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Heterogeneous Methanolysis of Beniseed Oil to Biodiesel and its Characterization

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ABSTRACT: The heterogeneous methanolysis of Beniseed oil to biodiesel and its characterization were carried out. The oil from the seeds was extracted by solvent extraction methods using n-hexane. The catalyst was synthesized from waste eggshell by activating it with concentrated phosphoric acid (H_3PO_4) at a ratio of 1:4 (w/v) on weight basis. It was dried in a Memmert oven at 100 °C for 12 hours and characterized to determine its catalytic properties. The oil was extracted from the seed by solvent extraction with n-hexane and was characterized to determine its physiochemical properties. The biodiesel was produced and the effect of process parameters such as methanol/oil molar ratio, reaction time, temperature, amount catalyst and agitation speed on yield were investigated. The biodiesel was characterized to determine its physiochemical properties. The result indicated that the extracted oil yield 52 % from the seeds using n-hexane solvents was within the quantity of oil obtained by some researchers. The low acid value, iodine value and saponification value of the oil enable it to undergo direct transesterification without treatment with the acid activated eggshell. The biodiesel synthesized by transesterification of beniseed oils has a maximum yield between 70 – 80% and the process parameters had significant effects on the biodiesel yield. The properties of the biodiesel were within acceptable standard.

KEYWORDS: Acid activated Eggshell, biodiesel, beniseed oil, Transesterification reaction.

I. INTRODUCTION

In recent years, it has been a growing importance to explore new energy resources as substitutes to fossil fuels. Fuel and energy crisis and the concern of the society for the depleting world's nonrenewable energy resources led to a renewed interest in the quest for alternative fuels [1, 2]. One of the most promising alternatives fuel is the vegetable oils and their derivatives. The first use of vegetable oil in a compression ignition engine was first demonstrated through Rudolph Diesel who used peanut oil in his diesel engine. The use of oils from coconut, soy bean, sunflower, safflower, peanut, linseed, rape seed and palm oil amongst others have been attempted. The long-term use of vegetable oils led to injector coking and the thickening of crankcase oil which resulted in piston ring sticking. Therefore, vegetable oils are not used in diesel engines because of atomization issues [3, 4]. To overcome this problem, various modifications of vegetable oils have been employed such as transesterification, micro-emulsion formation and the use of viscosity reducers. Among these, transesterification was considered as the most suitable modification because technical properties of esters are nearly similar to diesel.

Transesterification is usually carried out using primary and secondary alcohols. Fukuda et al.,[5] reported that methanol and ethanol are most frequently used in the production of biodiesel but methanol is more preferred due to its low cost. Through transesterification, vegetable oils are converted to the alkyl esters of the fatty acids present in the vegetable oil [6, 7, 8]. These esters are commonly referred to as biodiesel.

Biodiesel is an alternative fuel that is renewable in the sense that its primary feedstock has a sustainable source. Some other feedstocks that can be converted to biodiesel are waste restaurant grease and animal fat [9]. Vegetable oils are



becoming attractive as the renewable source for biodiesel production due to its high lipid contents, high availability and low cost [10].

In view of the current instability in oil prices, biodiesel stands as an attractive source of alternative energy. By adopting and increasing the use of biodiesel, Nigeria will be free from her over-dependence on crude oil reserves [11]. Besides, conventional fossil fuel has been reported as being finite. The emissions produced from biodiesel are cleaner compared to petroleum-based diesel fuel. Particulate emissions, soot, and carbon monoxide are lower since biodiesel is an oxygenated fuel [12].

Owing to their availability, various oils have been in use in different countries as feedstock for biodiesel production. Rapeseed and sunflower oils in Europe, soybean oil in U.S., palm oil in Malaysia and Indonesia and coconut oil in Philippines are being used for biodiesel production. Also, the jatropha tree (*Jatropha curcas*), karanja (*Pongamia pinnata*) and mahua (*M. indica*) are used as major biodiesel fuel sources in India [13]. In spite of this, biodiesel production from conventional vegetable oils (soybean, sunflower, safflower, palm, rapeseed etc.) has progressively stressed food uses, price, production and availability of these oils [14]. Consequently, this has ignited the search for additional regional biodiesel raw materials. With 350 oil-bearing crops having been identified, recent studies on biodiesel from less common or unconventional oils include *Moringaoleifera*[15], *Micheliachampaca* and *Garcinia indica*[16], pumpkin [17], sea mango [18] and desert date [19] oils but use of beniseed is limited.

Beniseed (*Sesamum indicum* L), is an herbaceous plant in Nigeria as well as in India, China, Sudan, Burma, Bangladesh, Indonesia, Egypt, Tunisia, belongs to the family of Pedaliaceae. Beniseed belongs to seeds with very high oil contents of about 35-50% and is considered to be the oldest oilseed crop known to man, highly resistant to drought and has the ability of growing where most crops fail[20]. The seed colour varies from cream-white to charcoal black but it is mainly black. In Nigeria, the notable colours of sesame seed are white, yellow and black [21]. The major world producers include India, Sudan, China and Burma while Nigeria and Ethiopia are also major producers and exporters in Africa [22]. The main fatty acid composition of the oil is oleic, linoleic, palmitic, and stearic acids, contributing to suitable feedstock for FAME production [23]. Therefore, this study focused on synthesis and characterization of biodiesel from beniseed oil using acid activated eggshell catalyst.

II. MATERIALS AND METHODS

A. MATERIALS

Beniseeds were purchased from Ogbete Market Enugu, Enugu State, Nigeria while the waste eggshell was sourced from different fast food restaurants in Enugu State Nigeria. The methanol, and other chemicals were sourced from De-Cliff Integrated Services Ltd, Enugu, Nigeria and they are of analytical grade.

B. EXTRACTION OF OIL FROM BENI SEED.

The oil was extracted by cold solvent extraction. 1.5 kg of the Beniseed was weighed on an analytical weighing balance, pulverized to particle size of 850 μm using an industrial blender and soaked with 2 liters of n-hexane in a container for two days. The container was covered and made air tight to avoid evaporation of n-hexane. The solvent was separated from the oil using rotary vacuum evaporator (Laborota 4000) and was collected in the receiving flask. The oil which was remained in the sample flask was weighed after the process was completed [24]. The percentage yield of the oil was calculated as thus:

$$\% \text{ yield} = \frac{\text{weight of the oil extracted}}{\text{weight of the sample used}} \times 100 \quad (1)$$

C. DETERMINATION OF BENI-SEED OIL PROPERTIES

The extracted oil from Beni-seed was characterized using appropriate AOAC [24] for physiochemical properties and gas chromatography mass spectrometer (GCMS, ThermoFinnigan Trace GC/Trace DSQ/A1300) for fatty acid profile respectively.

D. PREPARATION AND ACTIVATION OF THE CATALYST

Egg shells were washed thoroughly in tap water to remove any unwanted material adhered on its surface, and rinsed twice with distilled water. The washed egg shells were then dried in hot air oven at 105 °C for 24 h and were reduced to particle size of 350µm. The catalyst was activated by chemical means (acid activation). The prepared eggshell was impregnated with concentrated phosphoric acid (H₃PO₄) at a raw material to acid ratio of 1:4 (w/v) on weight basis. The saturated sample was dried in a Memmert oven at 100 °C for 12 hours. After the activation, and slow cooling in air at room temperature, the slurry was washed with distilled water several times to reduce the pH value of the samples, filtered to be free from acid and then dried at a temperature of 110 °C for 4 hours and finally grounded into a fine powder, sieved and stored in desiccators for further usage.

E. CHARACTERIZATION OF THE CATALYST

The synthesized catalyst was characterized to determine its morphology, elemental compositions, functional group, mineralogy and surface area using scanning electron microscope (SEM), X-ray fluorescence (XRF, ARL 9400XP), Fourier transform infra-red spectroscope (FTIR BUCK model M530), X-ray diffractometer (XRD) and Brunauer-Emmett-Teller (BET, ASAP 2020) respectively.

F. SYNTHESIS OF BIODIESEL

The beniseed oil (BSO) was quantitatively transferred into a flat bottom flask placed on a hot magnetic stirrer. Then specific amount of catalyst (by weight of oil sample) mixed with the required amount of methanol was added. The reaction flask was kept on a hot magnetic stirrer under constant temperature with defined agitation throughout the reaction. At the defined time, sample was taken out, cooled, and the biodiesel (i.e. the methyl ester in the upper layer) was separated from the by-product (i.e. the glycerol in the lower layer) by settlement overnight under ambient condition. The percentage of the biodiesel yield was determined by comparing the weight of layer of biodiesel with the weight of oil used.

$$Y = \frac{\text{weight of biodiesel}}{\text{weight of oil used}} \times 100 \quad (2)$$

The procedure was repeated by varying the factors affecting the transesterification reaction such as; time, catalyst concentration, temperature, alcohol/oil molar ratio and agitation speed.

III. CHARACTERIZATION OF BIODIESEL

The fuel properties of biodiesel was characterized to determine its physiochemical properties using the method employed by Onukwuli et al., [25] and according to ASTM D6751-02 [26].

A. DETERMINATION OF ACID VALUE AND FFA

5 g of biodiesel was poured into a conical flask. About 50ml of neutralized ethanol solution was added to the biodiesel and the solution heated for about 10 minutes at temperature of 45 °C. After the heating, two drops of phenolphthalein indicator was added. The mixture was then titrated against 0.25 mol dm⁻³ sodium hydroxide (NaOH) solution from the burette until the appearance of pink colour. The acid value (A.V) was then calculated using the equation:

$$A.V = \frac{T \times N \times 56.1}{W} \quad (3)$$

Where,

T = Titre value, N = Normality of NaOH, W = Weight of the biodiesel

The FFA was determined using the equation:

$$\%FFA \approx \frac{1}{2} A.V \quad (4)$$

B. DETERMINATION OF SAPONIFICATION VALUE

2 g of biodiesel was put into a flask. 25 ml of ethanol-KOH solution, which is 75% ethanol was added to the sample. The flask was heated on a rotary evaporator for 1 hour at temperature of 40°C. After the heating, the solution was cooled and 2 drops of phenolphthalein indicator was added into the flask and titrated against 0.5 mol dm⁻³ of

tetraoxosulphate (VI) (H_2SO_4) acid from the burette until the pink colour disappeared. The procedure was repeated without the biodiesel and the corresponding reading was noted for the blank titration. The saponification value (S.V) was calculated using the equation:

$$S.V = \frac{(B - T) \times N \times 56.1}{W} \quad (5)$$

Where,

B = Titre value of Blank, T = Titre value of sample containing biodiesel
N = Normality of the acid, W = Weight of biodiesel used

C. DETERMINATION OF IODINE VALUE

0.25 g of biodiesel was put into a flask. 10ml of chloroform was added and the mixture was warmed slightly for 10 minutes at temperature of 40 °C and cooled thereafter. 25ml of iodine tetrachloride-glacial acetic acid solution was added to the flask and the mixture shaken vigorously. The flask was kept in a dark place for 30 minutes. Thereafter, 10 ml of potassium iodide solution was added and the mixture was titrated against 0.1 $mol\ dm^{-3}$ sodium thiosulphate solution from the burette until the appearance of yellow colour. 1ml of starch indicator was added to the initially titrated mixture and the colour changed to blue and the mixture was again titrated against sodium thiosulphate until the blue colour disappeared. The procedure was repeated without the oil and the corresponding reading was noted for the blank titration. The iodine value (I.V) was calculated using the equation:

$$I.V = \frac{(B - T) \times N \times 12.69}{W} \quad (6)$$

Where,

B = Titre value of Blank T = Titre value of sample containing biodiesel N = Normality of the acid W
= Weight of biodiesel used

D. DETERMINATION OF DENSITY AND SPECIFIC GRAVITY

A clean empty specific gravity bottle was weighed on an electronic balance and the mass (W_1) noted. It was then filled with the biodiesel, in turn, at the required temperature and its mass (W_2) and volume noted. The mass of each oil (W_s) was the difference between W_2 and W_1 . The density of biodiesel, ρ , was calculated using the equation:

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}} \quad (7)$$

The bottle was washed, dried and filled with equal volume of water at the required temperature and the mass (W_3) was noted. The mass of water (W_w) was the difference between W_3 and W_1 . The specific gravity of biodiesel was determined using the equation:

$$\text{Specific gravity} = \frac{\text{Weight of biodiesel}}{\text{Weight of equal volume of water}} \quad (8)$$

That is:

$$\text{Specific gravity} = \frac{W_2 - W_1}{W_3 - W_1} \quad (9)$$

E. DETERMINATION OF VISCOSITY

The viscosity was measured with a digital viscometer made by Searcher instruments, England. The spindle was selected and fixed on the instrument. The spindle was inserted in the sample to be analyzed till the level mark on the spindle reached the surface of the sample. The enter button on the instrument was pressed and the dynamic viscosity, μ , of the sample was displayed on the screen. The kinematic viscosity, ν , was then determined by using the equation:

$$\nu = \frac{\mu}{\rho} \quad (10)$$

F. DETERMINATION OF CALORIFIC VALUE

Bomb calorimeter was used to measure the calorific value of the biodiesel. The weight of the biodiesel was measured in grams. The sample was poured into a crucible. Two ends of the ignition thread (nichrome wire) of noted length were fixed on two electrode poles and they were made to keep a good touch on the sample to be evaluated. 10ml of distilled water was poured into the oxygen bomb and the cover was screwed down. Oxygen at a pressure of 2.9 MPa was made to flow into, and fill the bomb. The oxygen bomb was put onto the clamp in the inner canister. The temperature sensor was put into the canister. The power was turned on and the stir button was pressed. The water was allowed to stir until the temperature reading stabilized and the initial temperature was noted as T_0 . The fire button was pressed and the instrument automatically measured and saved the data. When testing counts got to about 31 counts, the experiment was finished. The final temperature was noted as T_f . The stirring was stopped and the temperature sensor was pulled out. The lid was opened and the bomb was removed. The oxygen inside was released before opening the bomb. The length of the unburned firing wire was measured. The inner lining of the oxygen bomb and crucible were washed with distilled water. 2 drops of methyl red indicator were added into the solution and titrated with 0.0709 N sodium carbonate. The titre volume V was recorded. The calorific value was calculated using the equation:

$$\text{Calorific value} = \frac{E\Delta T - \phi - V}{w} \quad (11)$$

Where,

w = Weight of sample
 E = Energy equivalent of the calorimeter per degree Celsius
 ΔT = Change in temperature
 ϕ = Correction for heat of combustion of firing wire
2.3
burnt length (cm)
 V = Volume of titre used during titration

G. DETERMINATION OF FLASH POINT

The sample of the biodiesel was poured into the test cup up to the specified level. The cover was then fitted into position on the cup and the sample was heated and stirred at a slow and constant rate. At every 2 °C temperature rises, a flame was introduced over the test cup at a very slow rate for a moment with the help of a shutter. The temperature at which a flash appeared in the form of sound and light was recorded as the flash point.

H. DETERMINATION OF CLOUD POINT

The sample of biodiesel was put into a test tube containing a thermometer and sealed with a cork. After being heated to within 48 °C, the sample was cooled in a series of cooling baths. The temperature at which a haze or cloud was first seen at the bottom of the test tube was noted as the cloud point.

I. DETERMINATION OF POUR POINT

The sample of biodiesel was put into a test tube containing thermometer and sealed with a cork. After being heated to within 48 °C, the sample was cooled in a series of cooling baths. At each 3 °C reduction in temperature, the tube was removed and tilted until no movement of the sample occurred for 5 seconds. The pour point was recorded as the temperature 3 °C above the temperature at which no movement was observed.

J. DETERMINATION OF CETANE NUMBER

The cetane number was determined using degree API at specific gravity at 60 °F (15.56°C) of the sample and its aniline point (AP). The aniline point of biodiesel was determined by adding 10 ml of aniline solution to 10 ml of the biodiesel in a beaker. The mixture was heated on a heater while being stirred until the two merge into a homogeneous solution. Heating was stopped and thermometer was inserted into the beaker while the beaker and its content were allowed to cool. The temperature at which the two phases separated was observed and was recorded as the aniline point. The degree API and Diesel index of the sample were determined using the formula below.

$$\text{Degree API} = \frac{141.5}{\text{Specific gravity at } 60^{\circ}\text{C}} - 131.5 \tag{12}$$

$$\text{Diesel Index (DI)} = \frac{\text{Degree API} \times \text{Aniline point}}{100} \tag{13}$$

Finally, the cetane number of the sample was determined using the formula:

$$\text{Cetane Number} = 0.72\text{DI} + 10 \tag{14}$$

IV. RESULTS AND DISCUSSION

A. OIL YIELD AND ITS CHARACTERIZATION

52% of oil was extracted from the beniseed. The oil yield is above the yields of some oil such as soybeans, 50% and cotton seed, 47% [14]. The oil yield of Beniseed makes it suitable and economical for biodiesel production, as any seed that yields up to 30% oil is regarded as suitable feedstock for industrial production of biodiesel[27].

The physiochemical properties of the beniseed oil is depicted in the Table 1. From the table, specific gravity has been described as one of the most basic and vital properties of the feedstock for FAME production [11] because of its correlation with cetane number, heating values feedstock storage and transportations [28]. The specific gravity obtained for Beniseed oil (BSO) lies within the standard range 0.87 – 0.98 for triglycerides [11]. The acid value of Beniseed oil extracted for this work is 6.10mgKOH/g hence, the value indicates that it has good quality for biodiesel production. The result also reveals that the oil has moderate free fatty acid value of 3.0%. This value suggests pre-treatment step on the raw-oil before the transesterification step using homogeneous catalyst but the process could be avoided using heterogeneous catalysts. Saponification value of the feedstock was between the ranges of the standard 175 – 205 mgKOH/g oil [27]. The Saponification values of BSO was found to be 184.3 mgKOH/g oil, this value indicates that the Beniseed is a normal triglyceride and suitable for FAME production. The physicochemical properties of the raw oil compare favorably with those of some other oils such as *Pongamiapinnata*[29], *Jatropha curcas*[30], *Madhuca indica*[31].

The density and high viscosity of the oil will make its atomization difficult in internal combustion engine, hence it cannot be used directly as bio-fuel. The low pour point shows that the oil will hardly solidify at room temperature hence can be stored for a long time. The oxidation stability of the oil was high and is good for production of biodiesel.

Table 1: The characterization results of the Beniseed oil (BSO).

Properties	BSO
Density (g/cm ³)	0.91
Kinematic viscosity (mm ² S ⁻¹ at 40°C)	46.01
Free fatty acid (mgKOH/g oil)	3.00
Iodine value (g/100g oil)	39.00
Saponification value (mgKOH/g oil)	184.30
Refractive index	1.42
Peroxide value (meq/kg)	0.53
Moisture content (%)	0.02
Acid value (mgKOH/g oil)	6.10
Calorific value (MJ/g)	30.01
Boiling point (°C)	199.00
Flash point (°C)	263.00
Fire point (°C)	273.00
Molecular weight (g/mol)	827.80
Oxidation stability 11°C (Hour)	5.10

B. FATTY ACID COMPOSITION OF BSO USING GC –MS

The fatty acid compositions of BSO is presented in Table 2. From the table, the main fatty acid components of the oil are: palmitic, stearic, oleic, Lignoceric, linoleic, Caproic, Lauric acid and Linolenic acid. Linoleic acid is the most abundant with 50.03% of the total fatty acid present. BSO consists of 24.94% of saturated acids (stearic acid, palmitic acid, Caproic acid, lauric acid and Lignoceric acid) and 75.06% unsaturated acids (oleic, linoleic, Linolenic acid,). The dominant unsaturated fatty acid of the oil is linoleic acid, which accounted for 50.03% of the total fatty acid content, hence, the oil belongs to oleic acid category [32]. The oleic acid content of BSO as reported in Table 2 is comparatively higher than 7-40% reported for coconut oil, palm oil and cottonseed oil [14, 33]. This shows that BSO oil is highly unsaturated triglycerides. However, the fatty acid components of the BSO was found to be consistent with the fatty acids present in typical oils used for FAME production.

Table 2: Fatty acid composition of BSO oil.

Fatty acid	Structure	Composition (%)
Caproic acid	C6:0	7.70
Stearic acid	C18:0	7.89
Palmitic acid	C16:0	5.90
Oleic acid	C18:1	24.65
Linoleic acid	C18:1	50.03
Lignoceric acid	C24:0	0.32
Lauric acid	C12:0	3.13
Linolenic acid	C18:3	0.38

B. X-RAY FLUORESCENCE ANALYSIS OF EGG SHELL CATALYSTS

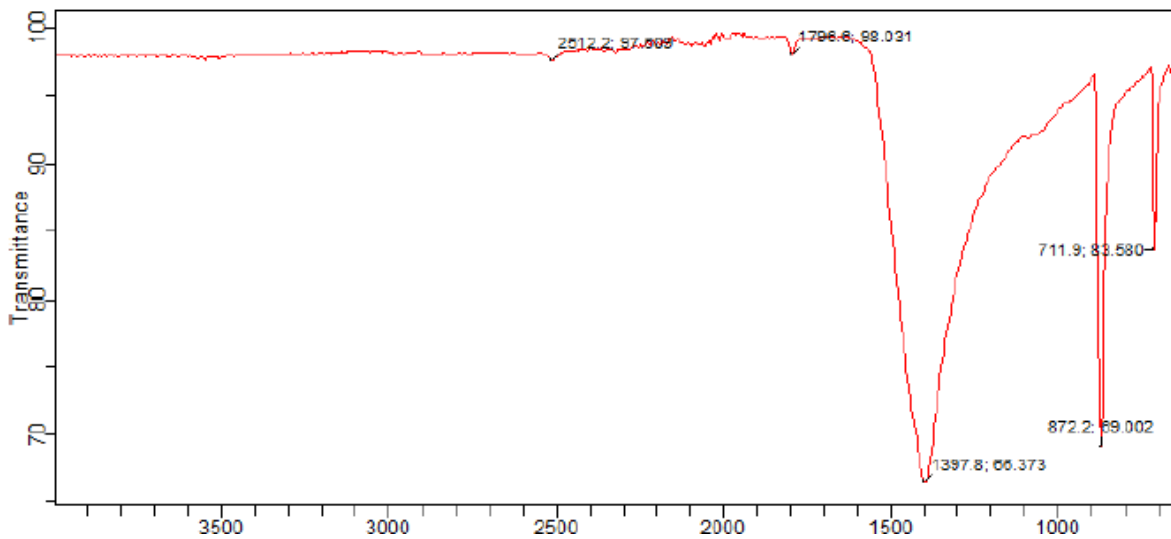
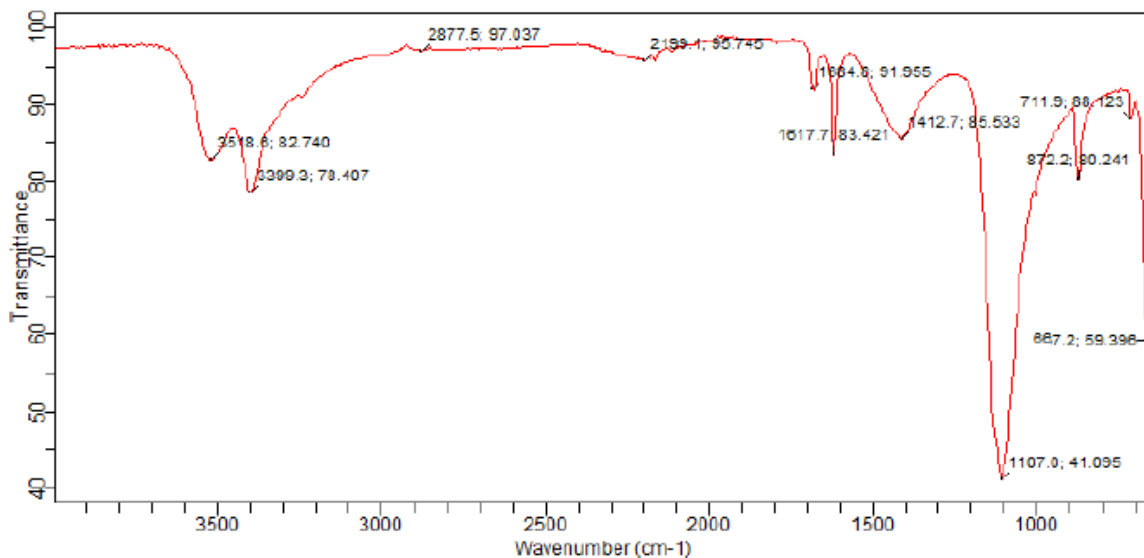
The chemical compositions of raw and acid activated eggshell are presented in Table 3. The main compositions of the egg shell are Ca, P, S, K, Al, CL, Si and Sr. Eggshell had high amounts of Ca and Al. The modification of egg shell by acid activation increased the quantity of CaO, SiO₂ and eliminates SO₃, Na₂O and Mn₂O₃. After the activation process, the percentage of calcium increases rapidly. Moreover, the presence of lower amounts of other elements (MgO, Fe₂O₃, P₂O₅, K₂O, Al₂O₃ and Cl,) is noticeable, which will be considered as impurities of the CaO catalyst. The high calcium content of the activated eggshell used in this work suggests that this material could be a promising material to biodiesel production.

Table 3: X-ray fluorescence (XRF) of egg shell catalysts.

Elements	Raw egg shell	Acid activated egg shell
Na ₂ O	0.331	0.000
MgO	0.130	0.412
Al ₂ O ₃	0.428	0.297
SiO ₂	2.170	2.360
P ₂ O ₅	0.299	0.258
SO ₃	32.514	0.000
Cl	0.059	0.136
K ₂ O	0.086	0.097
CaO	63.817	96.564
Mn ₂ O ₃	0.005	0.000
Fe ₂ O ₃	0.032	0.011
SrO	0.126	0.216

C.FOURIER TRANSFORMS INFRA-RED (FTIR) ANALYSIS OF EGG SHELL CATALYSTS

Fourier transform infra-red (FTIR) spectroscopy of the raw egg shell and acid modified egg shell catalysts were done to ascertain the functional groups present in them as shown in the Figures 1(a & b). The spectra band range of 2500-3639.68 cm^{-1} is detected for the catalysts (acid modified eggshell) which can be assigned to the presence of O-H stretching vibrations of $\text{Ca}(\text{OH})_2$. While peak at 1413 –1436 cm^{-1} detected corresponds to the bending vibration of Ca-O stretching. Besides that, from the FTIR result, it can be said that all CaCO_3 component in the egg shell waste was converted to CaO because no peak appeared for the CaCO_3 component in the modified catalyst. Hence, it can be said that the derived CaO from modified eggshell has the same potential as the commercial CaO to be a catalyst in the biodiesel production.

**Fig. 1a FTIR of raw egg shell.****Fig. 1b FTIR of acid activated eggshell catalyst.**

D. SCANNING ELECTRON MICROSCOPES (SEM) OF EGG SHELL CATALYSTS

The morphologies of the raw and acid activated egg shell catalyst were performed by SEM, as presented in Figures 4.2 (a & b). The SEM micrographs display that raw eggshell has structure of irregular and heterogeneous distribution of particle sizes (CaCO_3 and organic matter) (Figure 2a), while the SEM micrograph of acid egg shell catalyst exhibits particles with lower particle size and more homogeneous distribution probably due to exothermic process that takes place in the activation process (Figure 2b).

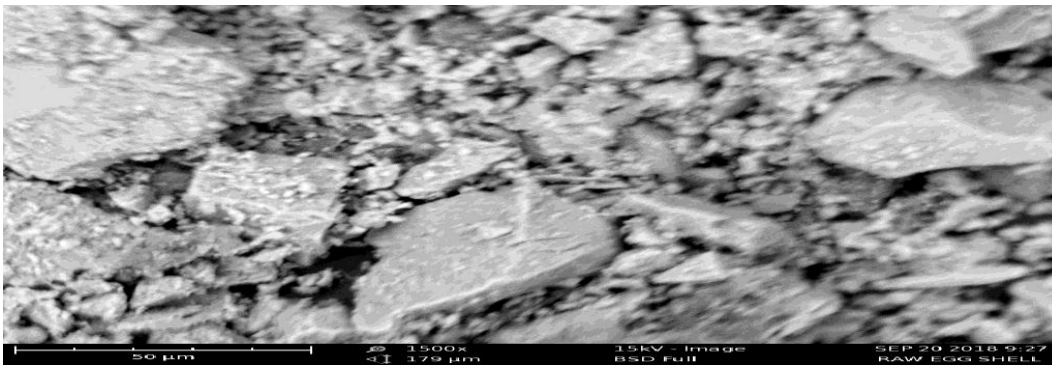


Fig. 2a SEM of raw egg shell.

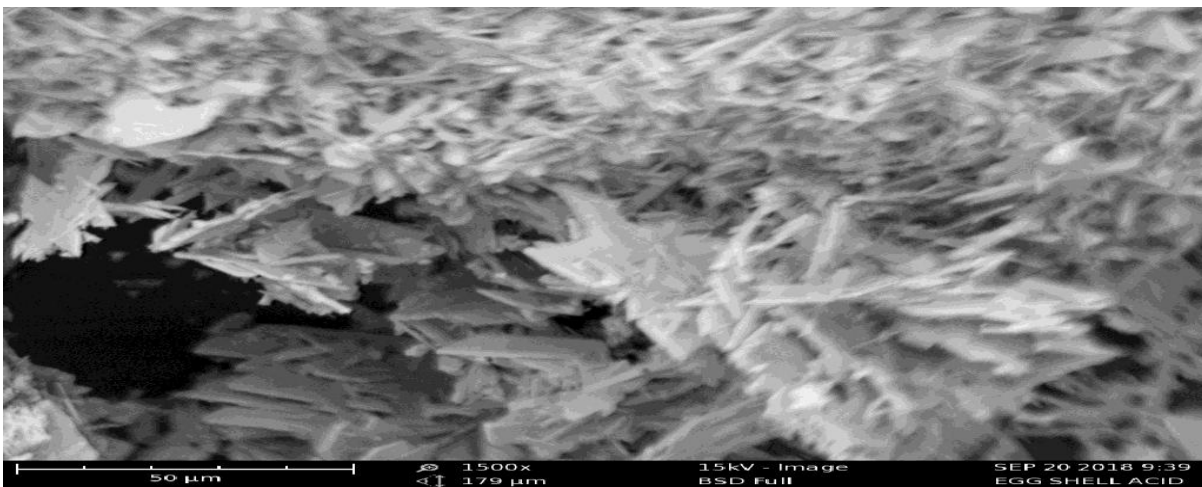


Fig. 2b SEM of acid activated egg shell.

E. X-RAY DIFFRACTION PATTERN OF THE EGG SHELL CATALYSTS (XRD)

The mineralogical identification of raw egg shell and acid activated egg shell was carried out using X-ray Diffraction (XRD). Figures 3 (a & b) present the X-ray diffraction pattern of the egg shell catalysts and its modified form. Discarding the presence of other crystallographic phases, raw Eggshell presents diffraction lines located at 2θ /degree which has been ascribed to the presence of rhombohedra calcite (CaCO_3). After the activation process, the diffraction lines attributed to CaCO_3 disappear, with new diffraction lines arising at 2θ /degree and corresponding to lime (CaO).

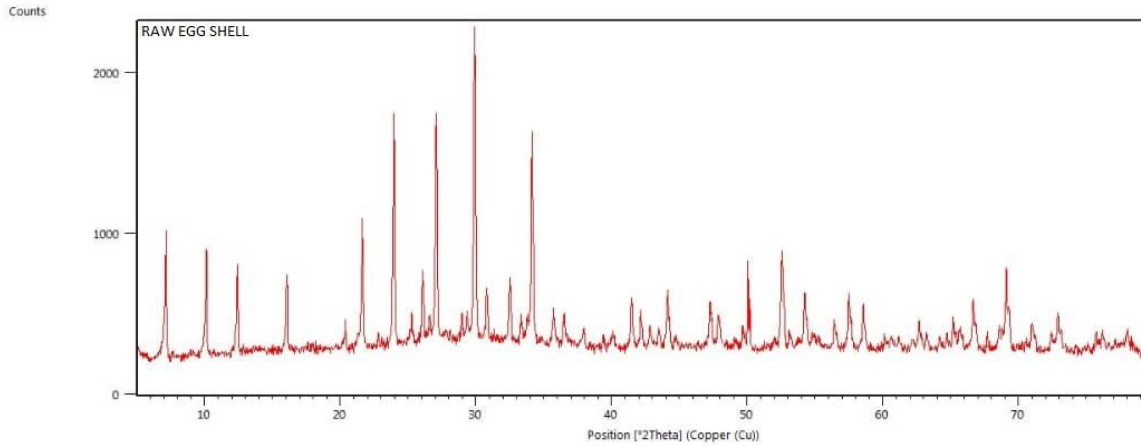


Fig. 3a XRD of raw egg shell.

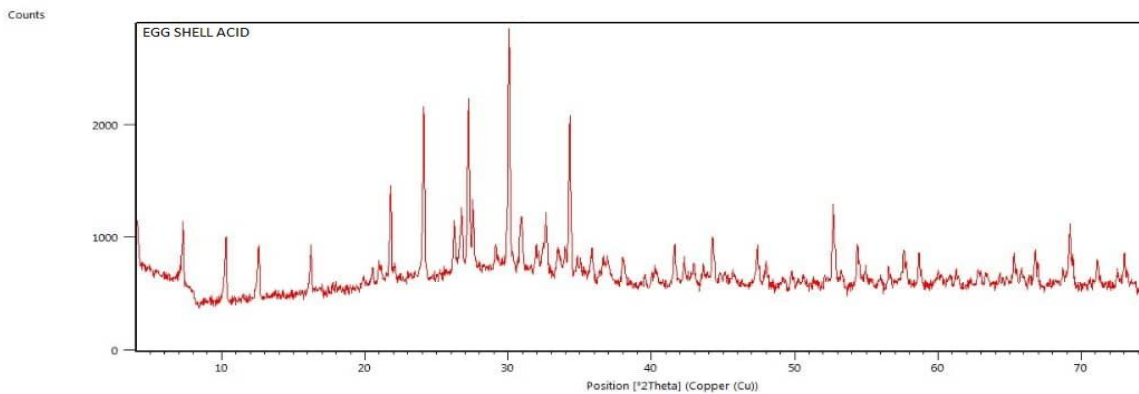


Fig. 3b XRD of acid activated egg shell.

F.PHYSIOCHEMICAL PROPERTIES OF EGGSHELL CATALYST

The BET studies confirmed that higher surface areas and well-developed pore volume were obviously found on the surface of acid activated eggshell compared to raw. Chemical activation normally develops more porosity and gives high surface area and pore volume when compared with the raw eggshell[34].

Table 4: Physiochemical properties of raw and acid activated catalysts.

Sample name	Raw eggshell	Acid activated eggshell
Surface area (m ² /g)	276.3	477.6
Pore volume (cm ³ /g)	12.67	24.3

Pore size A°	2.447	4.423
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G. EFFECT OF CATALYST CONCENTRATION ON BIODIESEL YIELD

The effect of catalyst weight was premeditated between 1%-5%wt (based on weight of the oil) while other variables were constant. In a chemical reaction, the bonds holding the reactants together must first be fragmented before the reaction can take place. Breaking bonds requires energy, and the minimum energy needed to start a reaction is referred to as activation energy. Catalysts provide alternative reaction pathways for breaking and remaking of bonds. It was observed from Figure 4 that as catalyst weight increases, the yield of biodiesel also increased up to 4% weight of catalyst and decreased with further increase in catalyst weight. The higher yield of biodiesel with increase in catalyst weight is due to the higher availability of catalyst in the reaction medium. Increasing the catalyst weight beyond 4% weight showed decrease in the amount of biodiesel yield. This may be due to excess catalyst causing dispersion and mixing bottlenecks, thereby inhibiting the formation of FAME [35].

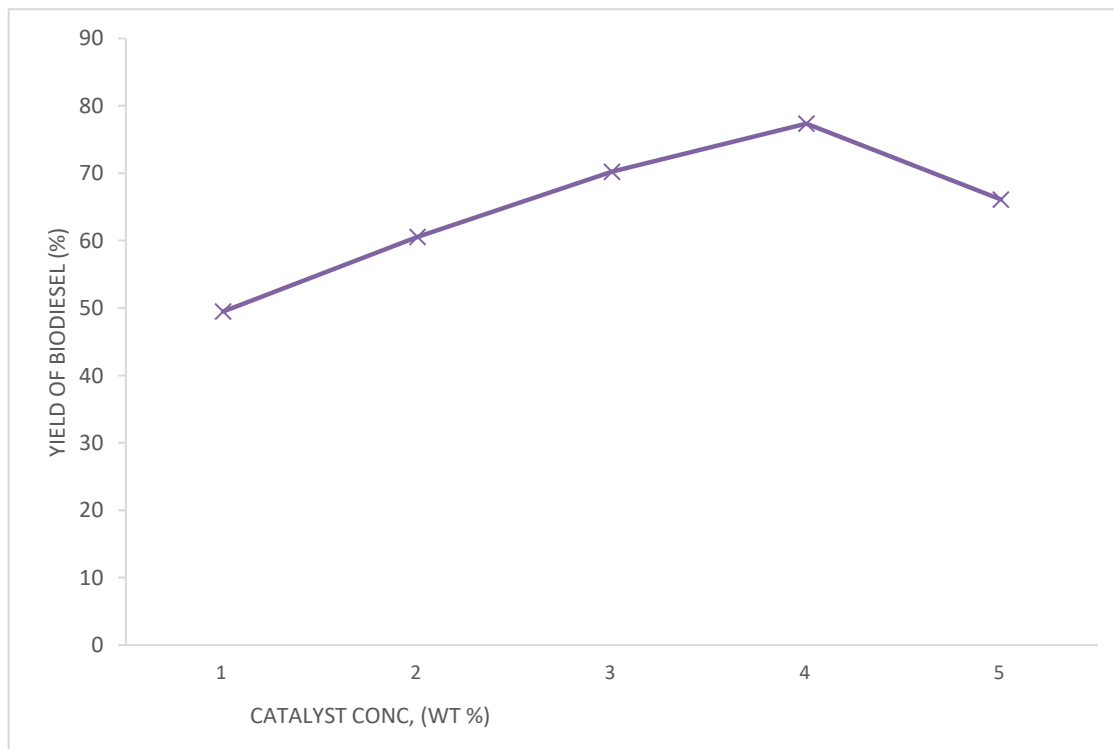


Fig. 4Effect of Catalyst Conc. on biodiesel yield: Reaction conditions: Time= 3 hr, Temperature= 60°C, Speed= 250rpm, mole ratio = 12:1

H. EFFECT OF METHANOL/OIL MOLAR RATIO ON FAME YIELD.

Figure 5 depicts the effect of methanol/oil molar ratio on the yield of biodiesel produced. Methanol to oil molar ratio was studied between the range of 6:1 to 14:1 and other variables were constant. The result from the figure, indicates that methanol oil molar ratio has significant impact on biodiesel yield. The maximum yield was obtained at a methanol/oil molar ratio of 12:1. The higher molar ratio resulted in higher yield of biodiesel. The yield reduced when the molar ratio was beyond 12:1. This may be due to decrease in the catalyst activity with increased in methanol content and difficulty in glycerol separation. Also, it could be that methanol has polar hydroxyl group which act as an emulsifier causing emulsification that made the separation of the ester layer from the water layer very difficult at high volume of the methanol thus, causing loss in the yield of the ester [36].

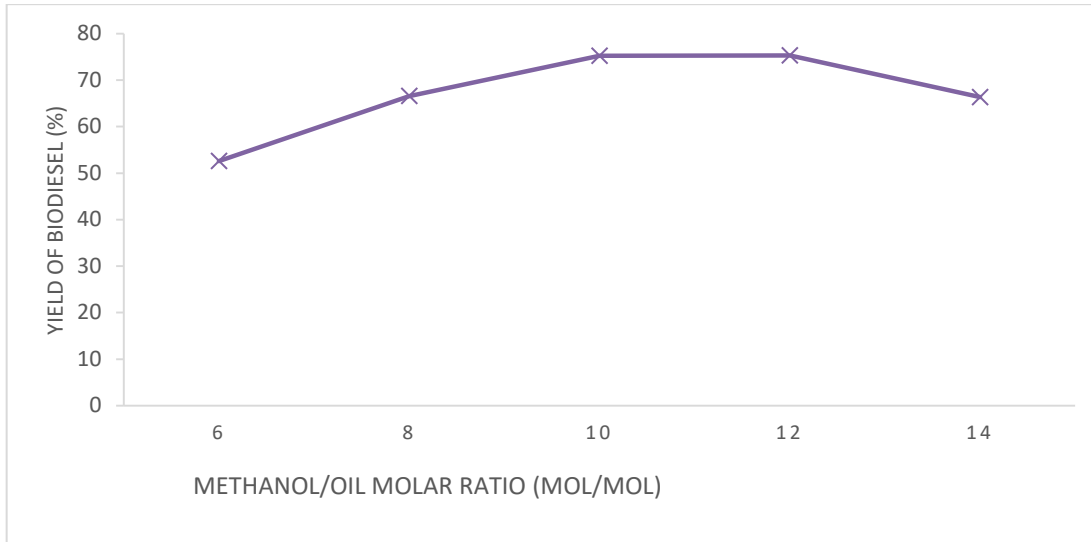


Fig. 5 Effect of methanol /oil molar ratio on biodiesel yield. Reaction conditions: Time= 3hr, Temperature 60 °C, Speed= 250 rpm, catalyst conc. = 3.0 wt. %.

I. EFFECT OF TEMPERATURE ON BIODIESEL YIELD

Effect of temperature on reaction rate can be explained through the theory of chemical reaction kinetics. An increase in temperature will result in increasing fraction of molecules that have a high speed and therefore has a high kinetic rate. The effect of temperature between 45 °C to 65 °C on biodiesel yield was studied keeping other parameters constant. As shown in Figure 6, the reaction rate was slow at low temperatures, but biodiesel yield first increased and then decreased with the increased of the reaction temperature beyond 60°C. However, a more rapid reaction rate could be obtained at high temperatures, but at high temperatures, methanol was vaporized and formed a large number of bubbles, which inhibited the reaction on the two-phase interface. Similar result was reported by Ude and Onukwuli[35].

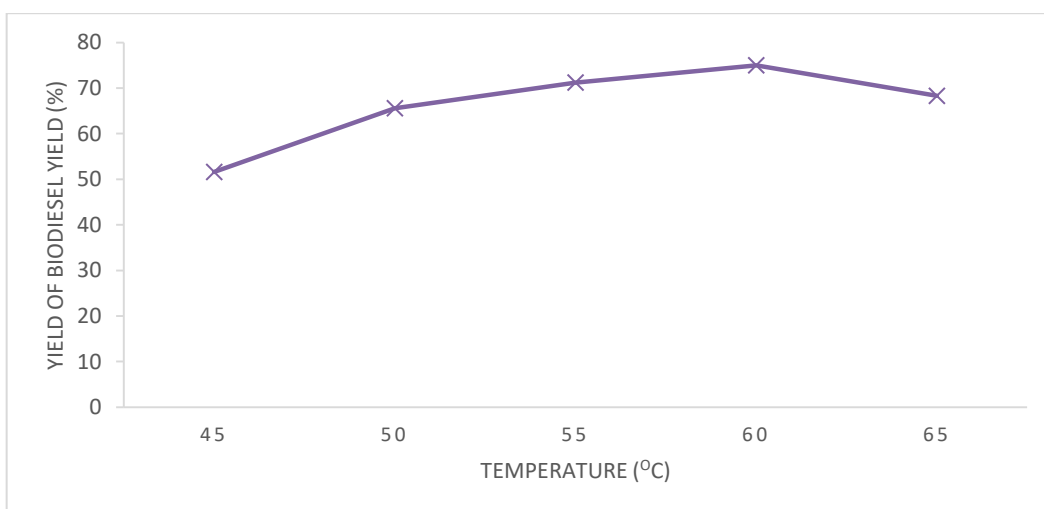


Figure 6: Effect of temperature on biodiesel yield. Reaction conditions: Time = 3hr, molar ratio =12:1, Speed= 250rpm, catalyst= 3.0 wt. %

J. EFFECT OF SPEED OF AGITATION ON BIODIESEL YIELD

Transesterification was conducted in this study at different agitation rate such as 150, 200, 250, 300 and 350 revolution per minutes (rpm). Mixing is particularly very important for transesterification process; it ensures homogeneity within the reaction mixture. The biodiesel yield at different rate of mixing is shown in Figure 7. At the lowest stirring speed of 150 rpm it was observed that the reaction was practically incomplete as it only exhibited a yield which was difficult to separate and as such was very low. The yield was observed to decrease as the stirring rate went above 300 rpm for both feed stocks. The backward reaction could be as a result of high entropy of the reacting system and reduction of contact time of the reactants thereby retarding the formation of biodiesel. These results are in conformity with observations made by Ogunsuyi[37], who studied the effect of agitation speed on the transesterification of non-edible oil and concluded that higher agitation promoted the homogenization of the reactants and thus led to higher yields.

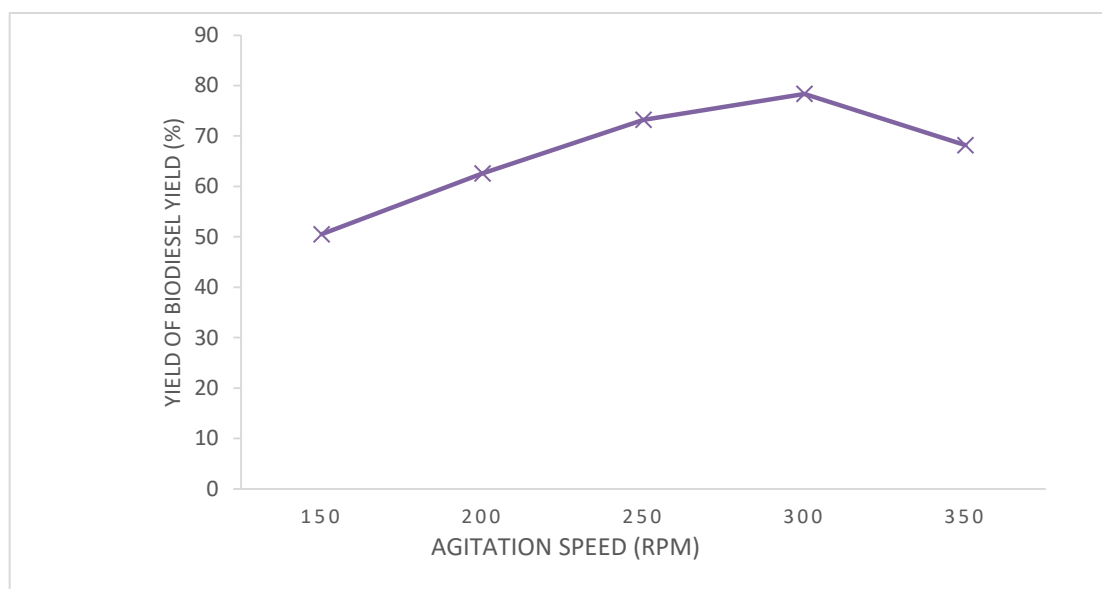


Fig. 7 Effect of agitation speed on biodiesel yield. Reaction conditions: Time= 3hr, Temperature = 60 °C, molar ratio=12:1, catalyst= 3.0 wt.%.

K. EFFECT OF TIME ON BIODIESEL YIELD

Reaction time was studied from 1 to 5 hours on biodiesel yield while every other parameter was kept constant. From Figure 8, it shows that the reaction was very slow initially due to dispersion and mixing of methanol and catalyst into BSO from 1 hour. But as the reaction time increased an increase in the yield of biodiesel was observed as the 3 hours were enough retention time for reactions to occur and then yield started decreasing as the reaction time further increased. This was because the reaction has reached equilibrium hence a reverse reaction starts to occur. From the figure, it shows that the maximum ester yield of 70% was obtained from transesterification of beniseed oil(BSO) with acid activated eggshell. The figure also indicated that an increase of the reaction time from 4 hours to 5 hours would not yield further increase in biodiesel yield but leads to a reduction in the product yield. This is because longer reaction time enhanced the hydrolysis of esters (reverse reaction of transesterification), resulting in loss of esters [38]. Similar result was also reported by Deepak et al., [39].

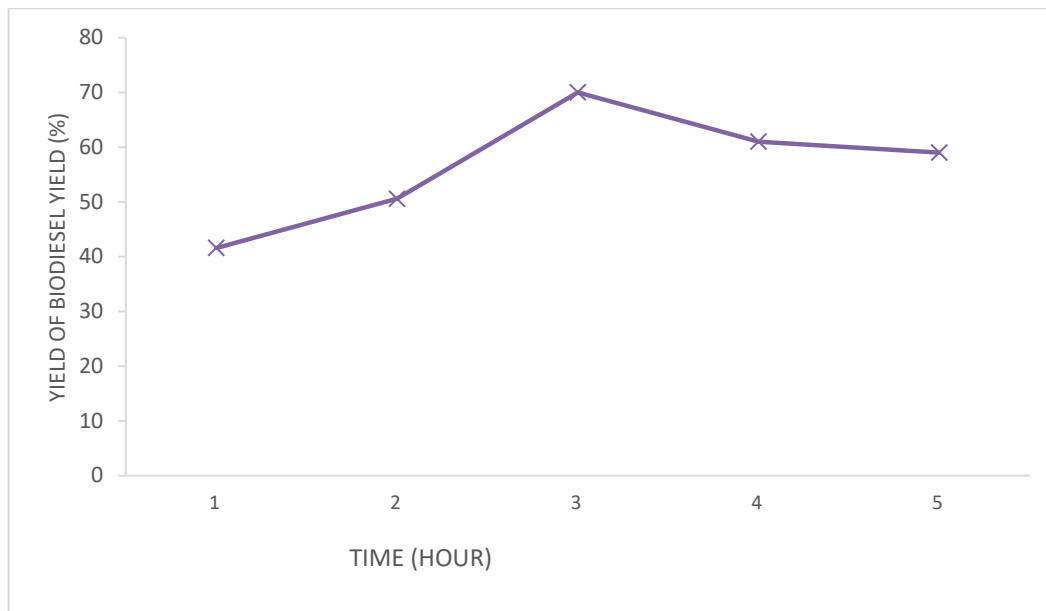


Fig 8: Effect of time on biodiesel yield. Reaction conditions: methanol/oil molar ratio= 12:1, Speed= 250 rpm, catalyst= 3.0 wt. %.

L. CHARACTERIZATION OF BIODIESEL

The fuel properties of biodiesel produced are presented in Table 5, and the limits that they were compared with (ASTM D 6751 (2002) standards).

Viscosity of BSO are always high and they cause serious problems in unmodified engines. The increase in viscosity results in poor atomization and incomplete combustion which leads to coking of injector tips. This results in engine power loss. Biodiesel has higher viscosity than Petro-diesel. Viscosity decreases with unsaturation but increases markedly with contamination by mono, di or triglycerides. The increase in viscosity results in poor atomization and incomplete combustion which leads to coking of injector tips, engine power loss. Low-viscosity fuel produces a very subtle spray and cannot get into the combustion cylinder thus forming the fuel rich zone which led to the formation of soot [40, 41]. From the result it can be inferred that the viscosity of biodiesel is 3.90 cSt. That is to infer that biodiesel from BSO via acid activated eggshell has a good injection and atomization performance. Furthermore, it will offer lubrication and protection for the moving parts of an engine superior to those of the diesel.

Density is an important fuel property, because injection systems, pumps, and injectors must deliver an amount of fuel precisely adjusted to provide proper combustion. The density values must be maintained within tolerable limits to allow optimal air-to-fuel ratios for complete combustion. Biodiesel generally has a higher density than Petro-diesel. This has a significant impact on fuel consumption as fuel introduced into the combustion chamber is determined volumetrically. High-density biodiesel or its blend can lead to incomplete combustion and particulate matter emissions. The default value of 40 °C density specified in ASTM D6751 is 0.82–0.90 g cm³. Density depends upon the feedstocks used for biodiesel fuel production with negligible catalyst effect. The results from Table 5 show that the density value of biodiesel obtained meet the density value specified by the ASTM for biodiesel.

The flash point is a determinant for flammability classification of materials. The typical flash point of pure biodiesel is ≥130 °C, classifying them as “non-flammable”. However, during production and purification of biodiesel, not all the methanol may be removed, making the fuel flammable and dangerous to handle and store if the flash point falls below 130 °C. The flash point for the biodiesel produced from BSO falls within the ASTM standard, and makes it safe for handling and storage.

Determination of acid value (AV) is an important test to assess the quality of a biodiesel produced. The AV of the feedstock can play an important role on the % fatty acid methyl ester of the final product. The maximum level of AV for pure biodiesel, as specified in ASTM standard D6751 is 0.8 mg KOH /g. The AV of the biodiesel produced from BSO is 0.50mgKOH/g. This value are significantly lower than the maximum value approved by ASTM D6751 standard fuels.

The iodine value, IV is the measure of degree of unsaturation in oil or FAME produced. It is constant for a particular oil or fat. The IV is a useful parameter in studying oxidative rancidity and chemical stability properties of different biodiesel fuels. A higher quantity of double bonds in the sample has greater potential to polymerize and, hence, lesser stability. Iodine value above 125 are classified as drying oils; those with an IV of 110–140 are classified as semidrying oils and those with IVs less than 110 are considered as non-drying oils. The IV of the obtained biodiesel is 44.33 g I₂/100 g oil, indicating that it is a non-drying biodiesel invariably it is non-volatile.

Furthermore, this value is significantly lower than the maximum value (120 I₂/100 g) approved by ASTM D6751 for standard fuels. IV is useful for determining the overall degree of saturation of the biofuels, which is important for viscosity and cloud points. The lower the IV, the better the fuel will be as a biodiesel. Biodiesel from vegetable oils with high amounts of saturates (which mean low IVs) will have a higher cetane number (CN), while biodiesel from vegetable oils with high amounts of un-saturates (high IVs) will have a lower CN. Unsaturation in the fatty acid chain is the most significant cause of lower CNs. IVs greater than 50 may result in decreased engine life but give better viscosity characteristics in cooler conditions.

Cetane number is a measure of ignition quality of a fuel. This is the most pronounced change from vegetable oil to the trans-esterified product (biodiesel). Fuels with low cetane numbers show an increase in emission due to incomplete combustion. The lower limit for cetane index is 47 by ASTM standards. The cetane number of the BSO biodiesel is greater than 50 as presented in Table 5, which is above the lower limit for cetane number. The result obtained is acceptable.

Table 5: Fuel properties of Biodiesel compared with ASTM limits.

PROPERTY	UNITS	ASTM METHODS	BSO FAME by AES	ASTM LIMITS
Density	kg/m ³	ASTM D-1298	865	830-880
Kinematics Viscosity	Cst	ASTM D-445	3.90	1.6-6.0
Flash Point	°C	ASTM D-93	165	≥130
Pour Point	°C	ASTM D-97	7	+15 max
Cloud Point	°C	ASTM D-2500	1.2	-15 to 5
Acid Value	mgKOH/g	ASTM D-974	0.5	≤ 0.80
Low Heating Value	MJ/kg		45.9	≥ 35
Aniline Point	(°C)	ASTM D-4737	179	
Higher Heating Value	MJ/Kg		50	
Cetane number		ASTM D-130	59	47 min



Iodine Value	¹² /100g	ASTM D6751	44.33	120
				Max

V. CONCLUSION

The production of biodiesel from Beniseed oil using heterogeneous catalysts (Acid activated eggshell, AES) were carried out. The oil from the seeds was extracted by solvent extraction methods using n-hexane. The result indicated that the extracted oil yield from the seeds using n-hexane solvents was reasonably enough for biodiesel production. The low acid value, iodine value and saponification value of the oil enable it to undergo direct transesterification without treatment with the acid activated eggshell. The biodiesel synthesized by transesterification of beniseed oil has a maximum yield between 70 – 80%. Increase in process parameters such as reaction time, catalyst concentration, methanol/oil ratio, reaction temperature and agitation speed increase the yield of biodiesel to a reasonable point before it decreased. The density, viscosity, cetane index, oxidative stability and higher heating values of biodiesel produced meet the ASTM standard and were within the acceptable limits.

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