RSM Optimization of Biodiesel from Waste Cooking Oil Using Snail Shell Derived Heterogeneous Catalyst

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1 Introduction

The need for biofuels has emerged as a result of the imminent threat of the depletion of fossil fuel, and as per statistics [1], the proven reserve of oil, natural gas, and coal will last for 54, 49, and 139 years respectively. When compared to fossil fuels, biodiesel mostly consists of fatty acid methyl esters (FAME) and provides several environmental advantages, such as low CO_2 and CO emissions, low sulfur content, and biodegradable nature [2]. Additionally, biodiesel can be combined with diesel and utilized in engines without any modifications or with minimal changes [3]. The presence of a catalyst in the transesterification of biodiesel accelerates the reaction time [4]. Even though researchers claim that acid transesterification produces a better yield, it is constrained by the higher catalyst cost. Commercially, sodium hydroxide and potassium hydroxide are frequently used as a catalyst for transesterification as it is affordable and widely accessible. But the fundamental problem with homogeneous catalysts is that it leads to saponification when used with high free fatty acid (FFA) feedstock such as WCO and also produce toxic water waste while washing [5]. Although acids can esterify FFA, the process is less desirable due to its sluggish rates and high cost. Many researchers have already identified potential sources such as chicken egg shells, scallop shells, animal bones, etc. as a source for base heterogeneous catalysts [6]. Previously, researchers claimed that heterogeneous catalysts produced higher ester conversion yields than homogeneous catalysts [7].

When snail shell is utilized as a heterogeneous catalyst during the synthesis of biodiesel, it is stated to have a conversion rate of 92.5% when used cooking oil is used as the feedstock [8]. As a result, it is crucial in developing a low-cost, environmentally friendly catalyst that can overcome the shortcomings of base homogeneous and acid

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Fig. 1 **a** Shell of ningkhabi tharoi (*Bellamya crassa*), **b** lai tharoi (*Thiara* tuberculate) and **c** labuk tharoi (*Angulyagra oxytropis*)

catalysts. Therefore, given the above-mentioned facts, three different varieties of snail shells namely labuk tharoi (*Angulyagra oxytropis*), ningkhabi tharoi (*Bellamya crassa*), and lai tharoi (*Thiara tuberculate*) were selected in this study to produce calcium oxide heterogeneous catalyst, and the best catalyst was chosen out of the three based on crystal size and elemental composition.

2 Experimental Methodology

2.1 Materials

Five liters (5 L) of waste cooking oil and two kilograms (2 kg) of Waste snail shells known locally as labuk tharoi (*Angulyagra oxytropis*), ningkhabi tharoi (*Bellamya crassa*), and lai tharoi (*Thiara tuberculate*) were collected from hotels situated in Imphal, Manipur, as shown in Fig. 1. Chemicals utilized throughout the experiment were procured locally from Imphal, India and of standard grade.

2.2 Catalyst Preparation

To remove organic materials from the snail shells, the shells were washed several times with distilled water and then sundried for 7 days. The snail shells were grounded separately using ceramic mortar and pestle and sieved through a mesh size of 200–250 μm. The powdered snail shells were calcinated separately in a muffle furnace at a temperature range of 800–1000 °C for a time interval of 3–5 h. A total of 27 catalyst samples, were obtained. Figure 2 shows nine calcinated samples for one type of snail shell.

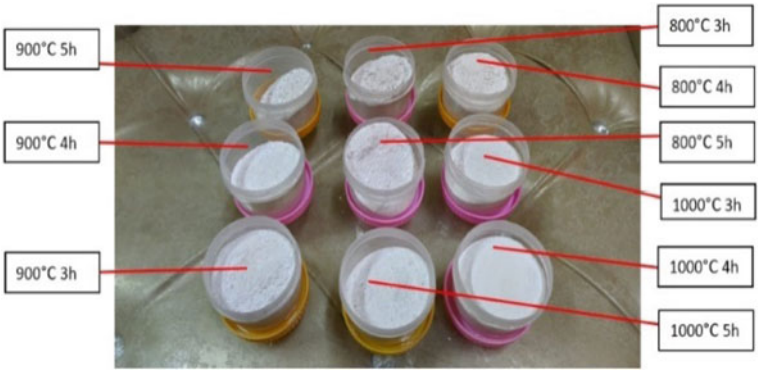

Fig. 2 Snail shell calcinated at a temperature of 800, 900, and 1000 °C and time of 3, 4, and 5 h

2.3 Characterization of the Catalysts

X-ray diffractometer (XRD), Fourier transform infrared spectroscopy (FTIR), and Energy dispersive X-ray (EDX) were performed for raw and calcined snail shells to analyze the crystal structure, chemical makeup, and elemental composition of the catalyst. The XRD diffractions patterns of the CaO samples were recorded using Bruker AXS; Model: D8-Advance powder XRD equipped with l $\lambda = 1.5406$ Å of Cu-Kα radiation over the Bragg angle 2θ range of 20°–80° and a step size of 0.04° at room temperature. FTIR was performed for uncalcined and calcined snail shells using PerkinElmer; Model: Spectrum Two FTIR spectrometer to investigate the functional group present in the samples in the spectrum range of 2200–400 cm^{-1}.EDX analysis was carried out for both uncalcined and calcined snail shells to determine the elemental composition.

2.4 Transesterification Reaction and FAME Analysis

The Waste Cooking oil (WCO) was filtered using filter paper and is transferred to a glass container and heated to about 90 °C in an electric oven for about 15 min to remove moisture content from the oil. The FFA content of the WCO was determined by titration of the WCO with 0.1 M NaOH with methanol as solvent and phenolphthalein as indicator. The value of the FFA content was found to be 0.47%, hence there was no requirement for esterification. The transesterification reaction was carried out using WCO and the synthesized catalyst under different reaction parameters considered for the present study. Alcohol-to-oil molar ratio, catalyst loading, and reaction time have been fixed at, 12:1, 5 wt.%, and 1.5 h respectively for all the experimental runs. Transesterification of the WCO was carried out by mixing the prescribed amount of catalyst with 30.39 g of methanol preheated at 40 °C and

Table 1 Parameter levels employed for calcination

S. no.	Parameters	Symbol	Levels		
			−1	0	+1
1	Calcination temperature (°C)	A	800	900	1000
2	Calcination time (h)	B	3	4	5
3	Reaction temperature (°C)	C	55	65	75

mixing with 80 g of WCO in a 500 ml conical flask (Make: Borosil). The solution was then heated for transesterification as per the prescribed reaction temperature using a magnetic hot plate stirrer (Make: Tarsons Digital Spinot) at an rpm of 800. The FAME yield of the WCO has been calculated using Eq. (1).

$$\text{Biodiesel yield} = \frac{\text{weight of biodiesel}}{\text{weight of WCO}} \times 100\% \tag{1}$$

2.5 Design of Experiment Using CCD-RSM

The response surface methodology (RSM) is used in the current study to examine how different parameters influence the outcome and how the parameters interact with each other. Three independent variables were considered for this study namely calcination temperature (800–1000 °C), calcination time (3–5 h), and reaction temperature (55–75 °C) as shown in Table 1. Based on the 3 independent parameters with 3 levels each, the total number of experiments was found to be twenty as shown in Table 2.

3 Results and Discussion

3.1 XRD of Calcinated Snail Shells

XRD patterns of the snail shells of Lai tharoi, Ningkhabi tharoi, and labuk tharoi calcined at 900 °C for 4 h were recorded and analyzed. From Fig. 3. Intensity peaks of Lai tharoi, Ningkhabi tharoi and Labuk tharoi calcined at 900 °C for 4 h were observed at 2 theta values of 32.60, 37.83, 54.43, 64.86, 67.65 and 32.63, 37.78, 54.28, 64.56, 67.7, and 32.64, 37.79, 54.29, 64.57, 67.76 respectively, which correspond to the (111), (200), (220), (311) and (222) planes as reported by other researchers as well [9]. The high-intensity peaks of ningkhabi tharoi and labuk tharoi show good crystalline formation in the synthesized catalyst.

Table 2 Design of experiments using RSM (CCD)

Run order	Calc. temp. °C	Calc. time h	Reaction temp. °C	Actual value	Predicted value	Residual
1	1000	3	55	94.52	94.51	0.0111
2	900	4	65	94.85	94.83	0.0242
3	1000	5	55	94.23	94.22	0.0071
4	800	3	75	94.41	94.4	0.0111
5	800	3	55	94.22	94.21	0.0071
6	900	4	65	94.81	94.83	-0.0158
7	800	5	75	94.3	94.29	0.0071
8	1000	5	75	94.96	94.95	0.0111
9	1000	4	65	94.53	94.58	-0.0493
10	900	4	65	94.88	94.83	0.0542
11	900	3	65	94.84	94.89	-0.0493
12	1000	3	75	95.18	95.16	0.0201
13	900	4	65	94.9	94.83	0.0742
14	900	4	75	95.17	95.22	-0.0493
15	900	4	65	94.87	94.83	0.0442
16	900	5	65	94.67	94.69	-0.0233
17	800	4	65	94.08	94.1	-0.0233
18	900	4	65	94.79	94.83	-0.0358
19	900	4	55	94.74	94.76	-0.0233
20	800	5	55	93.53	93.53	-0.0019

3.2 FTIR of Calcinated Snail Shells

Lai tharoi, Labuk Tharoi, and Ningkhabi shells were calcined at 900 °C for 4 h, and FTIR spectra were taken to identify the material's absorption bands. Figure 4 displays the FTIR spectra for calcined snail shells, and the major absorption bands are found at 891 $cm^{-}1$, 865 cm^{-1}, 863 cm^{-1}, 1449 cm^{-1}, 1443 cm^{-1}, and 1442 cm^{-1} respectively [10]. The $CO_3{}^{2-}$ lost during the calcination process of the snail shells, caused a shift in the absorption bands when exposed to high energy due to a reduction in the decreased mass.

3.3 EDX of the Calcinated Snail Shells

EDX analysis of the Labuk Tharoi shells calcined at 900 °C for 4 h was carried out to find the major elements present in the calcined snail shells. The major elements Ca (95.22 wt.%), O (2.93 wt.%), C (1.58 wt.%) and Mg (0.27 wt.%) were found in the samples.

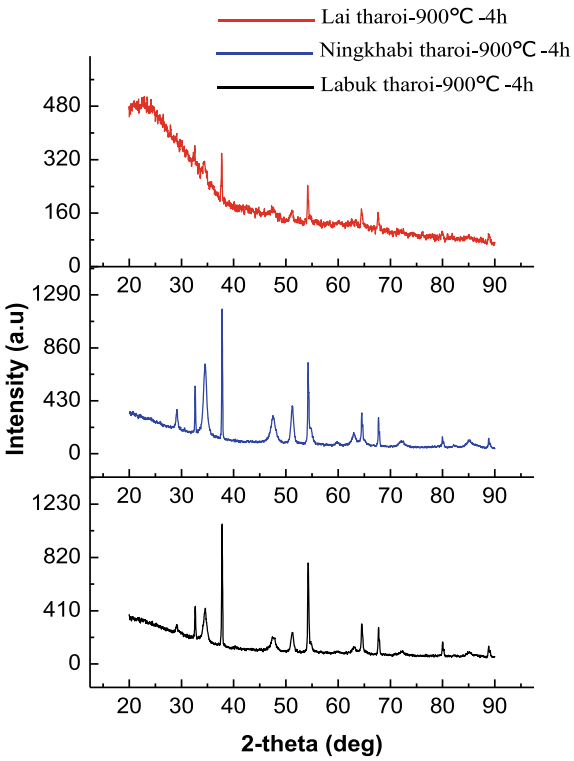

Fig. 3 XRD of lai tharoi, labuk tharoi, and ningkhabi tharoi calcinated at 900 °C for 4 h

3.4 Selection of the Best Catalyst

Labuk tharoi was selected as the most suitable catalyst since it showed the highest XRD intensity peak with a crystal grain size of 39.23 nm when compared to lai tharoi (121.68 nm) and ningkhabi tharoi (40.89 nm). EDX analysis also shows a high CaO composition of 95.22% for the selected catalyst.

3.5 Design of Experiment and Statistical Analysis By RSM

A quadratic model with a high *F*-value of 109.45 and a low *p*-value of 0.0001 was selected as the best model. The correlation between the response i.e., yield and the independent variables in biodiesel synthesis is shown in Eq. (2) where A represents calcination temperature, B calcination time, and C reaction temperature.

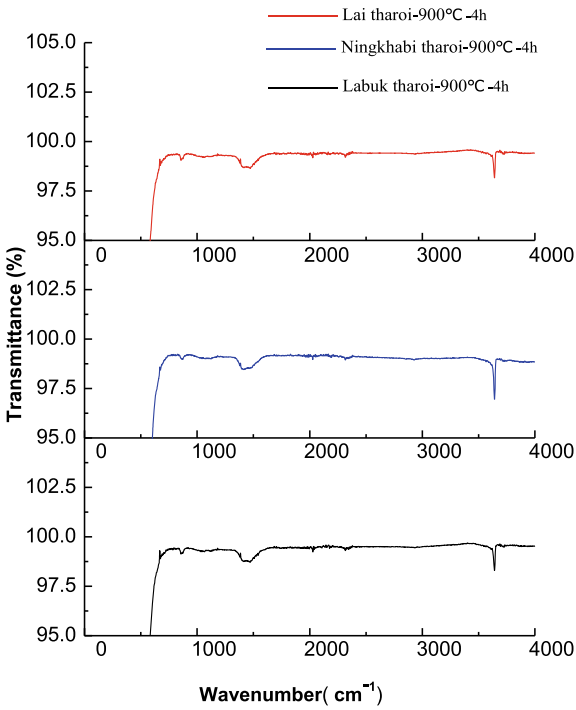

Fig. 4 FTIR of lai tharoi, labuk tharoi, and ningkhabi tharoi calcinated at 900 °C for 4 h

$$\begin{aligned}\text{Biodiesel Yield} = {} & 65.1265 + 0.0830919 * \text{A} + 0.292739 * \text{B} \\ & - 0.304416 * \text{C} \; - 0.0002625 * \text{AB} \\ & + 0.00011625 * \text{AC} + \; 0.001875 * \text{BC} \\ & - 0.000048 * \text{A}^2 - 0.0345455 * \text{B}^2 + 0.00165455 * \text{C}^2 \end{aligned} \quad (2)$$

To determine the significance of the independent parameters, the *p*-value and *F*-value of ANOVA were examined as shown in Table 3. Thus, for the synthesis of biodiesel from WCO using waste snail shell catalyst, calcination temperature ($F = 253.55$), calcination time ($F = 42.99$), and reaction temperature ($F = 232.69$) were found with a significance of 24.94%, 4.22%, and 22.89% respectively. The minor difference of 0.2 between the predicted R^2 of 0.9676 and adjusted R^2 of 0.9809 indicates that all the paraments taken are significant in the biodiesel synthesis. The high value of predicted R^2 of 0.9676 indicates that the predicted response is in line with the experimental yield [11].

Table 3 ANOVA for quadratic model

Source	Sum of squares	d*f*	Mean square	*F*-value	*p*-value	Remarks
Model	2.2	9	0.244	109.45	< 0.0001	Significant
A-Calcination temperature	0.5664	1	0.566	253.55	< 0.0001	
B-calcination Time	0.096	1	0.096	42.99	< 0.0001	
C-reaction temperature	0.5198	1	0.519	232.69	< 0.0001	
AB	0.0055	1	0.005	2.47	0.1473	
AC	0.1081	1	0.108	48.39	< 0.0001	
BC	0.0028	1	0.003	1.26	0.2881	
A^2	0.6457	1	0.645	289	< 0.0001	
B^2	0.0033	1	0.003	1.47	0.2534	
C^2	0.0753	1	0.075	33.7	0.0002	
Residual	0.0223	10	0.002			
Lack of fit	0.0133	5	0.002	1.48	0.3382	Not significant

3.6 Confirmation of Experimental Design

The optimum solution of calcination temperature 931.8 °C, calcination time 3.5 h, and reaction temperature 70.8 °C was obtained from the RSM (CCD) and a confirmation test was carried out with these observed values. Three consecutive experiments were conducted, and the biodiesel yield obtained was 95.91 ± 0.15% which is superior to the predicted yield of 95.24% as predicted by RSM.

3.7 Effect of Parameters on Biodiesel Production

To study the effect of the independent parameters on biodiesel yield, the 3-D surface graphs of the CCD were used as shown in Fig. 5. From Fig. 5a it is observed that with an increase in reaction temperature from 55 to 75 °C, the biodiesel yield increases [12]. This is because, with an increase in reaction temperature, the kinetic energy between the triglycerides of the Waste Cooking Oil, catalyst, and the methanol increases [13]. The catalyst temperature also plays a very significant role in improving the yield of biodiesel. From Fig. 5c it can be seen that with an increase in calcination temperature from 800 to 900 °C, the biodiesel yield increases from 93.53 to 95.22 [14]. Further increasing the calcination temperature reduces the biodiesel yield which may be due to the formation of ash at higher temperatures in the catalyst sample. From Fig. 5b it is observed that the calcination time is not so significant in improving the yield of biodiesel.

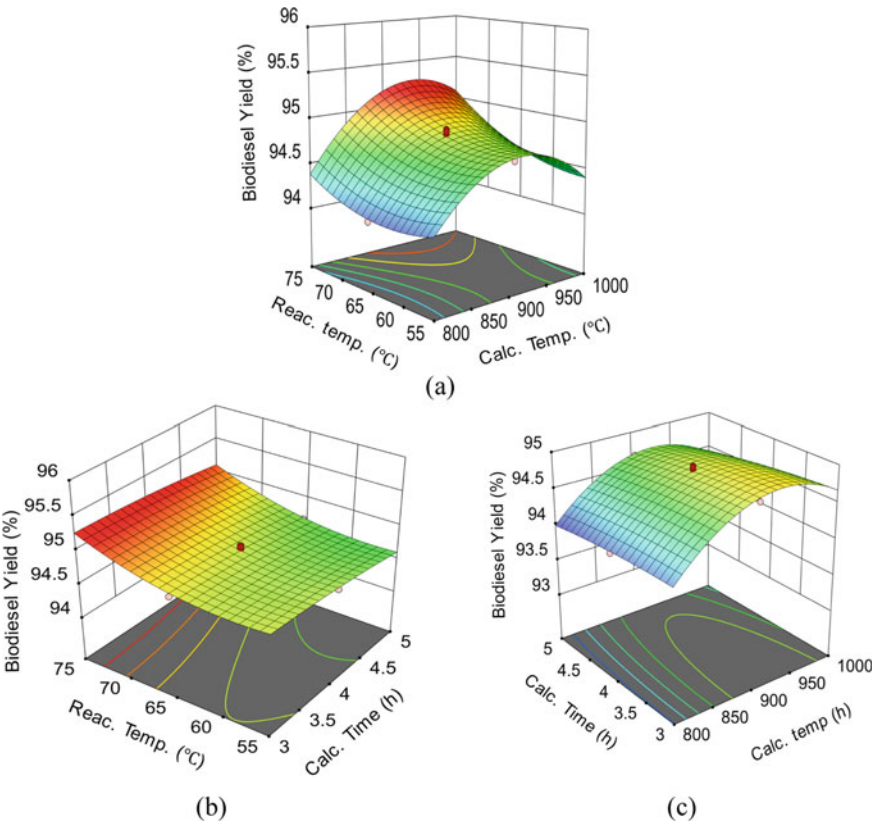

Fig. 5 Surface plot of RSM **a** calcination and reaction temperature versus biodiesel yield b calcination time and reaction temperature versus biodiesel yield **c** calcination temperature and calcination time vs biodiesel yield

3.8 Properties of Biodiesel

3.8.1 FTIR of Biodiesel

FTIR of the extracted FAME is shown in Fig. 6. It is observed that the stretching at 3010.312 cm^{-1} with 93.99% transmittance shows C-H bond presence, 2923.035 cm^{-1}, and 2853.706 cm^{-1} and 723.093 cm^{-1}shows CH2 presence. C=O ester presence is detected at 1461.654 cm^{-1}. (CO)–O–CH3 is detected at 1435.553 cm^{-1} and C–O ester is detected at 1169.710 cm^{-1}.

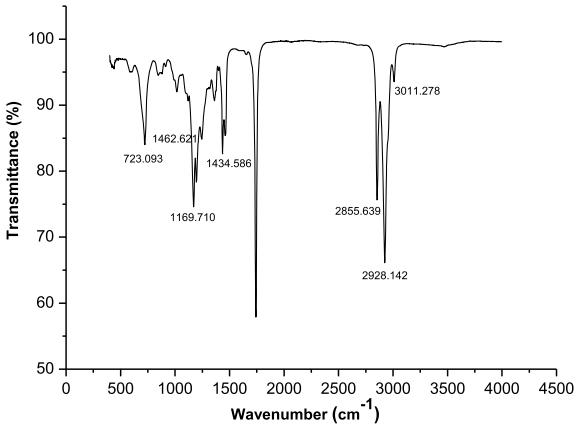

Fig. 6 FTIR of biodiesel (FAME)

Table 4 Methyl ester and fatty acid profile of biodiesel

Retention time (min)	Identified compounds	Corresponding acids	Chemical formulae	Values
42.22	Methyl docosenoate	Behenic acid	$C_{23}H_{46}O_2$	45.67
35.55	Methyl oplopanone	Pentadecadienoic acid	$C_{15}H_{26}O_2$	24.33
35.43	Methyl 9–12 octadecadienoic	Linoleic acid	$C_{19}H_{34}O_2$	16.89

3.8.2 GCMS of Biodiesel

A gas chromatography-mass spectrometer was used to find out the composition of FAME. Table 4 shows the composition of the esters and the corresponding fatty acids present in the sample. The result shows the presence of behenic acid, pentadecadienoic acid, and linoleic acid, as the main composition.

4 Conclusion

An eco-friendly, cost-effective, and reusable heterogeneous catalyst was developed by calcination of three different types of waste snail shells known locally as labuk tharoi (*Angulyagra oxytropis),* ningkhabi tharoi (*Bellamya crassa*) and lai tharoi (*Thiara tuberculate*) found at Imphal, Manipur. Labuk tharoi was selected as the most suitable catalyst as it contains the highest percentage of CaO (98.15%) as per EDX analysis. The catalyst was found to be highly crystalline as per XRD analysis. WCO was employed as feedstock as it is readily and cheaply available. A high biodiesel yield of 95.91 $\pm$ 0.15% was achieved under optimized reaction

conditions of calcination temperature of 931.8 °C, calcination time of 3.5 h, and reaction temperature of 70.8 °C which is more than the RSM predicted yield value of 95.24%. Most of the researchers fail to study the effect of independent parameters such as calcination temperature and calcination time while optimizing biodiesel yield using RSM. In this study, it was observed that calcination temperature (24.94%) plays a significant contribution in optimizing biodiesel yield. The characterization of the biodiesel and the synthesized catalyst shows that high-grade biodiesel has been obtained by deploying WCO as a feedstock and waste snail shell as a source for heterogeneous catalysts.

References

1. Statistical Review of World Energy globally consistent data on world energy markets. and authoritative publications in the field of energy (2021)
2. Parida S, Singh M, Pradhan S (2022) Biomass wastes: a potential catalyst source for biodiesel production. https://doi.org/10.1016/j.biteb.2022.101081
3. Shrivastava P, Verma TN, Pugazhendhi A (2019) An experimental evaluation of engine performance and emisssion characteristics of CI engine operated with Roselle and Karanja biodiesel. Fuel 254:115652. https://doi.org/10.1016/j.fuel.2019.115652
4. Adepoju TF, Victor E, Ekop EI, Emberru RE, Balogun TA, Adeniyi AD (2022) Residual wood ash powder: A predecessor for the synthesis of $CaO–K_2O–SiO_2$ base catalyst employed for the production of biodiesel from Asimina triloba oil seed. Case Stud Chem Environ Eng 6:100252. https://doi.org/10.1016/J.CSCEE.2022.100252
5. Brahma S, Basumatary B, Basumatary SF, Das B, Brahma S, Rokhum SL, Basumatary S (2023) Biodiesel production from quinary oil mixture using highly efficient Musa chinensis based heterogeneous catalyst. Fuel 336:127150. https://doi.org/10.1016/j.fuel.2022.127150
6. Abdullah SHYS, Hanapi NHM, Azid A, Umar R, Juahir H, Khatoon H, Endut A (2017) A review of biomass-derived heterogeneous catalyst for a sustainable biodiesel production. Renew Sustain Energy Rev 70:1040–1051. https://doi.org/10.1016/j.rser.2016.12.008
7. Singh TS, Verma TN (2019) An assessment study of using Turel Kongreng (river mussels) as a source of heterogeneous catalyst for biofuel production. Biocatal Agric Biotechnol 20:101185. https://doi.org/10.1016/j.bcab.2019.101185
8. Kaewdaeng S, Sintuya P, Nirunsin R (2017) Biodiesel production using calcium oxide from river snail shell ash as catalyst. Energy Proc 138:937–942. https://doi.org/10.1016/j.egypro.2017.10.057
9. Ashine F, Kiflie Z, Prabhu SV, Tizazu BZ, Varadharajan V, Rajasimman M, Joo S-W, Vasseghian Y, Jayakumar M (2023) Biodiesel production from Argemone mexicana oil using chicken eggshell derived CaO catalyst. Fuel 332:126166. https://doi.org/10.1016/j.fuel.2022.126166
10. Pandit PR, Fulekar MH (2017) Egg shell waste as heterogeneous nanocatalyst for biodiesel production: optimized by response surface methodology. J Environ Manage 198:319–329. https://doi.org/10.1016/j.jenvman.2017.04.100
11. Shi X, Karachi A, Hosseini M, Yazd MS, Kamyab H, Ebrahimi M, Parsaee Z (2020) Ultrasound wave assisted removal of ceftriaxone sodium in aqueous media with novel nano composite g-C_3N4/MWCNT/Bi2WO6 based on CCD-RSM model. Ultrason Sonochem 68:104460. https://doi.org/10.1016/j.ultsonch.2019.01.018
12. Nongbe MC, Ekou T, Ekou L, Yao KB, Le Grognec E, Felpin FX (2017) Biodiesel production from palm oil using sulfonated graphene catalyst. Renew Energy 106:135–141. https://doi.org/10.1016/j.renene.2017.01.024

13. Abukhadra MR, Sayed MA (2018) K+ trapped kaolinite (Kaol/K+) as low cost and eco-friendly basic heterogeneous catalyst in the transesterification of commercial waste cooking oil into biodiesel. Energy Convers Manag 177:468–476. https://doi.org/10.1016/j.enconman.2018.09.083
14. Singh TS, Verma TN (2019) Taguchi design approach for extraction of methyl ester from waste cooking oil using synthesized CaO as heterogeneous catalyst: response surface methodology optimization. Energy Convers Manag 182:383–397. https://doi.org/10.1016/j.enconman.2018.12.077