

A Novel Green Bio-composite Heterogeneous Catalyst Synthesis for the Optimized Transesterification of Linseed-Marula bi-oil Methyl Ester Production

Anietie Etim¹, Paul Musonge^{1,2} and Andrew C. Eloka-Eboka³

Abstract— Waste biomass materials contribute immensely towards environmentally friendly and cost-effective clean energy production. In this study, a bio-composite catalyst was developed from waste biogenic materials (waste chicken eggshells and banana peels) and was used in the transesterification of linseed-marula bi-oil methyl ester. The two materials were prepared and calcined separately at different temperatures; eggshells at 900 °C and banana peels at 700 °C. The calcined ash of each of the materials was fused together in equal amounts via the wet impregnated method, and further activated at 800 °C to obtain bio-composite nanoparticles (catalyst). The synthesized catalyst was characterized to determine its catalytic potentials and was used in the transesterification of linseed-marula bi-oil. Transesterification process was optimized using Taguchi design (TD) of the Response Surface Methodology, which was used to generate 9 experimental conditions for the investigation of the effect of methanol to oil molar ratio, catalyst loading, reaction time and temperature. Result of the characterization shows that Ca and K are the dominant elements present in the synthesized bio-composite catalyst. Optimum experimental condition for the transesterification of the bi-oil was established at methanol-to-oil ratio of 15:1, catalyst amount of 3.5 wt%, reaction time of 60 min and reaction temperature of 65 °C with 95.03 % of biodiesel yield. The quality of the biodiesel produced was within the ASTM, EN and SAN standards. The study shows that the combined effect of biogenic waste materials and linseed-marula bi-oil is a potential source of an effective and sustainable feedstock for biodiesel production.

Keywords—biomass waste, biodiesel, bi-oil, heterogeneous catalyst, transesterification, Taguchi design.

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I. INTRODUCTION

Globally, scientific contributions in the exploration of sustainable materials for biofuel production is increasing daily either to address the challenging issues of environmental pollution or the higher rate of petroleum fuel consumption. Biodiesel among liquid biofuels stands as the most auspicious and suitable fuel alternative to petroleum fuel due to their similarities in properties. The indigenous nature of biodiesel and its potency in greenhouse gases emission reduction makes it a desired fossil fuel substitute option. Biodiesel is a long chain fatty acid – alcohol - ester triglyceride produced in the presence of a catalyst through a chemical reaction called transesterification. Catalysts for biodiesel can be produced using locally available materials and waste resources.

Feedstock blends or mixtures are majorly designed to address the challenges of feedstock scarcity for biodiesel production. The fact that not all the feedstock could be found in a particular region indicates that they are different in their compositions as a result of climatic, geographical and territorial differences. In this case, co-mixing more than one feedstock is considered a viable approach in order to examine the effects on physicochemical properties based on the chemical and biological modifications. This process actually creates new feedstock with improved properties capable of enhancing effective production and biodiesel products. Deploying edible oils in biodiesel production not only increases the cost of production but also provides avenue for food versus oil contention. In transesterification reaction, alcohol is an important reactant, which brings about alkylation of esters during the reaction process. It is quicker to dissolve in a base than in an acid catalyst. Catalysts employed in transesterification reaction can be homogeneous or heterogeneous. Homogenous catalysts are associated with soap formation, difficulty in product isolation, catalyst recovery and spent water generation. Heterogeneous catalysts have extensively been reported as a solution to most of the homogenous catalysts' drawback being that they can be

recovered and reused. They are grouped into two, acid and base types. Acid heterogeneous catalysts are slow in reactions and are linked to longer reaction time and higher operational conditions. Base catalysts have become attractive due to their fast reaction time and mild operational conditions. Apart from these characteristics, base heterogeneous catalysts can be sourced from mineral-rich waste renewable resources. Wastes such as eggshells among other animal residues have been reported as the chief source of natural CaO, with the highest content of 80-90%; and they have been used extensively in biodiesel production [1]–[4]. Agricultural wastes such as banana peels, papaya peels and stem, cocoa pod husk have all been studied and reported as the major source of potassium based compounds such as K_2CO_3 , K_2O , KCl , K_2SO_4 and so on., with high catalytic performance converting up to 90-99% biodiesel yield [5]–[7].

Recently, several biochemical modification approaches applicable in the development of heterogeneous catalyst for biodiesel production has been established and reported by [8]. The purpose of which is to develop improved physico-chemical characteristics of the heterogeneous catalyst for effective transesterification and enhancement of pure biodiesel products. Biomass modified functional heterogeneous catalysts, with attachment of various homogenous catalysts at the surface of either commercial or natural derived CaO such as CaO-KOH, CaO-NaOH, CaO- Na_2SO_4 and CaO- H_2SO_4 to enhanced effective catalytic activities and purity product [9]–[11] has been the most attractive area in heterogeneous catalyst development. Attachment of support enhance increase of the active spores and the surface area of the synthesized catalyst [8]. However, these modifications although very effective are linked with compounds which are not environmentally friendly. In order to make the biomass derived catalyst a standalone venture and a completely green process, co-mixing of several agro-waste materials have to be investigated. Cocoa pod husk-kola nut husk and fluted pumpkin waste has been reacted together to produce a heterogeneous catalyst for the transesterification of yellow oleander-rubber oil blend and was reported effective by [12]. Mixed animal bones was also used to synthesize heterogeneous catalysts for the transesterification of waste cooking oil [13]. A case of a green biogenic modification using calcium and potassium rich sources was proposed in the last study of this authors using eggshells and papaya peels [14]. The current study therefor is the continuation of previous reported investigation using the same novel approach of heterogeneous catalyst development.

Unlike other RSM modelling such as central composite design (CCD) and Box Behnken design (BBD) which involves a large number of experiments, Taguchi method involves the smallest number of experiments. Only nine experimental runs are employed to perform its optimization function. It makes use of orthogonal arrays for optimization of different parameters controlling the process and their variation

magnitude. It allows for the assembling of data to decide on the most influential factor on the response from the least number of experiments [15]. It has been applied in many esterification and transesterification experiments and reported to be effective in optimizing the process variables [9], [16]–[18]. Although linseed and marula seed oil has been utilised, as single feedstock oil for biodiesel production, their combination (bi-oil) in transesterification process has not been investigated.

This study hence investigated the transesterification of the bi-oil of linseed and marula (LOMO) (50:50 w/w) using waste biomass modified functional base catalysts derived from eggshells and banana peels, which are the novelties behind this work. The process conditions were also modelled and optimized using a Taguchi design, the reusability of the synthesized catalyst was also investigated. The overall protocol is a contribution to an existing knowledge of waste development and effective biodiesel production approach.

II. EXPERIMENTAL MATERIALS USED

Commercial linseed and marula seed oils were supplied by United Scientific SA cc, Congella, South Africa. The chemicals and reagents used for experimentation are all analytical grades.

A. Preparation of the bio-composite catalysts and characterization

The waste materials were washed with distilled water to remove all the impurities at the surface and further dried in the oven for 48 h at 80 °C. The dried materials were milled to powder particle size of < 50 μm and then calcined separately in the furnace; eggshells was calcined at 900 °C for 3 h to generate CaO, while banana peels were calcined at 700 °C for 3 h. Equal quantities of the calcined eggshells (CE) generated CaO, denoted by (CE-CaO), and calcined banana peels ash (CBP) were dissolved in 100 ml warm distilled water in a beaker and stirred at 600 rpm for 3 h. The resultant slurry was oven dried for 24 h at 120 °C to remove excess water. The dried cake obtained from the process was pulverised and activated by further calcining at 800 °C to obtain a solid base nanoparticle catalyst designated as CE-CaO/ CBPA@ 800 °C NPs. This was then packed into an airtight bottle and kept in a desiccator for biodiesel production and further analyses.

B. Catalyst characterization

The basicity strength of the synthesized catalyst was determined using the Hammett indicator method with methanol and phenolphthalein (H₉₈) as a Hammett indicator. The surface morphology and elemental composition of the bi-composite catalyst, (CaO/CBPA-800 NPs) was determined using a scanning electron microscope (SEM) at a high resolution (Zeiss Germany) fitted to the energy dispersive X-ray (EDX) detector. The crystalline phase of the composite catalyst sample was confirmed by XRD, using D-8 an

Advanced diffractometer (Cu-K α radiation) fitted to a PSD detector (Bruker AXS Karlsruhe, Germany) using electron beam generated at 40 kV and 30 mA at ambient temperature. The identification of the active functional groups present in the developed catalyst sample was done by Fourier transform infrared (FT-IR) spectra, Perkin Elmer spectrum (version 10.5.4) at the range of 4000 – 500 cm⁻¹.

C. Preparation and characterization of the hybrid oil

The bi-oil of linseed-marula seed oil (LOMO) was found to have an acid value of 5.61 mg KOH/g with the corresponding FFA of 2.81 % and was converted using one-step pathway transesterification method. The bio-oil was then heated at 60 °C and stirred using a magnetic hot plate, for homogeneity and to remove all moisture present in the oil. The physico-chemical properties of the bi-oil and the biodiesel produced namely the density, viscosity, acid value, iodine value, cetane number, calorific value were estimated according to the standard protocol [19]. The values estimated were compared with the ASTM D6751, EN 14214 and SAN 833 standards.

D. Empirical design and statistical analysis

Taguchi design was used to investigate the effect of the process parameters viz a viz methanol-to-oil molar ratio, catalyst loading, reaction time and temperature. L9 orthogonal array method with three different levels and four parameters were considered in the study as presented in Table 1. This was selected to generate the nine number of experiments (L9) in order to achieve the desired results as shown in Table 2. The number of parameters and the variation levels determine the orthogonal array selection [20]. The triplicates of each experiment are to minimise the error. The performance characteristic of each parameter was assessed to predict the most significant parameter. The relationship with which the number of experiments can be evaluated is given by Eq. (1).

$$N = 1 + (L - 1)Z \quad (1)$$

Where N denotes the number of experiments, Z is the total number of control parameters studied and L is the corresponding levels.

The design, modelling, optimization and statistical analysis of data in this study was done using the design expert software (version 11.0). Mathematical quadratic model equation was developed using regression analysis by correlating the independent variables with the responses. The performance characteristics of the obtained experimental result could be computed using signal-to-noise ratio. Signal function of the expected outcome are serving as the objective optimization problem therefore, they are used to determine the extent of deviation of the quality function to the expected response [18]. A signal to noise ratio (SNR) is the mean value of the quality characteristics of FAME yield to its standard deviation, as expressed in Eq. (2).

$$SNR = -10 \log \left(\frac{1}{n} \sum_{i=1}^n \left(\frac{1}{y_i} \right)^2 \right) \quad (2)$$

Where n is the number of replicates of each experimental condition, y_i is the HOME yield of each experiment. The contribution of each variable to the response was determined by Eq. (3).

$$C_f (\%) = \frac{SS_f}{SS_T} \times 100 \quad (3)$$

Where C_f is the influence of each factor, SS_f is the sum of square of each parameter and SS_T is the total sum of squares of all the parameters. The linear regression model equation was developed to correlates the predicted response for all the process parameters

E. Transesterification process of the hybrid oil with CaO/CBPA-800 NPs catalyst

The transesterification process was conducted in a setup system consisting of 250 ml three-necked round bottom glass reactor equipped with a condenser, thermometer and magnetic stirrer. A specified amount of the bi-oil was placed in the reactor and preheated to a desired temperature. A certain quantity of methanol as justified by the methanol/oil ratio displayed in Table 2 was added to the oil in the reactor and allowed to stir for 5 min, followed by the addition of specified amount of (CE-CaO/CBPA-800 NPs) catalyst in weight %. The reaction time commenced immediately after the catalyst was added. A magnetic hotplate allows for adjustment of plate temperature to keep the mixture temperature constant for each run. Table 2 presents the Taguchi design matrix. At the end of the reaction, the content was transferred into a separating funnel and allowed to settle overnight. A three-phase layer separation was observed which include the biodiesel layer at the top, the glycerol and the catalyst layer at the bottom respectively. This was separated accordingly starting from the catalyst and then glycerol layer, the remaining crude biodiesel product in the separating funnel was washed thrice with warm distilled water at 50 °C and further dried by heating over Na₂SO₄. The yield of the purified biodiesel was determine gravimetrically using Eq. (4).

$$\text{Biodiesel yield (\%)} = \frac{\text{weight of purified LOMOB (g)}}{\text{weight of LOMO sample (g)}} \times 100 \quad (4)$$

TABLE I:
PROCESS PARAMETERS AND THEIR VALUES AT DIFFERENT LEVELS

Symbols	Parameters	unit	Levels		
			1	2	3
A	Methanol/oil	-	9:1	12:1	15:1
B	Catalyst loading	wt%	2.5	3.5	4.5
C	Time	min	50	60	70
D	Temp	°C	55	65	75

TABLE II:
TAGUCHI L9 EXPERIMENTAL MATRIX FOR LOMO
TRANSESTERIFICATION

Std Order	R un	Met h/O il ratio	Cat. load ing (wt %)	Tim e (mi n)	Te mp (°C)	LOM OB (%)	Predi cted Valu e	SNR
7	1	15	2.5	70	65	93.12	93.77	39.38
6	2	12	4.5	50	65	87.72	86.58	38.86
9	3	15	4.5	60	55	87.1	87.59	38.80
2	4	9	3.5	60	65	89.6	90.09	39.04
8	5	15	3.5	50	75	92.23	91.09	39.29
3	6	9	4.5	70	75	72.53	73.18	37.21
5	7	12	3.5	70	55	82.89	83.54	38.37
1	8	9	2.5	50	55	73.97	72.83	37.38
4	9	12	2.5	60	75	72.33	72.82	37.18

III. RESULT AND DISCUSSION

A. Characterization of bio-alkaline and hybrids

Basic strength

Hammett indicator test conducted for the basicity determination for the synthesized catalyst, CE-CaO:CBP@800 NPs showed the basic strength of H_{22.8}. This was taken to be higher than the weakest indicator (H_{9.8}). Thus, the higher basic strength observed in the catalyst is due to the present and the combined strengths of the two major active basic ions (K⁺ and Ca⁺), which are responsible for its high catalytic activities in the conversion process.

FT-IR

The infrared (IR) spectra of CE-CaO/CPB@800 NPs is depicted in Fig 1, which shows the bands of available functional groups. The strong band at 3642 cm⁻¹ are attributed to (—OH) of absorbed moisture on the catalyst surface [21]. This was also attributed to the hygroscopic nature of CaO. The characteristic band around 1411 and 873 cm⁻¹ can be accredited to the carbonyl (O—C—O) vibration of metal carbonate entities resulting to K—O and Ca—O vibrations at high calcination temperature. The broad band around 500 cm⁻¹ could be accredited to vibratory stretching of Ca—O and is clearly appeared in the spectrum. The EDX plot Fig.1a corroborate with the observed functional groups identified in the IR spectrum of the sample.

The XRD Analysis

The X-ray diffraction (XRD) intensity plot (Fig.1b) shows the crystalline characteristics of the catalyst structure of CE-CaO/CPB@800 NPs catalysts. The obtained peaks were compared with the Joint Committee on Powder Diffraction Standards (JCPDS) database. Distinct peaks were observed between 14-55° and this can be attributed to the efficacy of the calcination temperature. In Fig.1b CE-CaO:CBP@800 NPs majorly contain CaO, HN₄Al₃(SO₄)₂(OH)₆ and Na K Cl. The dominant and active compound present in calcined eggshells is CaO. The result showed that the new compounds HN₄Al₃(SO₄)₂(OH)₆ and Na K Cl were formed because of the

impregnation process. The peaks at 17.65°, 29.57°, 47.43° 52.16° can be ascribed to the presence of rhombohedral structure of Ammoniolunite – Ammonium Aluminium Sulphate (HN₄Al₃(SO₄)₂(OH)₆). While the peaks at 28.6°, 40.9°, 50.7° and 67° indicates the presence of a FCC lattice structure of sodium potassium chloride (Na K Cl) which is suggested to be contributed by the CBP. This clearly indicates that these mineral particles were properly absorbed on the surface of the CaO through the impregnation process and are responsible for the effective catalytic activity of the catalyst.

SEM-EDX Analysis

The micrograph displaying the morphology of the powdered CE-CaO/CPB@800 NPs is depicted in Fig.1c. The hybrid NPs catalyst CE-CaO/CPB@800 shows the aggregate of numerous porous and spongy nature of the ash mineral particles as a result of high temperature of calcination. The particle size distribution of the non-uniform structure on the surface of the hybrid catalyst might be attributed to the merging effect of the two biogenic materials during synthesis, which clearly indicate the modified surface structure of pure CaO due to attachment of other mineral particles from the CBP catalyst. Moreover, the EDS analysis as shown in Table 3, indicated that CE contain only two major elements which are Ca and O while CBP was found to be mainly composed of a high content of K, O and Cl with little amount of P, Mg and Si. However, the hybrids of the two biogenic materials CE-CaO/CPB was found to contain majorly O, Ca, K with small amount of Cl and Si. The content of Ca was observed to increase which was minimal in CBP. The existence of an increase in K and Cl was found to be present in pure CaO, indicating the effectiveness of impregnation and calcination processes.

TABLE III:
THE EDX OF CES, CPB AND CE-CAO/CPB@800

Calcined materials	Element Composition (%)								
	O	Ca	K	Cl	P	S	Mg	Na	Si
CES @ 900°C	49.2	50.8	0.00	0.00	0.0	0.0	0.0	0.0	0.0
CPB @ 700°C	38.5	1.21	44.1	14.1	0.3	0.0	0.7	0.0	0.9
CES/CPB -800°C	44.3	34.9	18.6	1.41	0.0	0.0	0.0	0.0	0.6
	9	3	2		0	0	0	0	5

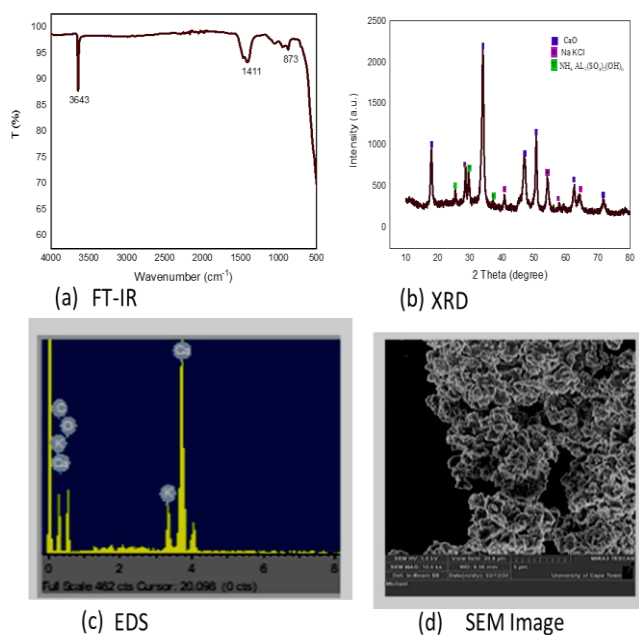


Fig. 1 (a-c): Characterization of CE-CaO/CBP @ 800 NPs catalyst (a) FT-IR, (b) XRD and (c) SEM

B. Mathematical modelling equation

The multiple regression model analysis was done to determine the effect of each parameter on LOMOB yield. The numerical value obtained for each significant parameter coefficient at 95% confident level are expressed in terms of mathematical equation for prediction of FAME yield and is presented in Eq. 5.

$$Y = 83.50 - 4.80A [1] - 2.52A [2] - 3.69B [1] + 4.74B [2] - 2.18D [1] + 6.65D [2] \quad (5)$$

Where Y is the biodiesel yield, A[1] and A[2] is methanol to oil ratio at first and second level, B[1] and B[2] is catalyst loading at first and second level and D[1] and D[2] is the reaction temperature at first and second level respectively as shown in Table 1. The equation is useful for identifying the relative impact of the factors by comparing the factor coefficients. The model equation only comprised the significant parameters viz methanol to oil, catalyst loading and temperature. The insignificant parameter (reaction time) was eliminated from the model equation. The plot of experimental values and the predicted values is depicted in Fig. 2. The plot shows that both values are in good agreement, which indicate the significance and accuracy of the model in evaluating the yield(s).

The result of the transesterification process of LOMO together with the predicted yields are presented in Table 2. The analysis by ANOVA was used to determine the significance of the model for the optimization process together with individual parametric effect on the response. Table 3 shows the ANOVA of the transesterification process of the linseed oil-marula oil biodiesel (LOMOB). The result majorly

focuses on the mean performance characteristics established by Fischer's test value (F-value) estimation. The F-value and the sum of squares are used to explain the impact and the status of each parameter on the yield. The p-value measures the probability of obtaining the F-value due to noise and the value below 0.05 indicate the significance of a specific parameter. The high sum of square value of 567.14 obtained for the model in the study was enough to indicate that the model is significant. The ANOVA also shows that out of the four selected parameters for the study, the significant effect of the two parameters is well pronounced on the yield. Nevertheless, the effect of catalyst loading with the p-value of 0.05 is less significant while the effect of reaction time is completely negligible in the chosen range of parameters. Among the three parameters in Table 4, methanol/oil ratio has the highest influence on FAME yield with F-value and sum of square of 42.17 and 248.77 respectively. Reaction temperature also have an influence on FAME yield with an F-value of 35.04 and sum of square of 206.73 and 2.7 % chance to obtain its high value due to noise. The catalyst loading also have effect on FAME yield but with less significant than methanol/oil ratio and temperature. The significance of each parameter could also be demonstrated with the estimation of the contribution factors of individual parameter in the process. The contribution factors are evaluated by Eq. 3 and the results obtained is displayed in Table 5. The contribution factor of methanol/oil molar ratio was found to be 43.86, which significantly influenced the process with strong impact, reaction temperature was found with 36.45 contribution factor which also shows strong impact on the yield and the catalyst loading with only 18.92 contribution factor which indicate less influence on FAME yield as compared to the other two parameters.

The analyses of the process that was also used to evaluate the significance and the applicability of the chosen model for the transesterification of the LOMO are displayed in Table 4. This include the correlation coefficient R^2 , adjusted R^2 and predicted R^2 . The value of correlation coefficient R^2 (0.9897) obtained signifies the accuracy and the good fit of data in the chosen model. The adjusted R^2 (0.9588) and predicted R^2 (0.7915) indicates good agreement between each other with acceptable difference of 0.16 which is less than the maximum allowable difference of 0.2. This shows the extent of variation explained by the model about the mean and the prediction aptitude of the response within the satisfactory range. Adequate precision ratio of 13.833 greater than the allowable ratio of 4 is desirable and indicate adequate response to predict and optimise the yield. The low standard deviation value of 1.72 and the coefficient of variance of 2.06 % implies the validity of the model and its capability to predict the best condition with high precision.

TABLE IV:
ANOVA FOR THE SELECTED FACTORIAL MODEL

Source	Sum of Squares	df	Mean Square	F-value	p-value
Model	567.14	6	94.52	32.04	0.030
A- Methanol/oil	248.77	2	124.39	42.17	0.023
B-Catalyst	111.63	2	55.82	18.92	0.050
D-Temp	206.73	2	103.37	35.04	0.027
Residual	5.90	2	2.95		7
Cor Total	573.04	8			

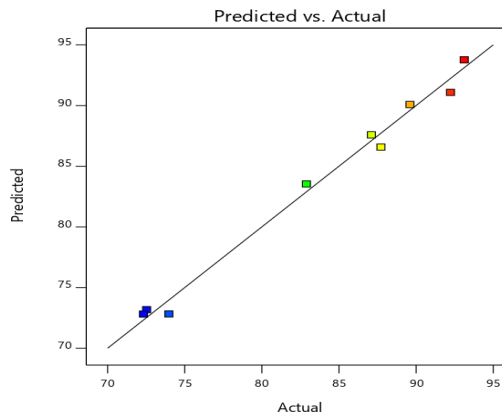


Fig. 2: Predicted versus actual values of LOMOB yield

C. Effect of process parameters on LOMOB yield

The effect of the process variables on LOMOB production can be adjudged based on the experimental result. From the ANOVA investigations and the contribution factor of individual parameter (Table 3 and 4), it is observed that methanol to oil molar ratio, catalyst loading, and reaction temperature were the significant parameters that influences LOMOB yield and hence their impacts are studied. The effect of time is not discussed because it appears insignificant with a negligible impact on LOMOB yield. The reaction time selected were within the range studied for the maximum yield conversion of LOMO. Although the reaction time is a vital factor in the conversion reaction process but in this case, it was insignificant since there was less variation in FAME yield within the range of time chosen.

TABLE V:
FIT STATISTICAL OF THE MODEL FOR LOMOB PRODUCTION PROCESS

R ²	0.9897	Standard deviation	1.72
Adjusted R ²	0.9588	Mean	83.50
Predicted R ²	0.7915	C.V. (%)	2.06
Adeq Precision	13.8334	PRESS	119.47
BIC	37.12	-2 Log Likelihood	21.74
AICc	147.74		

TABLE VI:
PERCENTAGE CONTRIBUTION OF EACH PROCESS PARAMETER ON THE YIELD

Parameter	Contribution factor (%)
Methanol-to-oil molar ratio (A)	43.86
Catalyst Loading (B)	19.68
Temperature (D)	36.45
Reaction time (C)	Insignificant

Effect of methanol to oil molar ratio

Methanol to oil molar ratio is observed to be the most influential parameter affecting LOMOB yield (Fig 3). The investigation of the impact of this parameter was done by varying the three levels at 9:1, 12:1 and 15:1. The optimum LOMOB yield was observed at methanol-to-oil ratio of 15:1 as confirmed by Figure 3. As the transesterification reaction is reversible in nature, large amount of methanol is required to sustain the reaction in the forward direction which favours the product formation [8]. However, precaution must be taken to avoid dilution of catalyst with excess methanol, which may lead to deactivation of the activity of the catalyst in the reaction process. Thus, excessive increase of methanol to oil ratio hinders glycerol separation leading to decrease in biodiesel yield [9].

Effect of catalyst loading

Catalyst concentration is another important variable that influence biodiesel yield. The effect of CE-CaO/CBP@800 loading was studied by varying the weight from 2.5 to 4.5 wt%. As displayed in Fig.3, by increasing the catalyst from the lowest level (2.5 wt%), leads to gradual increase in LOMOB till 3.5 wt%. Further increase at this drastically reduces the yield. This because excessive use of CE-CaO/CBP@800 is

found to form emulsion resulting on higher viscosity of the reaction mixture, thereby promoting poor agitation and hinders biodiesel formation [23]. In this study, the impact of catalyst loading was less pronounced on LOMOB maximum yield as compared with that of methanol/oil ratio and temperature. The catalytic activity of the chosen range of catalyst loading during the transesterification reaction was able to convert all LOMO to LOMOB.

Effect of reaction temperature

Reaction temperature is observed to be another most influential factor aside methanol to oil ratio on LOMOB yield. Temperature effect on FAME yield was studied by varying the values in the order of 55, 65 and 75 °C at three different levels (Table 1). The maximum yield was observed at the temperature of 65 °C. Fig. 3 shows that LOMOB yield increases from the temperature of 55 °C to maximum at 65 °C, thereafter decreases drastically at further increase in temperature. Although, increase in temperature increases the rate of the reaction, excessive increase in temperature above the boiling point of methanol during production do not favour the molar ratio of methanol in the reaction mixture due to evaporation. The resultant effect may lead to a shift of the reversible equilibrium toward the backward reaction, which favour triglyceride formation (soap). Moreover, the selected temperature within the study range was capable to convert LOMO to LOMOB without much loss of methanol.

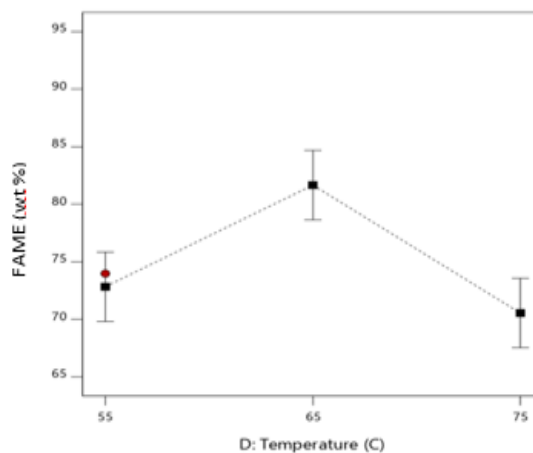


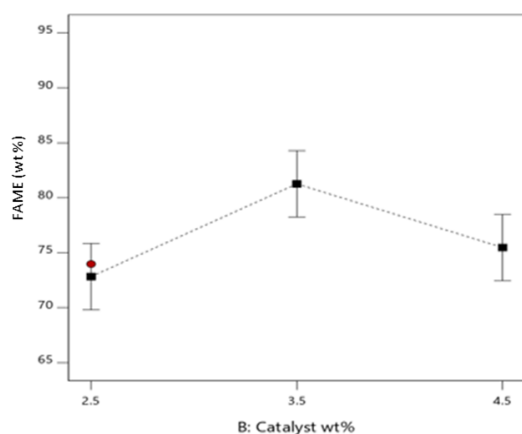
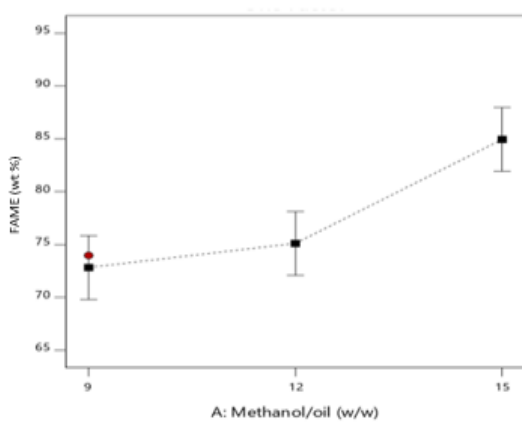
Fig. 3: the plot of FAME yield versus process parameters

D. Optimization of the process parameters and model validation

The process optimization was achieved by solving the regression equation (Eq. 4). The optimum predicted values obtained are methanol to oil ratio of 15:1, CE-CaO/CBP@800 loading of 3.5 wt.%, reaction time of 50 min, and temperature 65 °C with LOMOB yield of 95.53 wt.%. The predicted condition was validated by conducting a triplicate confirmatory experiment with an average yield of 95.03 wt.%.

E. Reusability Test

Eco-friendliness and economic viability of heterogeneous catalysts are based on their recyclability. The reusability test of CE-CaO/CBP@800 was investigated in biodiesel production by repeated reused of the recovered catalyst in subsequent transesterification reaction. This was achieved under optimum condition by decanting of the spent catalyst after each round of experiment and then washed with hexane, filtered and dried in the oven for 6 h at 120 °C and further activated at 700 °C for 2 h. The activated catalyst was then used in subsequent cycle of production. FAME yield of 85.2% was observed at the 6th cycle (Fig. 4). A similar method has also been reported in literature with a minimal decrease of 6.2 % after the 5th cycle when a gold-core-shell was used to transesterify sunflower oil [24]. The decrease in FAME yield however might be attributed to the weakening of the catalyst activity as a result of leaching and blockages of the catalyst active sites by FAME and water molecules [25]. However, CaO catalyst is noted for its severe leaching characteristics due to its hygroscopic nature. Attachment of K from banana peels on the surface of CaO (eggshells) coupled with high temperature calcination prevent leaching [26]. The reusability process was studied up to 6 cycles with infinitesimal decrease in LOMOB yield (Fig. 4). Thus, the result confirm that the developed catalyst has appreciable heterogeneous qualities, which can be adopted at industrial level.



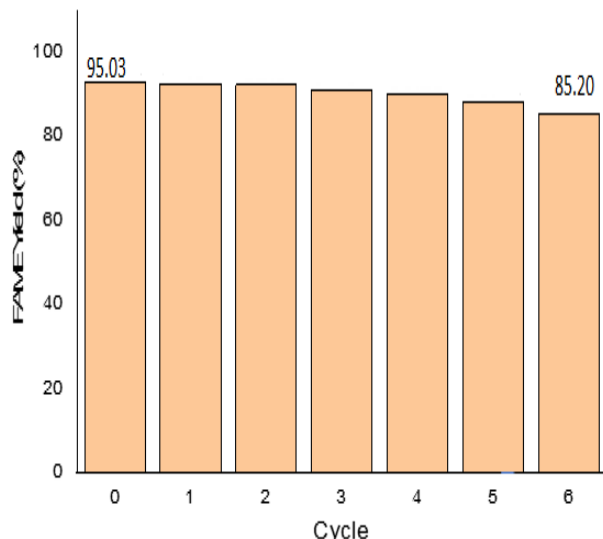


Fig. 4: Reusability test of CE-CaO/CBP@800

F. Fuel characterization

The quality of LOMOB produced was ascertained through its physiochemical properties. The obtained result compared with the ASTM D6751, EN 14214 and SAN 833 standards (Table 6). LOMOB is a good substitute fuel for diesel engines, due to all its properties which were within the standard specifications for biodiesel. The Cetane number of 58 is above the minimum required, which shows that LOMOB produced has a short ignition delay, which will lead to an effective cold start-up of a diesel engine [27]. The high calorific value of LOMOB suggest its improved energy capacity [28]. The low acid value of LOMOB suggest that the metal part of the engine will not be damaged and the associated problem such as injector fouling, fuel filter plugging and deposit formation will be minimised when LOMOB is applied in diesel engines [14].

TABLE VI:

PHYSIOCHEMICAL PROPERTIES OF LOMOB

Property	Unit	LOMOB	ASTM D6751	EN 14214	SAN 833
Physical state/colour	-	Liquid/golden yellow	-	-	
Density @ 25 °C	g/cm ³	0.864	0.850	0.86 – 0.90	0.86 – 0.90
Kinematic Viscosity @ 40 °C	mm ² /s	3.69	1.9 – 6.0	3.5 – 5.0	3.5 – 5.0
Acid Value	mg KOH/g	0.42	0.5 max	0.5 max	0.5 max
Saponification value		175.31	-	-	
Iodine Value	g I ₂ /100 g	79.27	-	120 max	140 max
Calorific value	MJ/kg	40.4	-	35	-
Cetane number		58	47 min	51 min	51 min

IV. CONCLUSION

A new bio-composite catalyst was successfully developed from waste biomass material of eggshells and banana peels. The synthesized catalyst showed the presence of high alkali elements. The crystal structure of the catalyst contains majorly of calcium and potassium compounds, which are responsible for the high catalytic function of catalyst in the transesterification of LOMO. The transesterification process was designed and modelled by the Taguchi approach. The optimum values obtained was methanol to oil ratio 15:1, CE-CaO/CBP@800 of 3.5 wt%, reaction temperature of 65 °C and time of 60 min, which led to a validated average LOMOB yield of 95.03 wt%. The study indicates that the CE-CaO/CBP@800 catalysed transesterification with methanol was effective. The properties of the final product obtained were within the biodiesel specification standards. The CE-CaO/CBP@800 could be reused for six reaction cycles with high yield. Thus, the combined effect of biogenic waste materials and the blend linseed-marula oil are potential source of an effective and sustainable feedstock for biodiesel development.

REFERENCES

- [1] P. R. Pandit and M. H. Fulekar, "Egg shell waste as heterogeneous nanocatalyst for biodiesel production: Optimized by response surface methodology," *J. Environ. Manage.*, vol. 198, pp. 319–329, Aug. 2017. <https://doi.org/10.1016/j.jenvman.2017.04.100>
- [2] W. U. Rahman *et al.*, "Biodiesel synthesis from eucalyptus oil by utilizing waste egg shell derived calcium based metal oxide catalyst," *Process Saf. Environ. Prot.*, vol. 122, pp. 313–319, 2019. <https://doi.org/10.1016/j.psep.2018.12.015>
- [3] N. Tshizanga, E. F. Aransiola, and O. Oyekola, "Optimisation of biodiesel production from waste vegetable oil and eggshell ash," *South African J. Chem. Eng.*, vol. 23, pp. 145–156, Jun. 2017. <https://doi.org/10.1016/j.sajce.2017.05.003>
- [4] A. Marwaha, P. Roshia, S. K. Mohapatra, S. K. Mahla, and A. Dhir, "Biodiesel production from Terminalia bellerica using eggshell-based green catalyst: An optimization study with response surface methodology," *Energy Reports*, vol. 5, pp. 1580–1588, 2019. <https://doi.org/10.1016/j.egy.2019.10.022>
- [5] V. O. Odude *et al.*, "Application of Agricultural Waste-Based Catalysts to Transesterification of Esterified Palm Kernel Oil into Biodiesel: A Case of Banana Fruit Peel Versus Cocoa Pod Husk," *Waste and Biomass Valorization*, vol. 10, no. 0123456789, pp. 877–888, 2019. <https://doi.org/10.1007/s12649-017-0152-2>
- [6] M. Gohain, A. Devi, and D. Deka, "Musa balbisiana Colla peel as highly effective renewable heterogeneous base catalyst for biodiesel production," *Ind. Crops Prod.*, vol. 109, no. August, pp. 8–18, Dec. 2017. <https://doi.org/10.1016/j.indcrop.2017.08.006>
- [7] G. Pathak, D. Das, K. Rajkumari, and L. Rokhum, "Exploiting waste: Towards a sustainable production of biodiesel using: Musa acuminata peel ash as a heterogeneous catalyst," *Green Chem.*, vol. 20, no. 10, pp. 2365–2373, 2018. <https://doi.org/10.1039/C8GC00071A>
- [8] A. O. Etim, P. Musonge, and A. C. Eloka-Eboka, "Effectiveness of biogenic waste-derived heterogeneous catalysts and feedstock hybridization techniques in biodiesel production," *Biofuels, Bioprod. Biorefining*, vol. 14, pp. 620–649, 2020. <https://doi.org/10.1002/bbb.2094>
- [9] S. H. Dhawane, T. Kumar, and G. Halder, "Biodiesel synthesis from Hevea brasiliensis oil employing carbon supported heterogeneous catalyst: Optimization by Taguchi method," *Renew. Energy*, vol. 89, pp.

- 506–514, 2016.
<https://doi.org/10.1016/j.renene.2015.12.027>
- [10] I. M. Ogbu, V. I. E. Ajiwe, and C. P. Okoli, "Performance Evaluation of Carbon-based Heterogeneous Acid Catalyst Derived From Hura crepitans Seed Pod for Esterification of High FFA Vegetable Oil," *Bioenergy Res.*, vol. 11, no. 4, pp. 772–783, 2018.
<https://doi.org/10.1007/s12155-018-9938-8>
- [11] J. Nisar *et al.*, "Enhanced biodiesel production from Jatropha oil using calcined waste animal bones as catalyst," *Renew. Energy*, vol. 101, pp. 111–119, 2017.
<https://doi.org/10.1016/j.renene.2016.08.048>
- [12] A. O. Falowo and E. Betiku, "A novel heterogeneous catalyst synthesis from agrowastes mixture and application in transesterification of yellow oleander-rubber oil: Optimization by Taguchi approach," *Fuel*, vol. 312, no. December 2021, p. 122999, 2022.
<https://doi.org/10.1016/j.fuel.2021.122999>
- [13] Y. H. Tan, M. O. Abdullah, J. Kansedo, N. M. Mubarak, Y. S. Chan, and C. Nolasco-Hipolito, "Biodiesel production from used cooking oil using green solid catalyst derived from calcined fusion waste chicken and fish bones," *Renew. Energy*, vol. 139, no. November 2014, pp. 696–706, 2019.
<https://doi.org/10.1016/j.renene.2019.02.110>
- [14] A. O. Etim, P. Musonge, and A. C. Eloka-Eboka, "An effective green and renewable from the fusion of bi-component transesterification of linseed oil methyl ester," *Biofuels, Bioprod. Biorefining*, pp. 1–12, 2021.
- [15] A. P. Bora, S. H. Dhawane, K. Anupam, and G. Halder, "Biodiesel synthesis from Mesua ferrea oil using waste shell derived carbon catalyst," *Renew. Energy*, vol. 121, pp. 195–204, 2018.
<https://doi.org/10.1016/j.renene.2018.01.036>
- [16] S. H. Dhawane, A. P. Bora, T. Kumar, and G. Halder, "Parametric optimization of biodiesel synthesis from rubber seed oil using iron doped carbon catalyst by Taguchi approach," *Renew. Energy*, vol. 105, pp. 616–624, 2017.
<https://doi.org/10.1016/j.renene.2016.12.096>
- [17] S. H. Dhawane, B. Karmakar, S. Ghosh, and G. Halder, "Parametric optimisation of biodiesel synthesis from waste cooking oil via Taguchi approach," *J. Environ. Chem. Eng.*, vol. 6, no. 4, pp. 3971–3980, Aug. 2018.
<https://doi.org/10.1016/j.jece.2018.05.053>
- [18] R. Kumar, K. Sureshkumar, and R. Velraj, "Optimization of biodiesel production from Manilkara zapota (L.) seed oil using Taguchi method," *Fuel*, vol. 140, pp. 90–96, 2015.
<https://doi.org/10.1016/j.fuel.2014.09.103>
- [19] D. Kumar, T. Das, B. S. Giri, E. R. Rene, and B. Verma, "Biodiesel production from hybrid non-edible oil using bio-support beads immobilized with lipase from *Pseudomonas cepacia*," *Fuel*, vol. 255, no. February, p. 115801, 2019.
<https://doi.org/10.1016/j.fuel.2019.115801>
- [20] P. Kumar *et al.*, "Characterization, activity and process optimization with a biomass-based thermal power plant's fly ash as a potential catalyst for biodiesel production," *RSC Adv.*, vol. 5, no. 13, pp. 9946–9954, 2015.
<https://doi.org/10.1039/C4RA13475C>
- [21] G. Chen, R. Shan, J. Shi, and B. Yan, "Transesterification of palm oil to biodiesel using rice husk ash-based catalysts," *Fuel Process. Technol.*, vol. 133, pp. 8–13, 2015.
<https://doi.org/10.1016/j.fuproc.2015.01.005>
- [22] G. Y. Chen, R. Shan, J. F. Shi, and B. B. Yan, "Transesterification of palm oil to biodiesel using rice husk ash-based catalysts," *Fuel Process. Technol.*, vol. 133, pp. 8–13, 2015.
<https://doi.org/10.1016/j.fuproc.2015.01.005>
- [23] P. Verma and M. P. Sharma, "Review of process parameters for biodiesel production from different feedstocks," *Renew. Sustain. Energy Rev.*, vol. 62, pp. 1063–1071, 2016.
<https://doi.org/10.1016/j.rser.2016.04.054>
- [24] M. Banerjee, B. Dey, J. Talukdar, and M. Chandra, "Production of biodiesel from sunflower oil using highly catalytic bimetallic gold-silver core-shell nanoparticle," *Energy*, vol. 69, pp. 695–699, 2014.
<https://doi.org/10.1016/j.energy.2014.03.065>
- [25] N. Mansir, S. Hwa Teo, M. Lokman Ibrahim, and T. Y. Yun Hin, "Synthesis and application of waste egg shell derived CaO supported W-Mo mixed oxide catalysts for FAME production from waste cooking oil: Effect of stoichiometry," *Energy Convers. Manag.*, vol. 151, 2017.
<https://doi.org/10.1016/j.enconman.2017.08.069>
- [26] A. S. Yusuff, O. D. Adeniyi, M. A. Olutoye, and U. G. Akpan, "A Review on Application of Heterogeneous Catalyst in the Production of Biodiesel from Vegetable Oils," *J. Appl. Sci. Process Eng.*, vol. 4, no. 2, pp. 142–157, 2017.
<https://doi.org/10.33736/jaspe.432.2017>
- [27] A. O. Etim, P. Musonge, and A. C. Eloka-eboka, "Transesterification via Parametric Modelling and Optimization of Marula (*Sclerocarya birrea*) Seed Oil Methyl Ester Synthesis," *J. Oleo Sci.*, vol. 93, no. 1, pp. 77–93, 2021.
<https://doi.org/10.5650/jos.ess20258>
- [28] M. K. Yesilyurt, C. Cesur, V. Aslan, and Z. Yilbasi, "The production of biodiesel from safflower (*Carthamus tinctorius* L.) oil as a potential feedstock and its usage in compression ignition engine: A comprehensive review," *Renew. Sustain. Energy Rev.*, vol. 119, no. October 2019, p. 109574, 2020
<https://doi.org/10.1016/j.rser.2019.109574>