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ORIGINAL ARTICLE

Thermal modification of chicken eggshell as heterogeneous catalyst for palm kernel biodiesel production in an optimization process

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Abstract

Synthesis of the heterogeneous chicken eggshell catalyst (CEC) using thermal treatment at temperatures of 800 °C (CEC800) and 900 °C (CEC900) for palm kernel biodiesel (PBD) production was undertaken. The morphology, chemical composition, and surface area of the catalysts were determined. Catalyst's efficiency in the production of biodiesel from palm kernel oil was studied using a definitive screening design of optimization technique. The optimization parameters investigated were calcination temperature, catalyst quantity, methanol:oil molar ratio, and reaction time. The stability of the catalyst after the 5th cycle of repeated usage was studied. The CEC900 contained the highest chemical composition of 32.36% (wt) calcium with the morphology of highly porous, uniformly distributed spherical shape, with no agglomeration. A surface area of 120.4 m^2/g and a smaller pore size of 1.324 nm were obtained from the CEC900. The optimal operating parameters of 4% (*w*/*w*) catalyst quantity, 10:1 methanol:oil molar ratio, 50 °C reaction temperature, 1 h reaction time, and 900 °C calcination temperature were obtained to yield optimum biodiesel of 97.10%. Qualitative characterization confirmed that the CEC900 is suitable to produce quality PBD of ASTM standard. Reduction in the catalytic activity of 6% PBD was noticed in the 5th cycle. Therefore, thermal-modified CEC is a suitable and low-cost catalyst for biodiesel production.

Keywords Transesterification · Biodiesel · Eggshell · Catalyst · Calcination · Optimization

1 Introduction

Increasing demand in energy coupled with petroleum price increase has necessitated the need for alternative sources of energy [17]. Biodiesel, alternative fuel to diesel, is a non-toxic and environmentally friendly fuel derived from renewable sources. It is mainly obtained through transesterification of oils/fats from vegetable or animal origin and alcohol in the presence of a catalyst to produce a mixture of fatty acids alkyl esters and glycerol.

Biodiesel is popularly produced with the use of homogeneous base catalysts [6]. However, such catalysts exhibit major disadvantages resulting in the high cost of biodiesel production. The shortcomings include the fact that they cannot be reused or regenerated; they are difficult to separate from the products and require more equipment. These have resulted in a high cost of biodiesel production. Thus, heterogeneous catalysts are good alternatives worthy of research to overcome all of these challenges associated with homogeneous catalysts.

Heterogeneous catalysts are of various types which include supported catalysts, alkali earth oxides (calcium oxide (CaO), and magnesium oxide (MgO)), and hydrotalcite catalyst [37]. Recent studies include the use of eggshells and mollusk shells as heterogeneous catalysts for biodiesel production, which have been reported to be re-useable without loss of activity. The catalyst preparation from waste eggshells was found to be simple [6]. Chicken eggshells consist of protein fibers, accompanied by carbonates of calcium and magnesium, calcium phosphate and organic substances and water [39]. Calcium

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carbonate was reported as the major constituent of chicken eggshell constituting more than 90% of the oxides which are essential ingredients in the heterogeneous catalyst for biodiesel production.

Several researchers have reported the potential of eggshells as a biodiesel production catalyst [33]. Not less than 95% biodiesel yield was obtained at 4 h calcination time and 800 °C calcination temperature [37]. The high calcination time could increase the energy cost of biodiesel production. Wei, Xu, and Li [38] studied the catalyst synthesis by calcination of chicken eggshell at different temperatures for transesterification and obtained a yield of 95% biodiesel with a 3% (*w/w*) catalyst, a calcination temperature of 1000 °C at 2 h and reaction temperatures of 65 °C. The high calcination temperature of 1000 °C might not be cost-effective. Chen, Shan, Shi, and Yan [7] studied waste ostrich eggshell as a biodiesel production catalyst using palm oil in an ultrasonic-assisted transesterification and obtained a maximum yield of 92.7% at 8% (*w/w)* catalyst quantity, 9:1 MeOH:oil ratio, 60 min reaction time and 60% amplitude ultrasonic power. In this case, the reaction process was ultrasonic-assisted and the procedure is more complex. Since it requires additional technical and scientific enhancement to achieve commercialization and industrialization. The ultrasonic power must also be under control to avoid soap formation in fast reaction during the process [27]. Moreso, palm oil was used and the optimization procedure employed was a linear form, deprived of interaction effects of the variables on the biodiesel yield. Shi, Jiang, Zhou, and Gao [29] investigated eggshell as a catalyst with the use of acetone as a solvent and obtained 93% yield of biodiesel from jatropha oil at 7 wt% catalyst, 1:1 (acetone/oil) weight ratio, 9:1 MeOH:oil ratio, 2 h reaction time at 65 °C. The use of acetone as the co-solvent in their study could increase the cost of biodiesel production. Modification of eggshell as a biodiesel production catalyst was also investigated by Niju, Begum, and Anantharaman [21]. The result obtained indicated that the FAME conversion was 67.57% and 94.52% for commercial grade CaO and eggshell CaO, respectively. However, the eggshell modification procedure being more time consuming, and complex can increase the cost of biodiesel production. Goli, Mondal, and Sahu [11] developed a heterogeneous catalyst from chicken eggshell for biodiesel production using soybean oil to obtain 93% optimum biodiesel yield. Although various calcination temperatures of between 500 and 1100 °C were carried out, its effects on the biodiesel yield in an optimization study were not investigated, hence this study.

Nowadays, non-edible seed oil has greatly received attention as feedstock for biodiesel production to avoid food-fuel debate. Such oils include palm kernel oil (PKO), *Jatropha curcas*, and neem seed oil [31]. The PKO is produced from the kernel of the palm tree (*Elaeis guineensis)* which is abundantly found in West African countries and Nigeria in particular [1]. Several works have been reported on PKO biodiesel production. The homogeneous catalyst for PKO transesterification was reported by Alamu, Akintola, Enweremadu, and Adeleke [5]. Aladetuyi, Olatunji, Ogunniyi, Odetoye, and Oguntoye [4] reported the conversion of PKO to biodiesel by a heterogeneous catalyst, but the catalyst was from *Cocoa pod ash*. Viele, Chukwuma, and Uyigue [36]; Jaturong, Boonyarach, Kunchana, Pramoch, and Peesamai [13]; Igbokwe and Nwafor [12] and Tarigan, Prakoso, Siahaan, and Kaban [35] reported various works on biodiesel production from PKO. However, the use of CaO of chicken eggshell origin as a PKO biodiesel catalyst in an optimization study using definitive screening design is yet to be reported, to the best of the authors' knowledge.

Several experimental design techniques such as central composite, box–behnken, full factorial, mixture designs, taguchi experimental design, orthogonal array design [3, 30, 40] and definitive screening design (DSD) can be employed for optimization study. But among them, DSD has not been extensively utilized for biodiesel production, despite its numerous advantages over others. The DSD is an experimental design tool that possesses maximal precision and a mid-sizeable number of operating variables with a minimal number of experimental runs to optimize a process [15]. It is highly innovative in terms of screening of variables where main variables are not aliased with each other or with two-way interactions, but allows estimation of quadratic terms. Among other advantages of DSD over the traditional experimental designs is the efficient estimation of main and quadratic variables with no or fewer trials. In the DSD, if the important variables are few it collapses the design to a "one-shot" design that supports a response-surface model. However, if many variables are significant, the DSD can augment the variables to support a response-surface model [1].

The study focuses on the determination of the calcination temperature effect on the quality of the chicken eggshell catalyst (CEC) and the corresponding PBD produced by employing a definitive screening design for optimization study. This is in a bid to enhance the development of chicken eggshell as a value-added product for biodiesel production. The determination of the calcination temperature effect on the quality of the CaO catalyst in this study is novel. Besides, the optimization of biodiesel production from PKO using CaO of chicken eggshell has not been reported. It is noteworthy that this study used CaO obtained from chicken eggshells by calcination only. This is to reduce the processing time and cost-effectiveness of the biodiesel production.

2 Experimental

2.1 Materials

Chicken eggshells were gathered from a restaurant in Ilorin metropolis, Kwara State, Nigeria, and washed twice by distilled water to eliminate impurities and unwanted whitish organic

material at the internal eggshell surface. Palm kernel oil (PKO) was purchased from a local market in *Obaagun*, Ifelodun Local Government, Osun State, Nigeria. The physicochemical properties of the PKO were determined by methods of the Association of Official Analytical Chemists (AOAC). Anhydrous methanol (MeOH) of analytical grade was purchased from Sigma-Aldrich. A batch reactor of 2 L working volume manufactured by Armfield and computer interphase used in this study are shown in Figure 1 a and b, respectively.

2.2 Eggshell catalyst synthesis

The prepared sample of the eggshell was dried in an oven for 24 h at 100 °C and ground to powder form. It was screened with a mesh size of < 180 μm, charged into a polyethylene bag and kept inside a desiccator. The prepared eggshell was calcined in a muffle furnace at various temperatures of 800 and 900 °C to synthesize chicken eggshell catalysts of CEC800 and CEC900, respectively. The calcination process was to obtain highly active calcium oxide (CaO) from the eggshell. The CEC800 and CEC900 were kept in the desiccator to prevent the reaction from humidity and carbon dioxide available in the air.

2.3 Thermogravimetric analysis (TGA) of eggshell

PerkinElmer TGA 4000 (Netherland) was used to determine the thermal stability of the eggshell. Nitrogen gas at a flow rate of 60 ml/min and heating rate of 10 °C/min from 25 to 1000 °C was considered as the operating conditions for the analysis.

2.4 Eggshell catalysts characterization

The developed catalysts of CEC800 and CEC 900 were characterized for their major functional group and absorption band by Fourier transform infrared spectroscopy (FTIR). The FTIR

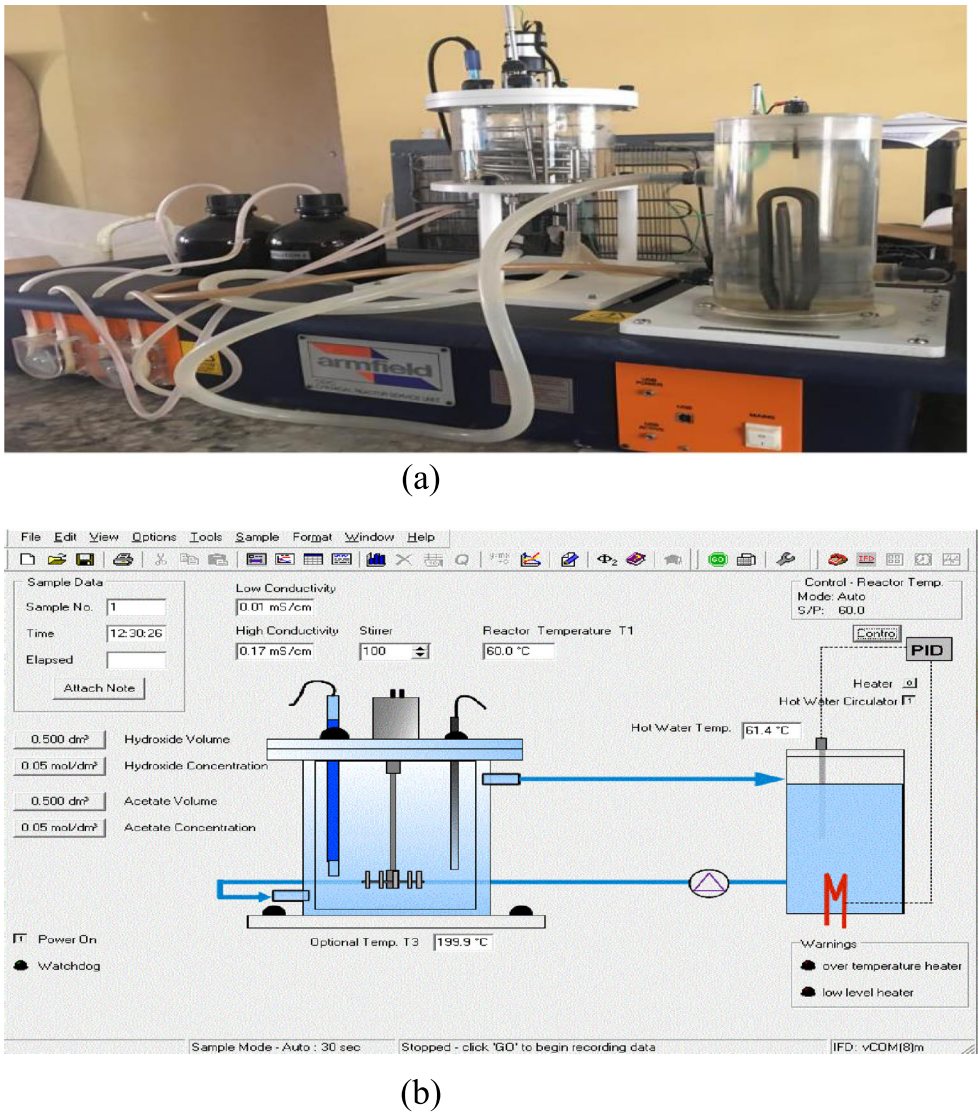


Fig. 1 Pictorial representation of **a** batch reactor setup and **b** computer interface of the armfield reactor

Shimadzu (8400S) spectrometer model was used within the wavenumber range of 450–4000 cm^{-1} and 4 cm^{-1} resolution.

The morphological structures of the catalysts were investigated by a high-resolution Scanning electron microscopy (SEM, FEI ESEM Quanta 200) at Energy Dispersive (EDS) mode. The specific surface area, pore size, and volume of the catalysts were measured with the use of Brunauer–Emmett–Teller (BET) (Nova Quantachrome version 11.03) by adsorption of nitrogen at the boiling point of liquid nitrogen (77 K). The surface area was calculated with the BET equation, as well as the pore volume and pore size.

The procedure described by Kouzu, Kasuno, Tajika, Sugimoto, Yamanaka, & Hidaka [16] was employed to analyze the strength and basicity of the catalysts. The strength of CEC was determined by the color change of the indicator. While basicity was measured by dispersing the catalyst in a toluene solution using the indicator method through the titration process. The indicator used was phenolphthalein (pK_{BH} = 9.3). The strength of the CEC site was expressed by an acidity function (H) as shown in Eq. 1.

$$H \equiv pK_{BH} + \log^{[B^-]}/_{[BH]} \quad (1)$$

where $[BH]$ = concentration of the indicator, $[B^-]$ = concentration of the conjugate base, and pK_{BH} = logarithm of the dissociation constant of the indicator.

2.5 Biodiesel production

2.5.1 Experimental design of biodiesel production by the eggshell catalysts

The design of experiment (DOE) was done using DSD of a SAS JMP Statistical Discovery version 11.0. The design was to optimize the %yield of PBD (Y, Response) by varying process parameters; MeOH:oil mole ratio (X_1), temperature (X_2), catalyst quantity (X_3), reaction time (X_4), and the catalyst (CEC800 and CEC900) (categorical factor) (X_5) as shown in Table 1. Table 2 shows the experimental runs as obtained from the DOE using the aforementioned process parameters. Equation 2 is the quadratic model equation proposed by the DSD for analysis of the response, Y:

$$Y = b_0 + b_1X_1 + b_2X_2 + \ldots + b_nX_n + \sum b_{ik}X_iX_k + \sum b_{ii}X_i^2 \quad (2)$$

Multiple regression was used for the analyses (linear and interaction effects of the process parameters for the response, Y). The coefficient of each process parameter and their interactions were observed for their significance using p values from analysis of variance (ANOVA).

2.5.2 Transesterification reaction of PKO by the eggshell catalysts

Five hundred grams (500 g) of PKO was measured into the reactor and heated to the desired temperature (55, 60, or 60 °C), MeOH in the ratio of PKO (1:6, 1:8, or 1:0, *w*/*w*) and catalyst (4, 6, or 8%, *w*/*w* to oil) were added. The agitation of the reactor was turned on to 100 rpm to mix the mixture thoroughly throughout the reaction time (1, 2, or 3 h). At the expiration of the reaction time, the mixture was cooled to room temperature. The catalyst was immediately removed from the product mixture via centrifugation. The supernatant was poured into the separating funnel for 24 h to ensure complete separation of the excess methanol, fatty acid methyl esters (FAME), and glycerol. The glycerol phase being at the bottom was removed and the fatty acid methyl esters (biodiesel) was poured in a laboratory-scale rotary evaporator, which removed the excess methanol. The biodiesel phase was further purified following an adapted procedure of Mishra, Nayak, Ghosh, Ukamanal, and Sahu [19]. The resulting FAME layer obtained was measured using a weighing balance. The %yield of biodiesel was calculated using Eq. 3.

$$\text{Biodiesel yield} = \frac{\text{Weight of biodiesel produced}}{\text{Weight of PKO used}} \quad (3)$$

Table 1 Definitive screening design for response and process parameters

Response name		Goal	Lower limit	Upper limit
%Yield of biodiesel		Maximize	–	–
Process parameters				
Name	**Codes**	**Roles**	**Values**	
MeOH:oil mole ratio (*w*/*w*)	X_1	Continuous	6	10
Temperature (°C)	X_2	Continuous	55	65
Catalyst quantity (*w*/*w*)	X_3	Continuous	4	8
Reaction time (h)	X_4	Continuous	1	3
Catalyst calcination temperature (°C)	X_5	Categorical	800	900

Table 2 Experimental matrix for the process parameters from the DSD

Exp. runs	MeOH:oil mole ratio (*w*/*w*)	Temperature (°C)	Catalyst quantity (%, *w*/*w*)	Reaction time (h)	Catalyst calcination temperature (°C)
1	8	55	8	1	800
2	6	55	8	3	900
3	6	55	4	2	800
4	10	55	4	1	900
5	8	60	6	2	800
6	6	65	8	3	800
7	10	65	8	2	900
8	10	65	4	1	800
9	8	65	4	3	900
10	8	60	6	2	900
11	10	65	6	3	800
12	6	60	4	3	900
13	10	60	8	1	800
14	10	55	4	3	800
15	6	65	4	1	800
16	10	55	8	3	900
17	6	55	6	1	900
18	6	65	8	1	900

3 Results and discussion

3.1 TGA analysis of the chicken eggshell

The result of the TGA is shown in Fig. 2 where the temperature at which chicken eggshell decomposes in a heated controlled environment is presented as a three-step weight loss. The initial weight loss of 20% occurred at a temperature of 350 °C and maintained constant weight until 600 °C. The weight loss at this point can be attributed to the removal of moisture content from the chicken eggshell. The second step reveals a significant weight loss of 50% between 600 and 675 °C which can be as a result of organic matters decomposition. At the third stage, about 15% weight loss was also noticed between 675 and 750 °C. The loss can be attributed to release of carbon dioxide from calcium carbonate to give calcium oxide. This shows that the temperature above 750 °C would be the most suitable to transform calcium carbonates of chicken eggshell to calcium oxide. The pattern of weight loss observed in this study is similar to the findings of Omojola, Freddie, & Emmanuel [25]. The effect of this temperature informed the choice of 800 and 900 °C calcination temperature adopted for this study which is adequate for complete decomposition of $CaCO_3$ to CaO.

3.2 Characterization of chicken eggshell catalysts

Figure 3 presents the absorption band in (a) chicken eggshell [2], (b) CEC800, and (c) CEC900. In Fig. 3a, the minor band at 1650 cm^{-1} can be assigned to the symmetric stretching vibrations of O-C-O bonds of unidentate carbonate at the surface of the calcium oxide [8]. While major absorption bands that occur in Fig. 3a at 1412, 879, and 711 cm^{-1} are attributed to; an asymmetric stretch of CO_3^{-2}, out of plane bend vibration mode of CO_3^{-2} and Ca-O bond, respectively [11]. Effect of calcination shows that the chicken eggshell loses carbonate. This leads to the movement of absorption bands of CO_3^{-2} molecules to the wavenumber of 1381, 871, and 712 cm^{-1} for CEC800 in Fig. 3b, and 3637.60, 1397, 868, and 709 cm^{-1} for CEC900 in Fig. 3c. The shift in the bands can be attributed to the reduction in the functional group mass attached to the CO_3^{-2} ions. The band at 3650 cm^{-1} for CEC900 is attributable to OH stretching vibration due to residual water. The presence of OH in Ca $(OH)_2$, which was adsorbed by CaO catalyst is attributed to the hygroscopic nature of CEC900 [20]. Figure 3 b and c rarely show dissimilarity to chicken eggshell (Fig. 3a) except for the difference in their energy level. However, due to heat treatment at 800 and 900 °C, eggshell gradually loses carbonate which is showed by a shift in the absorption band of CO_3^{-2} molecules wavenumber. The reason for shifting is due to the reduction and eventual destruction in the mass of the functional group associated with CO_3^{-2} ions, during thermal treatment [11]. The peaks that appeared at below 500 cm^{-1} for all the samples is attributed to CaO vibration [33].

Figure 4 presents morphology and elemental composition obtained from scanning electron microscopy (SEM) and EDS, respectively, for (a) chicken eggshell [2], (b) CEC800, and (c)

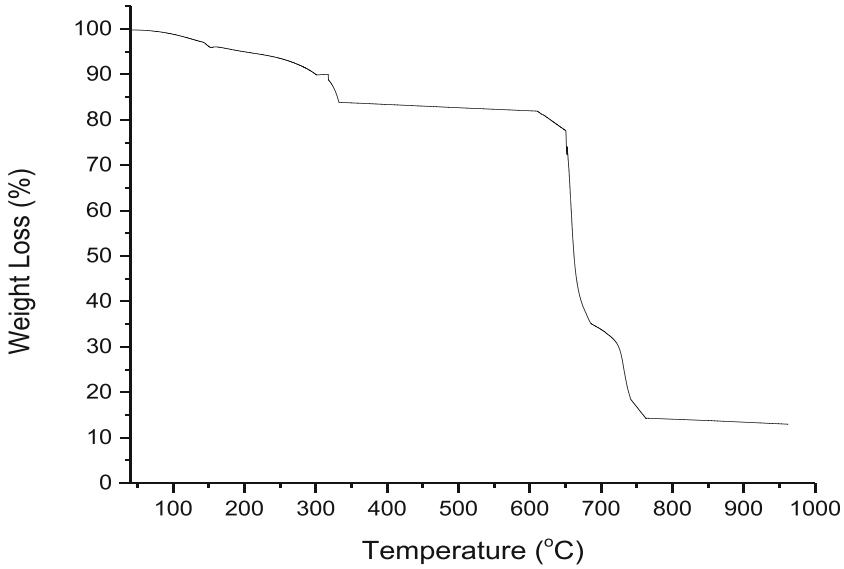


Fig. 2 TGA curve of chicken eggshell

CEC900. These SEM images (Fig. 4a–c) show dissimilarity among the three samples. Figure 4a demonstrates the presence of $CaCO_3$, which is the main substance of chicken eggshell, mixed with some granular material, agglomerated in the form of a rocky surface. Whereas Fig. 4b shows improved surface catalyst with less degree of agglomeration from the large particles and irregular crystal form, an indication of the effect of heat treatment. However, Fig. 4c shows an image with high porosity, uniformly distributed spherical morphology, with no agglomeration and decreased particle size. The smaller size of the grains and aggregates could offer higher specific surface areas [26]. This indicates that the higher temperature of 900 °C created an improved effective surface area for high catalytic activity. The change in the structural image of the samples show a similar effect in the EDS as revealed in Fig. 4a–c. The EDS of Fig. 4c (CEC900) shows highest calcium composition of 32.36 wt% and lowest carbon of 29.48 wt% among that of Fig. 4b (CEC800) calcium composition of 26.64 wt% and carbon of 31.94 wt%, and Fig. 4a (chicken eggshell) calcium composition of 21.17 wt% and carbon of 38.52 wt%. This shows that the increase in the calcination temperature increased the percentage elemental composition of calcium. This was achieved by the decomposition of calcium carbonate in the eggshell to calcium oxide and carbon dioxide. Thus, decreasing the particle sizes of CEC900 catalyst [33].

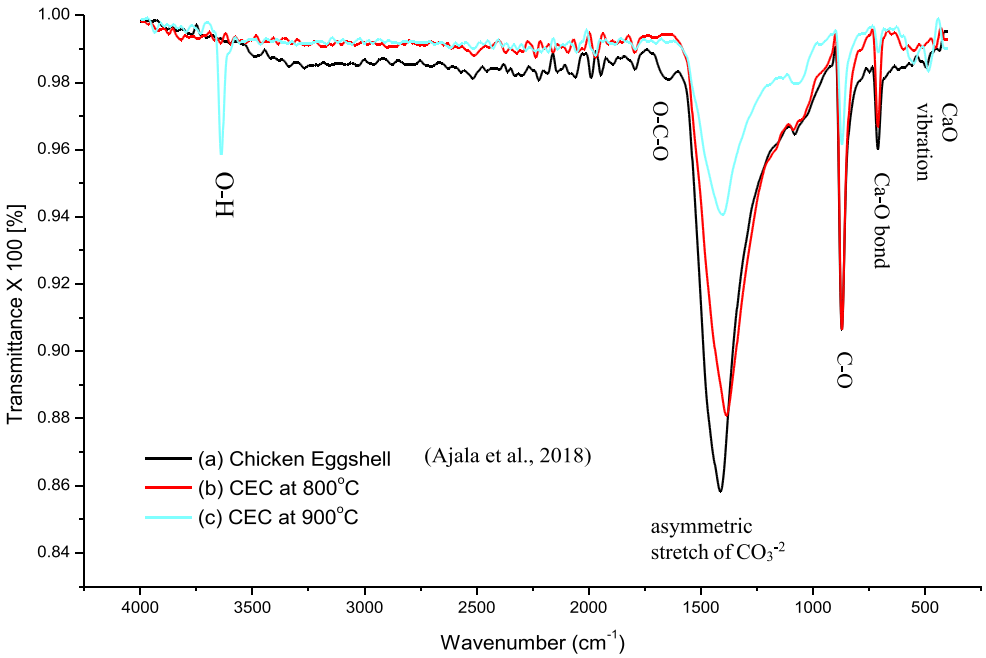
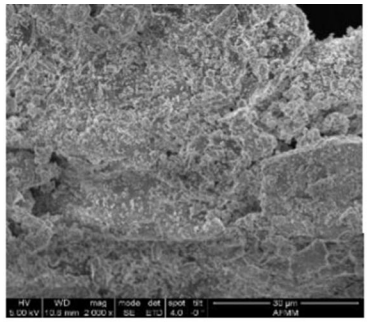
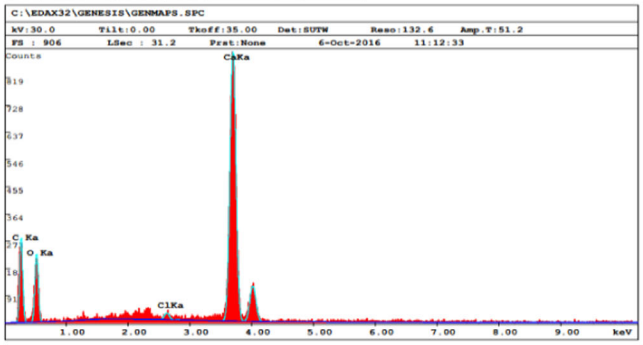


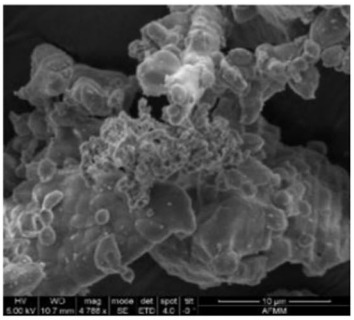
Fig. 3 FT-IR spectra of **a** chicken eggshell, **b** CEC800, and **c** CEC900



EDS Quantitative Results

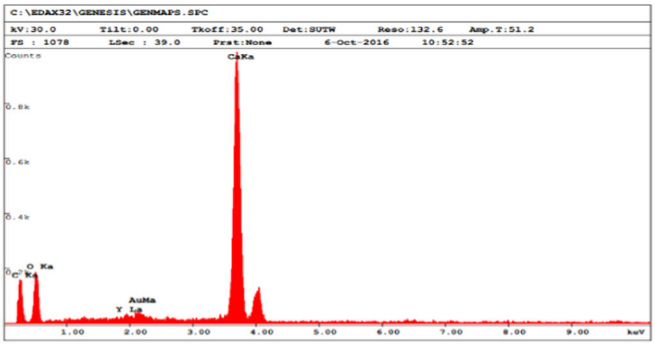
Element	Wt%	At%
CK	38.52	51.40
OK	39.88	39.94
ClK	0.43	0.20
CaK	21.17	8.46





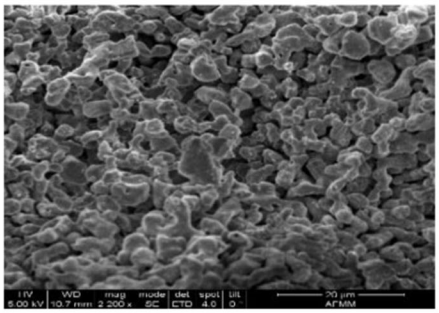
EDS Quantitative Results

Element	Wt%	At%
CK	31.94	46.22
OK	38.33	41.64
YL	1.18	0.23
NbL	1.91	0.36
CaK	26.64	11.55



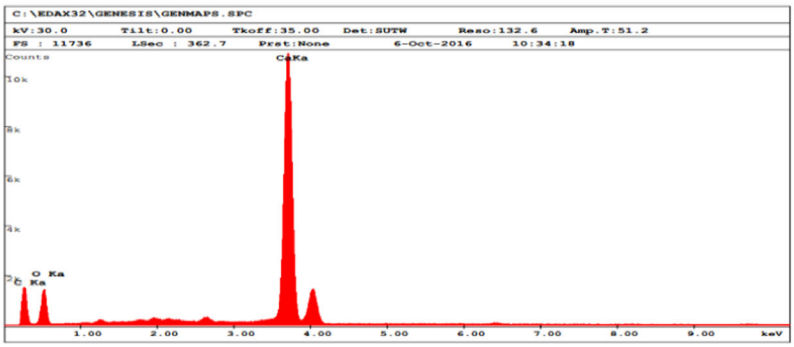
(a)

(b)



EDS Quantitative Results

Element	Wt%	At%
CK	29.48	43.46
OK	38.16	42.24
CaK	32.36	14.30



(c)

Fig. 4 The morphology structure and EDS of **a** chicken eggshell (Ajala, Eletta, et al., 2018), **b** CEC800, and **c** CEC900

The surface area, pore volume and pore size of the CEC800 and CEC900 obtained by the BET are shown in Table 3. The specific surface area of CEC900 (120.4 m^2/g) is greatly higher than that of CEC800 (97.90 m^2/g). This shows that the CEC900 has a higher catalytic activity than CEC800. Since the surface area of a solid catalyst has a direct impact on its catalytic activity. Hence, the higher the surface area of a solid catalyst, the higher the catalytic activity [21, 35]. This shows that the higher calcination temperature of 900 °C plays a vital role in improving the catalyst quality due to the increase of the BET surface area of CEC900. As shown in the table, the pore volumes are 0.1184 and 0.1428 cc/g for CEC800 and

Table 3 Properties of chicken eggshell catalysts

Properties	CEC800	CEC900
Surface area (m^2/g)	97.90	120.4
Pore volume (cc/g)	0.1184	0.1428
Pore size (nm)	1.324	1.324
Basic strength (H)	8.7 < H < 14.4	15.4 < H < 18.2
Basicity (mmol/g)	0.10	0.14

CEC900, respectively. However, the pore size of 1.324 nm is the same for CEC800 and CEC900, an indication that they are both micropores catalysts. Therefore, the BET results showed that the CEC900 was expected to have high catalytic activity due to its higher surface area [35].

The basic strength and basicity of the catalysts are thus presented in Table 3 as $8.7 < H < 14.4$, and $15.4 < H < 18.2$ for CEC800 and CEC900, respectively. These results are similar to those reported by Salamatinia, Hashemizadeh, & Ahmad [28] in literature. This shows that the CEC900 has high basic strength than the CEC800. The measured basicity of the CEC800 and CEC900 are 0.10 and 0.14 mmol/g, respectively. This reveals that the CEC900 was found to be highly basic compare to the CEC800.

It is worthy of note that the basic properties of CEC900 are better than those of CEC800. Meanwhile, major characteristics that influence the catalytic activity of basic catalysts are strength and basicity. These govern the electronegativity of the conjugated metal cation in the catalyst. Since the larger the electronegativity, the more the intensity of the attractive force of the electron for the conjugated metal cation, which weakens the oxygen anion [28].

3.3 Optimization of %yield of PBD by the CEC

3.3.1 Statistical analysis

The complete design matrix with actual and predicted %yield of PBD is presented in Table 4. The result shows that the actual %yield varied between 91.27 and 97.08%. With the minimum %yield achieved at 6:1 MeOH:oil molar ratio, 65 °C reaction temperature, catalytic quantity of 8 wt%, 3 h reaction time, and 800 °C catalyst calcination temperature; whereas the maximum %yield of PBD was achieved 10:1 MeOH:oil molar ratio, 55 °C reaction temperature, catalytic quantity of 4 wt%, 1-h reaction time, and 900 °C catalyst calcination temperature. The actual %yield of PBD obtained from the design was subjected to statistical analysis using analysis of variance (ANOVA).

The ANOVA is a strong tool to determine the significance and validation of a model and those of individual parameters in a mathematical model equation. Hence, ANOVA of the experimental results was performed and the results obtained are shown in Table 5. From the table, the quality fit of the

Table 4 Experimental matrix for the process conditions and response for the DSD

Exp. runs	MeOH:oil mole ratio (*w*/*w*)	Temperature (°C)	Catalyst quantity (%, *w*/*w*)	Reaction time (h)	Catalyst calcination temperature (°C)	Actual %yield of PKB	Predicted %yield of PKB
1	8	55	8	1	800	92.62	92.60
2	6	55	8	3	900	95.45	95.26
3	6	55	4	2	800	93.37	93.30
4	10	55	4	1	900	97.08	97.01
5	8	60	6	2	800	92.67	91.75
6	6	65	8	3	800	91.27	92.01
7	10	65	8	2	900	95.47	95.22
8	10	65	4	1	800	93.45	93.27
9	8	65	4	3	900	95.59	96.01
10	8	60	6	2	900	95.70	95.77
11	10	65	6	3	800	93.08	92.79
12	6	60	4	3	900	96.01	96.00
13	10	60	8	1	800	92.50	92.64
14	10	55	4	3	800	93.81	94.08
15	6	65	4	1	800	92.78	92.61
16	10	55	8	3	900	95.94	96.03
17	6	55	6	1	900	96.05	95.85
18	6	65	8	1	900	94.40	94.56

model equation was expressed by the coefficient of regression (R^2) as 0.988 of the model. The value is close to unity, which signifies that the experimental data linearly fit in the model. The adjusted R^2 of 0.983 is reasonably close to the R^2 with the difference value of 0.005, which is lower than the maximum allowable difference of 0.2. Fischer's statistical test (F value) obtained for the model is 195.1230 which is large enough to prove the significance of the model. The F values of the process parameters (Table 5) were also relatively high apart from reaction time, which indicates the significance of the process. A low probability (p) value of 0.01% was observed to obtain the F value due to noise. This shows an adequate signal of the final response without much chaos in the model [9]. The ANOVA shows that MeOH:oil mole *ratio* (X_1), temperatures (X_2), catalyst quantity (X_3), and the catalysts (CEC800 and CEC900) (categorical factor) (X_5) are significant parameters with $p < 0.0001$, respectively. However, reaction time (X_4) has a low F value of 0.2662 with 61.53% chances that this low F value can occur due to noise, which makes this parameter insignificant. The significant effect of the individual parameter on the biodiesel yield was further estimated using the contribution factor as shown in Fig. 5. The figure revealed that the calcination temperature is the most dominating factor that affects the eggshell catalytic activity for biodiesel yield of PKB with LogWorth of 11.712, followed by catalyst quantity with LogWorth of 6.033. The next is the reaction temperature with LogWorth of 4.486 followed by MeOH: oil molar ratio of 4.314. The lowest contributing factor to the process is the reaction time with LogWorth of 0.433, hence neglected from the model equation that predicts the %yield of PKB. These results show the response of the model as it is capable enough to predict the %yield of biodiesel. The model further confirms that all the parameters considered except reaction time have a significant effect on the %yield of PBD. Therefore, the model is an effective tool to optimize the PBD using the CEC.

3.3.2 Mathematical model equation analysis

To further establish the most influential parameters for improving the %yield of PBD in the process, the regression analysis was performed. The coefficients obtained for each parameter with a 95% confidence level in terms of the mathematical equation of actual factors to predict the biodiesel yield is as shown in Eq. 4:

$$\begin{aligned}\%\text{Yield of PBD} = {} & 94.294125 + \text{Match}(\pm 0.215100\ \{Block\}) \\ & -0.532785714\,X\left(\frac{\left(\text{Catalyst quantity}\left(\%, \frac{w}{w}\right) - 6\right)}{2}\right) \\ & +0.3585\,X\left(\frac{\left(\text{MeOH : oil mole ratio}\left(\frac{w}{w}\right) - 8\right)}{2}\right) \\ & -0.375785714\,X\left(\frac{\left(\text{Temperature}\left(^{\circ}\text{C}\right) - 60\right)}{5}\right) \\ & \pm \text{Match}(\text{Calcination temperature}\ (^{\circ}\text{C}))\end{aligned} \quad (4)$$

Note that the ± in the predicted expression means − 1.5095 for calcination temperature at 800 °C and + 1.5095 for calcination temperature at 900 °C.

The reaction time, being an insignificant parameter in the process was eliminated from the developed model equation (Eq. 4), as it has less impact on the catalyst activity to obtain an optimum yield of biodiesel. Thus, the equation predicts the response (%yield of PBD) at given levels of each parameter. Therefore, the equation can be employed to analyze the relative impact of the process parameters by evaluating their coefficients. The %yield of PBD predicted by the model equation as compared to the actual yields obtained from the experimental runs are shown in Fig. 6 and Table 4. The figure shows that the actual and predicted values are in a comparable range and the table further reveals that they are in close range. This proves that the model is accurate in predicting the %yield of PBD when CEC was used. The adequate precision obtained as compared between the predicted and the actual results for the

Table 5 ANOVA and statistical values estimated for the process parameters of the model

Source	Sum of squares	*df*	Standard error	*t* Ratio	*F* ratio	Prob > ItI
Model	45.693155	5	0.0581	1621.6	195.1230	< 0.0001*
MeOH:oil mole ratio (*w*/*w*)	1.769815	1	0.059738	6.00	36.0150	< 0.0001*
Temperature (°C)	1.944599	1	0.059738	− 6.29	39.5717	< 0.0001*
Catalyst quantity (%, *w*/*w*)	3.908900	1	0.059738	− 8.92	79.5444	< 0.0001*
Reaction time (h)	0.013080	1	0.052576	− 0.52	0.2662	0.6153
Catalyst calcined Temperature [800]	39.061547	1	0.05354	− 28.19	794.8855	< 0.0001*
Residual	1.75310	12				
R^2	**R^2 Adj**	**Root mean square error**		**Mean of response**	**Observations (or sum wgts)**	
0.988	0.983	0.216414		94.29111	18	

Source	LogWorth	p value
Calcination Temperature (°C)	11.712	0.00000
Catalyst Quantity (%, w/w)(4,8)	6.033	0.00000
Temperature (°C)(55,65)	4.486	0.00003
MeOH: Oil Mole Ratio (w/w)(6,10)	4.314	0.00005
Reaction Time (h)(1,3)	0.433	0.36932

Fig. 5 Rate of contributing effect of each of the process parameters

model indicates that the model has enough strong signal suitable for the optimization of the process.

3.3.3 The individual effect of the parameters on the transesterification of PKO by CEC

Effect of methanol:oil molar ratio Considering Figs. 7a–d and 8e–f where methanol:oil molar ratio of range 6:1 to 10:1 is depicted with other parameters, as it affects the %yield of biodiesel from PKO using the CEC800 and CEC900. In the figures, MeOH:oil molar ratio of 6.1 and 10:1 yielded < 96% and ≥ 97% of PBD, respectively, at various parameters. This shows an increase in the biodiesel yield at higher MeOH:oil molar ratio of 10:1, as higher MeOH:oil molar ratio is required due to the vaporization of methanol at high temperature [41]. Moreso, because of the reversibility of the transesterification reaction, a higher alcohol ratio is needed to shift the equilibrium forward to increase the %yield of PBD [33]. Low MeOH:oil molar ratio can also result in a poor suspension of the reactants mixture thereby causing mass transfer problems with low activity of the CEC. The increase in the %yield of PBD revealed that higher MeOH:oil molar ratio facilitates the suspension of the CEC to eliminate mass transfer problems [24]. Hence, a high MEOH:oil molar ratio is important to increase the %yield of PBD using the CEC. Excess of alcohol in the reaction ensures complete conversion of PKO to biodiesel.

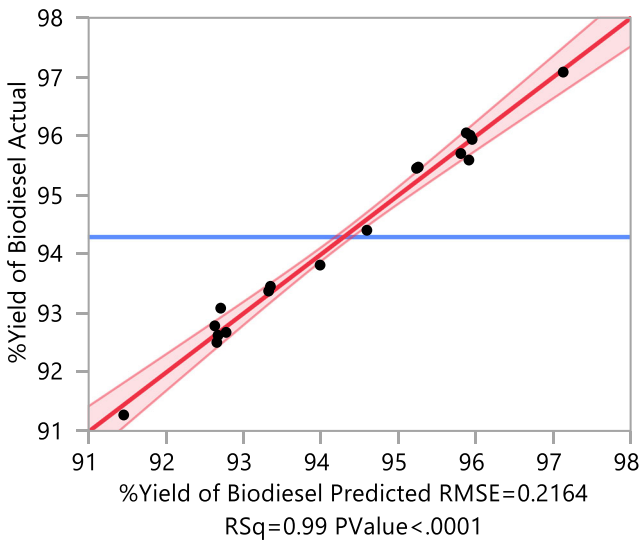


Fig. 6 Plot of actual yield vs predicted yield of PBD

Effect of reaction temperature Figure 8 a–f shows the effect of the reaction temperature in the range of 55–65 °C on the %yield of PBD at various parameters for CEC800 and CEC900. It was observed that 55 °C gave a higher yield of ≥ 96.8% when CEC900 was used, compare to 65 °C which yielded < 95.5% of PBD as shown in Fig. 8d. Although, it was expected that a higher reaction temperature should increase the kinetic energy by improving the collision between the molecules that would increase the biodiesel yield [24]. However, a lower temperature of 55 °C gave a better yield of PBD, because, at a much higher temperature, MeOH vaporizes into the gas phase and resulted in poor contact with the PKO [41]. Thus, reaction temperature had a significant effect on the reaction as a lower temperature of 55 °C gave a higher yield of ≥ 96.8% PBD. This is due to the occurrence of an unwanted side reaction, such as a saponification reaction at a higher temperature of 60 °C which lowered the PBD yield to < 92.2% [10, 24].

Effect of catalyst quantity The effect of the CEC quantity in the range of 4–8% (*w*/*w*) on the transesterification of PKO to PBD was investigated. The results obtained are shown in Figs. 7a, b, 8c, d, and 9a, b with the %yield of biodiesel of ≥ 96.8% and < 91.5% when CEC quantity were 4 and 8% (*w*/*w*), respectively. The maximum %yield of PBD was obtained at a low CEC quantity of 4% (*w*/*w*). While the CEC quantity of 8% (*w*/*w*) gave a reduced %yield of PBD. This is attributed to the relatively high content of catalyst quantity which leads to aggregation of catalyst particles, mass transfer limitation and a decrease in the interaction among the reactants (active sites, PKO, and methanol) [18]. The effect of too much catalyst quantity was possibly due to the difficult mixing of liquid reactants, as a higher solid catalyst quantity of 8% (*w*/*w*) could lead to the saponification of biodiesel [41]. This revealed that a little quantity of CEC is required to accelerate the formation of biodiesel by providing an alternative pathway, which lowers the activation energy for the reaction to complete fast [24]. The high %yield of PBD (≥ 96.8%) at low CEC quantity (4%, *w*/*w*) shows that the available active sites of the catalyst are sufficient to complete the reaction at minimum reaction

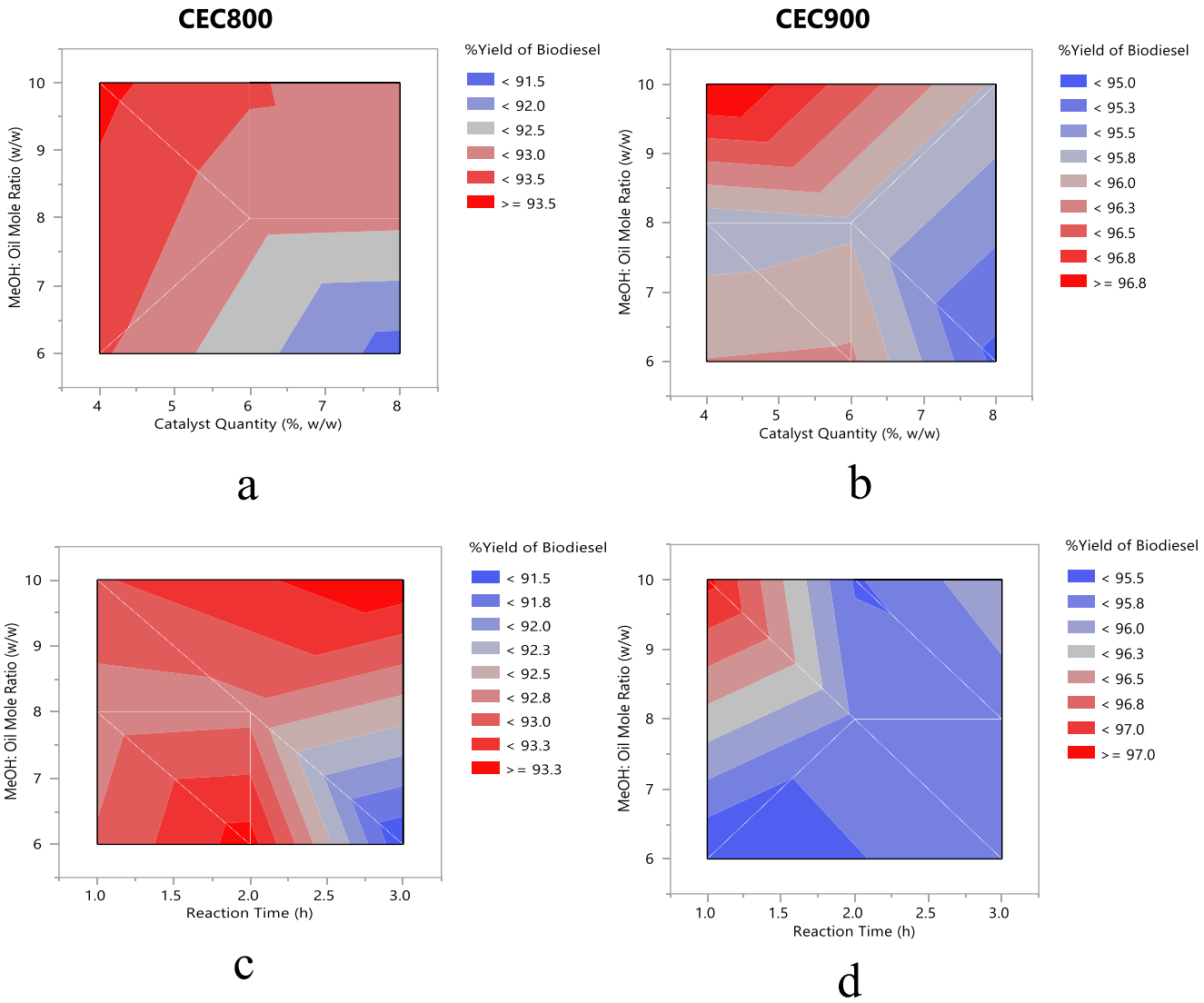


Fig. 7 %Yield of PBD by interaction between MeOH:oil mole ratio (*w*/*w*) and other parameters for CEC800 and CEC900

time possible, since catalyst quantity determines the number of active sites and the contact surface area. The phenomenon enables the reaction to attain equilibrium at a faster rate/low reaction time. High CEC quantity could not increase the %yield of PBD due to all the reactant, molecules that have occupied the active sites of the catalyst as the excess active sites are unoccupied. The reaction rate, therefore, is controlled by the diffusion rate of reactants to the active site instead of the number of active sites. Lower catalyst quantity of 3% (*w*/*w*) instead of 6% (*w*/*w*) was reported as the most suitable quantity in the report of Olutoye et al. [24] when the solid catalyst was also used for biodiesel production. Thus, 4% (*w*/*w*) catalyst quantity was sufficient to provide the active area needed for the collision of reactants with the catalyst. As higher catalyst quantity of 6 and 8% (*w*/*w*) decreased the biodiesel yield. This might be due to the increasing viscosity of the slurry that enhances the mass transfer resistance in multiple phases (liquid–liquid-solid), and complicate the mixing of the reactants with the catalyst [32].

Effect of reaction time In order to obtain a maximum yield of biodiesel, a sufficient amount of time is required for reaction completion. The sufficient time would afford the reaction to reach an equilibrium state and have enough contact time between reactants and catalyst for maximum biodiesel yield. However, longer reaction time might sometimes be inefficient as it results in solvent loss and by-product formation such as olefins and fatty alcohol [22]. Hence, the reason for the optimization of the reaction time between 1 and 3 h for the transesterification of PKO by the CEC. The effect of reaction time on the %yield of biodiesel is as shown in Figs. 7c, d, 8a, b, and 9a, b. From Figs. 7c, 8a and 9a, where CEC800 was used for the transesterification, it was observed that after 1 h, 92.8% optimum yield of biodiesel was attained. Afterward, the %yield of biodiesel (93.5%) remained nearly constant as a result of

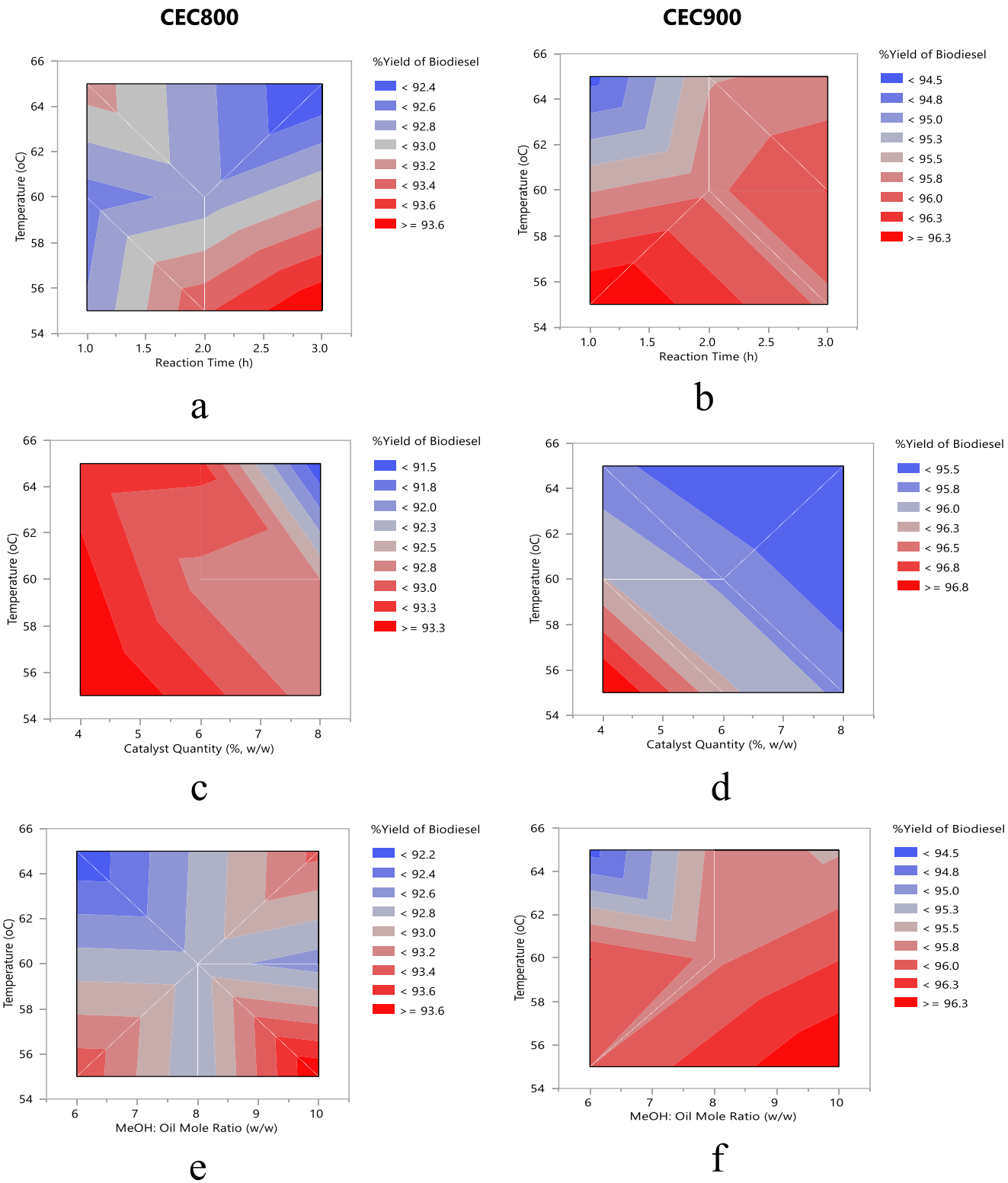


Fig. 8 %Yield of PBD by interaction between temperature (°C) and other parameters for CEC800 and CEC900

near-equilibrium conversion [22]. This shows that 1 h is sufficient for the CEC800 to attain equilibrium and complete the reaction. For the CEC900 as shown in Figs. 7d, 8b, and 9b, the maximum ≥ 97.0, ≥ 96.3, and ≥ 96.8% yields of biodiesel were attained at 1 h and decrease as time progresses to 3 h (< 96.0, < 95.8, and < 96.0% yields of biodiesel) respectively. This shows that after 1 h of reaction, solvent loss and by-product formation (such as olefins and fatty alcohol) took place in the reaction

medium and reduces the %yield of biodiesel. The finding in this study is similar to the report in the literature [18, 41]. However, optimum 1 h reaction time in this study is better than the finding of Jazie, Pramanik, Sinha, and Jazie [14], where reaction time of 3 h yielded 96% biodiesel from rapeseed oil.

Effect of calcination temperature Calcination temperature effect on the catalytic activity of the prepared catalyst of CEC800 and CEC900 at different temperatures of 800 and 900 °C was investigated. The activity of the catalysts (CEC800 and CEC900) was studied for the transesterification reaction of PKO. The various yields of biodiesel obtained are shown in Figs. 7, 8, and 9. From the figure, CEC calcined at 900 °C (CEC900) was found to be the most suitable temperature for the catalyst as it yielded ≥ 97.0% biodiesel (Fig. 7d) compare to CEC800 that gave ≥ 93.6% biodiesel (Fig. 8a) at given process parameters. The higher biodiesel yield of CEC900 is due to the higher surface area which gives a large area for the dispersion of homogeneous calcium oxide on the surface and ultimately enhances the productivity [9]. The catalytic activities of the CEC800 and CEC900 as obtained in the study corroborate the findings of Olutoye et al. [24] that a low level of activity can be obtained at a low calcination temperature. This occurs because of the effect of higher calcination temperature on the crystalline and molecular structure of the metal oxide as was aforementioned under characterization studies. The CEC900 shows increased activity compare to CEC800 because the increase in the calcination temperature transformed the metals in the chicken eggshell into the soluble form, which enhanced the integration of the metals to form active composite solid [24]. Furthermore, higher calcination temperature increases the activity by increasing the surface area of CEC900 as revealed in Table 3. Therefore, adequate calcination temperature plays crucial roles in the catalytic activity of solid catalyst by determining the crystal and structure of catalysts; producing much active site of mixed oxides and the decomposition of the organic matters in the CEC [18, 34].

3.3.4 . Interactive effects of process parameters on the transesterification of PKO by CEC

Interactive effects of the *process parameters* on the %yield of PBD are represented in contour plots as shown in Figs. 7a–d, 8a–f, and 9a–b. The contour plots of %yield of PBD against MeOH:oil molar ratio and catalyst quantity reveal highest PBD yield of ≥ 93.5% and ≥ 96.8% at MeOH:oil molar ratio of 10:1 and catalyst quantity of 4% (*w*/*w*) for both CEC800 (Fig. 8a) and CEC900 (Fig. 8b), respectively. Furthermore, Fig. 7 c and d are the contour plots of %yield of PBD against MeOH:oil molar ratio and reaction time for CEC800 and CEC900, respectively. The figures show that MeOH:oil molar ratio of 10:1 and reaction time of 3 h (CEC800) and 1 h (CEC900) yielded PBD of ≥ 93.3 and ≥ 97.0% for CEC800 and CEC900, respectively. The interactive effects of MeOH:oil molar ratio and reaction temperature on the yields are shown in Fig. 8 e and f for CEC800 and CEC900, respectively. A %yield PBD of ≥ 93.6 for CEC800 was obtained as shown in Fig. 8c, while Fig. 8f shown a %yield PBD of ≥ 96.3 for CEC900. This highest %yield of PBD was obtained at 10:1 MeOH:oil molar ratio and 55 °C reaction temperature. These show that lower temperature favor the transesterification reaction at a higher MeOH:oil molar ratio for biodiesel production using CEC.

Considering the interactive effects of reaction temperature and reaction time as shown in Fig. 8a, and b on %yield of PBD

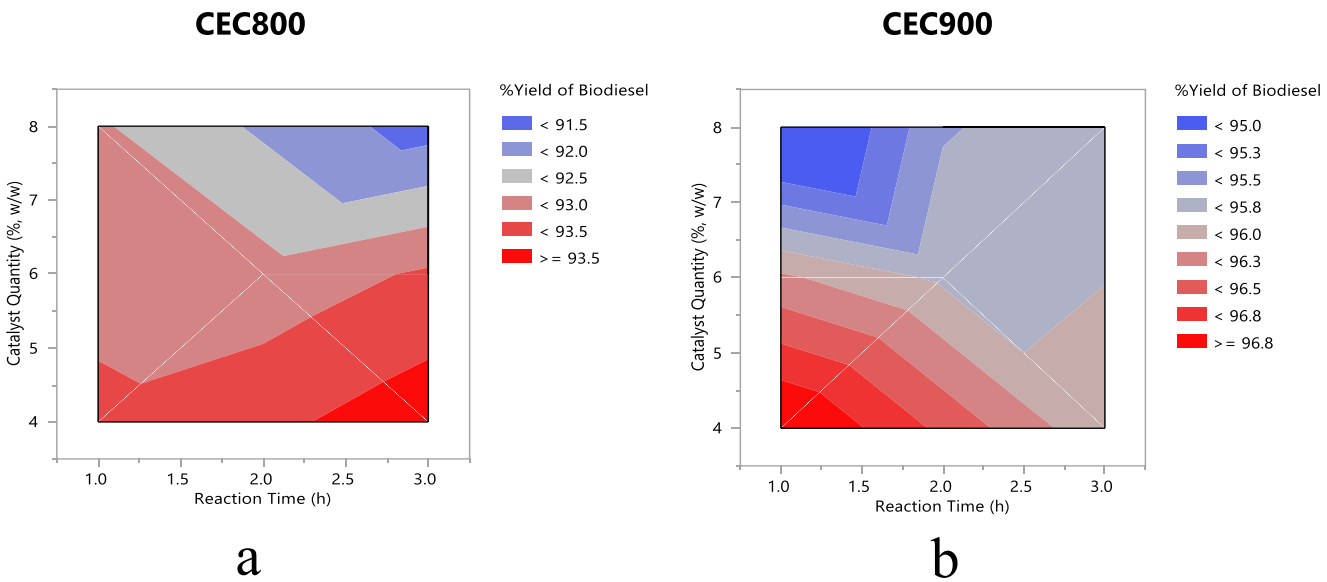


Fig. 9 %Yield of PBD by interaction between catalyst quantity and reaction time for CEC800 and CEC900

Table 6 Optimal parameters for %yield of PBD using CEC

Objective	Process parameters				%Yield of biodiesel				
	MeOH:oil mole ratio (*w*/*w*)	Reaction temperature (°C)	Catalyst quantity (%, *w*/*w*)	Reaction time (h)	Calcination temperature (°C)	Actual	Predicted	Lower CI	Upper CI
Optimal	10:1	55	4	1	900	97.10	97.07	96.79	97.36

for CEC800 and CEC900, respectively. The highest PBD of ≥ 93.6 and ≥ 96.3% were obtained for CEC800 and CEC900, respectively at a reaction temperature of 55 °C and reaction time of 3 h (CEC800) and 1 h (CEC900). Interactive effects of temperature and catalyst quantity on %yield of PBD for CEC800 and CEC900 are shown in Fig. 8 c and d, respectively. Higher %yield PBD of 93.3 and 96.8 were obtained for CEC800 and CEC900, respectively, at 55 °C and catalyst quantity of 4% (*w*/*w*). Similarly, the interactive effects of catalyst quantity and reaction time on the %yield of PBD for CEC800 and CEC900 are shown in Fig. 9a, b. The figures revealed the highest %yield of ≥ 93.5 and ≥ 96.8 for CEC800 and CEC900, respectively at 4% (*w*/*w*) catalyst quantity and reaction time of 3 h (CEC800) and 1 h (CEC900).

3.3.5 Optimization and experimental validation of the model

From the study, both the CEC800 and CEC900 are suitable solid catalysts for biodiesel production through transesterification process. However, to achieve the desired optimal process parameters for the CEC to attain optimum yield of PBD, optimization analysis was performed using Eq. 2 by the DSD. The optimal process parameters obtained from the analysis are as shown in Table 6, which include MeOH:oil molar ratio of 10:1, reaction temperature of 50 °C, catalyst quantity of 4% (*w*/*w*), reaction time of 1 h and calcination temperature of 900 °C with the predicted value of 97.07% yield of PBD. To obtain the actual %yield of PBD, a validation experimental run was carried out using the optimal parametric setting. The actual yield of PBD obtained was 97.10%, which when compared with the predicted value shows a variation of 0.03%, a value < 5%, which confirms the adequacy of the model.

3.4 Catalyst stability

The stability and ability of a solid catalyst to be recycled in the production of biodiesel are among its most important features. The reusability extent of the CEC900 was examined for 5 cycles using the optimal parameters obtained. At the end of each experimental cycle, the solid catalyst was retrieved from the reaction mixture by filtration, washing with methanol to remove the adsorbed stains and oven-dried at 100 °C for subsequent use. Figure 10 shows that a high PBD yield of ≥ 90% was achieved after the 5th cycle. However, there was a decrease of about 6% in the yield of PBD from the 1st to 5th cycle, which could be due to leaching of active component in the CEC900 with the increase in the reaction cycle. Furthermore, the decrease can be attributed to catalyst deactivation due to blockage of the catalyst pores by large molecules that inhibit the diffusion of PKO molecules into the pores [32]. Reduction in the amount of active component in the process of washing, purification, and the recovery of the catalyst for reuse can reduce its activity [24]. Other responsible factors for the decrease may include; aggregation of the catalyst after cycles, and a deposit of the PBD on the catalyst site [41, 23].

3.5 Qualitative and FAME characterization of the PBD catalyzed by the CEC

Figure 11 shows the pictorial representation of PKO and PKB at different stages of biodiesel recovery. It is pertinent to ascertain the quality of the PBD to ensure meeting the international standards and for commercial suitability. Therefore, the specific analytic method of the America Standard Testing Methods (ASTM) standard was employed to determine density, cloud point, flash point, kinematic viscosity, pour point, water content, and sulfur content as shown in Table 7. Table 8 shows the FAME

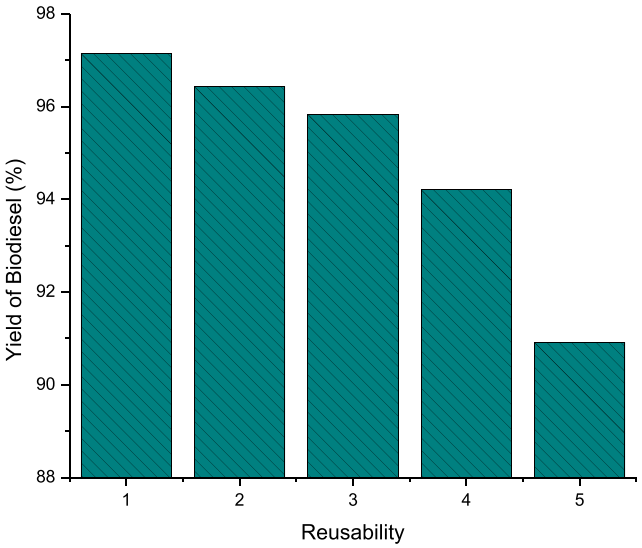


Fig. 10 Stability of the chicken eggshell catalyst for PBD production

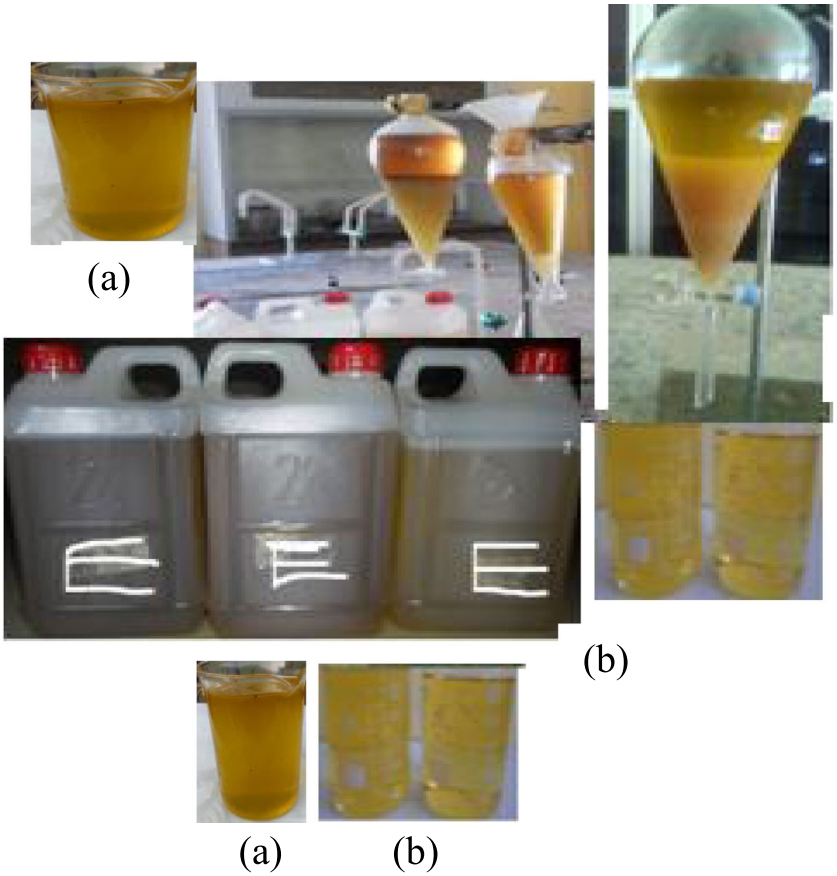


Fig. 11 Pictorial representation of **a** palm kernel oil and **b** palm kernel biodiesel

profile of the PBD by the CEC. Considering all the characteristics investigated, the PBD is within the expected range of the ASTM standard. The FAME profile revealed that methyl laurate which is a saturated FAME is the highest composition of 34.38%, followed by methyl oleate, which is an unsaturated FAME with the composition of 32.81%. The FAME content of 97.09% was obtained for the PBD, which is higher than the standard of 96.5% as shown in the table. The qualitative characterization, therefore, confirms that the PBD by the CEC is of a great quality suitable for commercial application in diesel engines.

4 Conclusions

Synthesis of a solid catalyst from chicken eggshell for PBD production in an optimization process is a novel study. This increases the feasibility of cost-effective synthesis of a highly active solid catalyst obtained from the chicken eggshell for biodiesel production. The study, therefore, concludes that:

- A highly active catalyst from waste chicken eggshell can be synthesized through adequate calcination temperature without any chemical modification.

Table 7 Physicochemical properties of PKO, PBD produced by CEC, and biodiesel standard

Fuel properties (units)	PKO	PBD	ASTM standard
FAME content (%)	–	97.09%	96.5
Density at 15 °C (g/cm^3)	0.922	0.868	0.860–0.900
Kinematic viscosity at 40 °C (mm^2/s)	16.29	2.49	1.9–6.0
Flash point (°C)	186	130	≥ 130
Cloud point (°C)	16.5	8	− 3–12
Pour point (°C)	11.2	1.1	− 15–10
Water content (*%w/w* oil)	< 0.005	<0.005	≤ 0.05
Sulphur content (*%w/w* oil)	< 0.005	< 0.005	≤ 0.005

Table 8 Profile and quantitative analysis of FAMEs in PBD produced by CEC

Peak no.	Retention time (min)	FAMEs present	Molecular formula	% composition
1	26.83	Methyl laurate	$C_{12}H_{24}O_2$	34.38
2	31.05	Methyl myristate	$C_{14}H_{28}O_2$	12.13
3	35.01	Methyl palmitate	$C_{16}H_{32}O_2$	13.09
4	38.26	Methyl oleate	$C_{18}H_{34}O_2$	32.81*
5	–	Others	–	4.68

*The unsaturated fatty acid methyl ester

- The calcination temperature of 900 °C that was used to synthesize CEC900 provides the highest surface area of 120.4 m^2/g with the highest calcium oxide composition of 32.36 wt%. The SEM image of the CEC900 revealed a high porous, uniformly distributed spherical morphology, and decreased particle size catalyst.
- The optimum yield of 97.10% PBD was attained at methanol to oil molar ratio of 10:1, temperature of 50 °C, catalyst quantity of 4 wt%, a reaction time of 1 h and calcination temperature of 900 °C. The order of contributing effect confirmed that the calcination temperature is the most influential parameter that affects the yield of PBD, followed by catalyst quantity, temperature, MeOH:oil molar ratio and reaction time.
- The stability of CEC investigated revealed that it can be reused for 5 times successfully with little reduction in the %yield of biodiesel.
- The evaluated qualitative characteristics of the PBD were found to be within the standard range of values set for conventional biodiesel as provided by the ASTM standard. The FAME profile studied assured that the PBD contains an appropriate and adequate proportion of the fatty acid methyl esters.

The chicken eggshell is a sustainable and efficient feedstock suitable for the development of a solid catalyst for biodiesel production.

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