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BIODIESEL PRODUCTION FROM PALM KERNEL OIL USING BENTONITE CLAY-SUPPORTED FE-CO NANOCATALYST

Aderibigbe F.A.[1*], Adewoye T. L.[1], Mustapha S. I.[1], Mohammed A. I..[1], Amosa M. I.[2], Saka H. B.[3], Muhammed-Nuhu R. A.[1], Adejumo A. L.[4] and Owolabi R. U.[5]

[1]*Department of Chemical Engineering, Faculty of Engineering and Technology, University of Ilorin, Ilorin, Nigeria*
[2] *Waste Management Unit, HSE Division, Department of Petroleum Resources, 7, Sylvester Ugoh Crescent, Jabi, Abuja-FCT, Nigeria.*
[3]*Quality Control Department, Segmax Oil Nigeria Limited, Kere-Aje, Ogbondoroko, Kwara State, Nigeria*
[4]*Department of Chemical Engineering, Osun State University, Osogbo, Nigeria*
[5]*Department of Chemical Engineering, University of Lagos, Lagos Nigeria*
*Corresponding Author: Aderibigbe.fa@unilorin.edu.ng , +2348033822123

ABSTRACT

This study is focused on the development of a heterogeneous Fe-Co bimetallic nanoparticle on Pindiga bentonite clay support to be used in the production of biodiesel. The local clay was beneficiated and used in the preparation of catalyst by wet impregnation method. The X-ray Fluorescence analysis (XRF) of the bentonite clay showed the presence of several metals and metallic oxides with good catalytic effect. Characterization of the prepared catalyst using Fourier Transform Infared Ray (FTIR), Energy Dispersive Spectrometer, (EDS) X-Ray Dispersion (XRD) and Scanning Electron Microscopy (SEM) confirmed the functional groups, elemental compositions, crystallinity, and morphology of the catalyst respectively. The catalyst was evaluated in biodiesel production using Box-Behnken optimization by varying the methanol: oil mole ratio, reaction temperature, reaction time, and catalyst concentration. An optimum yield of biodiesel (93.8 %) was obtained at process condition of 15:1 methanol: oil mole ratio, 55 °C reaction temperature, 1 h, reaction time, and 15 % (w/w) catalyst concentration. Physicochemical properties of the biodiesel produced using the developed Fe-Co/ bentonite nanocatalyst showed that the biodiesel is of good quality. This was further confirmed by the FAMEs profile. Therefore, the Fe-Co/bentonite nanocatalyst showed potential application as heterogeneous nanocatalyst for the trans-esterification of vegetable oil to biodiesel, an alternative and sustainable replacement for conventional petroleum diesel.

Keywords: Box Behnken design; biodiesel; heterogeneous catalysis; trans-esterification; pindiga bentonite.

Introduction

The worldwide energy utilization is increasing due to fast population growth and industrial development. Without energy, humans will find it tough, if not impossible to sustain both their living standard and economic growth Sanjay (2013). Bulk of these energy requirements are supplied by coal, petrochemical resources, natural gases, petroleum, hydroelectricity and nuclear energy (Dennis *et al*., 2010; Pei-jing *et al*., 2010). Out of all these resources, petroleum has been mostly channeled toward the development of industries, transportation and agricultural sector in order to satisfy the needs of humanity (Basha *et al*., 2009). Due to high level of utilization, the price of petroleum has up surged. Moreover, there have been continual depletion of the petroleum fuel and the exponential emission of their poisonous exhaust into the eco-system.

Due to the emissions of pollutant gases such as CO_2, HC, NOx, SOx, there have been an increase in the world temperature which has consequently leads to the continual global warming crisis. This crisis has encouraged researchers to go in search of an alternative source of fuel Jaimasith & Phiyanalinmart (2007). According to Chouhan & Sarma (2011), the introduction of an eco-friendly green technology is the current focus of the human society in the production of energy. One of the major breakthroughs of green technology is the use of biomass as fuels (biofuel). Consequently, biofuel has become more important because of its environmental benefits such as its biodegradability, nontoxicity and neutral carbon emissions profile. Aside from other biofuels, biodiesel have become more acceptable and simpler to synthesize. Biodiesel is a renewable source of energy produced from vegetable oils and animal fats in the presence of reacting species such as methanol, ethanol or propanol. This process is called transesterification method Ma & Hanna (1999).

The industrial synthesis of biodiesel has been carried out by several methods but the most widely used is the trans-esterification reaction. This

reaction can be catalyzed with homogenous, heterogeneous and enzymatic catalysts. Heterogeneous catalysts are by far more advantageous due to their reusability and the ease to separate easily from the reactant products Sivasamy *et al*. (2009). These heterogeneous catalysts could be made of metal oxides, metal hydroxides, metal complexes and various transition metals Masoud *et al.* (2009).

Aliyu *et al.*(2007) reported that transitions metals possess high surface area and are of high advantage due to their capability to perform an excellent catalytic activity with exceptional mechanical strength. Supporting these catalysts on precursors enhance a more promising activity by increasing the surface area of the catalysts and the catalytic performance. This consequently, increases the yield of biodiesel Hu *et al*. (2011). Different transitions metals such as copper, zinc, nickel, chromium, vanadium, their alloys e.t.c have been researched on over the years.

Supports and fillers from minerals or biomass materials are often used as support system for the nanoparticles. Perfect support for metal composites is clay minerals such as dolomite, zeolite, bentonite, montmorillonite, sepionite, palygorskite, halloysite Zhang *et al*. (2010). These clays are employed due to their environmental and economic advantage. They can be easily found everywhere at no or low cost. Clays generally, possess high chemical and mechanical stability, good specific surface area and structural properties. Swelling and adsorption properties of clay make them an excellent base support for nanoparticles Motshekga *et al*. (2013).

In this study, iron (Fe) and cobalt (Co) were used as a bimetallic nano-sized heterogeneous catalyst. In order to enhance the catalyst performance, the catalyst was also supported on clay material to improve its performance.

Materials and Method

The materials used in this study such as Fe $(NO_3)_3.9H_2O$, $Co(NO_3)_2.6H_2O$, analytical grade methanol and hexane were obtained from Sigma-Aldrich. The palm kernel oil and the Pindiga bentonite clay were obtained from Kwara State, and Gombe State, Nigeria respectively.

Preparation and Beneficiation of the Pindiga Bentonite Clay

The lumped clay of 5 kg was soaked in 50 L of distilled water in a plastic container. The colloidal mixture was stirred for 3 h at room temperature, after which it was allowed to remain in the container for 48 h. This was done in order to obtain fine bentonite particles after gravitational settling of the particles. The colloidal solution was then decanted off, separating the fine particles and discarding the coarse quartz impurities. The fine clay solution was then allowed to settle and then decanted off again. The resulting solution was oven dried at 100 °C for 48 h in order to eradicate the water molecules retained in it. The produced perfectly dried clay was then ground in to powder. The powdered clay was sieved through 80 mesh to obtain uniform particle size. The beneficiated Pindiga bentonite clay was labelled and stored for future use.

Preparation of Catalyst

The method used in the synthesis of the catalyst was the wet impregnation of the metallic nitrates into the clay support. The step-by-step procedures adopted from (Mohammed *et al*., 2017; Kariim *et al*., 2015) are stated as follows: About 7.23 g of $Fe(NO_3)_3.9H_2O$ and 4.94 g of $Co(NO_3)_2.6H_2O$ was accurately weighed and mixed together for 1h. The mixture containing both Fe and Co nitrates was dried at 105 ^oC for 24 h and then ground to obtain fine powder. The fine powder produced was then dissolved in 100 cm^3 of deionized water. 20 g of Pindiga bentonite clay was then added to the solution and it was stirred continuously for 1 h. The resulting slurry was dried at a temperature of 105 ^oC for until constant weight was achieved. The cake produced was allowed to cool to room temperature, ground, and sieved through 150 nm. The resulting powdered catalyst was thermally treated in a furnace at 500 °C for 2 h in order to decompose the nitrate. The calcined sample was then allowed to cool and then sieved through 150 nm.

Characterization of Pindiga Clay and the Catalyst

X-Ray fluorescence spectrometry was used for elemental and chemical analysis of the Pindiga bentonite clay used as a support for the bimetallic catalyst. The synthesized Fe-Co/ Bentonite catalysts was characterized for its crystalline nature, morphological property, elemental compositions, functional groups, and thermal stability using X-ray powder diffraction (XRD), scanning electron microscope with an energy dispersive X□ray spectrometer (SEM□EDS), and FTIR, respectively.

The XRD analysis was performed on a Bruker AXS D8 Advance (USA) with Cu-Kα radiation. A portion of the crystals were sprinkled on a de-greased glass slide, and diffractograms were recorded between diffraction angles of 15º and 80º. The SEM morphology result of the synthesized catalyst was acquired using a high-resolution Zeiss Auriga (USA). A crystal sample (1 mg) was sprinkled onto a carbon adhesive tape and sputter coated with Au-Pd using a Quorum T15OT for 5 min prior to the analysis. The microscope was operated with an electron high tension at 5 kV for imaging. In the FTIR analysis, infrared light in the range 500–4000 cm-1 was used to scan the sample. The sample was prepared using a standard potassium bromide (KBr) and was then placed on a crystal in the Nicholet iS5 spectrometer.

Biodiesel Production

The transesterification reactions were carried out in a shaker. The varying parameters were; temperature 50 ℃, 55 ℃ and 60 ℃; reaction time 1, 2 and 3 h; weight percentage of catalyst 5 %, 10 % and 15 %; methanol: oil ratio 10:1, 15:1 and 20:1 to determine how the biodiesel yield is affected by various combinations of these variables. The reaction stirring speed and initial amount of oil were maintained. The amount of oil required (1 g) were weighed and the catalyst concentrations required were added to different conical flask. After which 2 mL of hexane and the methanol required were added to the mixtures. These mixtures were then charged into the shaker. At the end of the transesterification reaction, the products; biodiesel and glycerol were separated into two separate phases by adding 5 mL of hexane and 5 mL of distilled water and the mixtures separated using separating funnel. The biodiesel contained in the hexane phase was obtained by evaporating the hexane from the mixtures at 70 ^{o}C. The yield of the biodiesel produced from the transesterification reaction was estimated with the Equation 1.

$$yield(\%) = \frac{weight\ of\ biodiesel}{weight\ of\ oil} \times 100 \quad (1)$$

Optimization Process

The experiments were performed according to the Box-Behnken design a response surface methodology (RSM) in design expert Santya *et al.* (2019), a collection of statistical and mathematical techniques useful for modelling and analysing the problems in which a response of interest is influenced by several variables and the objective is to optimize the response. It is an empirical technique developed for analysing and studying the relationship between set of controlled experimental factors and observed results.

To analyse a process mutually with a response Y which mainly depends on the input factors X_1, X_2, X_3....., X_n, the correlation between the response and the input process parameters are described as $Y= f(X_1, X_2, X_3.....,X_n) + \epsilon$, where f is the response function and ϵ is the error. In this design, four independent factors were evaluated, each at three levels and experimental trials were evaluated for all 27 possible combinations generated. Methanol to oil molar ratio, reaction temperature, reaction time and catalyst concentration were chosen as independent variables strength and the biodiesel yield was the dependent variables.

The reaction runs were designed using the design of experiment (DOE) expert. This is as shown in Table 1.

Table 1. Box-Behnken Design Response and Process Condition

Factors	Code	Lower Limit (-1)	Medium Limit (0)	Upper Limit (+1)
MeOH: Oil Molar Ratio (w/w)	X_1	10:1	15:1	20:1
Temperature (℃)	X_2	50	55	60
Reaction time (hr.)	X_3	1	2	3
Catalyst concentration (wt. %)	X_4	5	10	15

Biodiesel Characterization

The produced biodiesel using/ the synthesized catalyst was characterized by Gas Chromatography-Mass Spectrometry. The chemical composition of the biodiesel was determined using a gas chromatograph equipped with capillary column, DB-WAX (30 m, 0.15 mm) and a flame ionization detector with helium as carrier gas. The physico-chemical properties such as density, flash point, pour point, and cloud point were determined for the biodiesel produced and the result was compared to the American Society for Testing and Materials (ASTM) standard to check for conformity.

Results and Discussion

Characterization of Pindiga Bentonite Clay

The elemental composition of the beneficiated Pindiga bentonite clay and the oxide composition and loss in ignition (LOI) were shown in Table 2 and Table 3 respectively. A high loss on ignition (LOI) value was recorded for the clay having a quantitative composition of Silicon, 12.736%; Iron, 3.948%; Aluminium, 1.882%; Magnesium, 0.576%; Titanium, 0.522%; Potassium, 0.908% and Calcium, 0.404 %, Sulphur, 0.276%. The high silicon oxide, iron oxide and aluminium oxide composition indicates that it has a crystalline texture which preludes a purely colloidal explanation of its physical properties. This property gives the bentonite great adsorptive power which is essential on its use as a support for the catalysts during transesterification reaction. The high adsorptive power of the Pindiga bentonite clay ensures high bimetallic catalyst attachment to the surface and the pores of the clay thereby increasing the reactivity of the catalyst in the reaction.

Characterization of Catalyst
FT-IR spectrum of the catalyst

The FT-IR spectrum of the catalyst (Figure not shown) indicates the major absorption bands occurred at 3620.05, 3430.08, 1625.33, 529.82, 469.66 cm^{-1} which are attributed to asymmetrical stretch, out of plane bend and in-plane bend vibration modes denoting alcohols (O-H STRETCH), sulfonic acid (SO_3^-, O-H STRETCH), carboxylic acid salts and sulphur compound (S-S STRETCH) respectively. Also, a major absorption band occurred at 1036.41 cm^{-1} which denotes the presence of sulfoxide. This major absorption bands can be attributed to the thermal treatment of the catalyst indicating high energy levels and decomposition of the nitrate group.

Elemental composition analysis

The chemical characterization of the Fe-Co/Bentonite catalyst was observed from the EDS in Fig. 1. It was observed that the elemental features of the catalyst could be attributed majorly to the bentonite clay and a considerable amount of the principal catalyst iron and cobalt. As reported by the EDS spectrum, the dispersion of the Fe-Co nanoparticles on the bentonite shows that the Fe, Co, Si, Al, O were present in the sample. The spectrum further qualitatively confirms the chemical components of the Fe-Co/Bentonite catalyst. Also, absence of nitrate compound in the elemental composition indicates proper thermal treatment of the catalyst. This result shows that the nitrates were properly decomposed during the thermal treatment of the process.

Table 2. Elemental Composition of Pindiga Bentonite Clay

Element	Amount (%)	Element	Amount (%)	Element	Amount (%)
Loss on ignition (LOI)	78.648	**Zirconium**	0.015	**Arsenic**	<LOD
Silicon	12.736	**Strontium**	0.012	**Selenium**	<LOD
Iron	3.948	**Barium**	0.007	**Niobium**	<LOD
Aluminium	1.882	**Chlorine**	0.007	**Molybdenum**	<LOD
Potassium	0.908	**Zinc**	0.006	**Palladium**	<LOD
Magnesium	0.576	**Rubidium**	0.002	**Silver**	<LOD
Titanium	0.522	**Lead**	0.002	**Cadmium**	<LOD
Calcium	0.404	**Phosphorus**	<LOD	**Tin**	<LOD
Sulphur	0.276	**Manganese**	<LOD	**Tungsten**	<LOD
Vanadium	0.016	**Cobalt**	<LOD	**Aurum**	<LOD
Chromium	0.015	**Nickel**	<LOD	**Bismuth**	<LOD
Antimony	0.014	**Copper**	<LOD	Total	**99.996**

LOD: Low Detection

Table 3. Oxide Composition of Pindiga Bentonite Clay

Oxide	**Amount (%)**	**Oxide**	**Amount (%)**
SiO_2	27.255	Cr_2O_3	0.023
Fe_2O_3	5.645	ZnO	0.007
Al_2O_3	3.558	CuO	0
MgO	0.955	NiO	0
TiO_2	0.872	MnO	0
CaO	0.566	Loss on ignition (LOI)	61.119
		Total	100.000

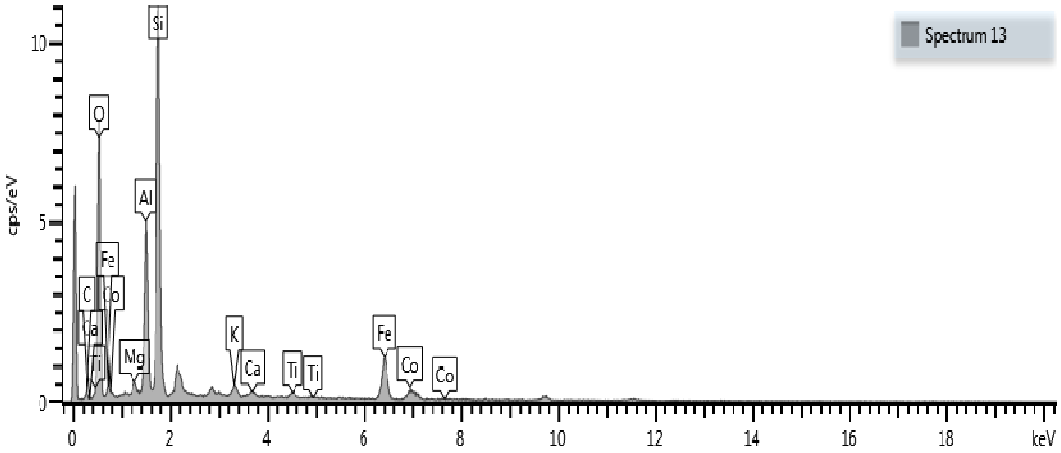


Fig. 1. EDS Spectrum of the Fe-Co/bentonite Catalyst

XRD Analysis

The crystallographic structure of the Fe-Co/Bentonite catalyst as viewed using an Advance X-Ray Diffractometer is represented in Fig. 2. The major peak was observed at 26° showing the intensity of crystallinity. This peak represents quartz (SiO_2) present in the clay which is a highly crystalline substance. The remaining peaks on the plot represent the presence of orthoclase ($KAlSi_3O_8$) and montmorillonite (Na_x (Al, $Mg)_2Si_4O_{10}(OH)_2$. zH_2O) in the catalyst composition which are components of the bentonite clay used. The high crystallinity of the catalyst is an important property on its behaviour, since highly crystalline solids will be easily separable from the reaction mixture.

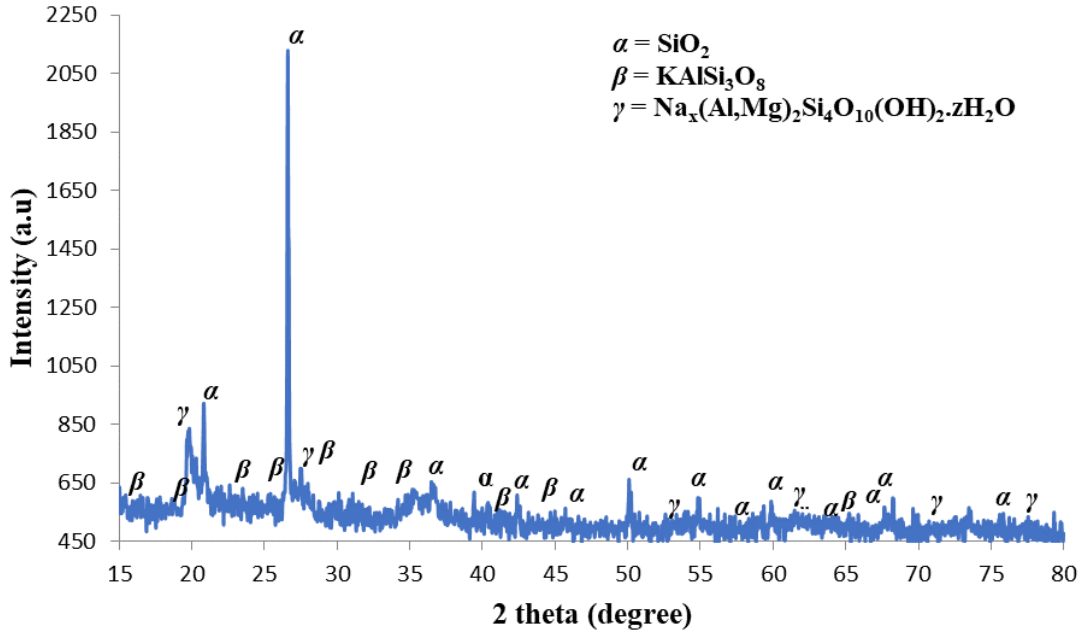


Fig. 2. X-ray Diffractograph of the Fe-Co/bentonite Catalyst

Morphological analysis of the catalyst

.Fig. 3 (a-d) are the SEM images at various magnifications and 20 µm, 200 nm and 100 nm scales. The SEM image as presented in Fig. 3 (a) shows granules of the catalyst material fused by the clay bentonite. It can also be described as highly crystalline, which has been earlier confirmed by the XRD image. Fig. 3 (b), shows the nanoparticles are sparsely distributed on the bentonite support showing few clusters of the nanoparticles and it identifies pores occurring between the composite layers and not within the nanoparticle itself. At higher magnification, Fig. 3 (c), shows that the size of the Fe-Co nanoparticle can be said to be about 80 nm and at lesser magnification in Fig. 3 (d), the dispersion of the catalyst is clearly seen and the

shape of the Fe-Co catalyst on the support material is flaky. This is an important property denoting clay material. The nanoparticle shape and size play a large role on the density, and porosity characteristic of the catalyst.

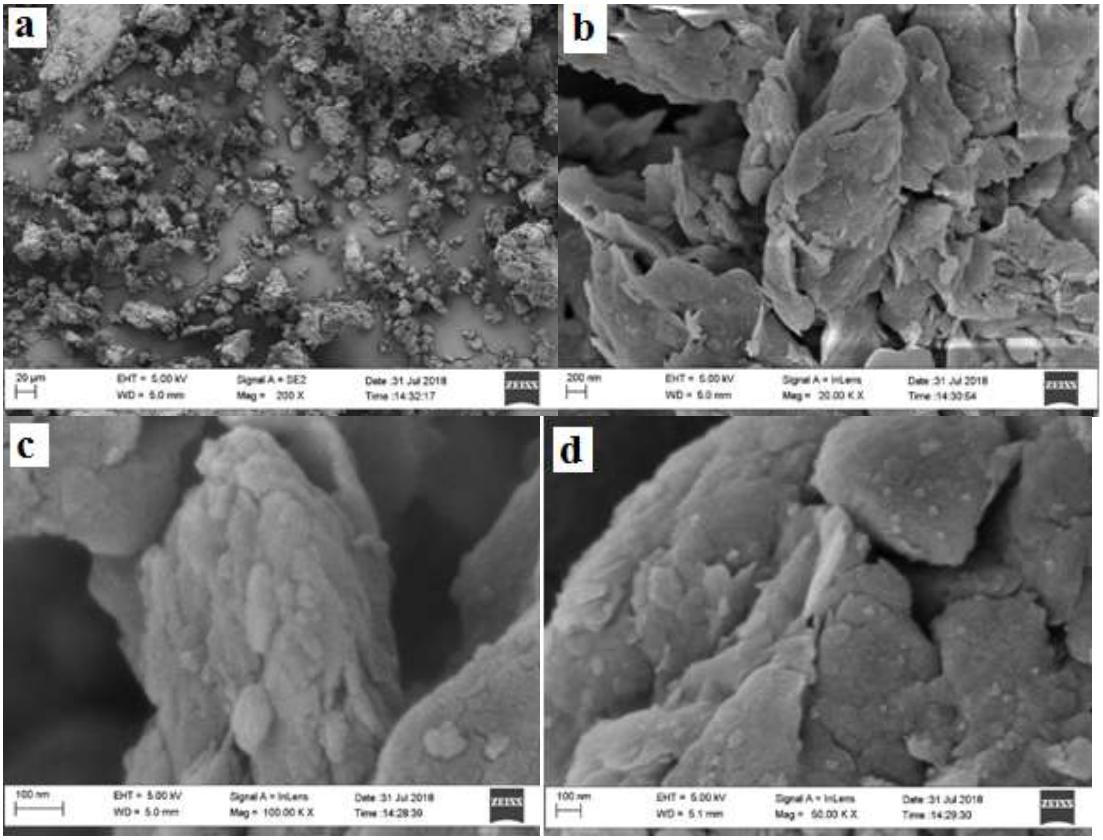


Fig. 3. HRSEM Image Showing Nanoparticles of Fe-Co Dispersed on Bentonite Support at (a) 20 µm, (b) 200 nm, and (c), (d) 100 nm scales.

Optimization of biodiesel produced using the prepared catalyst

The effect of each variable parameter on the yield of biodiesel is presented in Table 4. Experiment run 4 shows the optimum yield of biodiesel of 93.80 % with methanol/oil ratio 15:1 at 55 ^{0}C temperature, 1h reaction time and 15 % (w/w) catalyst concentration. The stoichiometric ratio for transesterification reaction involves three moles of alcohol and one mole of triglyceride to produce three moles of fatty acid ester and one mole of glycerol. The molar ratio of methanol to vegetable oil is also one of the most important variables affecting the yield of methylesters. Higher molar ratios result in greater ester production in a shorter time. Mazaheri *et al*. (2018) reported a FAME yield of 93.5 % using *Chicoreusbrunneus* CaO nanocatalyst under the following conditions: calcination temperature of 1100 °C, catalyst content of 0.4 wt%, the reaction time of 120 min, and molar methanol to rice bran oil ratio of 30:1. In another study with the transesterification of sunflower oil in the presence of Calcium oxide catalyst at 525 K, the transesterification reaction was basically completed within 6 min with 3 wt% CaO and 41:1 methanol/oil molar ratio Demirbas, (2007). Biodiesel yield was reported at optimum condition methanol/oil ratio of 6:1 and catalyst concentration of 2 % NaOH by Saifuddin and Boyce (2016). Optimum yield of FAME of 87.77 % for river catfish oil and 96.23 % for waste cooking oil catalyzed by waste chicken egg shells derived catalyst were obtained under the same optimum conditions of 12:1 of molar ratio of methanol/oil, 1.5 wt% of catalyst loading, 60 min and 60 °C were reported by Gopalan *et al.* (2019). Ghoreishi and Moein (2013) reported optimum predicted yield of 95.27 % (g/g) with 33.8:1 (methanol/oil molar ratio) 271.1 ^{0}C, 23.1 MPa and 20.4 min reaction time with transesterification reaction of waste vegetable oil in supercritical methanol.

Table 4. Summary of the Best Four of the Twenty-Seven Experimental Results for the Process Conditions and Response for the BBD

Run	MeOH: Oil Mole Ratio (w/w)	Temperature (°C)	Reaction Time (hr.)	Catalyst Conc. (wt. %)	Biodiesel Yield (%)
4	15:1	55	1	15	93.80
9	10:1	60	2	10	91.40
18	10:1	55	3	10	90.90
26	20:1	55	1	10	91.90

Characterization of Biodiesel Produced

1.Physiochemical characteristics of the biodiesel

The physiochemical properties of the palm kernel biodiesel give an appreciable result for density, flash point, cloud point and pour point as compared with ASTM standard are shown in Table 5. The physicochemical properties of the biodiesel produced conform to the ASTM standard.

Table 5. Fuel Properties of Biodiesel Produced and Biodiesel Standard

S/N	Fuel properties (units)	Biodiesel	ASTM standard for biodiesel
1	FAME content (%)	99.20	≥96.5
2	FFA (%)	63.52	—
3	Density @ 15 °C (g/cm^3)	0.864	0.860-0.900
4	Flash point (°C)	186	≥130
5	Pour point (°C)	-12	-15- 10
6	Cloud point (°C)	-5	-3- 12
7	Fire point (°C)	198	190
8	Acid Value (mg KOH/g)	0.78	≤0.80

Fatty Acid Methyl Ester (FAME) profile analyses

The GCMS analysis result reveals information on the nature of methyl esters present in the biodiesel. The graphical profile of the major esters is shown in Fig.4. The fatty acid profile of the biodiesel shows that 60.43 % are unsaturated fatty acids and 38.77 % are saturated fatty acids. This profile shows that the produced biodiesel has a high unsaturated fatty acid composition. According to Gopinath *et al*. (2010) biodiesel with high value of unsaturated fatty acids emits lower hydrocarbon, lower carbon monoxide, lower smoke emission, lower thermal efficiency and high NOx emission as compared to the biodiesel with more saturated fatty acid. Also, combustion of the unsaturated fatty acid biodiesel has longer premixed condition, high peak pressure and low heat release rate.

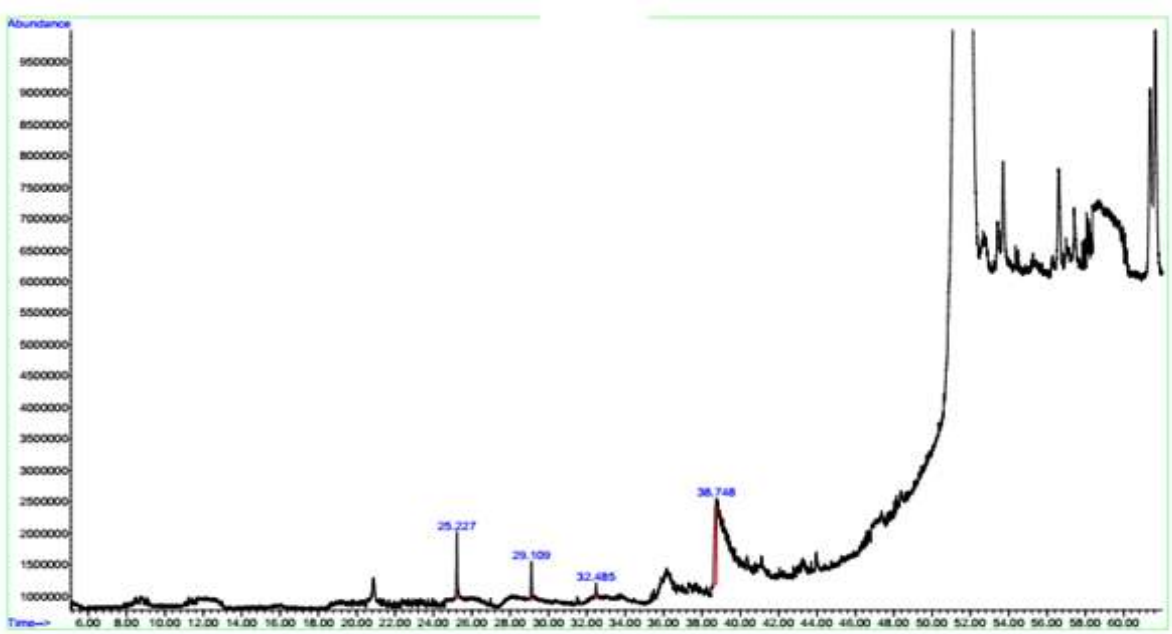


Fig. 5. Profile of Fatty Acid Methyl Ester of Biodiesel

Conclusion

It can be concluded that the optimal conditions for the optimum yield of 93.80 % biodiesel using the BBD were: MeOH: Oil mole ratio (15:1, w/w), reaction temperature (55 °C), reaction time (1 h) and catalyst concentration (15 wt. %). The physicochemical properties of the biodiesel produced conform to the ASTM standard. The fatty acid methyl esters (FAME) profile as shown by the GCMS further confirmed the quality of the biodiesel produced. Hence, the bimetallic nanocatalyst on a bentonite clay support synthesized was an effective heterogeneous nanocatalyst for biodiesel production.

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Disclosure of any Conflict of Interest

The authors declared that there is no conflict of interest

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