



Methanolic Synthesis of Fatty Acid Methyl Esters (FAME) from Waste Materials

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Authors' contributions

This work was carried out in collaboration among all authors. Authors ATM, VOA and EBA designed the study. Author ATM performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors ATM, VOA and EBA managed the analyses of the study. Author JY managed the literature searches. All authors read and approved the final manuscript.

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ABSTRACT

Waste materials (carbide slurry and waste cooking oil) were explored in esterification and transesterification reactions as a viable alternative to a sustainable transport fuel production. The Fourier transformed infrared spectroscopy (FTIR), Atomic absorption spectroscopy (AAS) and Scanning electron microscope (SEM) techniques showed that the prepared calcium oxide had improved basic sites, calcium content and surface morphology respectively. Reduced glycerol and free fatty acids enhanced mass transfer of moieties. Alkali was supported on the calcium oxide as a bimetallic catalyst. Biodiesel prepared from the esterified high FFA oils using prepared NaOH/CaO catalyst gave good quality yield and it compared favorably with other catalysts obtaining $92.2 \pm 0.31\%$ with the prepared catalyst, 90.2 ± 0.57 with $AlCl_3$ and 89.7 ± 0.16 with NaOH. The reusability of the prepared NaOH/CaO catalyst gave an appreciable yield of 74.5% on the fourth reaction cycle.

Keywords: Biodiesel; waste cooking oil; carbide slurry; calcium oxide; transesterification.

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1. INTRODUCTION

Industrialization processes have continued to grow globally in line with human population leading to the growing worldwide demand for petrochemical resources, coal and natural gases. This phenomenon has caused the depletion of fossil energy resources to increase exponentially with alarming environmental problems to the society [1]. In the last decade, many fuel developers have showed interests in alternative renewable fuels to substitute or compliment petroleum-based fuels. An alternative fuel should be easily available, environment eco-friendly and techno-economically competitive [2].

Biodiesel is considered as a “direct-pour” alternative fuel to petroleum diesel, as it requires almost no modification to most modern diesel engines. Biodiesel can be produced locally and therefore reduces foreign oil dependence. It has been reported that biodiesel combustion can result in less air pollutant emissions, such as carbon monoxide, sulphur dioxide, particulate matter, hydrocarbons, but with slightly higher nitrogen oxides [3]. Since the feedstock of biodiesel is mostly renewable, it significantly reduces carbon dioxide emission during its whole life cycle [4]. According to the American Standard Testing Methods (ASTM), biodiesel is defined as a fuel comprising mono-alkyl esters of long chain fatty acids derived from a renewable lipid feedstock, such as vegetable oil or animal fat. Which conform to ASTM D6751 specifications for use in diesel engines [5]. As an alternative fuel, biodiesel can be used in neat form or mixed with petroleum-based diesel. Biodiesel as an alternative fuel, has many merits. It is derived from a renewable resource, thereby relieving reliance and huge expenses on petroleum fuel imports. It is biodegradable and non-toxic. Compared to petroleum-based diesel, biodiesel has a more favourable combustion emission.

Though biodiesel production has currently not been commercialized worldwide mostly due to high cost of feed stock [6,7]. One way of reducing the cost of biodiesel is to employ low quality feed stock such as waste or used vegetable oils, non-edible oils, trapped grease and soap stock (by-product of vegetable oil refinery) which are cheaply available and can be regarded as attractive feedstock for biodiesel

production [8,9,10]. Even though the cost of biodiesel production is reduced, using such cheap feed stocks usually have the problem of high free fatty acid (FFA) in oil samples. These productions therefore, require a two-step process. FFA must first be converted to their methyl esters (biodiesel) via esterification using a catalyst preferably acid prior to transesterification with a homogeneous base catalyst. In the first step, FFA must be typically esterified to an acceptable level, (acid level less than one) in order to prevent soap formation and increase the biodiesel yield in the following alkaline catalyzed transesterification. Usually catalysts are used to enhance such reactions.

Esterification and transesterification of free fatty acids use catalysts to enhance the reaction rate. Catalysts that are commonly used in esterification include strong liquid mineral acid catalysts, heterogenous catalysts, enzymes among others. This homogenous catalysts though increases the biodiesel production, has its side reaction that affects the properties and yield of biodiesel produced. Heterogeneous substances, either acids or alkali are better catalysts due to their benefits not only in the purity of the secondary product glycerin, but also because it simplifies down streaming separation process, since it does not need much washing or neutralization. Particulate heterogeneous catalysts can be readily separated from products following reactions allowing the catalyst to be reused, generating less waste, and consuming less energy. Recycling and reactivating the catalyst have been studied and found to maintain efficiency for use in industries [2]. Researchers like, Liu et al. [11] and Ghiasi and malekzadeh, [12] have introduced heterogeneous catalyst for their experiment, examples are CaO, SrO, BaO, and $\text{Ca}(\text{OCH}_3)_2$. However, homogeneous catalysts have been widely used in industries and they include KOH, NaOH, and CH_3ONa [13]. Alkali metal hydroxides or alkoxides can be used as transesterification catalysts. Hydroxides are cheaper than alkoxides, but must be used in higher concentrations to achieve good reaction [14]. This research applies supported alkali on quick lime prepared from waste carbide slurry as a catalyst in transesterification of waste cooking oil (WCO) to biodiesel fuel, enhancing the economic viability and availability of biofuel as alternate fuel sources in developing countries like Nigeria since both catalyst and feed stock are prepared from readily available waste materials.

2. MATERIALS AND METHODS

2.1 Sample Preparation

Welder's carbide slurry was collected using a clean stainless steel spoon, washed and stored in a polythene bag. The waste carbide slurry was washed three times with distilled water after which it was heated in a muffle furnace at 700°C for three hours then cooled in a desiccator over silica gel. The catalyst was prepared by incipient wetness impregnation of CaO powder with an aqueous solution of NaOH. A known weight of the prepared calcium oxide (60 g) was measured into a beaker and impregnated with 50 cm³ 0.1 M sodium hydroxide (50 wt. %) solution. The mixture was stirred for one hour to homogenize after which the impregnate (NaOH/CaO) was dried in oven at 100°C overnight and further dried in a desiccators over silica gel [15].

Waste cooking oil (WCO) was collected and pretreated by warming at 60°C in a beaker on hot plate after which it was filtered under vacuum through cellulose filter paper to remove moisture and solid materials in the oil sample. The oil was then weighed and stored in a clean plastic container.

2.2 Esterification and Transesterification of WCO

In reducing the high free fatty acid content of the oil via esterification, the 200 g of the oil sample was added to a round bottom flask and warmed while stirring till temperature was 65°C. A measured quantity (v/v) of the catalyst and methanol was then charged into the flask making 6:1 ratio of oil to alcohol at 5% (v/v) of catalyst. After the designated time for the reaction has been reached, the flask was removed from the hot plate and the reaction was stopped by quickly submerging the flask in a water bath to cool the mixture to room temperature. The mixture was then transferred to a separatory funnel to allow separation of products and left to settle for 8 hours. When the mixture became biphasic, the upper and the lower layers were isolated by tapping off the lower layer. The upper layer, which mainly comprised of methyl ester, was later washed with distilled water to remove any impurities before heating in the oven at 105°C to remove traces of water and unreacted methanol, the acid value of the oil was then determined.

Transesterification was done to convert the triglycerides in the esterified waste cooking oil to

fatty acid methyl esters (FAME). The catalyst 2.50 wt% was dissolved in small amount of methanol and was gently charged into the reactor containing oil to methanol in the ratio 6:1 while stirring, the mixture was stirred continuously at 600 rpm for 2 hours to avoid the mass transfer limitations, a magnetic bar was used for stirring while maintaining the temperature between 60-65°C for the given time. After which the reaction was stopped and reactor removed from condenser and heater. The reaction mixture was transferred into a separation funnel and left for 8 hours undisturbed to allow separation of glycerol from the fatty acid methyl ester phase. The lower glycerol phase was then tapped off and a rotary evaporator was used to remove excess methanol. After separation, the crude biodiesel was washed 3-4 times with warm distilled water to remove trace amounts of catalyst and glycerol in the methyl ester. The washed biodiesel was then dried at 100°C in the oven and weighed. All experiments were repeated twice and the yield recorded. This was carried out for the prepared NaOH/CaO catalyst, AlCl₃ and NaOH catalysts. The percentage yield of biodiesel fatty acid methyl esters (FAME) was calculated as:

$$\%Yield = \frac{\text{Weight of biodiesel yield}}{\text{Theoretical weight of biodiesel yield}} \times 100 \quad (1)$$

2.3 Determination of Fuel Properties

2.3.1 Acid value

Acid value was determined following ASTM method (ASTM – D 974(00)). Sample (0.5 g), was weighed into 250 cm³ conical flask and 50 cm³ of neutralized ethyl alcohol was added. The mixture was heated on a water bath to dissolve the sample. The solution was allowed to cool and titrated against 0.1M KOH using phenolphthalein as indicator, after which the acid value and free fatty acid was determined as follows:

$$\text{Acid value} = \frac{A \times M \times 56.1}{w} \quad (2)$$

Where,

A = cm³ of 0.1M KOH consumed by sample

M = Molarity of KOH

W = weight in grams of the sample

$$\% FFA = \frac{A-B \times M \times 28.2}{w} \quad (3)$$

Where,

A = cm³ of 0.1M KOH consumed by sample

B= cm³ of blank

M= molarity of KOH

W= weight in gram of sample

2.3.2 Saponification value

American Standard for Testing Material (ASTM) method- (D 5558-95) was used for the determination. The sample (2.0 g) was weighed into the conical flask and 25 cm³ of 0.5M ethanolic solution of KOH was added and the resulting mixture was shaken for 20 minutes. This was subsequently titrated against 0.5M HCl with phenolphthalein as indicator. The resulting end point was obtained when the pink colour changed into colourless. The same procedure was used for the blank titration without the oil or biodiesel sample. The Saponification value (SV) was then calculated using the expression;

$$\text{Saponification value (S.V.)} = \frac{56.1 (B - S) \times M \text{ of HCl}}{\text{weight of sample}} \quad (4)$$

Where;

B – cm³ of HCl required by blank

S – cm³ of HCl required by sample

M- Molarity of HCl

2.3.3 Density

A 25 cm³ density bottle with a FA2004N digital precision electronic analytical weighing balance was used for density determination at 15°C according to ASTM D4052 method. The density bottle was first weighed empty, then with water in it and finally with the biodiesel sample. the density was then calculated as follows:

$$\text{Density} = \frac{W_3 - W_1}{W_2 - W_1} \quad (5)$$

Where,

w₃ = weight of bottle with sample

w₂= weight of sample with water

w₁= weight of empty density bottle

2.3.4 Viscosity

The viscosity was determined using kinematic viscosity recognizer item tool: KD R0515 according to ASTM-D445. A sample holder carried the sample and a calibrated thermometer

was held in upright position and inserted into the bath at set temperature of 40°C. The biodiesel was then allowed to freely flow and the time required for the meniscus to pass from the first to the second timing mark was noted. The viscosity reading is noted and compared with ASTM standards.

2.3.5 Iodine value

The sample (0.5 g) was weighed into conical flask and 20 cm³ of carbon tetrachloride was added to dissolve the oil. 25 cm³ of prepared Wigg's Reagent was added in a fume chamber. The flask was then stoppered and the content was vigorously swirled. The flask was then placed in the dark for 35 minutes. At the end of this period, 20 cm³ of 10% aqueous potassium iodide and 100 cm³ of water were added. The content was titrated with 0.1M sodium thiosulphate solution. Few drops of 1% starch indicator were added and the titration continued by adding the sodium thiosulphate drop wise until coloration disappeared after vigorous shaking according to EN 14111. The same procedure was used for the blank titration without the oil or biodiesel sample. The iodine value is given by the expression:

$$\text{Iodine Value (I.V)} = \frac{12.69C (v_1 - v_2)}{M} \quad (6)$$

Where,

C = concentration of sodium thiosulphate

V1 = volume of sodium thiosulphate used for blank

V2 = volume of sodium thiosulphate used for determination

M = mass of sample

12.69 = Constant.

2.3.6 Sediment and water content

The sample 50 cm³, was placed in a test tube and its content was stoppered and allowed to attain the laboratory temperature. The tube was placed in a trunnion cup opposite another filled tube to establish a balanced condition of the mechanical shaker. The samples were agitated at a speed of 1800 rpm for 10 minutes to ensure homogeneity. The oil was then separated from the fractions and weighed. The combined water and sediment at the bottom of the tube was the reported as percentage of sample (ASTM D2709 – 96).

$$\text{Moisture and Sediment} = \frac{(w_1 - w_2)}{w_1} \times 100 \quad (7)$$

W_1 = Initial weight of oil

W_2 = Final weight of oil

2.3.7 Cetane number

The cetane number was determined using automatic cetane analyzer tool; KD R3034 according to EN ISO 4264. The biodiesel sample (50 cm³) was placed in the inner sample holder and inserted into the outer sample holder, at room temperature. The machine gives the cetane reading of the sample.

2.3.8 Cloud point and pour point

The cloud and pour points were determined using the Haeckel Caton Changsha cloud and pour point analyzer tool; KD R1072 following ASTM D4539 method. For cloud point, sample was placed in the sample holder fitted with a thermometer. As the machine is set on the temperature begins to drop. The temperature at which the first crystal is formed was noted as the cloud point. For the pour point, the temperature of the machine starts to increase and the temperature at which the sample cannot move is noted as the pour point. 50 cm³ of sample was used in both cases. All results were compared to ASTM standards.

2.3.9 Flashpoint

The Haeckel Cation Changsha automatic flash point tester; KD R0211 was used in determining the point of ignition of the various biodiesel samples according to ASTM - D93. The sample is placed in a sample holder and the ignitor connected to a gas supply is placed on top the sample holder containing the sample, as the machine is set on and gas is supplied temperature begins to read and the temperature at which the sample flames up is recorded as the flashpoint.

2.4 Fatty Acid and FAME Profile

The profile of fatty acids and FAME present in the oil and biodiesel samples was analyzed using GC-MS. This is a combination of two techniques used for analyzing mixtures of components; The gas chromatography separates the components in the mixture using the principle explained while the mass spectroscopy characterizes each of the components individually. As the individual compounds elute from the GC column, they enter the electron ionization detector in the mass spectroscopy, from where they are bombarded with a stream of electrons causing them to break

apart into fragments. The analysis was carried out using a GC PERICHROM PR2100 equipped with a capillary column (50 m × 0.201 mm × 0.50 μm) with HP-PONA stationary phase and flame ionization detector. The carrier gas was helium at a flow rate of 0.6 ml/min. The GC column was kept at 120°C for 5 min, heated at a rate of 4°C/min up to 225°C and kept at 225°C for 20 min. The injector and detector temperatures were set at 250°C. External standard method was used for GC calibration. Standard solutions of methyl esters were prepared and injected into the GC under identical conditions. Then, calibration curve for each methyl ester was derived and used for quantification of methyl esters concentration in the samples. The preparation of the purified biodiesel samples for injection into the GC was carried out as follow: 0.3 g of the biodiesel sample was dissolved in 5 ml of *n*-hexane and 1 μL of this solution was injected into the GC machine.

2.5 Functional Group Analysis

To investigate the position and presence of characteristic organic functional groups, FTIR analysis was carried out using KBr. The FTIR spectra were recorded on a Shimadzu Fourier Transform Infrared Spectrometer (FTIR). The sample was mixed with Potassium bromide (KBr) and then smeared to give a small transparent disc of 13 mm diameter. A background spectrum of pure KBr was run before that of the spectrum of any sample to account for any absorption due to impurities in the KBr. The disc containing the sample was then placed in the infrared spectrometer and the spectrum of the samples was collected. A total of twenty (20) scans were collected for each measurement over the spectral range of 4000-400 cm⁻¹ with a resolution of 4 cm⁻¹. All spectra were presented without baseline correction or normalization. With this technique, vibrational excitation of bonds as a result of interaction between the certain wavelength of infrared radiation and molecules of the catalysts are observed depending on the functional group of the compound. The types of bond excitation that can occur are stretching (higher energy) and bending (lower energy) vibrations.

2.6 Preparation of Alkali Supported on Calcium Oxide (NaOH/CaO) Catalyst

The waste carbide slurry was washed three times with distilled water after which it was heated in a muffle furnace at 700°C for three hours after which it was cooled in a desiccator

over silica gel and pure CaO was obtained. The catalyst was prepared by incipient wetness impregnation of CaO powder with an aqueous solution of NaOH. A known weight of the prepared calcium oxide (60 g) was measured into a beaker and impregnated with 50 cm³ 0.1 M sodium hydroxide (50 wt. %) solution. The mixture was stirred for one hour to homogenize after which the impregnate (NaOH/CaO) was dried in an oven at 100°C for 7 hours and further dried in a desiccator over silica gel [15].

2.7 Size and Morphology of Carbide Slurry and Calcium Oxide

To determine the size and surface morphology of the samples, before and after calcination, Scanning Electron Microscopy (SEM) was carried out using a Phenom™X-pro Scanner. Minimal preparation includes the acquisition of the sample and placing it on a Clean Carbon strap that will be attached on the sample holder, which fit into the SEM chamber, and some accommodation to prevent charge build-up and also prevent the sample from making contact with the Detector.

3. RESULTS AND DISCUSSION

3.1 Physicochemical Properties

The physicochemical properties of waste cooking oil as shown in Table 1 suggests that the waste oil require esterification before it can be transesterified into biodiesel, since the high acid value of 3.8±0.74 mgKOH/g is far greater than the ASTM standard of <0.5 for biodiesel feedstock. Kulkarni et al. [16] also reported pretreatment for waste cooking oil biodiesel feedstock having an acid value of 5.3 mgKOH/g. The density of the waste cooking oil was found to be 0.89±0.07 g/cm³ which is within the ASTM standard of 0.86-9.0 g/cm³ for the density of biodiesel. This is lower than the density of 9.21 g/cm³ reported by Sanli et al. [10]. The viscosity of biodiesel feedstock is reduced after

transesterification into biodiesel, thus, the waste cooking oil viscosity of 18.6±0.36 mm²/s is above the 1.9-6.0 mm²/s ASTM standard, this is due to the prominence of palmitic fatty acid and other long chain fatty acids in the oil shown in Table 1 [17]. The Presence of moisture and sediment may lead to saponification during transesterification, the high moisture and sediment content of 3.6% for the waste cooking oil need to be reduced to <0.05% as required by the ASTM standard to avoid soap formation and deactivation of the catalyst during transesterification.

3.2 Fatty Acid Profile

The fatty acid composition of waste cooking oil determined by GC-MS showed the presence of fatty acids of different chain length compounds present in the sample as shown in Table 2. The fatty acid profile is one of the key factors that determine the suitability of any feedstock for use in biodiesel fuel production [5]. For this research, the fatty acid profile of the waste cooking oil (WCO) feedstock had the major fatty acids to be oleic, linoleic, palmitic, myristic and stearic acids, indicating the presence of mono and polyunsaturated as well as saturated fatty acids. This presence of triglycerides is what makes the oil a suitable feedstock for biodiesel production.

3.3 FT-IR Analysis of WCO

The FTIR spectrum of waste cooking oil (WCO) was carried out in the wave number range of 400 – 4000 cm⁻¹ to determine the functional groups present on the waste cooking oil (WCO). The FTIR spectra of the waste cooking oil sample are shown in Fig. 1 and it indicates the presence of methylene stretch at 2931.90 cm⁻¹. The presence of a broad peak at 1643.41 cm⁻¹ – 1737.92 cm⁻¹ shows the presence of free fatty acids attached to the carbonyl group of ester linkages [18], this confirms the high free fatty acid content reported in Table 2.

Table 1. Physicochemical properties of waste cooking oil (WCO)

Property	Unit	Value
Density	g/cm ³	0.89 ± 0.07
Acid value	mgKOH/g	3.80 ± 0.74
Free fatty acid	%	1.90 ± 0.21
Viscosity	mm ² /s	18.60 ± 0.36
Moisture and sediment	%	3.60 ± 0.22
Iodine value	g iodine/g	112.5 ± 0.54
Saponification value	mgKOH/g	248.1 ± 0.37

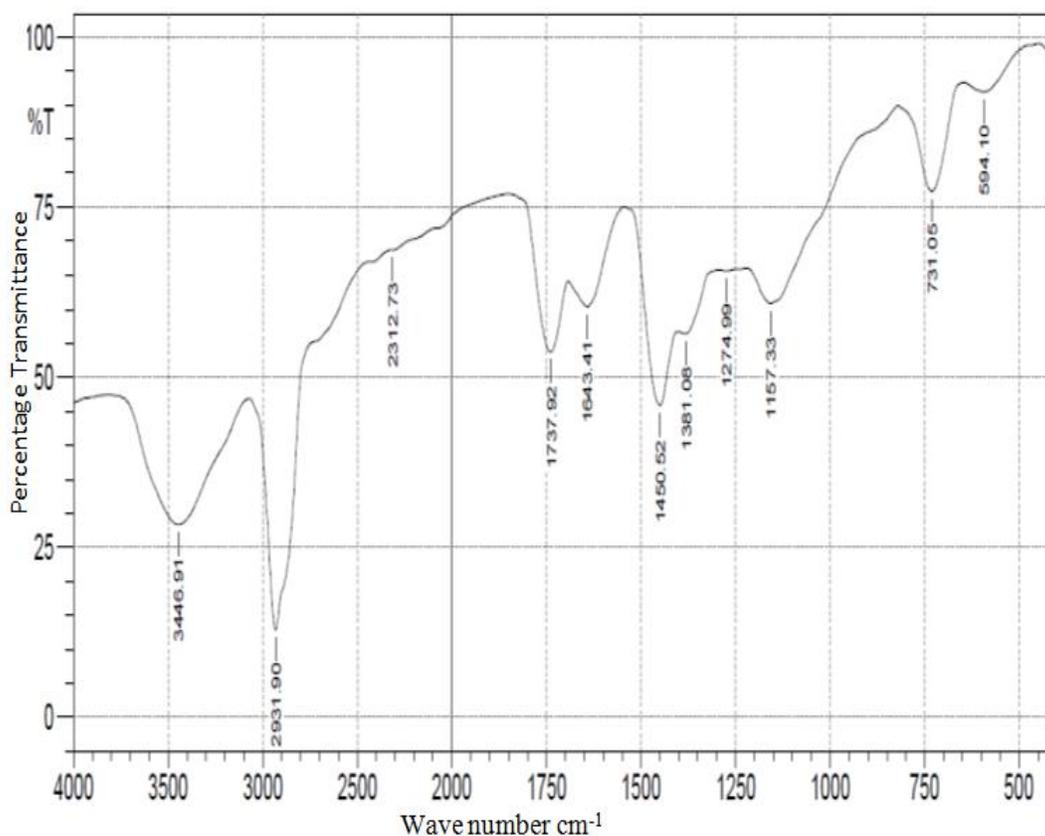
Table 2. Fatty acid profile of waste cooking oil

Methyl ester	Percentage composition
Palmitic acid methyl ester (C16:0)	42.50 ± 0.03
Myristic acid methyl acid ester (C14:0)	0.86 ± 0.31
Stearic acid methyl ester (C18:0)	9.00 ± 0.16
Oleic acid methyl ester (C18:1)	39.85 ± 0.09
Linoleic acid methyl ester (18:2)	2.10 ± 0.20

3.4 FT-IR Analysis of Prepared Calcium Oxide

Changes in the structure of the compounds will be observed through alterations in the infrared spectra [19]. A favorable dehydration and desorption is necessary for the preparation of a stable catalyst which is related to surface

regeneration process and reactivity. Fig. 2 (B) show the FTIR spectrum of the carbide slurry and indicate major peaks that are characteristic of inorganic compounds. The spectrum shows the absorption bands at 3540- 3645 cm^{-1} related to hydroxyl group (OH⁻) stretching mode and the peak at 1437 cm^{-1} correspond to the out of plane bending of CO_3^{2-} groups [11]. The FTIR spectrum of prepared calcium oxide is shown in Fig. 2 (A), the strong band at 3450-3513 cm^{-1} corresponds to the O-H bonds from the remaining hydroxide or from water molecules on the external surface of the samples during handling to record the spectra [12]. The broad band at 1438 cm^{-1} , as well as a weak band at 880 cm^{-1} indicates the C-O bond related to carbonation of CaO particles. The strong band at 465 cm^{-1} identified vibration of the Ca-O bond thus producing more basic sites due to CaO that are essential for trans esterification to occur [20]. There is a tiny dip in the spectra at 2340 cm^{-1} this may be due to the presence of atmospheric CO_2 .

**Fig. 1. Fourier transformed infrared spectra of waste cooking oil**

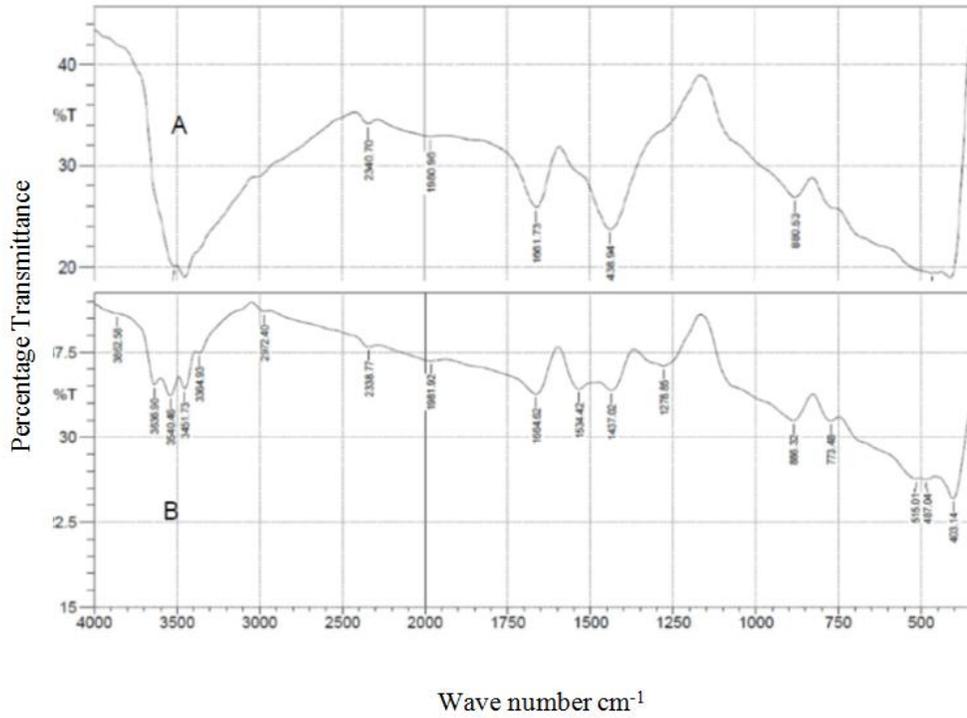
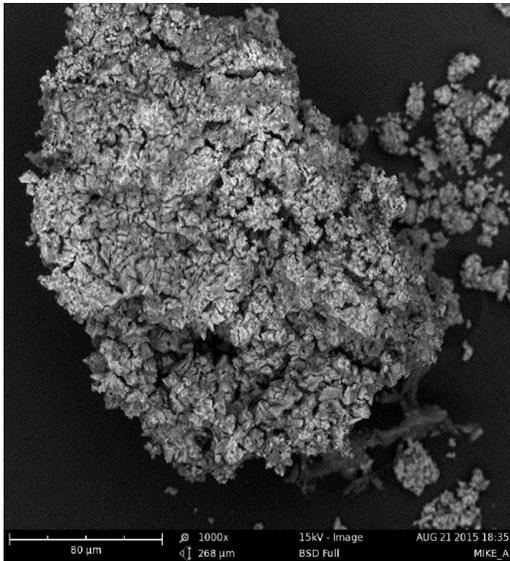
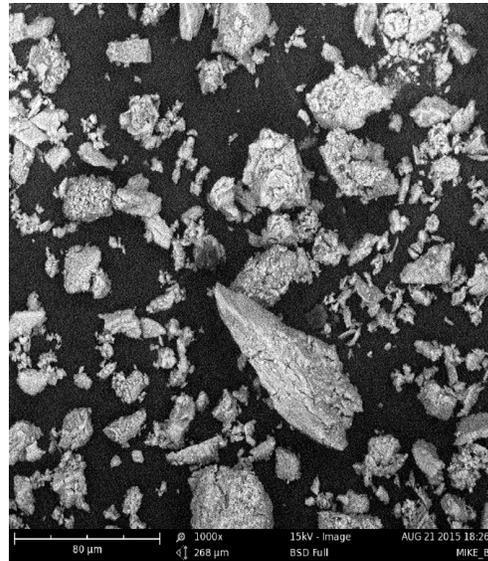


Fig. 2. Fourier transformed infrared spectra of carbide slurry (B) and calcium oxide (A)



(1)



(2)

Plate: Scanning Electron Micrograph of (1) Carbide slurry and (2) Calcium oxide

3.5 Scanning Electron Microscope (SEM) Studies

Plates 1 and 2 show the SEM surface morphology of the carbide slurry and calcium

oxide respectively. The carbide slurry (Plate 1) show massive, aggregated morphology, and in some instances, there are some bulky flakes. It is also observed that the prepared calcium oxide (Plate 2) showed a more heterogeneous

agglomeration in terms of dimension and particle size (polydispersity), comprising many particles of varying sizes and properties this may be due to the interactions. These results are in agreement with the findings of Hu et al. [21], where calcium oxide was prepared from egg shells. The shells displayed a typical layered architecture when the calcination temperature was increased from 700 to 1000°C. The microstructures of shells were changed significantly from layered architecture to porous structure [21]. In this study, it is of importance to note that the prepared calcium oxide show a significant change in morphology compared to the carbide slurry. These observations support the FTIR spectra in Fig. 2 indicating that at high temperatures, the curved plates in the carbide slurry transforms to flat layers showing that not only the basal spacing but also the morphology of the compound depends on the density and type of particles within the interlayer space.

3.6 FAME Yield

The prepared calcium oxide supported catalyst from carbide slurry waste was explored in transesterification of waste cooking oil to biodiesel and obtained a high biodiesel yield of $92.2 \pm 0.31\%$ with the prepared catalyst, 90.2 ± 0.57 with $AlCl_3$ and, 89.7 ± 0.16 with NaOH at high amount of reacting alcohol, this implies that the sufficient amount of alcohol enabled efficient transfer of alkyl moieties between triglycerides and alcohol and prevented any back reaction. Similarly Ghiasi M. & Malekzadeh A. [12], in his study on producing CaO as a solid base catalyst, the authors reported that besides the fact that the presence of water in the process has little effect on the catalyst, the use of CaO as a catalyst could provide many advantages such as: high activity, lengthened catalyst life and moderate condition of reaction. Catarino et al. [22] prepared biodiesel from waste cooking oils using waste foods as source for calcium oxide (CaO) as catalyst. A 65% yield was obtained mainly due to formation of soap from free fatty acids, proper esterification would have reduced these effect. Also Puna et al. [23] suggested that a little water is essential in enhancing the catalytic activity of prepared CaO, in his use of calcium oxide as a catalyst, it was discovered that a sigmoid curve denotes the reaction, with the initial slow reaction enhanced with a little hydration of the catalyst and a faster kinetic rate observed with the catalyst in the methoxide phase before

eventually slowing down due to homogenous reaction in the diglyceride phase due to its solubility in glycerin. Overall it was observed that it was a suitable catalyst.

3.7 Physicochemical Properties of Catalyzed Biodiesels

The biodiesel samples in this research showed Acid values of 0.12 ± 0.21 mg/KOH/g for $AlCl_3$, 0.26 ± 0.10 mg/KOH/g for NaOH and 0.18 ± 0.24 mg/KOH/g for NaOH/CaO biodiesel samples as shown in Table 3. The acid value for NaOH/CaO catalysed transesterification was less than that catalyzed by NaOH, this could be due to incomplete transesterification as a result of water and soap formation with NaOH catalyst, while the slightly lower value for $AlCl_3$ may be due to the lack of interfering effects since same catalyst was used in the esterification and transesterification processes with little water formed. The standard limit in the European norm is < 0.5 mg KOH/g sample, whereas the American standard testing methods, allows slightly higher values of $< 1\%$ FFA [1]. Mahajan et al. [24] and Lang et al. [25] reported that the acid values of the ethyl esters of linseed oil, canola oil, sunflower oil and rapeseed oil were 0.884, 0.869, 0.876 and 0.873 mgKOH/g, respectively [26]. Therefore the acid values of the biodiesel samples produced in this study, falls within acceptable standard.

The saponification values (SV) of the biodiesel samples are in the range of 190.66 ± 0.44 - 205.29 ± 0.35 , with $AlCl_3$ catalyzed biodiesel having the highest value of 205.29 ± 0.35 , this could be due to the formation of water and reaction of the catalyst with residual free fatty acids. Kulkarni et al. [16], reported saponification values ranging from 184-194 for various biodiesel samples from waste cooking oil.

The changes in the fuel density will influence engine output power due to a different mass of fuel injected [27,12,28]. Density limits in the European EN norm (standard) are in the range of 860-900 kg/m³ [24]. The densities of the produced biodiesel samples are shown in Table 3. The trend in the densities was $0.88 \pm 0.28 > 0.86 \pm 0.31 > 0.86 \pm 0.35$ g/cm³ for transesterifications catalyzed by $AlCl_3 > NaOH > NaOH/CaO$ respectively. The density of the waste cooking oil was found to be high due to presence of free fatty acids in the oil.

Table 3. Physicochemical properties of AlCl₃, NaOH and NaOH/CaO catalyzed biodiesel

Property	Unit	NaOH	AlCl ₃	NaOH/CaO	Standards
Density 15 ^o C	g/cm ³	0.86 ± 0.31	0.88 ± 0.28	0.86 ± 0.35	0.86-0.90
Acid value	(mgKOH/g)	0.26 ± 0.10	0.12 ± 0.21	0.18 ± 0.24	Max 0.50
FFA	%	0.13 ± 0.11	0.06 ± 0.20	0.09 ± 0.24	< 1%
Cloud point	(°C)	11.0 ± 0.62	10.0 ± 0.53	12.0 ± 0.49	-3 to 12
Pour point	(°C)	6.0 ± 0.25	6.0 ± 0.36	7.0 ± 0.47	-15 to 16
Viscosity 40 ^o C	(mm ² /s)	4.1 ± 0.73	2.9 ± 0.19	4.2 ± 0.13	1.9 – 6.0
Flash point	(°C)	167 ± 0.51	158 ± 0.42	164 ± 0.51	Min 130
Cetane number	(°C)	61 ± 0.33	56 ± 0.58	64 ± 0.27	Min 47
Iodine value	(iodine/g)	119.60 ± 0.52	103.34 ± 0.71	124.21 ± 0.64	Max 120
Saponification value	(mgKOH/g)	197.08 ± 0.48	205.29 ± 0.35	190.66 ± 0.44	-
Moisture and sediment	(%)	<0.05	<0.05	<0.05	Max 0.05
%Yield of Biodiesel		89.7 ± 0.16	90.2 ± 0.57	92.22 ± 0.31	

Generally, levels of saturation of the various biodiesel samples might be responsible for the observed cloud points (CP) and pour points (PP) of 10.0±0.53 and 6.0±0.36, 11.0±0.62 and 6.0±0.25 and 12.0±0.49 and 7.0±0.47 for AlCl₃, NaOH and NaOH/CaO catalysed transesterification reactions. Petro-diesel has cloud point standard range of -15 to 5°C, and pour point standard range of -35 to -15 respectively, whereas biodiesel has much higher CP and PP standard values [26,29].

Biodiesel has a higher cetane number compared to petroleum diesel [30]. The cetane numbers of waste cooking oil biodiesel as shown in Table 3 was found to be 56.0±0.58, 61.0±0.33, and 64.0±0.27 for AlCl₃, NaOH and NaOH/CaO catalysed transesterification reactions respectively. These are within ASTM acceptable limits and can be seen to increase with degree of saturation. The standard ASTM D975 for conventional diesel fuel requires a minimum CN of 40, whereas the standards for biodiesel prescribe a minimum of 47 (ASTM D6751) or 51 (EN14214), [9]. The cetane number of the biodiesel samples are within acceptable limits and agrees with reports by van Gerpen [31] and Knothe et al. [32] who reported that feedstocks that are high in saturated fatty esters has a high CN, The oxidative stability of biodiesel fuels also increase with level of saturation.

The studied catalyst had viscosities within the acceptable limits as shown in Table 3, with AlCl₃ catalysed biodiesel having the best fuel viscosity at 2.90±0.19 mm²/s while NaOH/CaO catalysed transesterification has viscosity of 4.20±0.13 mm²/s this suggests that transesterification was not complete. Viscosity increases with increasing degree of saturation [33,26].

The highest iodine value for the biodiesel samples was 124.21 g iodine/g for NaOH/CaO while the lowest was 103.34 g iodine/g for AlCl₃. These iodine values can be seen to vary with degree of saturation, with AlCl₃ being the most saturated and least iodine value. Hilber et al. [34] reported that the iodine values of rapeseed, corn, soybean, sunflower and waste cooking oil were found to be 104, 94, 103, 97 and 82, respectively.

The combination of high viscosity and low volatility of a fuel causes bad cold engine start up, misfire and ignition delay [35]. The flash point of all biodiesel samples as shown in Table 3. are far above that of petro-diesel, reflecting the non-volatile nature of these fuels. Transesterification catalyzed with NaOH catalyst had the highest value of 167±0.51°C while AlCl₃ had the least 158±0.42°C due to the level of saturation in the various fuels. Canakci et al. [7] reported that inspite of the fact that the flash points of vegetable oils were reduced through transesterification.

Fuel contaminated with water can cause engine corrosion or react with the glycerides to produce soaps and glycerine. Therefore, <0.05% of water in fuels is what is accepted in the ASTM standard [26]. In this research, the produced biodiesels were routinely dried over anhydrous magnesium sulphate and recorded moisture contents for the biodiesels prepared was reduced to the accepted levels (< 0.05%).

3.8 Fatty Acid Profile of Catalyzed Biodiesels

Table 4 shows the fatty acid profile of the biodiesel samples with percentage yields. More levels of unsaturation were observed in biodiesel

produced from the prepared NaOH/CaO catalyst, these would influence the fuel properties of the biodiesel as it will have higher cold flow properties, oxidation and flash point but a lower energy content and density, while biodiesel prepared by AlCl₃ catalyst, had slightly higher levels of saturation. This can be compared to Felizardo et al. [36] analysis of waste cooking oil biodiesel and showed a high level of unsaturation with linoleic and oleic acid esters having highest compositions respectively.

3.9 FTIR Analysis of Catalysed Biodiesels

The changes in the percentage (%) transmission and functional groups showed the modifications that occurred during the transesterification process as shown in Fig. 3. In the transesterification of waste cooking oil, the FTIR

spectra of the raw oil and biodiesel are very similar because of high chemical similarities that exist among triglycerides and methyl ester at the 2900, 1750 and 1100 cm⁻¹. All biodiesel produced, showed the methylene stretch peak at 2800-2900 cm⁻¹. However, small differences are observed as a shift or intensity in the peaks in the other regions (C=O ester, CH₃ and C-O ester). The strong ester peak at 1750 cm⁻¹ (C=O ester) and at 1170 – 1200 cm⁻¹ (C-O ester) are clearly present in the spectra at 1744.67 cm⁻¹ and 1164.08 cm⁻¹ for NaOH/CaO catalyzed biodiesel and was observed for the other samples too. This is in agreement with the study of Knothe, [5] who stated that the wave frequency (cm⁻¹) for (C=O ester) functional group is 1750 – 1725 cm⁻¹ and indicates a reduction in glycerol and free fatty acids [15]. Outside these two regions, another characteristic peak that

Table 4. Fatty acid methyl ester (FAME) profile

Methyl ester	NaOH	AlCl ₃	NaOH/CaO
Palmitic acid methyl ester (C16:0)	31.66	24.61	1.08
Myristic acid methyl ester(C14:0)	1.52	8.60	35.90
Stearic acid methyl ester(C18:0)	7.96	9.31	6.35
Oleic acid methyl ester(C18:1)	34.35	30.26	46.30
Linoleic acid methyl ester(C18:2)	9.27	11.14	7.94
% Yield of biodiesel for:	89.7	92.20	92.22

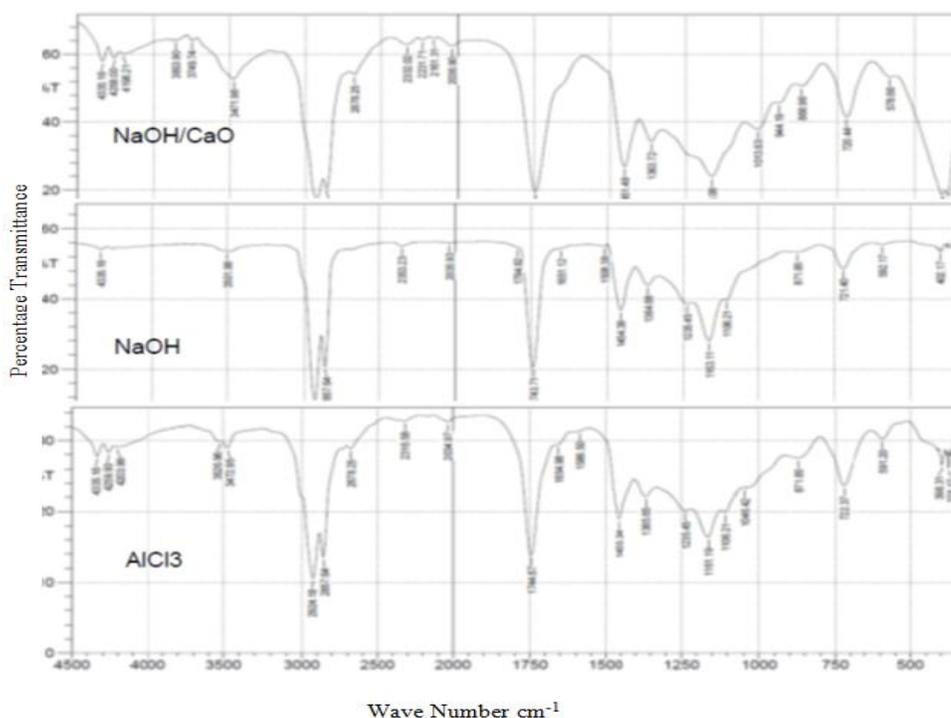


Fig. 3. FTIR analysis of catalyzed biodiesels

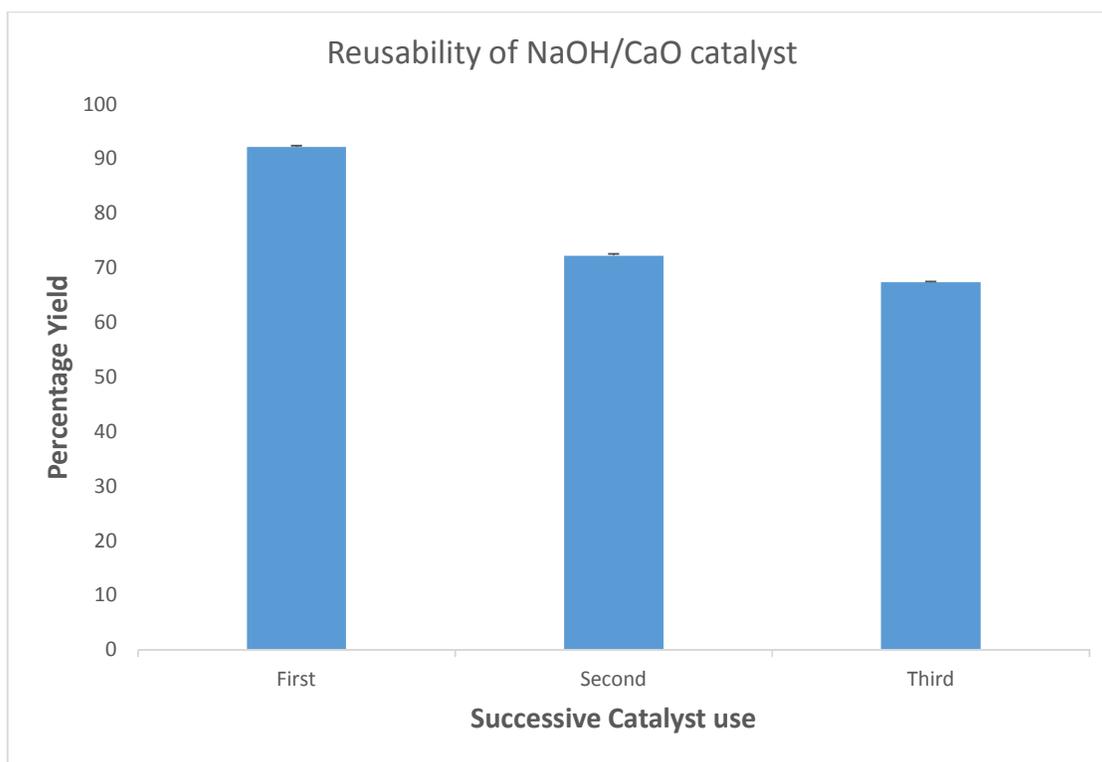


Fig. 4. Reusability of NaOH/CaO catalyst and biodiesel yield

indicates the presence of ester group in the mixture of methyl ester can be observed at 1454.38 cm^{-1} . Similar result was reported by Szybist et al. [35] and Yun et al. [6].

3.10 Reusability of Prepared NaOH/CaO Catalyst

The reusability of the prepared NaOH/CaO catalyst that gave $92.2 \pm 0.31\%$ biodiesel yield, through three transesterification reaction cycles of esterified waste cooking oil is shown in Fig. 4. After the second reaction cycle that gave a $72.3 \pm 0.18\%$ biodiesel yield, the catalyst still gave a favourable yield of $67.4 \pm 0.09\%$ for the third cycle, though less than the previous yields. This suggests to the fact that adsorption of transesterification reaction products such as residual methyl ester, glycerol, water and oil containing impurities on catalyst surface, may have hindered the interaction of fatty acids and methanol to acidic sites of NaOH/CaO catalyst. The catalytic performance of the spent catalyst can be partially recovered by intensive and sequential washing with methanol and dilute acids (50% v/v). It was also observed that the gradual decrease of biodiesel after each subsequent yield after each reaction cycle was

also due to the presence of water which also has an adverse effect on the equilibrium of transesterification reactions. Obtained results suggest that NaOH/CaO catalyst can be a suitable and durable catalyst for successful catalytic transesterification reactions.

4. CONCLUSION

Based on results of this study, it can be concluded that; it is economical to produce biodiesel using waste materials, alkali supported on CaO as a catalyst in biodiesel preparation competes favorably with conventional heterogeneous and homogeneous catalysts. A high amount of alcohol is required to obtain esters with this catalyst in a short time, Physicochemical and methyl ester profile of the waste cooking oil and its corresponding esters from various catalysts analysed by GC-MS, FTIR and ASTM methods indicated a gradual decrease in acid value from waste cooking oil, esterified and transesterified methyl esters, due to loss in weight from free fatty acids and glycerol obtaining high yields of $92.2 \pm 0.31\%$ with the prepared catalyst, 90.2 ± 0.57 with AlCl_3 and, 89.7 ± 0.16 with NaOH. Generally, the methyl ester profile showed variation in levels of

saturation, this effect is seen in the various fuel properties for cloud and pour point, cetane number and iodine number, these will influence their oxidative stability. Hence, waste resourced catalysts can be suitable catalysts for biodiesel preparation. Also, the use of waste materials carbide slurry and waste cooking oil as precursors for catalyst and feedstock in preparing biodiesel could reduce production cost and save environmental pollution.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Abdullah AZ, Salamatinia B, Mootabadi H, Bhatia S. Current status and policies on biodiesel industry in Malaysia as the world's leading producer of palm oil. *Energy Pol.* 2009;37(12):5440–5448.
2. Park YM, Chung SH, Eom HJ, Lee JS, Lee KY. Tungsten oxide zirconia as solid superacid catalyst for esterification of waste acid oil (dark oil). *Bioresour Technol.* 2010;101(17):6589–93.
3. Graboski MS, McCormik RL. Combustion of fat and vegetable oil derived fuels in diesel engines. *Prog. Energ. Combust.* 1998;24(2):125-164.
4. Sheehan J, Camobreco V, Duffield J, Graboski M, Shapouri H. An overview of biodiesel and petroleum diesel life cycles. Report NREL/TP-580-24772, NREL, Golden, CO; 1998.
5. Knothe G. Analyzing biodiesel: Standards and other methods. *J. Am. Oil Chem. Soc.* 2006;83(10):823-833.
6. Yun HT, Nurul FA, Mahiran B. Biodiesel production via transesterification of palm oil using NaOH/Al₂O₃ catalysts. *Sains Malaysiana.* 2011;40(6):587-594.
7. Çanakçı M, Şanlı H. An assessment about the reasons of NO_x rise in biodiesel's exhaust emissions. *Deniz Bilimleri ve Mühendisliği Dergisi.* 2005;3(1).
8. Ali Y, Hanna MA, Cuppett SL. Fuel properties of tallow and soybean oil esters. *J. Am Oil Chem Soc.* 1995;72:1557–1564.
9. Jian-Xun WANG, Huang QD, Huang FH, Huang QJ. Lipase-catalyzed production of biodiesel from high acid value waste oil using ultrasonic assistant. *Chinese Journal of Biotechnology.* 2007;23(6):1121-1128.
10. Sanli H, Canakci M, Alptekin E. Characterization of waste frying oils obtained from different facilities. In *World Renewable Energy Congress-Sweden*; 8-13 May; 2011; Linköping; Sweden (No. 057). Linköping University Electronic Press. 2011;479-485.
11. Liu T, Zhu Y, Zhang X, Zhang T, Zhang T, Li X. Synthesis and characterization of calcium hydroxide nanoparticles by hydrogen plasma-metal reaction method. *Materials Letters.* 2010;64(23):2575-2577.
12. Ghiasi M, Malekzadeh A. Synthesis of CaCO₃ nanoparticles via citrate method and sequential preparation of CaO and Ca(OH)₂ nanoparticles. *Crystal Research and Technology.* 2012;47(4):471-478.
13. Lu H, Liu Y, Zhou H, Yang Y, Chen M, Liang B. Production of biodiesel from *Jatropha curcas* L. oil. *Computers & Chemical Engineering.* 2009;33(5):1091-1096.
14. Freedman B, Pryde EH, Mounts T. Variables affecting the yields of fatty esters from transesterified vegetable oils. *Journal of the American Oil Chemists' Society.* 1984;61:1638-1643.
15. Kang M, Bae YS, Lee CH. Effect of heat treatment of activated carbon supports on the loading and activity of Pt catalyst. *Carbon.* 2005;43(7):1512-1516.
16. Kulkarni MG, Dalai AK. Waste cooking oils an economical source for biodiesel: A review. *Ind. Eng. Chem. Res.* 2006;45: 2901-2913.
17. Tat ME, van Gerpen JH. The specific gravity of biodiesel and its blends with diesel fuel. *J. Am. Oil Chem. Soc.* 2000;77(2):115-119.
18. Zheng S, Kates M, Dubé MA, McLean DD. Acid-catalyzed production of biodiesel from waste frying oil. *Biomass and Bioenergy.* 2006;30(3):267-272.
19. He H, Frost RL, Zhu J. Infrared study of HDTMA⁺ intercalated montmorillonite. *Spectrochimica Acta. Part A, Molecular and Biomolecular Spectroscopy.* 2004; 60(12):2853–9. DOI: 10.1016/j.saa.2003.09.028
20. Tangboriboon N, Kunanuruksapong N, Srivat N. Mesoporosity and phase transformation of bird eggshells via pyrolysis. *Journal of Ceramic Processing Research.* 2012;13(4):413–419.
21. Hu S, Wang Y, Han H. Utilization of waste freshwater mussel shell as an economic

- catalyst for biodiesel production. *Biomass and Bioenergy*. 2011;35(8):3627–3635.
22. Catarino M, Ramos M, Dias AS, Santos MT, Puna JF, Gomes JF. Calcium rich food wastes based catalysts for biodiesel production. *Waste and Biomass Valorization*. 2017;8(5):1699-1707.
 23. Dias APS, Puna J, Gomes J, Correia MJN, Bordado J. Biodiesel production over lime. Catalytic contributions of bulk phases and surface Ca species formed during reaction. *Renewable Energy*. 2016;99:622-630.
 24. Mahajan S, Konar SK, Boocock DGB. Determining the acid number of biodiesel. *J. Am. Oil Chem. Soc.* 2006;83(6):567-570.
 25. Lang X, Dalai AK, Bakhsi NN, Reaney MJ, Hertz PB. Preparation and characterization of bio-diesels from various bio-oils. *Bioresource Technology*. 2001;80:53-62.
 26. Meher LC, Sagar Vidya D, Nnik SN. Technical aspects of biodiesel production by transesterification - a review. *Renewable and Sustainable Energy Review*. 2006;10:248-268.
 27. Alptekin E, Canakci M. Determination of the density and the viscosities of biodiesel fuel blends. *Renew. Energ.* 2008;33(12): 2623-2630.
 28. Encinar JM, Gonzalez JF, Rodriguez-Reinares A. Biodiesel from used frying oil. Variables affecting the yields and characteristics of the biodiesel. *Ind. Eng. Chem. Res.* 2005;44(15):5491-5499.
 29. Dunn RO. Cold weather properties and performance of biodiesel. In: Knothe, G.; van Gerpen, J.; Krahl, J., *The Biodiesel Handbook*, Chapter 6.3. AOCS Press, Champaign, IL, USA; 2005.
 30. Knothe G, Bagby MO, Ryan TW. Precombustion of fatty acids and esters of biodiesel. A possible explanation for differing cetane numbers. *J. Am. Oil Chem. Soc.* 1998;75(8):1007-1013.
 31. Van Gerpen JH. Cetane number testing of biodiesel. *Proceedings of the 3rd Liquid Fuel Conference: Liquid Fuel and Industrial Products from Renewable Resources*, American Society of Agricultural Engineers (ASAE), September 15-17, Nashville, TN, USA. 1996;197-206.
 32. Knothe G, Matheaus AC, Ryan TW. Cetane numbers of branched and straight-chain fatty esters determined in an ignition quality tester. *Fuel*. 2003;82(8):971-975.
 33. Knothe G, Steidley KR. Kinematic viscosity of biodiesel fuel components and related compounds. Influence of compound structure and comparison to petrodiesel fuel components. *Fuel*. 2005;84(9):1059-1065.
 34. Hilber T, Mittelbach M, Schmidt E. Animal fats perform well in biodiesel. *Render*. 2006;16-18. Available:<http://www.rendermagazine.com/pages/pastarticles2006.html> (Accessed on 30 August 2006)
 35. Szybist JP, Song J, Alam M, Boehman AL. Bio-diesel combustion; 2007.
 36. Felizardo P, Correia MJN, Raposo I, Mendes JF, Berkemeier R, Bordado JM. *Waste Manage.* 2006;26(5):487-494.

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