powder cow bone also contains hydroxyapatite ($(Ca)_5(PO_4)_3(OH)$) at an angle of 2θ: 34.2200°. Based on the diffractogram obtained from (b); Cow bone which was calcined at 900°C for 3 hours produced a new peak shows that new compounds have been formed such as CaO and Ca $(OH)_2$, as well as increasing the intensity of hydroxyapatite. (a) Diffraction peaks at an angle of 2θ: 31.8499°, 32.9875° and 39.8804° indicate the formation of hydroxyapatite as the main ingredient in the material. The peaks at 2θ: 32.2768° and 35.5528° shows CaO formation and 2 Ca: 18.8725°, 28.5600° and 34.1423 ° angles indicate the formation of Ca $(OH)_2$.

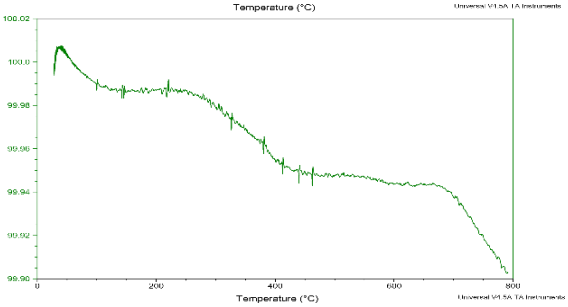
3.1.2 Thermal Analysis







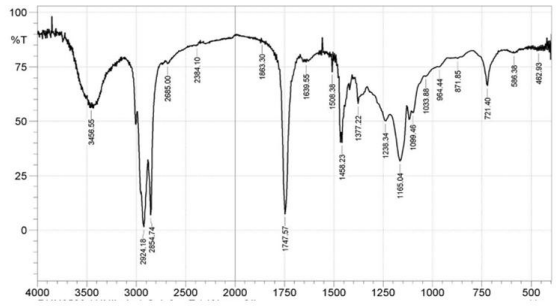




Results obtained for calcinations time, weight loss and percentage yield at various temperatures for the removal of organic matter and water. The carbon and oxygen content in the cow bone might have been lost after calcinations under high temperatures. The weight loss was more than 30% for the WCB at each temperature and time. The calcinations temperatures and time were progressively increased up to a maximum of 900^0C and 3 h respectively and the percentage yield under this condition was 76.4 %.

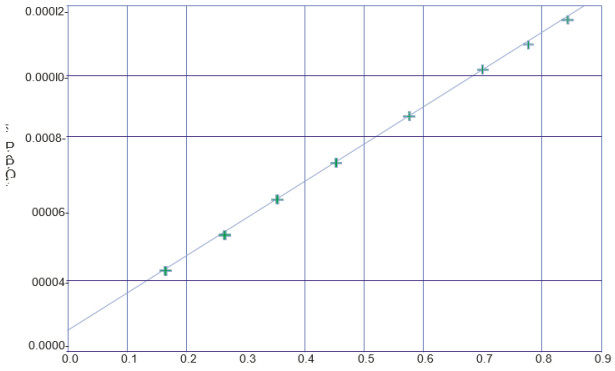
The crystalline structure of the cow bone changed after calcinations, which may be due to the decomposition of calcium carbonate ($CaCO_3$) to carbon (IV) oxide and calcium oxide (CaO) (Variya et al.,2010). As the temperature increase over the time, the yield was also observed to increases. High temperature increases the yield of heterogeneous catalysts. After the calcinations, the calcium oxide produced was doped with metal oxides to improve the surface area of the catalyst. No significant weight loss was observed between the metal oxides doped CaO and calcinated, indicating the complete removal of organic materials such as collagen, chondroitin sulfate, keratin sulfate, and lipids.

3.1.3 Brunauer Emmett-Teller (BET)

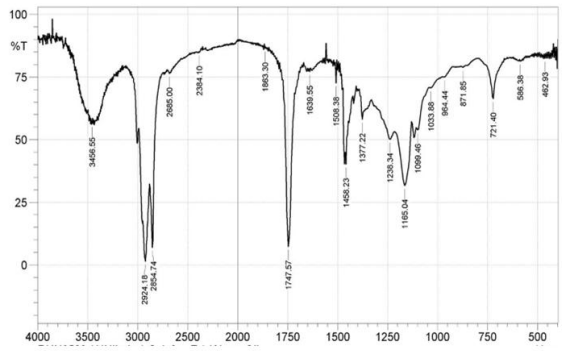


The catalyst prepared was characterized (BET) by using calcined form with a pore size (1.419 nm), surface area (4.369 m^2/g) and higher surface area(68.22 m^2/g, 65.22 m^2/g, 60.50 m^2/g) was doped with metal oxide to aided the reactants to diffuse easily into the interior of the catalyst (Niju *et al*.,2014). Sharma *et al*. (2012) reported that high pore size is desirable for better diffusion of reactant and product molecules. The pore volume of ($0.520cm^3/g$) obtained is high compared to the results reported by Birla *et al*., (2012) who recorded a pore volume of ($0.157\ cm^3/g$).

Properties	Calcined	CaO-Co	CaO-Zn	CaO-Mg
S/ Area(m^2/g)	4.369	50.220	60.500	68.220
Pore Vol(cm^3/g)	0.029	0.42	0.52	0.52
Diameter(nm)	1.419	30.260	30.230	24.220

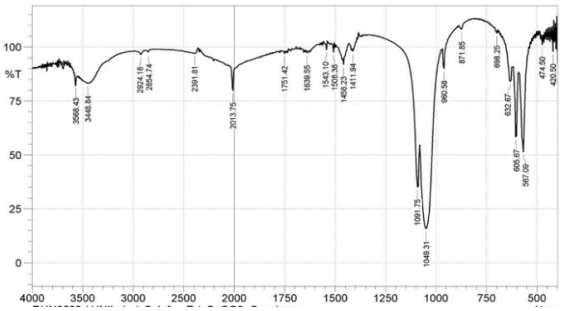


3.1.4 Fourier-Transform Infrared Spectroscopy Biodiesel

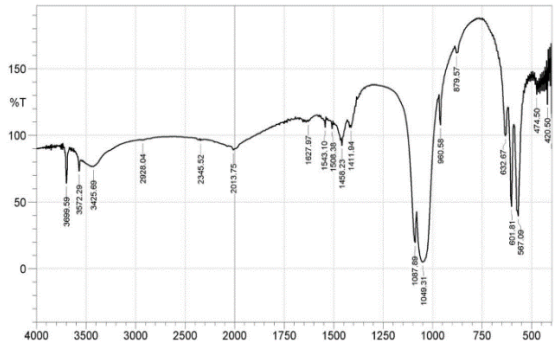


Waste oil

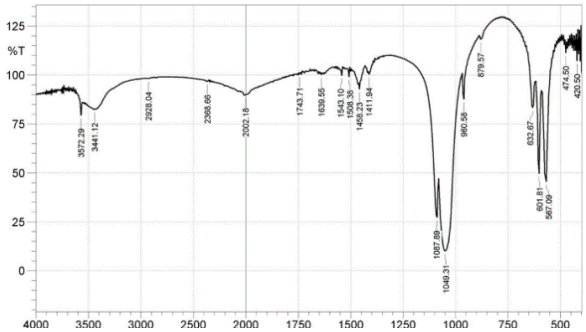
FTIR spectra of biodiesel produced from the WCO are illustrated in Figure (a) and (b). The spectrum region between 1500 and 900 cm^{-1} elaborates the chemical differences between biodiesel and vegetable oil (Nisar *et al*. 2017). The peaks located at 2924 and 2853 cm^{-1} show the symmetric and antisymmetric stretching vibrations of C-H in CH_2 and CH_3 groups, respectively. The strong peak located at 1765 cm^{-1} is because of the presence of C=O stretching vibration of carbonyl groups present in triglycerides and esters. The peaks at 1600–1400 cm^{-1} region confirmed the bending vibrations of CH_2 and CH_3 aliphatic groups, while the bending of HCH occurs at 1373 cm^{-1} and CH_2



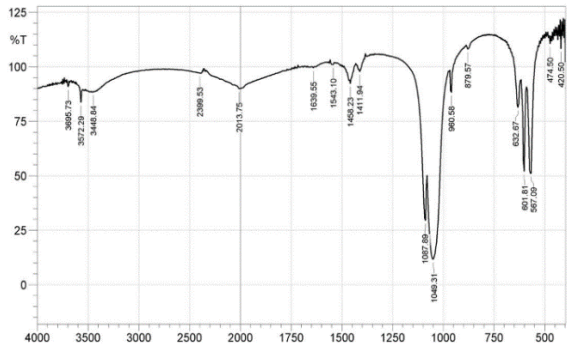
Calcined cow bone



Mg-doped CaO



Zn-doped CaO



Co-doped with CaO

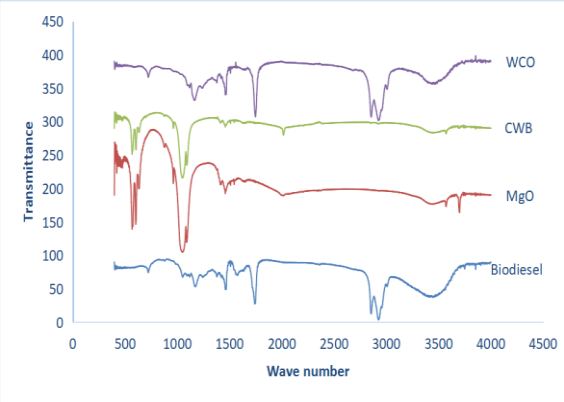
Calcined cow bone: Bones calcined at 900°C. scissoring at 1490 cm^{-1} respectively. The peaks situated in the region 1265–1245 cm^{-1} presented the stretching vibration of C-O ester. The peak at 1765 cm^{-1} confirmed the stretching vibration of C=O located in esters, and peaks present in the range 1500–1300 cm^{-1} also confirmed the C-O stretching vibrations (Shalaby and El-Gendy 2012; Tariq *et al*. 2011).

Mg-doped CaO: The sharp absorption peak at 3637cm^{-1} correspond to the stretching vibration of free O-H, indicating the formation of hydroxides such as Ca $(OH)_2$ on the surface of sample. The absorption peak at 1650cm^{-1} correspond to a bonding vibration of O-H, indicating the presence of chemisorbed H_2O on the surface of the sample. No broad absorption peak was found near 3500 cm^{-1} and CO_2 at 2352 cm^{-1}. The broad and strong absorptions peak near 500cm^{-1} corresponds to the vibration of Ca-O bands and the absorption peak near 545cm^{-1} is association with the vibration of Mg-O bonds. The appearance of these bands indicates the presence of CaO and MgO in the samples, which is consistent with the XRD analysis that the diffraction peak is larger than that of Ca-O, the absorption bands in this region overlap and became wide and weak with the increasing Mg content.

Zn-doped CaO: The FT-IR spectra for the catalysts with different Zn loading are presented in the peak which appears around 3600 cm^{-1} corresponds to the vibrations of OH group bonded to the metal ions and becomes more intense with Zn addition. The most obvious band assigned to ZnO is the one observed at around 850–900 cm^{-1}. The band around 1365–1587 cm^{-1} may have arisen due to the asymmetric stretching vibrations of Zn–O bond. The absorption peak at around 3400 cm^{-1} is attributed to O–H stretching vibration of H_2O. The peak observed at around 500–585 cm^{-1} is ascribed to stretching vibration of Zn–O bond.

Co-doped with CaO: The FT-IR spectrum of the Co-CaO nanoparticles are shown in which depicts mainly the incorporation of cobalt completely in the matrix of calcium oxide as discussed earlier in the XRD results too. The reason is that there is no distinguished peak for cobalt seen. The spectrum also reveals alteration of the crystalline structure of calcium oxide due to doping of cobalt. If we compare the peaks of calcined calcium oxide and calcium oxide doped, then there is a modification of the peak to a great extent. C-O stretching is at peak ~875 cm^{-1} which is due to the presence of carbonate ion. The peak assignments of Cobalt-doped calcium oxide at different temperatures are shown below in the table. The effect of catalyst loading on biodiesel conversion

was carried out with 0.5, 1, 1.5,2 and 2.5 wt.% of catalyst in algal lipid. The yield of biodiesel increased with increase in the concentration of the catalyst. The biodiesel yields are 72%, 86%, 98%, 94% and 88% respectively for the different dosage of the catalyst 3430 cm^1, 3447 cm^1, 3470 cm^1 are in O-H stretching vibrations of H_2O from the atmosphere. The peak 870 $cm^{1,}$ 860 cm^1,853 cm^1 is due to the metal to oxygen vibrations frequency which has made some micro structural changes to the addition of Co in CaO lattice. At 448 cm^1, 563 cm^1 peak shows the Ca-OH and Ca-O stretching vibration respectively. The 1544 cm^1, 1527 cm^1, 1515 cm^1 is due to H-O-H vibrations in the catalyst can be definitely due to the small amount water molecules in the catalyst.



3.1.5 Gas Chromatography-Mass Spectrometry Analysis

To detect the different FAME contents in the biodiesel, GC-MS analysis was performed. The results of the composition of methyl esters in the synthesized biodiesel are presented in the gas chromatogram (Figure 2. The various peaks appearing in the chromatogram were identified by comparing them with standard fatty acid methyl ester's (Biodiesel) chromatogram peaks as shown below. The chromatogram also confirms successful conversion of WCO into biodiesel. Fig 2 represents the chromatograms of biodiesel production by using the catalyst derived from animal bones calcined at 900°C. The results of the conversion of WCO into biodiesel are summarized in Table 2. The highest conversion was recorded when bones calcined at 900°C were used as catalyst to convert WCO into biodiesel of around 77.8%. The catalyst could be reused three times without losing much of its activity as depicted by the conversion of WCO to biodiesel that stayed around 76–78%. The composition of methyl esters present in the synthesized biodiesel is summarized below

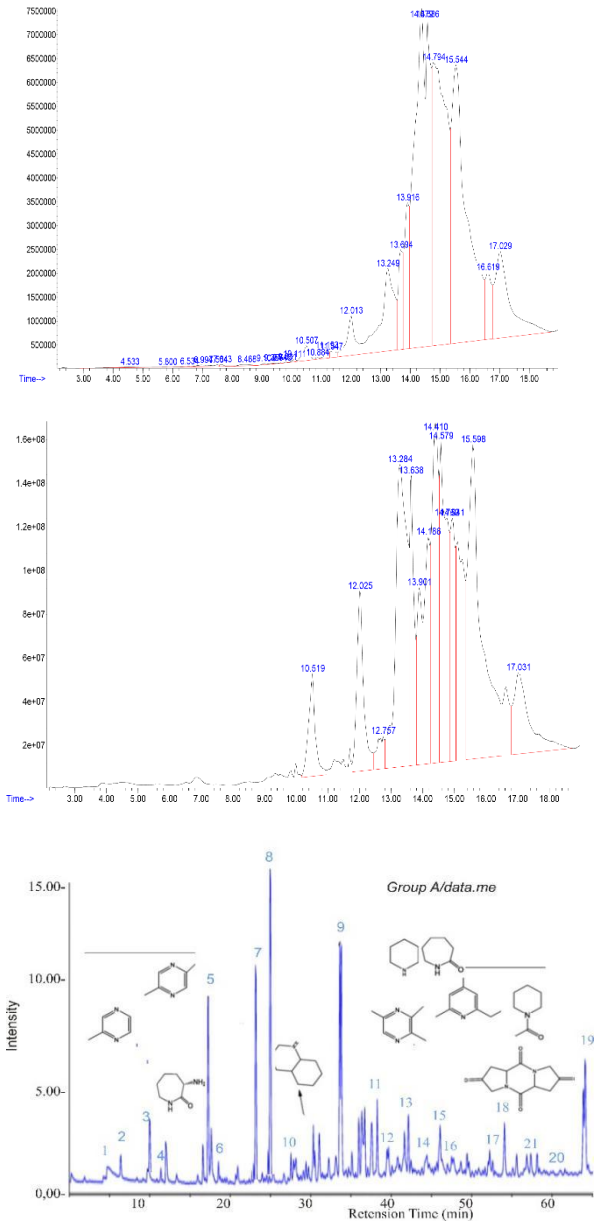


Figure 2. Gas chromatogram of the synthesized biodiesel through catalyst (cow bone) calcined at various temperature

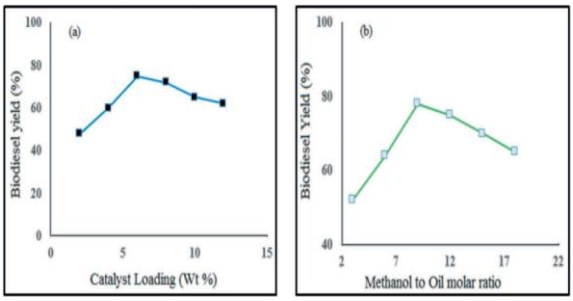
3.2 Optimization of the Transesterification Reaction Effect of Catalyst Loading

In order to optimize the amount of catalyst required for maximum biodiesel yield, experiments with various concentrations of catalyst (wt %) 2, 4, 6, 8, 10 and 12 were performed. The results are shown in (Figure 4(a)). Initially, the conversion of WCO to biodiesel was low at 2% (48% yield); FAME conversion increased by increasing catalyst loading up to 75% with 6% catalyst loading. Further increase in the amount of catalyst decreased the biodiesel conversion to a significant amount as the reaction

mixture became more viscous requiring a higher amount of stirring (Chen *et al*. 2015).

3.2.1 Effect of methanol-to-oil ratio

In order to optimize transesterification reaction, it is essential to optimize methanol-to-oil ratio. As the methanol-to-oil ratio increased from 3:1 to 9:1, the biodiesel yields significantly increased. The optimum value was recorded at 9:1 giving 78% conversion. At this ratio, the formation of methoxy species was observed on the catalyst surface which caused the shift in equilibrium in the forward direction (Nisar *et al*. 2017). Further increase in the methanol: oil molar ratio decreased the biodiesel yield as shown below. The reduction in FAME conversion is due to the deactivation of the catalyst. Therefore, excessive use of methanol decreased the conversion as the equilibrium is shifted toward the reverse direction. The higher amount of methanol also made the separation of biodiesel from glycerol difficult. The reaction temperature (65 ± 2°C) and reaction time (5 h) were also optimized.



CONCLUSION

Biodiesel production from transesterification of waste cooking oil using cost effective waste calcined cow bone is investigated was investigated in this study. The waste cow bone contains calcium carbonate ($CaCO_3$) that was calcined at 900^0C for 3 h and subsequently transformed to calcium oxide (CO_2) leaving the CaO to catalyzed the production of biodiesel from WCO. The optimum conditions for transesterification reaction were as follows: catalyst loading 6% weight of oil, methanol-to-oil ratio 9:1, reaction temperature 65 ± 2°C, and reaction time of 5 h. Under these conditions, 84% yield of biodiesel was obtained. Biodiesel properties were evaluated by standard method. All evaluated test parameters were in strong agreement with ASTM standards. Therefore,–waste cow bone has a high potential to serve as a low cost, commercial and eco-friendly.

REFERENCES

[1] Amani, H.; Ahmad, Z.; Hameed, B. Highly active alumina supported Cs-Zr mixed oxide catalysts for low-temperature transesterification of waste cooking oil. *Applied Catalysis. A General.*2014,*487*, 16–25.

[2] Balakrishnan, M.; Batra, V.; Hargreaves, J.; Pulford, Waste Materials-Catalytic opportunities: An overview of the application of large-scale waste materials as resources for catalytic applications. *Green Chemistry.*2011,*13*, 16–24.

[3] Bennett, J.A.; Wilson, K.; Lee, A.F. Catalytic applications of waste derived materials. *Journal of Material Chemistry. A* 2016,*4*, 3617–3637.

[4] Boro, J.; Deka, D.; Thakur, A.J. A review on solid oxide derived from waste shells as catalyst for biodiesel production. *Renewable and Sustainable. Energy Review.*2012,*16*, 904–910.

[5] Corro, G.; Sánchez, N.; Pal, U.; Bañuelos, F. Biodiesel production from waste frying oil using waste animal bone and solar heat. *Waste Management.*2016,*47*, 105–113.

[6] Gharby, S.; Harhar, H.; Bouzoubaa, Z.; Asdadi, A.; El Yadini, A.; Charrouf, Z. Chemical characterization and oxidative stability of seeds and oil of sesame grown in Morocco. *Journal of Saudi Society of Agricultural Science.*2017,*16*, 105–111.

[7] Gorji, A. Animal renewable waste resource as catalyst in biodiesel production. *Journal Biodiversity. Environmental Science.*2015,*7*, 36–49.

[8] Haider, A.; Haider, S.; Han, S.S.; Kang, I.-K. Recent advances in the synthesis, functionalization and biomedical applications of hydroxyapatite: A review. *RSC Advanced.*2017,*7*, 7442–7458.

[9] Hossain, N.; Bashir, S.; Badruddin, I.A.; Goodarzi, M.; Effect of Sr@ZnO nanoparticles and Ricinus communis biodiesel-diesel fuel blends on modified CRDI diesel engine characteristics. *Energy Sources* 2021,*215*, 119094.

[10] Karmakar, B.; Halder, G. Progress and future of biodiesel : Advancements in oil extraction and conversion technologies.*Energ Conversion* .2019,*182*, 307–339.

[11] Khan, H.M.; Ali, C.H.; Iqbal, T.; Yasin, S.; Sulaiman, M.; Mahmood, H.; Raashid,

M.;Pasha, M.; Mu, B. Current scenario and potential of biodiesel production from waste cooking oil in Pakistan: An overview. *China Journal of Chemical Enginneering.*2019,*27*, 2238–2250.

[12] Kumar, M.; Sharma, M.P. Selection of potential oils for biodiesel production. *Renewable and Sustainable Energy Review.*2016,*56*, 1129–1138.

[13] Lee, A.F.; Bennett, J.A.; Manayil, J.C.; Wilson, K. Heterogeneous catalysis for sustainable biodiesel production via esterification and transesterification. *Chemical Society.Review.*2014,*43*,7887–7916.

[14] Lee, A.F.; Wilson, K. Recent developments in heterogeneous catalysis for the sustainable production of biodiesel. *Catalysis. Today.*2015, vol.*242*, pp.3–18.

[15] Lohri, C.R.; Camenzind, E.J.; Zurbrügg, C. Financial sustainability in municipal solid waste management—Costs and revenues in Bahir Dar, Ethiopia. *Waste Management.*2014, *vol.34*, pp.542–552.

[16] Lu, Y.; Zhang, Z.; Xu, Y.; Liu, Q.; Qian, G. CaFeAl mixed oxide derived heterogeneous catalysts for transesterification of soybean oil to biodiesel. *Bioresource Technology.*2015,vol.190, pp.438–441.

[17] Luque, R.; Lovett, J.C.; Datta, B.; Clancy, J.; Campelo, J.M.; Romero, A.A. Biodiesel as feasible petrol fuel replacement: A multidisciplinary overview. *Energy of Environmental Science.* 2010,*3*, 1706–1721.

[18] Mujtaba, M.; Masjuki, H.; Kalam, M.; Ong, H.C.; Gul, M.; Farooq, M.; Soudagar,M.E.M.; Ahmed, W.; Harith, M.; Yusoff, M. Ultrasound-assisted process optimization and tribological characteristics of biodiesel from palm-sesame oil via response surface methodology and extreme learning machine-Cuckoo search. *Renewable Energy.* 2020, Vol.158, pp.202–214.

[19] Nisar, J.; Razaq, R.; Farooq, M.; Iqbal, M.; Khan, R.A.; Sayed, M.; Shah, A.; Rahman, I.U., Enhanced biodiesel production from Jatropha oil using calcined waste animal bones as catalyst. *Renewable Energy* 2017,*101*, 111–119.

[20] Niju, S., Meera, K.M., Begum, S. and Anantharaman N. 2014. Modification of eggshell and its application in biodiesel production. *Journal of Saudi Chemical Society*, 18, 5, pp. 702-706.

[21] Paterson, G.; Issariyakul, T.; Baroi, C.; Bassi, A.; Dalai, A. Ion-exchange resins as catalysts in transesterification of triolein. *Catalysis. Today.*2013, vol.*212*, pp.157–163.

[22] Piccirillo, C.; Silva, M.; Pullar, R.; Da Cruz, I.B.; Jorge, R.; Pintado, M.; Castro, P.M. Extraction and characterization of apatite-and tricalcium phosphate-based materials from cod fish bones. *Material Science Engineering.*2013, vol.*33*, pp.103–110.

[23] Semwal, S.; Arora, A.K.; Badoni, R.P.; Tuli, D.K. Biodiesel production using heterogeneous catalysts. *Bioresource Technology.*2011,*102*, 2151–2161.

[24] Shan, R.; Chen, G.; Yan, B.; Shi, J.; Liu, C. Porous CaO-based catalyst derived from PSS-induced mineralization for biodiesel production enhancement. *Energy Convers.Manag.* 2015, *106*, 405–413.

[25] Shan, R.; Shi, J.; Yan, B.; Chen, G.; Yao, J.; Liu, C. Transesterification of palm oil to fatty acids methyl ester using K2CO3/palygorskite catalyst. *Energy Conversion Management.*2016,*116*, 142–149.

[26] Soudagar, M.E.M.; Mujtaba, M.A.; Safaei, M.R.; Afzal, A.; Ahmed, W.; Banapurmath, N.R.; Mujtaba, M.; Cho, H.M.; Masjuki, H.; Kalam, M.; Ong, H.; Gul, M.; Harith, M.; Yusoff, M. Critical review on sesame seed oil and its methyl ester on cold flow and oxidation stability. *Energy Representation.*2020,*6*, 40–54.

[27] Su, F.; Guo, Y. Advancements in solid acid catalysts for biodiesel production. *Green Chemistry* 2014, *16*, 2934–2957.

[28] Synthesis in solvent-Free Conditions. *Journal Material Environmental Science.*2016, vol.*7*, pp.4580–4588.

[29] Taleb, M.A.; Mamouni, R.; Saffaj, N.; Mouna, A.; Taha, M.; Benlhachemi, A.; Bakiz, B.; Ezahri, M.; Villain, S. Animal Bone Meal as new recyclable and ecological catalyst for the oximes Synthesis in solvent-Free Conditions. *Journal Material Environmental Science.*2016,*7*, 4580–4588.

[30] Wan, L.; Liu, H.; Skala, D. Biodiesel production from soybean oil in subcritical methanol using $MnCO_3$/ZnO as catalyst. *Applied Catalysis Bioresource Environmental.* 2014, *152*, 352–359.

[31] Wei, Z.; Xu, C.; Li, B. Application of waste eggshell as low-cost solid catalyst for biodiesel production.*Bioresource Technology.*2009,*100*, 2883–2885.