

Quaternary blend of *Carica papaya* - *Citrus sinensis* - *Hibiscus sabdariffa* - Waste used oil for biodiesel synthesis using CaO-based catalyst derived from binary mix of *Lattorina littorea* and *Macra coralline* shell

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ABSTRACT

These studies focuses on synthesizing of an efficient CaO-based-catalyst derived from the binary mixture of *Lattorina littorea* (periwinkles shell) and *Macra coralline* (seashell), and apply it to transesterification of a quaternary mix of *Carica papaya* - *Citrus sinensis*- *Hibiscus sabdariffa*- Waste used. Details characterization of the developed catalyst was carried out using SEM, FTIR, and XRD to establish its catalytic potential. Process parameters optimization for the transesterification process was carried out to determine the optimum yield of biodiesel from oil blend. *Lattorina littorea* and *Macra coralline* were made into powder by milling after drying, the powdered were mixed in the same ratio to obtain a developed catalyst before characterization. Oil was extracted from *Carica papaya*, *Citrus sinensis*, *Hibiscus sabdariffa* seed powder through solvent extraction method, the extracted oil was mixed in quaternary ratio with waste used oil, the properties of the mixed oil was determined before the transesterification with ethanol. Process optimization was carried using response surface methodology (RSM) coupled with central composite design (CCD) by considering four independent variables (reaction time, derived calcined catalyst powder (DCCP) amount, reaction temperature, and EtOH/OMR). The catalyst recyclability test was carried out, and the biodiesel quality was determined through physicochemical properties. The results showed 25:25:25:25 quaternary blend produced oil with low viscous and high volatility. Thermal treatment of a developed catalyst (DP) from *Lattorina littorea* mix with *Macra coralline*, at 900 °C for 3 h produced CaO of 99.02 (% wt.) on XRD analysis result. The produced catalyst developed was re-used up to 3-cycles for base transesterification. The maximum experimental yield of 99.95 (% wt.) at a reaction time of 60 min, DCCP amount of 3.0 (g), reaction temperature of 70 °C, and EtOH/OMR of 6:1 (ml/ml), was obtained, but the statistical optimization predicted biodiesel yield of 99.8044 (wt. %) at a reaction time of 57.72 min, DCCP amount of 3.0 (g), reaction temperature of 69.54 °C, and EtOH/OMR of 6:1 (ml/ml), this yield was validated in triplicate and an average biodiesel yield of 99.7800 (%wt.) was obtained. Analysis of variance and the p-value showed that the selected variable factors were remarkably significant (p-value<0.0001). Based on fit statistics and model comparison statistics, the coefficient of determination (R squared) of 99.84% was obtained with the predicted R² of 99.06 in reasonable agreement with the adjusted R² of 99.68. The quality of biodiesel produced was within the specification limits of biodiesel standard.

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1. Introduction

To work towards a secure, sustainable future, increase energy security and avert conservational degradation, researchers have

tailored researches towards the use of renewable energy sources. Despite an awareness created by European Union Membership Countries and the United States to increase biofuel production, fossil fuels still exist as a double-edged sword for most countries. On one hand, they still make up a dominant piece of the current energy mix, and oil is still seen as a crucial resource for achieving geopolitical significance. It's no secret that fossil fuels are the driver for many socioeconomic around the world. Nevertheless, with the

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continuous uncertainty and increasing environmental impact associated with the utilization of petroleum-based diesel fuel, a need for replacement of fossil fuels with renewable, sustainable, economically feasible, environmentally friendly and clean energy biodiesel is a safe and sustainable future for all the countries [1].

Biodiesel was defined as a fatty acid methyl ester (FAME), and derived from vegetable oils and animal fats [2,3]. It is a sulfur-free, non-toxic, renewable, biodegradable, clean-burning, ester-based, and it is an oxygenated fuel [4–6]. In another study [7], define biodiesel as a derivative of biomass material produced through modern biological routes. Generally, biodiesel can be produced using edible and non-edible sources, but, owing to the edible source which is also consumed as food, a new avenue of producing biodiesel via a non-edible source crop such as the *carica papaya*, neem, *citrus lanatus* and sorrel seeds as potential feedstocks for second-generation biodiesel is necessary [8].

Carica papaya, *Citrus sinensis*, *Hibiscus sabdariffa* seeds are tropical fruits, mainly cultivated in tropical climates (Africa, Asian and South America), the fruits contained approximately 15–20% seeds, generated in the form of dregs and discarded as biomass wastes during the processing of the fruits, thereby causing an environmental problem. It has been reported that the seeds of these plants contained 13.9–34% oil for *Carica papaya* [9,10], 34–56% oil for *Citrus lanatus* [11,12], and 18–25% oil for *Hibiscus sabdariffa* [13–15]. Therefore, the oil can serve as feedstocks for industrial applications, such as the synthesis of biodiesel. Meanwhile, the percentage of free fatty acid (FFA) of any oil determines the process of biodiesel synthesis. Oil with FFA < 1.5 requires biodiesel synthesis via transesterification while oil with FFA > 1.5 always requires acid esterification before transesterification [16]. For transesterification of biodiesel, the use of homogeneous or heterogeneous catalysts have been tested [17–23]. The disadvantages of using homogeneous catalysts include; high price cost, toxic effect, in-ability to recycle, hygroscopic nature, time-consuming in washing process making it difficult to separate glycerol from biodiesel and utility wastage. Heterogeneous catalysts, however, comprises of many advantages over the use of homogeneous catalysts which includes non-toxic easily recycle and reuse, non-hygroscopic and availability at low cost. Meanwhile, heterogeneous catalysts can be obtained from biomass waste, animal bones, activated carbon-supported catalyst, and waste coral [24–29]. These catalysts are classified into different form and have been developed, employed for biodiesel synthesis. Further studies showed that the use of shells [30,31], agricultural wastes [17,32–37], cement clinker [38], hydrated lime [39], and quicklime [7,16,40–44] as a bio-base catalyst for the synthesis of biodiesel have been tested using various vegetable oil. Further reports on the use of solid based catalyst from waste materials and the reaction conditions are presented in Table 1.

Meanwhile, the use of a mixture of oils in different proportions

(70:30; 50:50; 25:75; 40:60), have been exploited for biodiesel synthesis, and the reports recorded high conversion yield of biodiesel [42,45–47], but, all of these reports utilized the mixture of two/three oils and also used homogeneous catalyst (KOH/NaOH) for transesterification process of biodiesel production apart from the work reported by Ref. [48], where heterogeneous based catalyst used was derived from elephant ear tree pod husk in biodiesel production intensification via microwave irradiation-assisted transesterification of two oil blend. Recently, more similar work was carried out by Ref. [49], where biodiesel synthesis from the blend of oil with a developed catalyst from the mixture of three agrowastes. However, the blend of the oils should not be seen as “likelihood approach” rather, it should be based on the oil physicochemical parameters to avoid internal engine problems when used. Therefore, the key factors to be considered to achieve proper oils blend are the viscosity, the specific gravity, and the acid value of such oil. The aforementioned researchers have never considered the key parameters for the oil blend which may lead to engine malfunctioning when used as fuel. This showed there is a lingering gap to be covered in the used of edible and non-edible oil blend. To cover this gap, this studies proposed new novel key factors to be considered when blending oil by employed the used of mixture of extracted oil from different seeds. To the best of our knowledge, there is no report found were the shells of *Lattorina littorea* was mixed with *Macra coralline* for used as heterogeneous catalyst, also, no single report found four (4) oil was quaternary blend for the synthesis of biodiesel via a mixed based catalyst developed from the shells.

Therefore, the aim of this research is to produce biodiesel from blend of non-edible oil using derived heterogeneous catalyst from the shells. The specific objectives focus on synthesis of a new novel heterogeneous base catalyst from the binary mixture of *Lattorina littorea* and *Macra coralline*. The heterogeneous catalyst is then apply to transesterification of a quaternary blend of non-edible oil of *Carica papaya* (CP) (pawpaw) seed, *Citrus sinensis* (CS) (orange seed), waste used (WU), and edible oil of *Hibiscus sabdariffa* (sorrel) (HS). The new novel heterogeneous catalyst was characterized using SEM, FTIR, and XRD to establish its catalytic perspective. The process parameters optimization was carried out by considering four variable factors through using response surface methodology (RSM). The quality of the biodiesel produced was determined with a view to ascertain its potential use as fuel engine.

2. Materials and methods

2.1. Materials

2.1.1. CP, CS, WU and HS

Freshly CP and CS were collected from a local fruits seller in the

Table 1
Early reports on the use of various bio-based catalysts for synthesis of biodiesel.

References	Oil	Catalysts	Variable conditions -OH/OMR Rxn time Cat. amt Rxn temp. (°C)				Optimization techniques
[50]	Canola oil	AlCl ₃ /ZnCl ₂	1:24	18 h	NS	110	Non
[51]	Soybean oil	Calcined sodium silicate	7.5:1	60 min	3.0 wt%	60	Non
[52]	Waste cooking oil	Mussel shell	24:1	1–8 h	9–12 wt%	NS	Non
[53]	Palm oil	Anadara Granosa shell	12:1	2 h	2.6%	70	Non
[54]	Palm oil	Limestone	40:1	2 h	NS	60	Non
[23]	Sunflower oil	Palm shell biochar	9:1	NS	3 wt%	65	CCD
[55]	Milk bush seed oil	Snail shell	9:1	2 h	3 wt%	65	BBD
[56]	Waste cooking oil	Lipase	6:1 to 11.6:1	50 min	9.8–10%	60	Non
[7]	Lucky nut oil	Pearl spar	0.15%	50 min	0.15 wt%	60	CCD
[57]	Soybean oil	Snail shell	6:1	7 h	3 wt%	Room temperature	CCD

-OH/OMR = alcohol to oil molar ratio, Rxn = Reaction, Cat. amt = catalyst amount, NS = Not stated, CCD = central composite design, BBD = Box Behnken design.

Eket market, HS was obtained from Ekim Market, while WU was obtained from Food Affairs in Eket, all in Akwa Ibom, Nigeria. The seeds (CP-SC-HS) were washed in distilled water, sun-dried for three days and then oven-dried to constant weight.

Both *Lattorina littorea* (periwinkles shell) and *Macra coralline* (seashell) were also obtained from Ibeno beach, Akwa Ibom State, Nigeria.

2.1.2. Chemicals

Concentrated H_2SO_4 , 99.5% pure methanol, 36 wt% HCl, HPLC grade n-hexane, chloroform, H_2SO_4 acid, ethanol acetic acid, Wij's solution, NaOH, starch indicator, etc., were of analytical graded and need no further purification obtained from Terasson Chemical Venture Nig., Ltd.

2.2. Methods

2.2.1. Oils extraction, preparation and quality characterization

The obtained WU was heated at 40 °C for 20 min, and then filtered to remove dirt. The cleaned WU was kept in a tightly cork-jar for further processing.

The dried seed was manually ground and sieved to achieve powders of particle sizes of 0.05 mm. The solvent extraction method was used to extract the oils from the powders (CP-SC-HS) by considering the three variable conditions (extraction time, solvent volume and powder weight) to achieve optimum yields of oils from the powders. The optimum conditions established by Ref. [58] for oil extraction from HS, were 2 h–157 ml–22 g; [11], established working conditions of 40 min–180 ml–40 g, for oil extraction from SC, while, a working condition of 10 min–100 min for oil extraction from CP was established by Ref. [59]. At these variable conditions, oils were mass-produced in 1000 ml capacity soxhlet extractor using n-hexane as solvent. Excess n-hexane in oils was recovered using a rotary evaporator.

2.2.2. Oils blend and characterization

To obtained oil with low viscosity, low density, and good volatility, there is a need for proper blending to allow for a synergistic effect within the blend. It is worthwhile to know that the action of oil is increased by mixing several oils. Hence, the order in which the oil is blended must be factor properly. Lighter with smaller molecules will produce less viscous oils with high volatility while heavier and larger molecules produce high viscous oils with low volatility. For these reasons, the extracted oils CP, CS, and HS were blended with WU oil in the ratio of 25:25:25:25 to form a quaternary mixture since the oils were of lighter oil with smaller molecules. The quaternary blend oil (QBO) was heated in a magnetic shaker at 70 °C for 30 min to achieve a homogeneous mixture.

The oils and the few drops of QBO were subjected to the recommended [60] standard test to evaluate the physicochemical properties. Qualities such as density, viscosity, moisture content, peroxide value, acid value, flash point, pour point, cold filter plugging point and other chemical properties were determined. Agilent 5973 N GCMS instrument control and data storage were used to determine the constituent of the volatile matter, long and branched-chain hydrocarbons, esters and alcoholic acids, and others.

2.2.3. Catalyst preparation and development

Lattorina littorea (periwinkles shell) and *Macra coralline* (seashell), each weighed 500 g were washed with warmed water heated at 50 °C to neutralized the salt content and the unwanted materials. The cleaned *Lattorina littorea* and *Macra coralline* were oven-dried to constant weight at 100 °C for 5 h. The dried samples were mixed, milled and separated into a particle size of 0.30 mm

powder before calcination. Since the efficiency of the calcination process transforms calcium carbonate to calcium oxide in the sample is often depended on the calcination temperature, heating rate, and particle size [61], the 0.30 mm powdery sample was calcined at 900 °C for 3 h in a muffle furnace. The calcined powder (DCCP) was then characterized. DCCP is the abbreviation used for the developed calcined catalyst powder obtained from *Lattorina littorea* and *Macra coralline* mixture.

2.2.4. DCCP characterization

The morphological characteristic of the DCCP at 900 °C was investigated by SEM, model 6300 F by JEOL solution for innovation, USA. The elemental analysis of the DCCP was carried out using EDX-ray to quantitative and qualitatively estimated the chemical compositions present in the catalyst. The chemical bond in the sample was confirmed by using the FTIR absorption spectrum. The spectra produce the shape of the sample as an individual molecular pattern that can be used to screen and scan the powder sample for different components. The angular scanning electron was performed in the range of $10^\circ < 2\theta < 70^\circ$ at a rate of 2 min^{-1} using the method earlier adopted by Ref. [17].

2.3. Synthesis of biodiesel

The acid value (FFA <1.50) of the blended oil was within the range of successful transesterification by the base catalyst, therefore, biodiesel was synthesis through the process route earlier adopted by Ref. [62] with few modifications. Here, a three-necked-reactor was used to carry out the production, four variables factors were considered namely; reaction time of 45–60 min, DCCP amount 1.5–3.0 g, reaction temperature of 55–70 °C and EtOH/OMR of 3–6, respectively. Initially, the 100 ml of the oil was preheated at 60 °C for 1 h, a measured catalyst amount was added to known ethanol in 250 ml flask, heated at 65 °C for 20 min, and then transferred into the preheated oil in the reactor, and the reaction was monitored for certain duration until it reaches completion. At the end of the reaction, the catalyst was separated by decantation and the biodiesel phase was separated from the ethanol phase by separating funnel. The leached catalyst in the biodiesel was removed by washing with a mixture of 2.0 g Na_2CO_3 and 40 ml ethanol thermally heated for 2 h under agitation. The mixture was filtered, washed with distilled water trice before the separation of biodiesel through gravity settling was carried out. The washed biodiesel was then dried over anhydrous Na_2SO_4 , and then separated by filtration to obtain pure biodiesel. The DCCP used was recycled for reuse at the end of the reaction with a reduction in the 4th and 5th cycles. Hence, the catalyst was reusability was stopped after 3rd usage. These processes were repeated based on experimental runs generated by the design expert. Detailed graphical schematic of the experimental set up is added in supplementary file.

2.3.1. Experimental design for biodiesel and its statistical analysis via optimization

A four-level four factors were used for laboratory experimental design for biodiesel production from QBO, the factors, the units, the symbols, and their levels are listed in Table 2. A CCED (central composite experimental design) was adopted to generate a total of 30 (thirty) experimental runs, which allows each numerical factors to be varied over three levels, with duplication for every combination of categorical factor, and a higher number of experimental runs to increase the axial and center points.

EtOH/OMR = Ethanol/oil molar ratio, DCCP = Developed calcined catalyst powder.

For statistical analysis, the regression parameter (RM), analysis

Table 2
Experimental design for transesterification of QBO.

Variables	Units	Symbol	Levels			
			−2	−1	0	1
Reaction time	(min)	X_2	45	50	55	60
DCCP amount	(g)	X_2	1.5	2.0	2.5	3.0
Reaction temp	(deg. C)	X_3	55	60	65	70
EtOH/OMR	(ml/ml)	X_4	3	4	5	6

of variance (ANOVA) and test of significant (TOS) were used to ascertain each variable influence on the response (biodiesel) yield. The statistical analysis further produced the predicted values which were compared and contrast with the responses obtained. The predicted value against the responses was plotted to show best-fit lines on the scatter plot (x-y graph), which proved the relationship among the variables. Furthermore, process optimization was carried by determining the p-value, the f-value the df, and the VIF, respectively. R-square, predicted R-square, adjusted and the adequate precision were also evaluated to confirm the model adequacy. Graphing a function with a two-input (X_1X_2 ; X_1X_3 ; X_1X_4 ; X_2X_3 ; X_2X_4 or X_3X_4) and one-dimensional output (biodiesel) requires plotting points in three dimensional spaces for a perfect interactive effect among the variables. The second-order model equation that relates the relationship between the biodiesel yield (BY) and the independent variables is mathematically express as Eqn. (1).

$$BY = \vartheta_0 + \sum_{i=1}^k \vartheta_i X_i + \sum_{i=1}^k \vartheta_{ii} X_i^2 + \sum_{i < j}^k \vartheta_{ij} X_i X_j + \varepsilon \quad (1)$$

Sources [27]. Where BY is the response (biodiesel) in percentage, ϑ_0 is the intercept, ϑ_i is the linear coefficient, ϑ_{ii} is the interaction coefficient, ϑ_{ij} is the quadratic coefficient terms, X_i , X_j are the four factors and is the residual error.

No assumption was made in this study, except the number of runs generated by design expert which were varied over five levels. The conditions for the variables are explained in details in the process optimization.

Table 3
Properties of oils and QBO blended oil.

Properties	CP oil	CS oil	WU oil	HS oil	QBO
Density (kg/m ³) @ 40 °C	965	944	958	945	950
Viscosity @ 40 °C/(mm ² /s)	21.50	12.22	13.50	14.30	14.67
Moisture content (%)	0.24	0.012	0.015	0.010	0.010
%FFA (as oleic acid)	1.80	1.22	0.60	0.22	0.67
Acid value (mg KOH/g oil)	3.60	2.44	0.30	0.44	1.34
Saponification value (mg KOH/g oil)	188.73	183.32	187.10	186.20	184.75
Iodine value (g I ₂ /100 g oil)	86.40	78.00	78.64	71.00	80.34
Peroxide value (meq O ₂ /kg oil)	6.71	8.60	5.60	7.30	6.82
HHV (MJ/kg)	40.40	40.74	40.58	40.73	40.65
Cetane number	55.78	56.18	55.43	57.51	55.35
Mean molecular mass	296.72	305.48	299.31	300.75	303.11
Flash point (°C)	120	120 min	120 min	120 min	120 min
Cloud point (°C)	+5	+5	+5	+5	+5
Fatty acid properties (%)					
Miristic acid (C14:0)	0.10	0.20	0.15	0.25	0.22
Palmitic acid (C16:0)	15.40	28.12	13.21	4.23	29.41
Palmitoleic acid (C16:1)	0.14	0.26	0.56	0.12	0.54
Stearic acid (C18:0)	5.92	8.12	7.13	4.21	12.62
Oleic acid (C18:1)	69.50	38.72	39.30	46.50	37.68
Linoleic acid (C18:2)	8.06	29.20	38.82	43.82	18.56
Linolenic (C18:3)	0.51	0.68	0.53	0.41	0.64
Others	0.37	0.84	0.30	0.46	0.33

CP = *Carica papaya*, CS = *Citrus sinensis*, WU = Waste used, and HS = *Hibiscus sabdariffa*, QBO = Quaternary blended oil.

2.3.2. Biodiesel properties

The pure BY produced needs to certify the recommended important properties biodiesel standards such as ASTM D6079, ISO 17828:2015, EN ISO 12937:2000, EN 14111, EN14112, EN 14103, STM D664, EN ISO 5165, ASTM D2015, (ASTM D6371), (ASTM D4530), (ASTM D93), (ASTM 2500), and (ASTM 97), respectively. These properties among all include: moisture content, density, kinematic viscosity, saponification value, iodine value, cetane number, higher heating value, oxidative stability cold, filter plugging carbon residue, flash point, cloud, and pour point.

3. Results and discussion

3.1. Properties of oils and QBO

The results of the characterization of the oils are presented in Table 3. For comparative purposes, the QBO mixture of the oils blend was also presented. From the table, there was a significant reduction in the important properties of the QBO when compared with the oils, it was observed that the density, the viscosity, and the moisture content of the oil reduced significantly base on QBO. These observations could be attributed to the order in which the oil was a blend. Lighter oils with smaller molecules were blended which produced less viscous oils, with low density and high volatility. The low moisture content indicates little or no impurities in the QBO with high shelf life [11]. The maximum value for non-rancid oil is 5, the value of 1.34 obtained for QBO showed the oil conveniently falls within the non-rancid oil [63]. The low peroxide value of the QBO along with the oils showed the oil has a low level of rancidity [64]. The iodine value of the QBO (80.34 g I₂/100 g oil) was higher than the CS, WU, and HS oils, but lower than the value of 86.40 g I₂/100 g oil obtained for CP-oil. This indicated that QBO has a moderate level of unsaturation of the oil and can be referred to as non-drying and semi-drying oil; hence the oil can be used for industrial purposes [11]. High saponification value of 184.75 mg KOH/g oil obtained for QBO indicated the oil contained a high percentage of triglycerides [7].

The high value of HHV obtained from QBO proved its suitability for biodiesel production, the higher the high heating value, the more suitable the oil for biofuel production. The cetane number is a

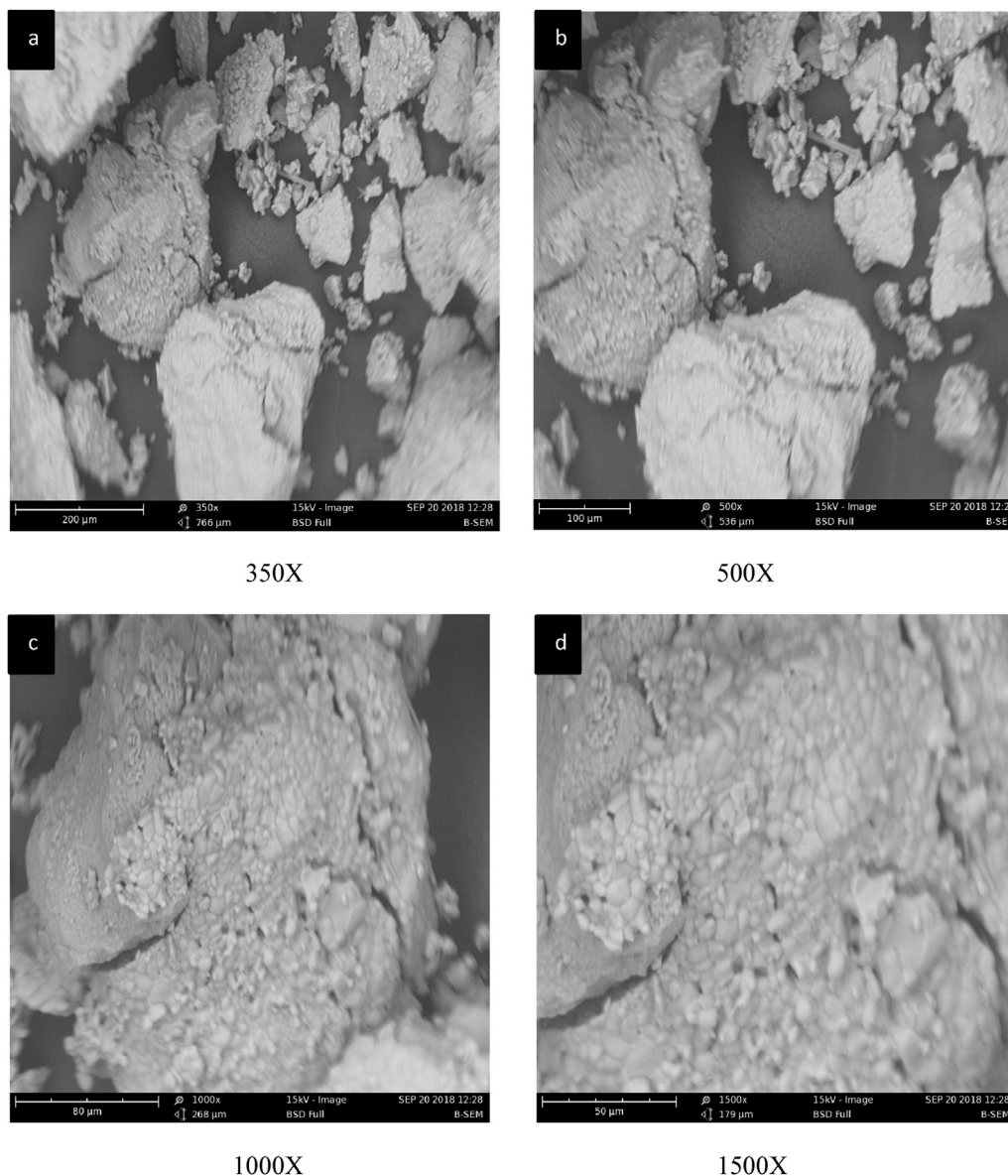


Fig. 1(a–d). SEM image of DCCP showing the morphological characteristic at different magnification.

fuel property, it values responsible for ignition delay and combustion qualities, the resultant QBO value obtained proved that the oil is of high fuel potential [16,65].

The fatty acid properties of the oil showed that the oil has moderate saturation and monounsaturated acid, although the CP, WU, HS and CS oils contain a high level of unsaturation, the blend of the oils resulted in a moderate level of unsaturated. This may be attributed to the proper blending which allows for a synergistic effect within the blend.

3.2. DCCP characterization and elemental analysis

The morphological characteristic of the DCCP at 900 °C was investigated by SEM at different wavelengths and magnification of 50 μm ; 1500x, 80 μm ; 1000x; 100 μm ; 500x, and 200 μm ; 350x, performed in the range of $10^\circ < 2\theta < 70^\circ$ at a rate of 2 min^{-1} (Fig. 1a–d). Observation from the images of DCCP showed the powder was of various shapes, non-uniform in size and with little porosity (1a&1 b). The semantic structure based on magnification

showed mineral sums and wholes (Fig. 1c and d) particles responsible for the spongy and glossy nature of the particle present. This observation could be likened to the abundance of calcium and oxygen present after high-temperature calcination which showed that no carbon remains after thermal treatment that resulted in the gaseous formation of CO_2 via decomposition of calcium carbonate (Fig. 1d).

FTIR analysis measures a sample's absorbance of infrared light at various wavelengths to determine the material's molecular composition and structure. It works to convert the raw data from the broad-band light source to obtain the absorbance level at each wavelength. Fig. 2 showed the result of the FTIR DCCP calcined at 900 °C for 3 h along with the infrared spectrum, which plots the intensity of infrared spectra. The absorbance's band corresponds with the various vibrations of the DCCP when it's exposed to the infrared region of the electromagnetic spectrum are indicated by the vibration line. The spectrum stretching is about thirteen displaying both wavelength and transmittance. The wavelength of 894.6 cm^{-1} at a transmittance of 75.548 stretched to the

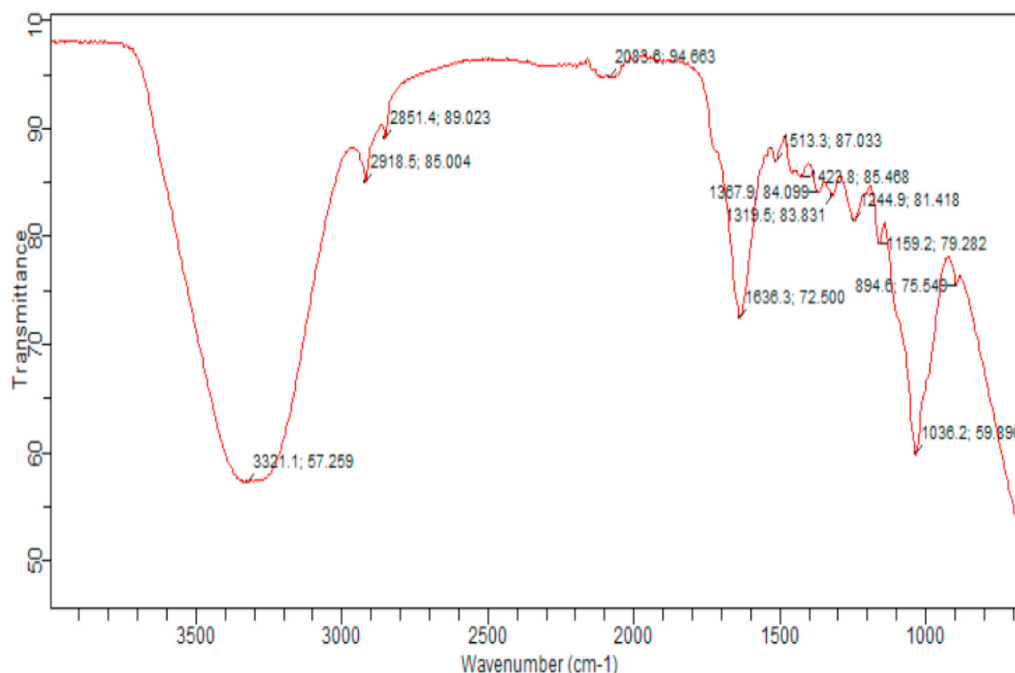


Fig. 2. FTIR spectrum of DCCP.

Table 4

Coded factors, experimental, predicted biodiesel yield, and residuals values.

Std Runs	X ₁ (min)	X ₂ (g)	X ₃ (°C)	X ₄ (ml/ml)	Exp. Bio (% wt.)	Pred. Bio (% wt.)	Residual
1	–1.000	–1.000	–1.000	–1.000	91.89	91.66	0.23
2	1.000	–1.000	–1.000	–1.000	93.19	93.22	–0.035
3	–1.000	1.000	–1.000	–1.000	92.05	92.09	–0.038
4	1.000	1.000	–1.000	–1.000	96.32	96.39	–0.073
5	–1.000	–1.000	1.000	–1.000	93.50	93.54	–0.038
6	1.000	–1.000	1.000	–1.000	90.92	90.99	–0.073
7	–1.000	1.000	1.000	–1.000	93.84	93.91	–0.071
8	1.000	1.000	1.000	–1.000	94.22	94.11	0.11
9	–1.000	–1.000	–1.000	1.000	90.35	90.39	–0.038
10	1.000	–1.000	–1.000	1.000	93.07	93.14	–0.073
11	–1.000	1.000	–1.000	1.000	93.49	93.56	–0.071
12	1.000	1.000	–1.000	1.000	99.17	99.06	0.11
13	–1.000	–1.000	1.000	1.000	95.59	95.66	–0.071
14	1.000	–1.000	1.000	1.000	94.42	94.31	0.11
15	–1.000	1.000	1.000	1.000	98.89	98.78	0.11
16	1.000	1.000	1.000	1.000	99.80	99.95	–0.15
17	–2.000	0.000	0.000	0.000	94.01	94.05	–0.039
18	2.000	0.000	0.000	0.000	97.11	97.00	0.11
19	0.000	–2.000	0.000	0.000	90.39	90.43	–0.040
20	0.000	2.000	0.000	0.000	96.83	96.72	0.11
21	0.000	0.000	–2.000	0.000	95.54	95.58	–0.040
22	0.000	0.000	2.000	0.000	98.68	98.57	0.11
23	0.000	0.000	0.000	–2.000	89.14	89.18	–0.040
24	0.000	0.000	0.000	2.000	94.08	93.97	0.11
25	0.000	0.000	0.000	0.000	95.18	95.18	0.000
26	0.000	0.000	0.000	0.000	95.18	95.18	0.000
27	0.000	0.000	0.000	0.000	95.18	95.18	0.000
28	0.000	0.000	0.000	0.000	95.18	95.18	0.000
29	0.000	0.000	0.000	0.000	95.18	95.18	0.000
30	0.000	0.000	0.000	0.000	95.18	95.18	0.000

wavelength of 1636.3 cm^{-1} at a transmittance of 72.500, indicated the infrared spectrum are highly characteristic of the molecule as a whole, explaining the details of what is going on within the molecule. The region showed the presence of aldehyde ($\text{C}=\text{C}$ stretch), ketone ($\text{C}=\text{O}$ stretch), ester, carboxylic acid, and amide while the stretched band noticed in the infrared spectrum located 1636.3 cm^{-1} wavelengths at a transmittance of

72.500–3321.1 cm^{-1} at transmittance 57.259 showed the presence of nitrile, carboxylic acid, and alcohol/phenol functional groups. The results of identifying and quantify minerals in the CCDP by XRD-ray contained 99.02% of CaO , 0.32% of P_2O_5 , 0.25% of MgO , and 0.41% of ZnO , respectively, by weight. At calcination temperature 600 °C, the main compound left is calcium carbonate, an increase in thermal temperature to 750 °C, decomposition of calcium

Table 5
Test of significance for every regression coefficient for biodiesel production.

Source	Sum of squares	df	Mean Square	F-value	P-value
Model	201.88	14	14.42	653.70	<0.0001
X ₁	13.07	1	13.07	592.42	<0.0001
X ₂	59.31	1	59.31	2688.86	<0.0001
X ₃	13.40	1	13.40	607.23	<0.0001
X ₄	34.39	1	34.39	1559.07	<0.0001
X ₁ X ₂	0.20	1	0.20	9.23	0.0083
X ₁ X ₃	4.42	1	4.42	200.29	<0.0001
X ₁ X ₄	6.15	1	6.15	278.94	<0.0001
X ₂ X ₃	22.28	1	22.28	1010.18	<0.0001
X ₂ X ₄	7.52	1	7.52	340.96	<0.0001
X ₁ ²	16.87	1	16.87	764.82	<0.0001
X ₂ ²	1.42	1	1.42	64.46	<0.0001
X ₃ ²	2.756E-003	1	2.756E-003	0.12	0.7286
X ₄ ²	7.55	1	7.55	342.20	<0.0001
Residual	11.54	1	11.54	523.27	<0.0001
Lack of Fit	0.33	15	0.022		0.6750
Pure Error	0.33	10	0.033		
Cor Total	201.88	14	14.42	653.70	<0.0001
Fits statistics					
R squared	99.84				
Adjusted R squared	99.68				
Predicted R squared	99.06				
Adequate precision	104.652				

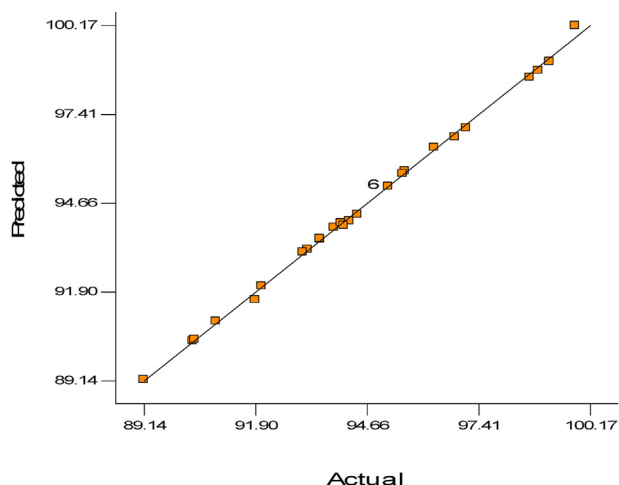


Fig. 3. Biodiesel yield vs. Predicted value.

ey: 6 is the values for six center points showing runs of the same replication (runs 25–30).

carbonate to form calcium (II) oxide started to occur. An increased to 900 °C, the only mineral present was calcium oxide with a trace amount of minerals <1. This observation agreed with the earlier reports that seashells generally composed of CaO (97.57%) owing to the presence of calcium carbonate, which is the main component of the waste sea shell [61,66] other minerals are less discoursed, but could also help the transesterification reaction process [29].

3.3. Transesterification of QBO to biodiesel using DCCP

3.3.1. Statistical optimization of transesterification of QBO

Statistical optimization of the transesterification of QBO to biodiesel was carried out by developing build-in information; design expert file version 12.0.3.0 was used with the study response surface as the type. Based on four-factor-four level-adopted, BBED was employed, and the quadratic model design was

chosen, the total build time was 15 min, the subtype was randomized and 29 runs were observed, and these runs were carried out as presented in Table 4. From the table, the highest biodiesel yield of 99.80 (wt. %) was obtained at the following conditions: reaction time of 60 min, DCCP amount of 3.0 (g), reaction temperature of 70 °C, and EtOH/OMR of 6:1 (ml/ml). These results were subjected to statistical analysis through transformation, fit summary, model effects, anova, diagnosis, and model graph. For transformation, $1/\lambda y^l = y$ was used, which showed the ratio of max to min is 1.11959, hence, the transformation of little effects was considered. For process fit summary and model effects, the model source was quadratic with 4° of freedom and P-value <0.0001 with the standard deviation of 0.15 for fit summary was suggested to improve the predicted yield. However, the analysis resulted in a predicted biodiesel yield of 99.8044 (wt. %) at a reaction time of 57.72 min, DCCP amount of 3.0 (g), reaction temperature of 69.54 °C, and EtOH/OMR of 6:1 (ml/ml). The predicted biodiesel yield was validated in triplicate and an average biodiesel yield of 99.7800 (wt. %) was obtained. This showed that the conversion of oil to be successful and the DCCP base-catalysed derived from *Lattorina littorea* and *Macra coralline* and applied to the transesterification of a quaternary mix of *Carica papaya* - *Citrus sinensis*- Waste used- *Hibiscus sabdariffa* proved to be a good agro waste-based catalyst. Furthermore, the results of 2nd-order polynomial through regression coefficients and significance of response surface quadratic equation was performed, the results of the second-order polynomial equation were as presented in coded factor Eqn. (2).

Based on the coefficient of the equation, the negative coefficient decreases biodiesel while a positive coefficient increases the biodiesel yield. All the linear variables have a positive influence on the response, however, X₂ (1.57) with f-value = 2688.86, and p-value <0.0001 is the Final equation in term of coded most positively significant variable among the selected variables. Furthermore, the model F-value of 653.70 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. Further analysis proved that all the selected variables considered for biodiesel production via ethanolysis of the DCCP catalyst were remarkably significant except the interaction of X₂X₃ (with p-value = 0.7286) that was a non-significant term (Table 5). The Lack of fit f-value of 0.6750 implies the Lack of Fit is not significant relative to the pure error which showed is goodness for the fit. Based on fit statistics and model comparison statistics, the coefficient of determination (R squared) of 99.84% obtained showed the proportion of the variances in the dependent variable that is predictable from the independent variable. Predicted R² of 99.06% was in reasonable agreement with the adjusted R² of 99.68 with high adequate precision of 104.652 > 4 which is required for any fit model. Based on the model graph, the plot of biodiesel yield was plotted against predicted yield; a straight line (Fig. 3) passing through the points indicated that the predicted values concord with the experimental results with non-significant residual value. Further, on the model graph, the linear interaction among the variables on biodiesel yield resulted in 3-dimensional plots; these plots are presented hitherto in contours from as in Fig. 4a-f. The plots of the DCCP amount interacting with the reaction time are indicated in Fig. 4a while Fig. 4b illustrates the interaction of reaction temperature and reaction time. Depicted in Fig. 4c is the interaction of reaction time and EtOH/OMR on biodiesel yield while Fig. 4d shows the interaction of reaction temperature and DCCP amount on the yield of biodiesel. The interaction of EtOH/OMR against the DCCP amount on biodiesel yield is presented in Fig. 4e with Fig. 4f showing further the interactive effects of EtOH/OMR against the reaction temperature on the biodiesel yield.

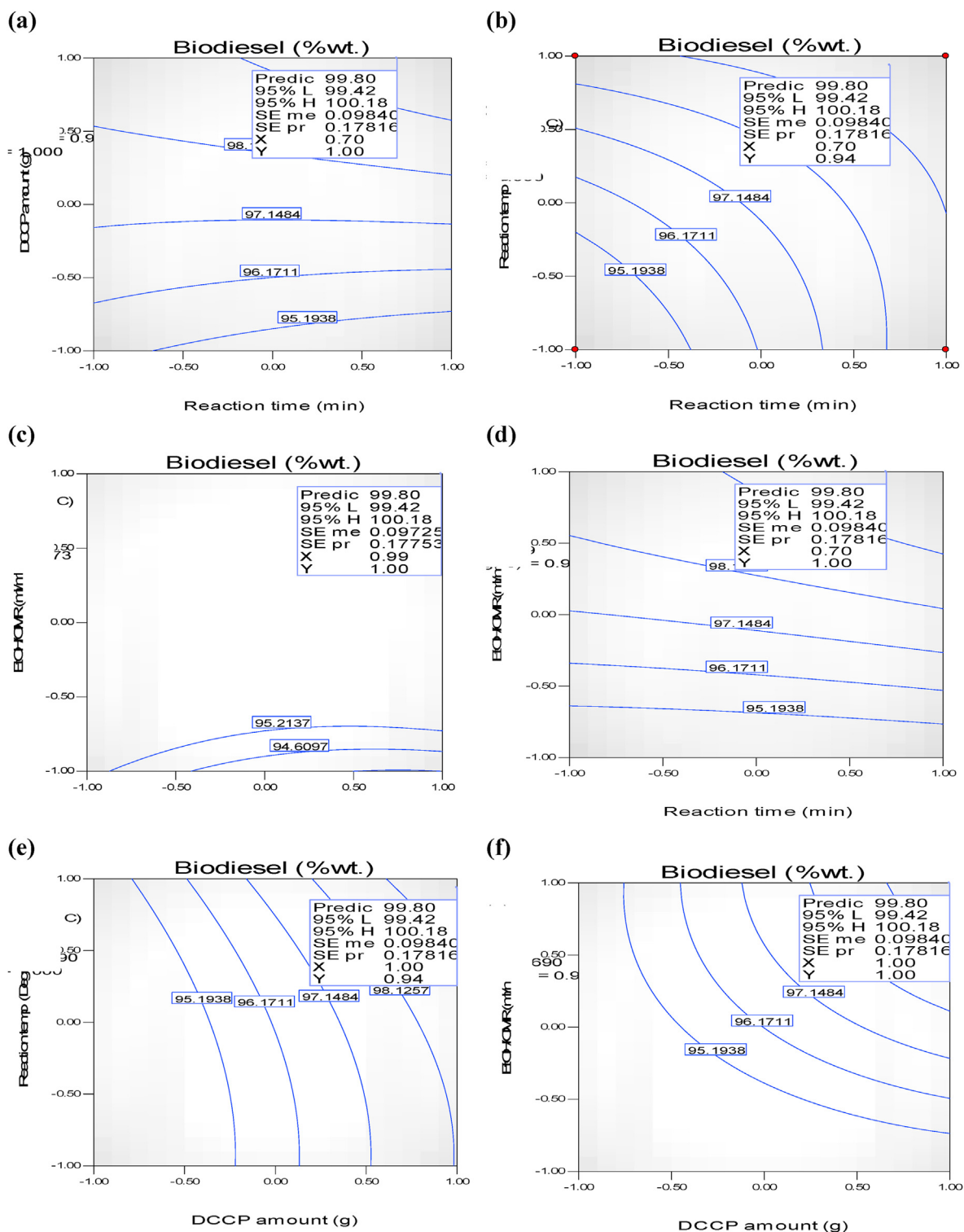


Fig. 4 (a–f). Contour plots of interaction among the selected variables on biodiesel yield.

$$\begin{aligned}
 \text{MOB (wt. \%)} = & 95.18 + 0.74X_1 + 1.57X_2 + 0.75X_3 + 1.20X_4 + 0.086X_1^2 - 0.40X_2^2 + 0.47X_3^2 \\
 & - 0.90X_4^2 + 0.69X_1X_2 - 1.03X_1X_3 + 0.30X_1X_4 - 0.013X_2X_3 + 0.69X_2X_4 + 0.85X_3X_4
 \end{aligned}
 \quad (2)$$

Sources: RSM-CCD

Observation from the plots showed the mutual interactions noticed in Fig. 4(a, c and f) are better than that observed in Fig. 4(c and d), however, Fig. 4d has the least mutual interaction on the biodiesel yield, this observation further supports the fact that X_1X_3 has the least negative effect on the response in Eqn. (2).

3.3.2. Quality of biodiesel

Since this study is a new novel ideal of biodiesel produced from quaternary oil blend (QBO) from *Carica papaya*-*Citrus sinensis* -*Hibiscus sabdariffa*-Waste used, literature reports are scarce for comparison purposes, hence, the quality of the biodiesel was compared with [67] European and [68] America standards and presented in Table 6. The results obtained showed the properties of the biodiesel were within the biodiesel specifications limit. Main

biodiesel properties such as density, viscosity, acid value, cetane number, higher heating value, iodine value, and saponification value are within the limits recommended by Refs. [67,68] standard. Fuel properties comprise of diesel index, flash point, pour point, and cold point agreed with the recommended values.

Other fuel properties such as:

Oxidative stability affects the stability of biodiesel during storage, hereby compromise fuel properties; damage fuel quality and engine performance. The minimum recommended value was 3 min, the value of 3.5 h obtained in this study showed that the biodiesel is more stable within a short period.

Cold filter plugging point (CFPP) indicates the lowest temperature at which a given volume of diesel fuel still passes through a standardized filtration device in a specific time when cooled under certain conditions. A high CFPP > 5 will clog up vehicle engines in

Table 6

Quality of biodiesel with biodiesel standard.

Properties	Biodiesel (QBOB) *this study*	[69,70]	Unit
Physical and Chemical Properties			
Density	872	None	860–900 kg/m ³
Kinematic viscosity @ 40 °C	1.82	1.9–6.0	3.50–5.00 mm ² /s
Moisture content	0.001	0.05	— (vol%)
FFA (as oleic acid)	0.18	—	— (%)
Acid value	0.36	0.5	0.5 mg KOH/g oil
Saponification value	178.24	None	None mg KOH/g oil
Iodine value	52.62	—	120 g I ₂ /100 g max
Mean molecular mass	—	—	— NU
Fuel Properties			
HHV	41.27	None	None MJ/kg
Cetane number	64.38	47	51 min
Diesel index	75.53	None	None NU
Flash point (°C)	130	93	101 °C min
Cloud point (°C)	–2	None	None °C
Pour point (°C)	–12	None	None °C
CFPP	3	None	None °C
Oxidative stability	3.5	3	8 h min
Carbon residue	0.02	0.05	None mass % max

API = American Petroleum Institute, CFPP = Cold Filter Plugging Point, NU = No unit, ND = Not Determine, LL = Lower limit, UP = Upper limit, 1 Btu/gal = 0.001055 MJ/US gallon.

Table 7

Comparative of this study with other researched work.

Oil and blend ratio	Catalysts mixed	C. temp.	Variable conditions $X_1 X_2 X_3 X_4$	Biodiesel yield (%)	References
Pig fat + Neem oil 60:40	Palm kernel shell husk +	800 °C for 3 h	5.9:1 57.45 min 2.179 g	59.91 °C 98.05	[27]
Cucurbita pepo + chrysophyllum albidum + papaya oil 33:33:34	Fermented kolanut pod husk <i>Citrullus lanatus</i> +	700 °C for 4 h	6.97:1 70 min 5.0 wt%	80 °C 93.45	[29]
Honne + Rubber seed + Neem oil 20:20:60	<i>Musa acuminata</i> Peels Cocoa pod husk +	500 °C for 4 h	12:1 60 min 1.158 wt%	65 °C 98.45	[49]
Carica papaya + Citrus sinensis + Hibiscus sabdariffa + Waste used oil 25:25:25:25	+ kola nut husk Lattorina littorea +	900 °C for 3 h	6:1 57.72 min 3.0 g	69.54 °C 99.78	This study
	Mactra coralline Shell				

cold temperature regions, the value of 3 obtained in this study showed that the diesel is of good qualities with low temperature clogging effect.

Carbon residue value showed the tendency of the fuel to form carbon deposits under high-temperature conditions in an inert atmosphere. Its low value (0.05 max) is required for a better fuel engine, the value of 0.02 obtained for biodiesel in this study showed the produced biodiesel is of good fuel properties.

3.3.3. Comparative study

The results obtained in this study were compared with earlier reports of other researchers, and the results are displayed in Table 7. Since the synthesis of biodiesel from the mixture of different vegetable oil in various ratios through alcoholysis of derived catalyst from mixed biomass wastes is a new novel approach, therefore only a few reported results were found and used as a source of comparison with the process conditions. From the results, it was observed that [27], used the blend of two oils in the ratio of 60:40 used to synthesized biodiesel from methanolysis of the derived catalyst from palm kernel shell husk and fermented kola-nut pod husk. The result of biodiesel yield was 98.05% (wt.) which was higher than the result of 93.45% (wt.) yield of biodiesel obtained when the three oils were blended in the ratio of 33:33:34. However, the yield of 98.45% (wt.) obtained by Ref. [49] when three oil was blended in the ratio of 20:20:60 was lower than the result of biodiesel yield of 98.78% obtained in this study. The high yield obtained in this study could be attributed to the synergy of the oil blend, the nature of derived catalyst (shells) and the nature of the oil mix. Shells obtained from animal waste usually required high thermal treatment than the biomass waste calcination temperature before use as based catalyst transesterification.

X_1 = methanol/oil molar ratio, X_2 = Reaction time, X_3 = Catalyst amount, X_4 = Reaction temperature, C. temp = Calcined temperature.

4. Conclusion

The following conclusion can be drawn from the study:

- i. Synergistic to oils quaternary blend produced oil with low viscous and high volatility.
- ii. Thermal treatment of a developed catalyst from *Lattorina littorea* mix with *Macra coralline*, at 900 °C for 3 h produced 99.02 %wt. Of CaO based on XRD analysis result.
- iii. The produced catalyst developed was re-used up to 3–cycles for transesterification
- iv. The maximum biodiesel produced was 99.68 (%wt.) at a catalyst amount of 2.0 (g), a reaction time of 70 min, a reaction temperature of 60 °C, and EtOH/OMR of 7:1 (ml/ml).
- v. Statistical optimization predicted biodiesel yield of 99.8044 (wt. %) at a reaction time of 57.72 min, DCCP amount of 3.0 (g), reaction temperature of 69.54 °C, and EtOH/OMR of 6:1 (ml/ml). The predicted biodiesel yield was validated in triplicate and an average biodiesel yield of 99.7800 (wt. %) was obtained.
- vi. The properties of biodiesel were within the specification limits of biodiesel standard.
- vii. The proposed novel approach of 1:1:1:1 blend was perfect for oil with low viscous and high volatility used for synthesized biodiesel.
- viii. CaO-based-catalyst derived from the binary mixture of *Lattorina littorea* and *Macra coralline* successfully converted the quaternary mixture of oil to biodiesel.

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CRediT authorship contribution statement

T.F. Adepoju: Conceptualization, Methodology, Software, Validation, Formal analysis, Investigation, Resources, Data curation, Writing - original draft, Writing - original draft, Supervision. **M.A. Ibeh:** Formal analysis, Investigation, Resources, Data curation, Provide Financial Support, Methodology, Software. **E.N. Udoetuk:** Methodology, Software, Investigation, Resources, Writing - original draft, Writing - original draft. **E.O. Babatunde:** Methodology, Software, Validation, Formal analysis, Methodology, Investigation, Resources.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.renene.2021.02.020>.

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