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Biofuel (FAEE) Synthesized from the Blends of Oil Using Calcined Submerged Fermented *Theobroma cacao* pod husk

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Abstract

This study utilized a combination of lard fat and waste cooking oil to synthesize biofuel, employing calcined submerged fermented Theobroma cacao pod husk as a catalyst. The oil blends were prepared in ratios of 20:80, 40:60, up to 100:0, with the aim of achieving oils with low viscosity and low acid values. The catalyst was developed and characterized through SEM, FTIR, XRD, and BET adsorption isotherm techniques. The properties of the resulting biodiesel were assessed and compared against international biodiesel standards. Results demonstrated that the blend ratio of BLW60 (60:40) yielded the optimal blended oil, characterized by low viscosity and low acid value. Catalyst analysis revealed a high CaO content of 87.65% as determined by XRD analysis. The biodiesel produced reached a maximum yield of 96.53% (wt./wt.) at a reaction temperature of 70 minutes, with a CSFCPA amount of 1.6 g, and an ethanol-oil molar ratio of 7:1. The properties of the biodiesel met international standards. The study concluded that the submerged process enhances the catalyst's basicity, and the biodiesel produced can serve as a substitute for conventional diesel.

Keywords: Blends oil; Submerged; Calcined; Fermentation; Biodiesel; Physicochemical properties; FAEE

1. Introduction

Numerous chemical reactions require one or more catalysts to achieve completion. The specific type of catalyst utilized in a given reaction is determined by the reaction conditions and the characteristics of the reactants involved. While catalysts are not consumed during the reaction, their presence accelerates or moderates the reaction rate, and they are recovered at the conclusion of product formation. Currently, various industries, including pharmaceuticals, polymers, petroleum, electronics, environmental treatment, chemicals, and agrochemicals, utilize catalysts to produce their final products. Catalysts are primarily classified into four categories: homogeneous catalysts, heterogeneous catalysts, heterogenized-homogeneous catalysis, and biocatalysts. Among these, a heterogeneous catalyst, typically a solid calcium-based compound derived from solid waste, is employed as a base catalyst in the conversion of oil to biodiesel due to its advantages such as

ease of recovery, reusability, non-toxicity, and low synthesis cost. Biodiesel is a bio-renewable, environmentally friendly, non-toxic, and sustainable alternative fuel produced from the synthesis of vegetable oils or fats. To bridge the gap between the efficiency of developed catalysts derived from single or mixed solid wastes and to introduce a novel blend ratio through BLW, BLW20, BLW40, ..., BLW100 at intervals of 20 between Lard Oil (LO) and Waste Used Cooking Oil (WUCO) for the process industry (bio-fuel or margarine), this study developed three CaO-based catalysts from submerged fermented calcined Theobroma cacao pod husk (SFCTCPH) and applied them for the synthesis of biodiesel from the BLW. The prepared catalysts were characterized using Scanning Electron Microscopy (SEM), FTIR, X-ray diffraction analysis (XRD), and BET isothermal adsorption. The suitability of the biodiesel for use in an internal combustion engine was assessed by evaluating its physicochemical properties.

2. Materials and Methods

2.1 Materials

WUCO was gotten from University cafeteria, Akwa Ibom State University; Lard fat (LF) was obtained from a slaughterhouse in Ikot Akpaden,Akwa Ibom State, Nigeria. The WUCO was thermally heated in a reactor pot at 130 ^{o}C placed on the temperature regulated hot plate for 20 min, and allowed to cool at at room temperature before sieved to eliminate impurities. The filtered oil made cleaned was kept in a 5 L tight keg for further used. Meanwhile, the LF was thoroughly washed in an open vessel with 1.0 N Na_2CO_3, and stirred for 10 min via mechanical mean. The resulting mix was centrifuged at 2500 revolution per minute for 12 min at a temperature of 35 ^{o}C using a polypropylene tube. The supernatant was separated by filtration, and 30 g of anhydrous Na_2SO_4 was added, stirred for 5 min, and was re-centrifuged again for 10 min at a temperature of 25^{o}C (Adepoju, 2020). The purified LF oil (LFO) acquired was kept in a tightly covered container for further use.

Cocoa pod husk was obtained from Cocoa processing factory in Ondo State, Nigeria. The pod husk was cleaned by washing with ionized water, and was decanted, kept overnight to allow proper draining. The drained cocoa pod was fermented in distilled water anaerobically (submerged) for 7 days, and then the fermented sample was separated from fermented water by decantation, dried in an oven at 100 ^{o}C until a constant weight was achieved (bone dried). The dried fermented sample was milled and sieved into powder of 0.25 mm particle size before calcined at 800 ^{o}C for 3 h in a furnace. The calcined sample was left in the furnace for 24 h for proper cooling, and then placed in cleaned container for further characterization to determine their potential as a heterogeneous catalyst for industrial application (biofuel production). The calcined submerged fermented cocoa pod ash is dented by (CSFCPA)

All chemicals used in this study were of analytical graded and need no further purifications, and were supplied by Sigma Aldrich.

2.2 Catalyst characterization

CSFCPA was characterized by SEM to study the surface morphology of the samples, while the XRD equipped with Kά and Cu radiation source, accelerated at 20 mA and 40 kV, to establish the angular scanning electron performed in the range of $10^{o}<2\theta<80^{o}$ at speed of 2.5^{o}C min^{-1}and to verify the elemental analysis of the samples and the quantitative composition of the samples. FTIR was used to confirm the presence of functional group and verify the presence of characteristic absorption bands of major elements present within the crystals powder structures. The pore volume, surface area, basic density site, and the total basic density were examined using BET isothermal adsorption.

2.3 Blending of oil (LW) and physicochemical properties

The key factors to be considered in blending of oils are the viscosity, volatility, and acid value. This study adopted the following blend ratios in volumetric ratios as; 20:80 (BLW_{20}), 40:60(BLW_{40}), 60:40 (BLW_{60}), 80:20 (BLW_{80}), 100:0 (BLW_{95}), respectively. These ratios were chosen to ascertain oil with low viscous, high

volatility, and low acid value that enhanced higher biodiesel yield using the derived CaO-based heterogeneous catalysts.

The blended oil in different ratios was properly mixed by heating at 50 ^{o}C on a hot plate for easy miscibility considering the instability in Lard fat oil nature. Each resulting mixture was examined for its viscosity, the acid value, and the specific gravity. The mixture with low acid value, low specific gravity, and low viscosity was used for biodiesel synthesis. Other properties of the blended oil were further determined using the association of official analytical chemists (AOAC 1997 and AOAC 1990).

2.4. Biodiesel production

Production of biodiesel was carried out through the ethanolysis of CaO-based catalyst derived from the CSFCPA. The reaction process take placed in a 1 L capacity-three-necked-reactor, 200 mL of the BLW was first preheated on a hot plate with a magnetic stirrer for 60 min at 110 ^{o}C. 2.5 (wt.) of CaO-catalyst was measured in a 250 ml dried-cleaned flask, and 50 ml of ethanol was measured and added to the ethanol flask to achieved EtOH/OMR of 1:4. The mixture was placed on a shaker for 15 min and then added to the preheated oil on the hot plate. Two layers were observed, the ethanol-catalyst layer, and the oil layer, the stirrer was inserted, and the reaction was monitored at 70 ^{o}C for 65 min.

At the reaction completion, the insoluble catalyst was separated through decantation, and the remained product (ethanol-biodiesel) was distinguished through gravity in a separating funnel. The obtained fatty acid ethyl ester (biodiesel) contained adherent catalyst (leached catalyst), which was removed by washing with hot methanolic sodium carbonate (1.0 g $NaCO_3$ dissolved in 20 ml methanol), and was well stirred. The washed mixture was filtered, and the filtrate-diesel was washed with distilled water twice before water-diesel separation through gravity settling. The water wet-diesel was dried over anhydrous Na_2SO_4, before separation by decantation to obtain pure biodiesel (fatty acid ethyl ester: FAEE). The residual residue filtered catalyst was collected for reused but was firstly purified. This process was conducted based on the number of productions carried out.

2.5 Properties of FAEE

Properties of the FAEE such as density, viscosity, moisture content, mean molecular mass, acid value, Saponification value, iodine value, peroxide value, cetane number, higher heating value, and API gravity were determined to ascertain its suitability as a replacement for conventional fuel in an internal combustion engine (I.C. engine), via AOAC, 1997. The results were compared with ASTM D6751 and EN 14214 recommended standard.

3. Results and discussion

3.1. Physicochemical properties of the BLW

Presented in Table 1 are the results of the physicochemical properties of the BLW in different ratios. Observation from the table indicated that the BLW in the different ratios have the same percentage moisture content of 0.02%, all other blends have different values. However, since the major key factor in the selection of any oil is the viscosity and specific gravity of the oil, therefore, the BTO_{60} with the low viscosity of 22.30 mm^2/s and a specific gravity of 0.890 was selected as BLW for FAEE production. This BLW produced lighter oil with low acid value and high API gravity (Adepoju et al., 2020).

Table 1: Physicochemical properties of the BLW

Blends	**Physicochemical Properties**						
Ratio (BLW)	MC (%)	SG	V @ 40 ^oC (mm^2/s)	AV (mgKOH/g oil)	SV (mg KOH/g oil)	IV (meq O_2/kg oil)	API g
BLW_{20}	0.020	0.912	24.90	0.303	189	60.03	23.65
BLW_{40}	0.020	0.905	23.50	0.283	186	59.80	24.85
BLW_{60}	0.020	0.890	22.30	0.249	180	58.88	27.49
BLW_{80}	0.020	0.911	22.86	0.272	188	59.94	23.82
BLW_{100}	0.020	0.914	22.96	0.277	191	59.89	23.36

M = Moisture content, SG = Specific gravity, V = Viscosity, AV = Acid value, IV = Iodine value, PV = Peroxide value,
SV = Saponification value, API g = API gravity

3.2. Characterization and analysis of catalysts

3.2.1 Scanning Electron Microscopy (SEM) analysis

The morphological characteristic of the catalyst was carried out by SEM analysis. Fig 1 displayed the result of SEM analysis of CSFCPA at magnification of 500x, but different structural outlook performed in 2θ diffraction with a peak from $20^o<2\theta < 70^o$ at speed of 2 ^oC/min. Observation from the morphological structure of CSFCPA indicated a uniformly distributed structure with smaller sizes and shapes and a high surface area. This could be due to *submerged fermentation* which involves *the* growth of *the* microorganism in a homogeneous medium (inter-particle space and *surface* area) of *the* substrate and moisture content. However, it was observed that the release of the CaO from $CaCO_3$ was complete at the calcination temperature of 800^oC (Betiku *et al*, 2017).

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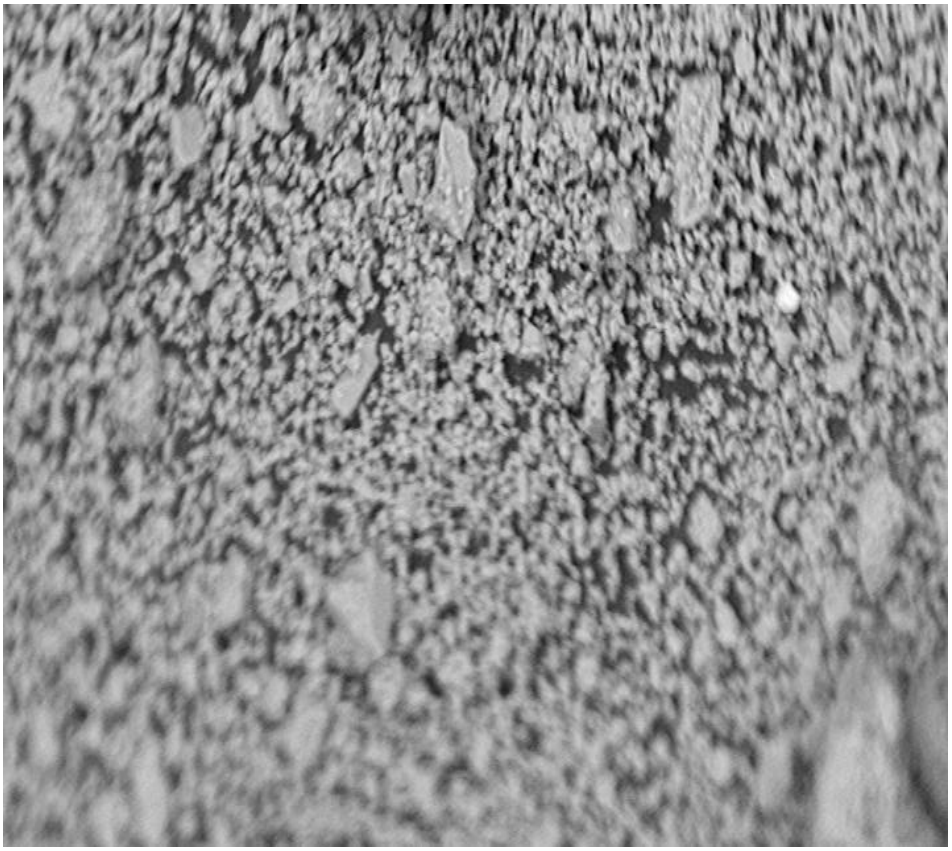

Fig. 1: SEM images of CSFCPA

3.2.2 Fourier-transform infrared spectroscopy (FTIR) analysis

The results of FTIR analysis of the CSFCPA catalyst was displayed in Fig. 2. The spectral showed a sinusoidal waveform at different peaks confirming the effects of heat on the thermal degradation of the catalyst. The vivid descriptions of the wavelengths at different peaks for the catalyst which showed the stretches and the bending vibration of organic-inorganic functional groups present are presented in Table 1. The bands between 752.9 – 913.2 cm^{-1}observed for CSFCPA, specified the presence chlorocarbon (C-Cl), O = C = O bending vibration, nitrogen to carbon bond waging and twisting, and the presence of CO_3^{2-} molecules at a lower temperature. The stretches range between 1036.2–1699.7 cm^{-1} observed in CSFCPA, indicated that fermentation process involved. Furthermore, the value range of 1893.5 – 2322.1 cm^{-1}observed in the wavelength bands of CSFCPA, indicated the presence of C=O of ketone, -CHO of aldehyde, C=C of ester, C-C of alkyne/acetylene, C-N of cyanogen, and O-H of complex molecules. Further observation also indicated the presence of O-H bending structure in alcohol and phenol, O=O of dioxygen, and NO of sp were found in CSFCPA at wavelength bands of 3641.6 – 3753.4 cm^{-1}, the long stretches (> 3500) found in CSFCPA showed the presence of amine and amide bonding structures (Arjun et al., 2019; Fayazishishvan et al., 2018). This showed that fermentation increased the presence of functional groups and the surface area of the sample.

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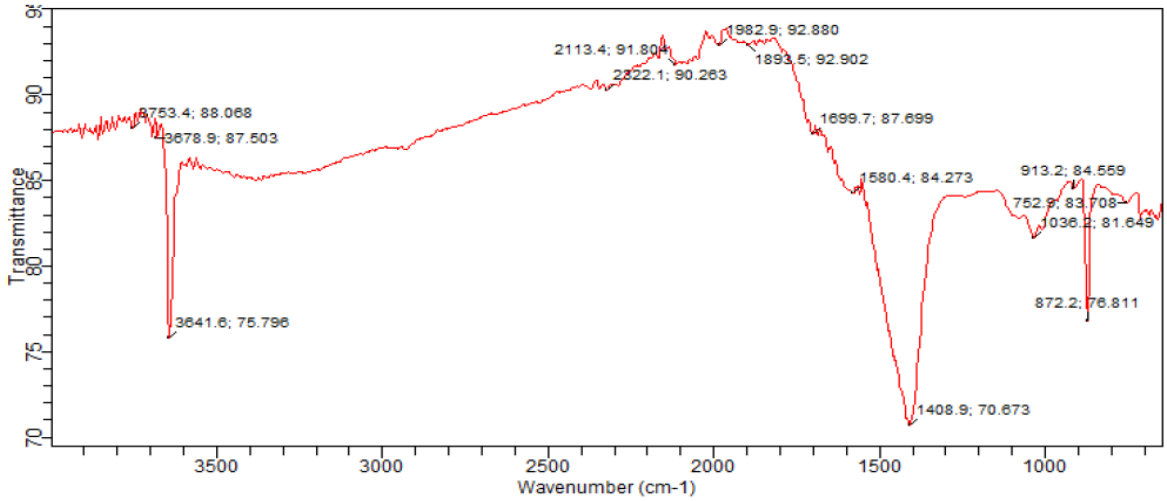

Fig. 2: FTIR spectral analysis of CSFCPA

Table 3: FTIR sample spectrum analysis of CSFCPA

SN	Wavelength (cm^{-1})	Transmittance (%)	Bonds and Functional groups
1	752.9 – 913.2	83.708 – 84.559	C-Cl, C-C. CO_3^{2-},N-H waging and twisting, O=C=O bending vibration
2	1036.2 - 1699.7	81.649 – 87.699	C-C, C=C, C=N, and O-Ca-O bending vibration
3	1893.5 – 2322.1	92.902 – 90.263	C=O, CHO, C≡C, C≡N, and O-H
4	3641.6 – 3753.4	75.796 – 88.068	O-H bending structure, O=O, N≡O, Amine, and Amide

3.2.3 Brunauer-Emmett-Teller (BET) and XRD analysis

Displayed in Table 3 are the results of the analysis of BET and XRD of the catalysts sample. A strong basic site (196) was found in the catalyst which suggested that the produced catalyst was capable to be used as heterogeneous catalysts for FAEE production, as well as for other industrial applications. The basic site density does not depend on the pore volume of the catalysts but depends solely on the surface area of the catalysts. The higher the surface area, the lesser the basic site density, hence, the value of 178.18 μmole/m^2 obtained. The results of XRD analysis showed that the total basic site was responsible for the high conversion of calcium carbonate to calcium oxide (CaO). Even, when the calcination temperature was responsible for the formation of CaO with gaseous evolution of CO_2, the reaction is not complete without the process route. Truly, the fermentation process increased the content of CaO obtained in the catalysts with high conversion yield of FAEE yield of 96.20% (wt./wt.).

Table 2: BET and XRD analysis of the catalysts

Catalysts	β (m^2/g)	λ (cm^3/g)	CaO (%)	BS (µmole.g^{-1}) 400<BS<650	>650	TBS	BSD (µmole/m^2)	FAEE %(wt./wt.)	CA (wt.%)
CSFCPA	1.10	0.0030	87.65	22	174	196	178.18	96.53	2.50

β = Surface area, **λ** = Pore volume, BS = Basic site, TBS = Total basic site, BSD = Basic site density, GD = Green diesel, CA = Catalyst amount

3.3. Biodiesel experimental results

Displayed in Table 4 are the results obtained for every experimental run carried out in the presence of constraint variables reaction time, catalyst amount, and ethanol-oil molar ratio using CSFCPA developed from cocoa pod husk. Observation from the table showed that FAEE highest yield of 96.53 % (wt./wt.) was obtained. This value indicated that the calcined submerge fermented cocoa pod husk powder produced highest FAEE yield at run 3 at reaction temperature of 70 min, CSFCPA amount of 1.6 g , and ethanol-oil molar ratio of 7:1, respectively. It's therefore concluded that fermentation increased the basicity of the catalyst hereby improved biodiesel yield (Adepoju et al., 2020c).

Table 4: The variables and the biodiesel yields

Runs	Reaction time (min)	CSFCPA amount (g)	ethanol-oil molar ratio (vol./vol.)	Biodiesel yield
1	50	1.2	3	92.40
2	60	1.4	5	94.12
3	70	1.6	7	**96.53**
4	80	1.8	9	95.42
5	90	2.0	11	92.20

3.4 Fatty acid ethyl ester (FAEE) qualities and its comparison with standard

Table 5 displayed the results of the qualities of the FAEE produced with the references to ASTM and EN. Observations from the table indicated; this could be attributed to the calcination process involved in the sample preparation, causing the gaseous evolution of CO_2 from the $CaCO_3$ at a controlled temperature more than burning. The properties of biodiesel produced were well within the recommended standard stated by ASTM D6751 [22] and EN 14214[23].

Table 5: Qualities of the produced FAEEs

Properties	FAEE (biodiesel)	ASTM D6751	EN 14214
Colour@ 27 °C	Light yellowish	-	-
State @ room temp	Liquid	Liquid	Liquid
Specific gravity	0.864	-	860-900
Viscosity @ 40 °C/ (mm^2/s)	2.78	1.9-6.0	3.5-5.0
Moisture content (%)	<0.01	<0.03	0.02
%FFA (as oleic acid)	0.018	0.40 max	0.25 max

Acid value (mg KOH/g oil)	0.036	0.80 max	0.50 max
Iodine value (g I_2/100g oil)	53.62	ND	120 max
Saponification value (mg KOH/g oil)	172.22	236.66-253.04	ND
Peroxide value (meq O_2/kg oil)	8.60	ND	12.85
HHV (MJ/kg)	41.52	ND	ND
Cetane number	65.92	57 min	51 min
API gravity	32.27	30-42	ND
Diesel index	52.04	50.4 min	ND

ND = Not Determine

Conclusion

The blending ratio of oil 60:40 (BLW_{60}) effectively produced a low oil acid value. Calcined Submerged fermented *Theobroma cacao* pod husk demonstrated a potential catalyst for FAEE production and its efficacy could be attributed to the high percentage of calcium present. High biodiesel yield (FAEE) of 96.53 %(wt./wt.) at reaction temperature of 70 min, CSFCPA amount of 1.6 g , and ethanol-oil molar ratio of 7:1, respectively Based on catalyst BET adsorption analysis, the percentage CaO-based obtained from the developed catalyst showed *Theobroma cacao* pod husks could be used as industrial feedstock, and the properties of the FAEE are within the ASTM D-6751 and EN 14214 biodiesel standard specifications.

Declarations

Ethics approval and consent to participate

Not Applicable

Consent for publication

All authors consented and agreed to take part in this study as research participant.

Competing interests

Authors declares no competing interests whatsoever

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AOAC. Official methods of analyses of the Association of Official Analytical Chemists. 1997

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