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Research paper

Optimization of Eggshell/Biochar Catalyst for Production of Sustainable Biodiesel

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Abstract

Biodiesel, a renewable and biodegradable fuel, offers a promising alternative to fossil fuels. This study investigates the production of biodiesel using a novel, cost-effective, and environmentally sustainable catalyst derived from waste materials. Specifically, biochar from pine fruit was used as the catalyst support, while eggshells, rich in calcium oxide, served as the active catalytic component. The catalyst and its support were characterized using FESEM, XRD, EDX, and FT-IR. The transesterification reaction was optimized using response surface methodology with Design-Expert 7.0.0 software, varying the oil-to-methanol volume ratio (1, 2, and 3 v/v), reaction time (60, 90, and 120 min), and eggshell percentage in the catalyst (20, 30, and 40 wt.%). The optimal conditions were determined to be an oil-to-methanol ratio of 2 v/v, a reaction time of 90 min, and an eggshell percentage of 30 wt.%, resulting in a biodiesel purity of 96.83%. These findings demonstrate the potential of utilizing waste-derived catalysts for efficient and sustainable biodiesel production, offering a promising avenue for future research focusing on process optimization and catalyst longevity.

1. Introduction

Fossil fuels are an important part of the economy and the main energy sources in today's world. Fuels derived from the products of these materials have long been a source of energy in internal combustion engines, and the existence of abundant underground reserves has contributed to the greater use of these fuels [1]. The increasing need for energy in the world and the reduction of fossil fuel resources on the one hand, and environmental problems caused by the combustion of these fuels, on the other, have led to extensive research in recent years to find alternative energies in different countries of the world. The use of alternative fuels - especially biodiesel - is generally regarded as one of the possible feasible solutions to

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these problems. Biodiesel is a clean fuel produced from natural, renewable sources such as vegetable oils, which could be used in combustion engines like fossil diesel without the need to make any modifications to the engine itself [2]. The use of biodiesel in a conventional diesel engine ultimately results in a drastic decrease in the amount of unburned hydrocarbon, carbon monoxide, and particulate matter being released into the atmosphere [3].

Biodiesel's use decreases the carbon content in particulate matter. The properties of biodiesel are fairly identical to conventional diesel; however, the resultant exhaust from biodiesel is much greener [4]. In addition, when compared with diesel fuels, there are many benefits of biodiesel, including enhanced lubrication, reduced emission rates of many pollutants such as soot, carbon monoxide, and sulfur dioxide, a higher boiling point, renewability, biodegradability, and, foremost, a reduction in the amount of greenhouse gas accumulating in the atmosphere [5].

The main industrial method followed for biodiesel production is the transesterification process; it is a very simple and highly cost-effective process. Its main purpose is to reduce the viscosity of the oil. It involves the purification of the oil or fat, which then reacts with an alcohol-mostly ethanol or methanol-with the help of various catalysts [6]. The sources of biodiesel production include various types of vegetable oilseeds, algae, various animal fats, and fatty wastes, and their availability and price are very important in choosing a source for biodiesel production, because the highest cost of biodiesel production (about 81%) is related to the raw material used [7].

The use of inexpensive sources such as waste cooking oils (WCOs) and animal fats instead of refined edible oils, in addition to reducing the final price of biodiesel, allows for the recovery and reuse of waste. Used cooking oils are a significant source of fat that is discharged into the environment and causes environmental pollution, which can be a good feedstock for biodiesel production [8]. Bases and acids have been used as catalysts in the transesterification reaction. Some of the most commonly used acidic homogeneous catalysts in this process include sulfuric acid, hydrochloric acid, and sulfonic acid. Basic homogeneous catalysts include sodium hydroxide, potassium hydroxide, and potassium methoxide. The use of homogeneous base catalysts in biodiesel production has disadvantages, such as producing more wastewater and being non-reusable; however heterogeneous catalysts are more promising because they reduce the high costs of biodiesel production. Heterogeneous catalysts are basic or acidic solids that include anion exchange resins, zeolites, enzymes, hydrotalcites, alkali metal salts, and alkaline earth metal oxides [9].

CaO is considered one of the most efficient catalysts for biodiesel production due to its high catalytic activity in transesterification, easy preparation, low solubility in methanol and biodiesel, and relatively low cost [10-13]. Various waste biomaterials such as eggshells, oyster shells, crab and snail shells, chicken

excrement, and animal bones have been used in research related to biodiesel production for the derivation of CaO catalysts [14-17].

Various studies have been conducted on CaO loading on distinct natural supports for biodiesel production [18-25], and a number of these studies are reviewed below. In their study Mohadesi et al. [18] reported the synthesis of biodiesel from WCO using a clay/CaO catalyst, under optimum conditions, i.e., a reaction temperature of 54.97ºC, catalyst concentration of 9.6 wt.%, oil-to-methanol volume ratio of 1.94 v/v, concentration of toluene as co-solvent of 16.13 wt.%, and reaction time of 74.32 minutes, yielding a conversion of 97.16%. Different studies represented by Kumar et al. [19] on the implementation of nanocatalysts in the transesterification process developed a further proposal for the extraction of biochar from waste biomass for use as a nanocatalyst. They found that nanocatalysts greatly enhance the efficiency of the transesterification process.

Foroutan et al. [20] prepared a biochar catalyst from brown algae *Sargassum oligocystum* and CaO from the shells of produced eggs and concluded that the maximum biodiesel production efficiency under optimal conditions would be 98.83%. Wang et al. [21] studied biochar from municipal sludge as a new structure for the synthesis of a series of heterogeneous calcium-based catalysts for biodiesel production. They found that the highest biodiesel yield was up to 93.77%. Kostic et al. [22] studied the production of biodiesel from sunflower oil in the presence of a biochar catalyst prepared from palm kernel shells. They found that under optimal conditions, the biodiesel production efficiency was 99%.

Zhao et al. [23] explored high-performance and stable CaO-based catalysts supported on rice husk biochar. The results indicated that efficiencies as high as 93.4% might be achieved upon loading 30 wt.% CaO and calcination at 700°C. Jung et al. [24]studied the use of biochar from poultry manure pyrolysis for biodiesel production as a greener approach. They found that the prepared biochar at 350°C gave better performance, achieving a 95.6% biodiesel yield.

Wang et al. [25] employed raw coal, a sort of solid waste, as a substrate for synthesizing a solid carbon-based acid catalyst in producing biodiesel from palm oil. They attained the highest biodiesel yield of 98.6% at optimum conditions. In agreement with this work, Sivan et al. [26] explored the production of biodiesel from cashew nut shell liquid using a sulfonated cashew nut shell biochar catalyst during the transesterification process. This was conducted under ideal conditions of a temperature of 65ºC, a reaction time of 1 h, and an oil-to-methanol molar ratio of 18:1, where the biodiesel production attained its maximum yield of 94.2%.

Mazaheri et al. [27] discussed the use of the *Chicoreus brunneus* shell to produce heterogeneous CaO nanocatalysts to be applied to rice bran oil transesterification in order to produce biodiesel. The results of their research indicated that the CaO catalyst derived from the *Chicoreus brunneus* shell had favorable results regarding biodiesel production, demonstrating considerably lower kinematic viscosity.

Lani et al. [28] researched rice husk and eggshells for biodiesel production via transesterification with hybrid catalysts prepared using the wet impregnation method and revealed that silica-supported CaO had higher activity than pure CaO in biodiesel production. Another research work was done by Kaewdaeng et al. [29] on the production of biodiesel using a calcium oxide catalyst obtained from the ash of the river snail shell. Under optimum operating conditions - a methanol-to-oil molar ratio of 9:1, a catalyst amount of 3 wt.%, and a reaction time of 1 hour- the maximum yield for biodiesel production was found to be 92.5%.
This research introduces a novel and sustainable approach to biodiesel production by utilizing a composite catalyst derived from waste materials: biochar from pine fruit as a support and eggshells as the active calcium oxide component. This combination offers a cost-effective and environmentally benign alternative to conventional catalysts, achieving a high biodiesel purity under optimized conditions determined through response surface methodology (RSM), demonstrating the synergistic potential of these readily available waste streams for efficient and sustainable biofuel production.

2 . Materials and Methods

2.1. Materials

In this study, WCO was selected for biodiesel production. This oil was obtained from restaurants and fast-food stores and was used in this research. Among the alcohols that can be used to produce biodiesel, methanol is a suitable choice; in this study, methanol with a purity of 99% was used. A calcium oxide catalyst based on biochar was employed. In this study, biochar was prepared from pine fruit, and calcium oxide was sourced from eggshells. Distilled water was used to wash the materials (eggshells and pine fruit).

2.1.1. Preparation of eggshell, biochar, and catalyst

The eggshells were cleaned with distilled water to remove dust and all kinds of impurities. Thereafter, the materials were dried in an oven at 100°C for 24 hours and then ground and sieved using a grinder to less than 45 μm. The eggshell material was then heated at a rate of 10°C/min and calcined at 1100°C for 2 hours [30]. Other cleaning of pine fruits with distilled water was followed by oven drying at 100°C for 24 hours and grinding/sieving to sizes finer than 45 μm. Pyrolysis of the prepared sample was conducted in a tubular furnace under inert gas at a heating rate of 5°C/min, holding at 550°C for 2 hours. In order to prevent the sample from absorbing humidity, the dried product was kept in an airtight container [31].
The preparation of the catalysts was carried out by mixing calcium oxide and biochar in an appropriate ratio with distilled water. Afterwards, it was stirred using a magnetic stirrer at room temperature for 24 h. Then, it was dried in an oven at 100°C for 24 hours. Finally, the prepared catalyst was treated under nitrogen gas flow in a tubular furnace at 550°C for 2 hours.

2.1.2. Preparation of waste cooking oil

In frying, the oil undergoes various physical and chemical changes that produce undesirable products like free fatty acids and water. The presence of these substances, above all water, seriously lowers the yield of biodiesel obtained and can even provoke a failure in the transesterification reaction. To neutralize this effect, WCO was previously submitted to a cleaning step by filtration to eliminate the suspended solids and fine particulates. Then, a 1 wt.% sulfuric acid treatment combined with a methanol-to-oil molar ratio of 6:1 for 2 hours was carried out to reduce the acid value of the substance [32]. Finally, the obtained oil was heated to 80°C for 12 hours to remove the trace amount of water.

2.2. Experimental procedure

All experiments were performed using WCO, methanol, and in the presence of a CaO/biochar catalyst. For each sample, 20 mL of WCO was used. A certain amount of methanol was added to a two-necked flask along with the WCO. The experiments were conducted under reflux at a constant temperature of 63°C with a stirring speed of 600 rpm and in the presence of an 8 wt.% catalyst [33, 34]. After the experiments, a separator funnel was used to separate glycerol from the produced biodiesel. Thereafter, the crude biodiesel obtained was washed several times with hot distilled water to remove residual impurities and dried in a hot air oven at 80°C for 12 hours. The purity of the biodiesel sample thus obtained was analyzed using GC-MS.

2.3. Experimental design

Biodiesel production relies on various parameters, such as reaction time, reaction temperature, mixing speed, oil-to-methanol ratio, type of catalyst, and catalyst concentration. Regarding this study, the influence exerted by the volume ratio of oil to methanol, reaction time, and eggshell percentage in the catalyst on biodiesel purity was considered. The values of the above variables can be identified from Table 1. The selection of process parameter levels was based on previous related literature[18, 34, 35].

Response surface methodology is one of the tools used in conducting regression analysis to find relationships among responses observed, which has been applied to study the effect of many variables on biodiesel production by several researchers. Within RSM, two popular experimental designs stand out: Box-Behnken design (BBD) and central composite design (CCD). While both aim to efficiently model the response surface, they differ in their approach and suitability for specific applications [36, 37]. In this study, the BBD was chosen due to its efficiency in exploring the design space with fewer runs compared to the CCD, particularly considering the number of factors being investigated. This minimized resource consumption while still providing sufficient data for model fitting and optimization [38].

As mentioned, experimental design has been carried out using the BBD. This multi-level method requires a total of 15 experiments based on three variables selected: oil-to-methanol volume ratio, reaction time, and the percentage of eggshell in the catalyst, each at three levels, including 13 unique experiments and 2 replicates at the central point.

Table 1. Operating parameters and their levels

Factor	Unit	Symbol	Levels		
			Low	Middle	High
Reaction time	min	t	60	90	120
Oil-to-methanol volume ratio	v/v	R_{OM}	1	2	3
Eggshell/(Eghshell+Biochar)	wt.%	EB	20	30	40

A full quadratic model describes the dependency of the dependent variable concerning the independent variables. Mathematically, a full quadratic model may be represented as:

$$Y = \beta_0 + \sum_{i=1}^{3} \beta_i X_i + \sum_{i=1}^{3} \beta_{ii} X_i^2 + \sum_{i=1}^{2} \sum_{j=i+1}^{3} \beta_{ij} X_{ij} \quad (1)$$

The above equation is explained as follows: Y, the response variable; X_i andX_j, independent variables; β_0, constant; β_i, coefficients for linear terms; β_{ii}, coefficients for quadratic terms; and β_{ij}, coefficients for interaction terms.

Analysis of variance was conducted for the proposed model of response. This method included the calculation of the regression coefficients of linear, interaction, and quadratic terms, as well as testing the integrity of the model equation through the coefficient of determination R^2. Furthermore, the adjusted coefficient of determination $R^2_{adj.}$ was measured to test the accuracy of the model. Unlike R^2, $R^2_{adj.}$ does not necessarily improve by including more factors in the model: it can decrease if irrelevant factors are included. Thus, it is a more conservative estimate of model precision [39].

The calculated p-value and F-value statistically analyzed the importance of model factors. In identifying the significance of the model, the first step is to calculate and compare the p-value to 0.05. When the calculated p-value is less than 0.05, the model is statistically significant. The comparative importance of the factors is made using the F-value, calculated by [39]:

$$F - \text{value} = \frac{MS_{reg.}}{MS_{res.}} \quad (2)$$

where $MS = \frac{SS}{DF}$ and mean square error and DF are the degrees of freedom and the subscripts $reg.$ and $res.$ indicate the regression and residual, respectively.

2.4. Samples characterization

XRD analysis (Philips PW 1730) was used to identify the chemical and crystalline composition of the synthesized samples (biochar, eggshell, and synthesized catalysts) in the 2θ range between 10 and 80°. Identification of the functional groups of the synthesized samples was carried out using FT-IR analysis (Thermo Nicolet AVATAR 360) with the KBr tablet technique. EDX analysis (TESCAN model MIRA II with SAMX detector) was also used to determine the compounds and elements present in the synthesized samples. In addition, the detection and determination of the surface properties and morphology of the synthesized samples were carried out using SEM analysis (TESCAN model MIRA III).

3. Results and Discussion

3.1. Characterization of synthesized samples

3.1.1. XRD analysis

XRD analysis was used to determine the crystalline structure of the synthesized samples. Figure 1 shows the XRD patterns for the biochar sample, eggshell, and different catalyst samples in this study. As can be seen in Figure 1, there are many similar peaks in the three different catalyst samples (20, 30, and 40 wt.%) at 18.1, 28.8, 34.2, 47.1, 51.2, 54.3, 59.5, 61.4, 62.2, 71.8, and 79.8°, all of which are indicative of $Ca(OH)_2$. There is a large variation in the peaks related to $Ca(OH)_2$, with the main peak at 34.2° [40]. As it is clear, there are two similar peaks at 23.2 and 29.4° related to the CaO phase. For the 30 wt.% and 40 wt.% samples, two dissimilar peaks at 50.9 and 62.6° related to the CaO phase are observed. According to Figure 1, for the eggshell sample, it is observed that the prominent diffraction values at 18.1, 28.8, 32.4, 34.2, 37.5, 47.5, 51.0, 54.0, 62.7, 64.2, 67.4, and 71.9° correspond to the $Ca(OH)_2$ phase and also to the CaO phase. As is clear, the main peak observed at 37.5° is related to the calcium oxide phase [41]. In addition, the XRD pattern for biochar, in the form of a broad peak with a peak at about 21° indicates carbon content that is amorphous in terms of crystalline structure [42, 43].

3.1.2. FT-IR analysis

Figure 2 shows the spectral information of biochar, eggshell, and various catalysts measured in this experiment. For the biochar sample, the peaks between 462 and 924 cm^{-1} represent the bond vibrations that make up the structure or fingerprint region of the biochar. Additionally, small peaks observed between 1013 and 1114 cm^{-1} can be assigned to the stretching vibrations of metals bonded within the biochar matrix. One strong peak at 1421 cm^{-1} was assigned to the vibrational modes of the aromatic C-C bonds, revealing the presence of aromatic organic compounds. The peak detected at 1575 cm^{-1} corresponds to the stretching vibrations of N-H bonds. A broad and weak peak at 3464 cm^{-1} belongs to the vibrations of the O-H bonds; thus, in this structure, there is slight moisture present. The absorption peaks from 522 to 929 cm^{-1} relate to the structural bond vibration or fingerprint region in the case of the eggshell and eggshell-biochar composite

samples. The absorption peaks between 1022 and 1110 cm^{-1} may correspond to the stretching vibration of different metal-oxygen bonds in the structure. The sharp peak at 1416 cm^{-1} is from the aromatic C-C bond vibration of aromatic organic compounds that initially existed in the sample.

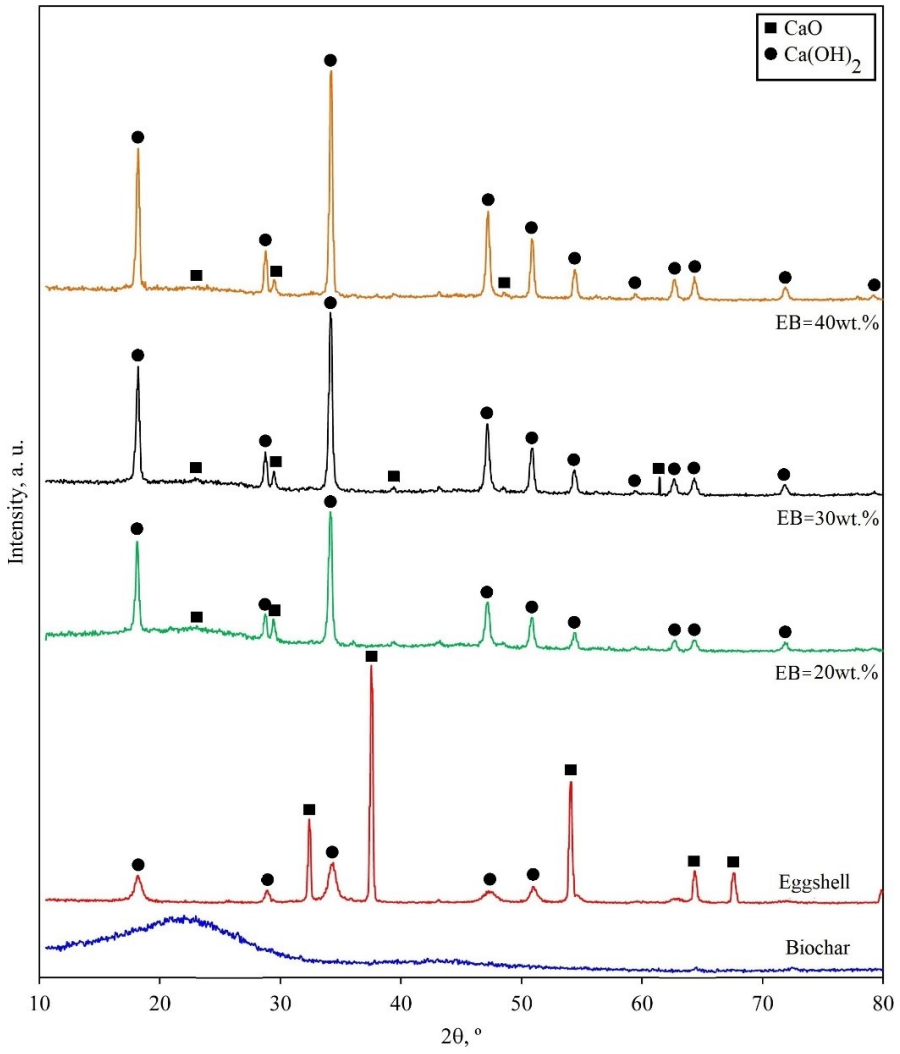

Fig. 1. XRD pattern for biochar, eggshell, and catalyst samples was used in this study.

The peak at 1570 cm^{-1} characterizes the stretching of the N-H bonds. The wide peak between 3469 and 3641 cm^{-1} corresponds to the stretching mode of the O-H bond due to slight moisture in the structure [41, 42].

3.1.3. EDX analysis

Table 2 shows the elemental analysis results for the biochar, eggshell, and various catalyst samples in this study. The EDX results confirm the elements constituting the phases identified in the XRD patterns. The

biochar sample consists of approximately 87% carbon, and the other elements indicate organic and inorganic residues present in the sample as impurities. The results also show the absence of oxygen in the biochar sample.

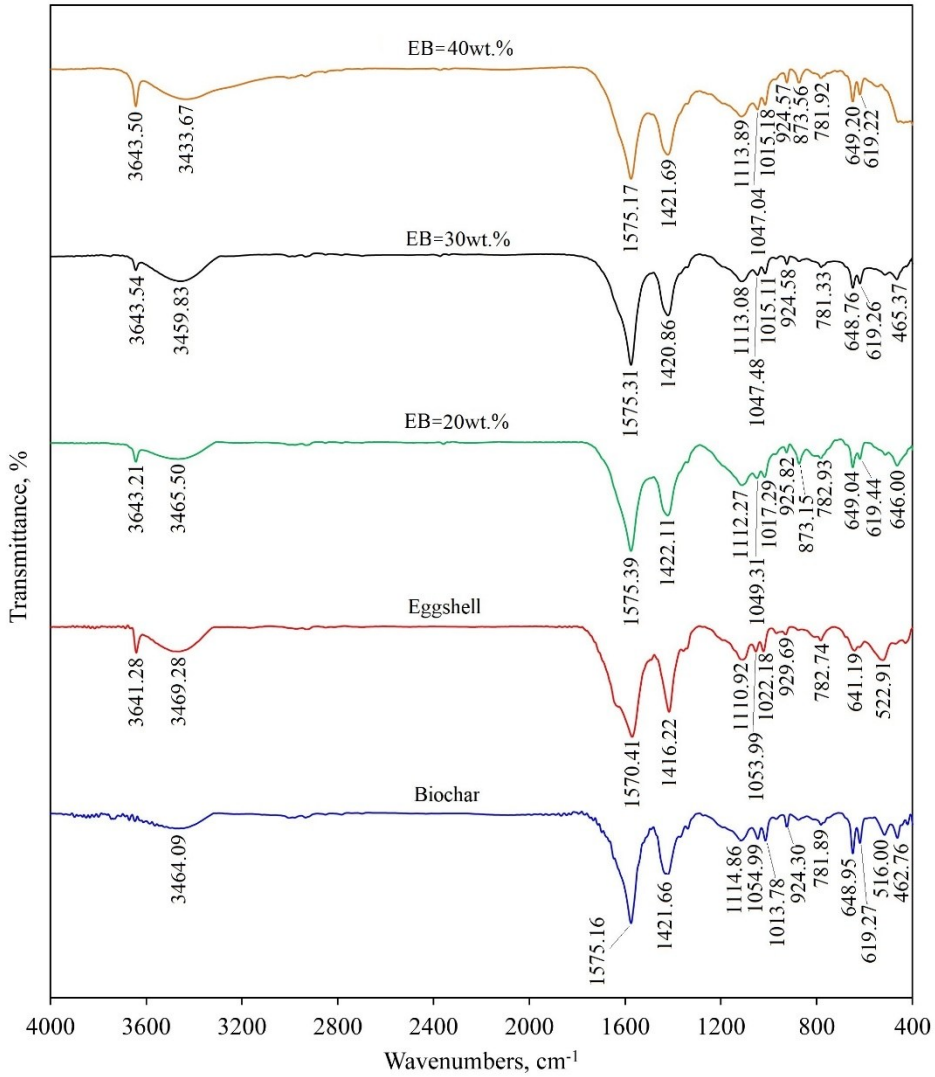

Fig. 2. FT-IR spectrum for biochar, eggshell, and catalyst samples was used in this study.

In the eggshell sample, the high levels of calcium and oxygen indicate different calcium oxides, which are consistent with the elemental analysis results in XRD. In the samples synthesized from different proportions of biochar and eggshell, the levels of carbon, calcium, and oxygen are the highest and are consistent with the phase results of these samples. In other words, the formation of a calcium carbonate phase due to the combination of biochar with eggshell indicates a chemical interaction between carbon atoms in biochar and calcium oxides in the eggshell sample.

3.1.4. FESEM analysis

FESEM analysis is one of the methods for determining the morphology and size of the particles constituting a sample. SEM images of the biochar sample, eggshell, and various catalyst samples in this study are presented in Figure 3. The SEM image for the biochar shows that, in terms of morphology, the particles constituting the sample are amorphous and lack a specific geometric shape [44]. Among the 80 particles measured, the smallest particle constituting the sample has a size of 0.06 nm, the largest particle constituting the sample has a size of 0.59 nm, and the average particle size is 0.18 nm.

Table 2. Composition of elements in biochar, eggshell, and catalyst used in this study using EDX analysis.

Element	Composition, wt.%				
	Biochar	**Eggshell**	***EB*=20 wt.%**	***EB*=30 wt.%**	***EB*=40 wt.%**
C	87.37	4.34	44.17	37.63	12.79
N	3.66	1.47	1.65	1.61	1.23
O	-	38.02	28.32	22.00	28.15
Na	0.94	1.49	1.19	1.05	1.04
Mg	-	2.33	1.58	1.33	1.43
Al	1.38	1.02	0.91	0.90	1.02
Si	2.15	0.84	0.94	1.02	0.94
S	0.94	0.90	0.70	0.76	0.74
K	0.89	-	-	-	-
Ca	2.61	48.79	19.86	33.20	52.63
Fe	0.07	0.79	0.69	0.51	0.02

As the SEM image of the eggshell shows, in terms of morphology, the particles constituting the sample are irregularly polyhedral [45]. Among the 24 particles measured, the smallest particle has a size of 0.47 nm, the largest particle has a size of 1.84 nm, and the average particle size is 0.97 nm. The SEM image of the catalyst containing 20 wt.% of the eggshell sample shows that the particles are cubic in terms of morphology. The SEM image of the catalyst containing 30 wt.% of the eggshell sample shows that the particles constituting the sample are a mixture of polyhedral to amorphous shapes in terms of morphology. The SEM image of the catalyst containing 40 wt.% of the eggshell sample shows that the particles are amorphous in terms of morphology. For all samples, the particle size distribution indicates that 100% of the particles have a size of less than 1 nm.

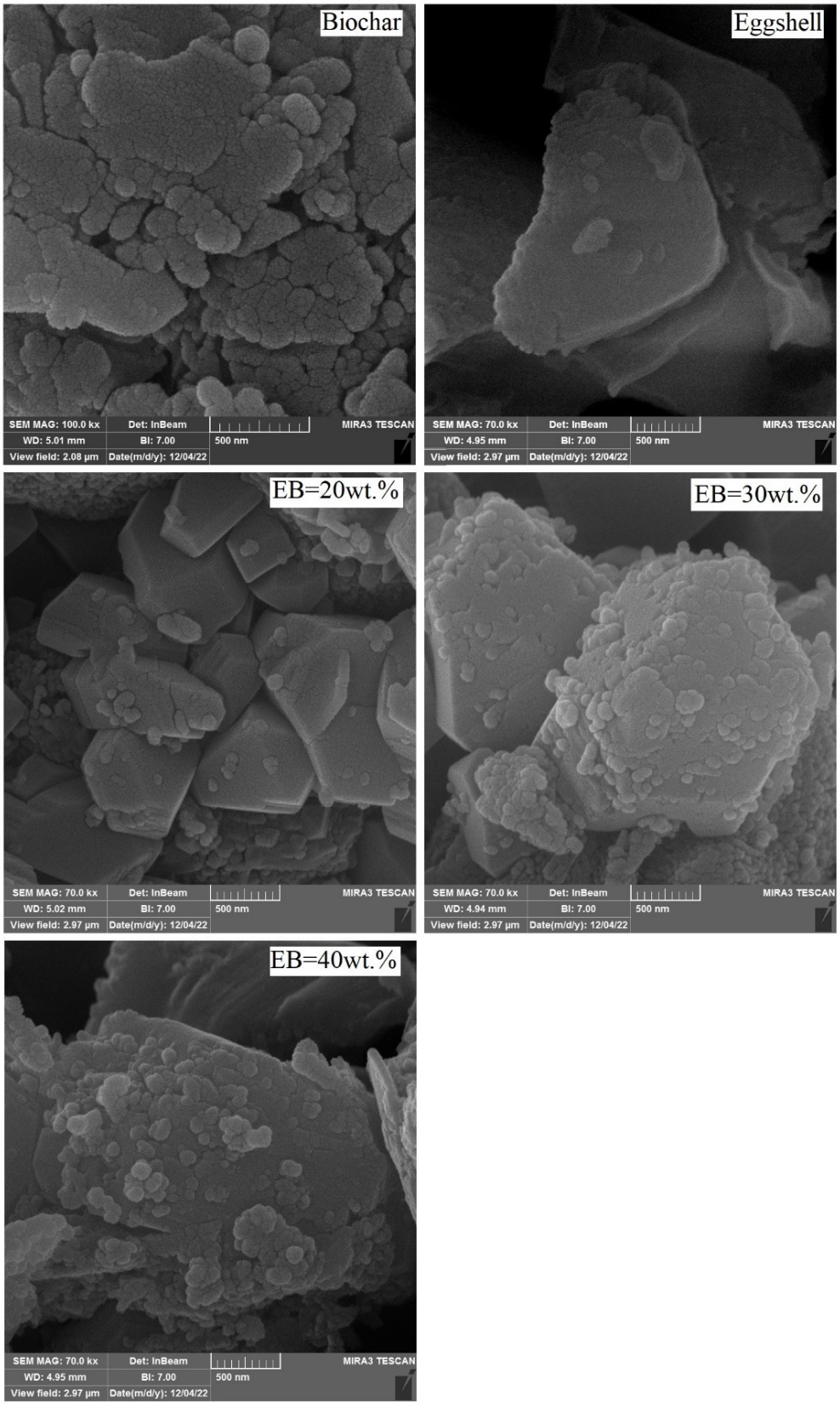

Fig. 3. SEM images for biochar, eggshell, and catalyst samples.

3.2. Investigation of the results and statistical analysis

In the present analysis, the three variables of interest were reaction time, oil-to-methanol ratio, and catalyst eggshell content at three levels: low, medium, and high. Their actual numerical values are shown in Table 1. The next section shows the Box-Behnken design of the experiment, while the results of the experiments carried out are summarized in Table 3. Table 3 presents that the highest biodiesel purity, based on FAME concentration, was achieved in experiment 15, using a reaction time of 90 minutes, an oil-to-methanol volume ratio of 2 v/v and an eggshell proportion of 30 wt.% in the catalyst, resulting in a purity of 96.83%. Meanwhile, the lowest purity was recorded in the test number 1: 60 minutes of reaction time, with an oil-to-methanol volume ratio of 2 v/v and catalyst material with eggshell at 20 wt.%, yielding a purity of 54.35%. Using the method of least squares, a quadratic model was designed to predict the purity of biodiesel, represented here as FAME:

$$FAME = 95.73 + 11.33X_t + 2.06X_{R_{OM}} + 7.67X_{EB} - 3.74X_t.X_{R_{OM}} - 1.84X_t.X_{EB} - 5.41X_{R_{OM}}.X_{EB} - 11.27X_t^2 - 7.55X_{R_{OM}}^2 - 8.41X_{EB}^2 \quad (3)$$

The respective coded values for reaction time, the volume ratio of oil to methanol, and % of eggshell in the catalyst can be defined by the use of X_t, $X_{R_{OM}}$, and X_{EB} in the model equation. The positive terms in the equation show a positive effect on purity, while the negative terms reflect a negative effect contributed by the respective variable. Table 4 shows the results of ANOVA for the quadratic model. The model is highly significant since the F-value is 94.92, and the p-value is below 0.0001. Furthermore, all the terms are significant since the p-values for all model coefficients are below 0.05. The three variables t, R_{OM}, and EB are involved since they have a significant influence on the purity of biodiesel. Interaction terms such as ($t.R_{OM}$, $t.EB$, and $EB.R_{OM}$), and quadratic terms like t^2, R_{OM}^2, and EB^2 represent remarkable significance with small p-values. The poor fit is also reflected by p-values higher than 0.05, reflecting a good agreement between the model and experimental data. The R^2 and $R_{adj.}^2$ determination coefficients are equal to 0.9942 and 0.9837, respectively. That would point to a very well-fitting and strong model.

3.2.1. Analysis of statistical plots

Figure 4 displays the statistical analysis of the results. In particular, Figure 4a presents the estimated values of purity in biodiesel as opposed to the actual experimental values. The high value of the correlation between calculated and actual values underlines a very good agreement between the model and experimental values.

The set of residual plots shown in Figures 4b, 4c, and 4d provides an additional explanation of the analysis of the results. The following plots are included: the residual plot for the predicted response (Figure 4b), normal probability plot for the residuals (Figure 4c), and residuals sorted by the order of the experiment (Figure 4d). In general, Figure 4b presents the residual plot of the predicted response, all with stochastic

scattering of points in such a way that their values fall within the two indirect lines, where any systematic errors would have appeared.

Table 3. Designing experiments using the Box-Behnken method and the results of them (C =8 wt.% and T=63 ºC)

Run	t, min	R_{OM}, v/v	EB, wt.%	FAME, %
1	60	2	20	54.35
2	90	3	20	79.15
3	60	2	40	72.65
4	90	1	20	64.34
5	60	1	30	60.92
6	90	1	40	91.22
7	90	2	30	94.87
8	90	2	30	95.50
9	120	3	30	85.42
10	90	3	40	84.39
11	120	1	30	88.65
12	120	2	20	83.13
13	120	2	40	94.06
14	60	3	30	72.67
15	90	2	30	96.83

Table 4. Variance analysis for the quadratic response surface model.

Source	Sum of squares	DF	Mean square	F-value	p-value Prob>F	Significance level
Model	2540.30	9	282.26	94.92	< 0.0001	highly significant
t	1027.63	1	1027.63	345.57	< 0.0001	highly significant
R_{OM}	34.03	1	34.03	11.44	0.0196	significant
EB	470.48	1	470.48	158.21	< 0.0001	highly significant
$t.R_{OM}$	56.10	1	56.10	18.87	0.0074	highly significant
$t.EB$	13.58	1	13.58	4.57	0.0856	possibly significant
$R_{OM}.EB$	117.07	1	117.07	39.37	0.0015	highly significant
t^2	469.21	1	469.21	157.79	< 0.0001	highly significant
R_{OM}^2	210.22	1	210.22	70.69	0.0004	highly significant
EB^2	261.33	1	261.33	87.88	0.0002	highly significant
Residual	14.87	5	2.97			
Lack of fit	12.87	3	4.29	4.28	0.1950	not significant
Pure Error	2.00	2	1.00			
Cor Total	2555.17	14				

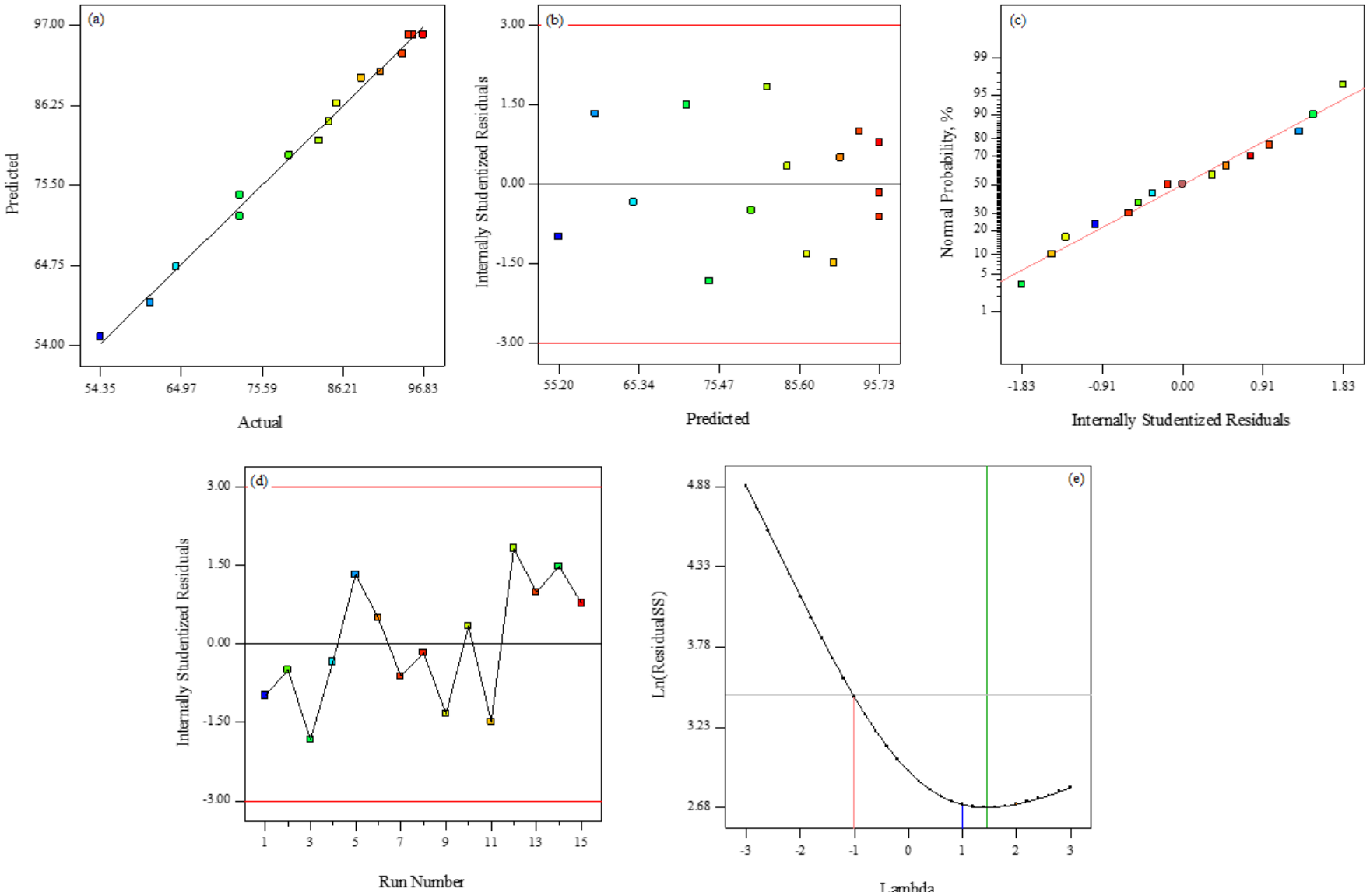

Fig. 4. (a) Comparison of predicted and actual biodiesel purity values, (b) Plot of residuals against predictor, (c) Residuals normal distribution plot, (d) Residuals plotted against the sequence of runs, and (e) Box-Cox plot for power transforms.

3.2.2. Effect of operating variables

Reaction time is one of the important variables in the transesterification process. Thus, reaction time was studied within the range of 60 to 120 minutes and is represented in Figure 5. When the reaction time is increased from 60 to 120 minutes at a fixed temperature of 63°C, catalyst concentration of 8 wt.%, and 30 wt.% eggshell content in the catalyst, the purity of biodiesel was considerably improved, as shown in Figure 5a. The purity reached its maximum value at approximately 110 minutes, which implies that the purity of biodiesel largely depends on variations in reaction time. The results of the experiments ae similar to the findings of a study by Mohadesi et al. [18].

Apart from that, the studied factor was the oil-to-methanol volume ratio at three different levels. The purity of biodiesel was highest at the lowest value of this factor (R_{OM}=1 v/v). On the other hand, the purity of the biodiesel produced decreased with an increasing volume ratio. The volume ratio of oil to methanol should be set at 2.4 v/v according to optimal conditions.

Figure 5b shows the effect of reaction time and the content of the eggshell inside the catalyst during fixed operating conditions, namely. An oil-to-methanol volume ratio of 2 v/v, a reaction temperature 63°C, and 8 wt.% catalyst concentrations. Up to 105 minutes, the reaction time increased the purity of biodiesel, and after that, it decreased with further increases in reaction time. Regarding the percentage of eggshell, increasing it from 20 wt. % to about 35 wt. % increased the purity of biodiesel dramatically. Beyond this level, an increase in the catalyst concentration progressively lowered the purity. The results show that the optimum percentage of eggshell in the catalyst is slightly above the average level for this factor, which can be due to the adverse reaction conditions that negatively affected the saponification of triglycerides [18].

Figure 5c combines the effect of the volume ratio of oil to methanol with respect to the percentage of eggshell in the catalyst on the purity of biodiesel under the following conditions: reaction time of 90 minutes, 63 ºC, and 8 wt.% catalyst concentrations. It can be realized from this figure (Figure 5c) that at the lowest volume ratio between oil and methanol R_{OM}=1 v/v, the purity of biodiesel was the lowest. However, with an increased volume ratio, the purity of biodiesel also increased. Beyond the average volume ratio, biodiesel purity started to decline due to the decreased percentage of eggshell in the catalyst. Further increases in the oil-to-methanol volume ratio resulted in reverse reactions. A similar trend has been reported in previous studies [46, 47]. The optimum oil-to-methanol volume ratio was 2.4 v/v.

Figure 5c also shows that increasing the catalyst eggshell percentage to the upper bound value (EB=40 wt.%) increased the purity of the obtained biodiesel considerably. The optimal value of the eggshell content for the maximum yield of biodiesel was found to be 37 wt.%.

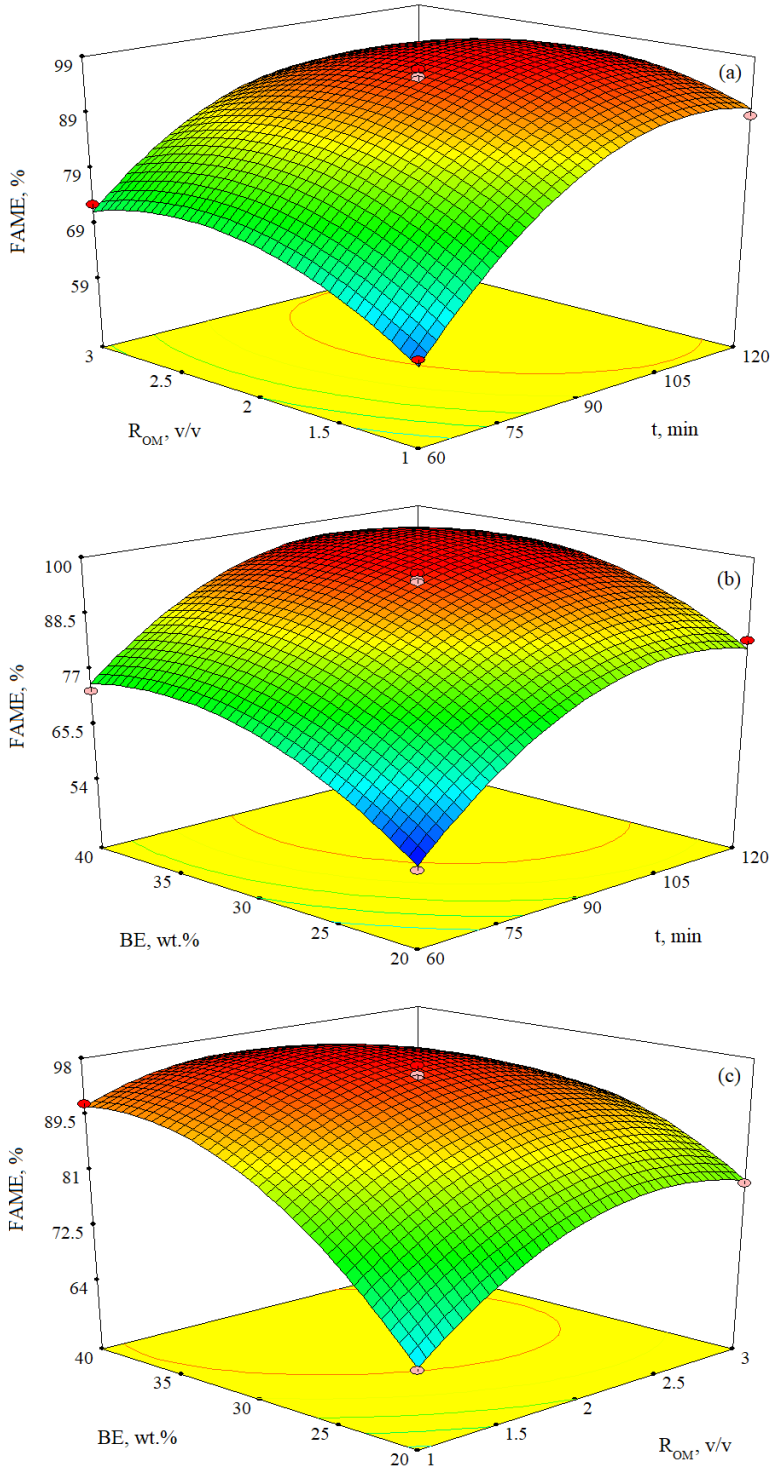

Fig. 5. (a) Interaction between reaction time and volumetric ratio of oil to methanol on biodiesel purity (C =8 wt.%, T=63 ºC, and EB=30 wt.%), (b) Influence of reaction time and eggshell/(eggshell + biochar) on biodiesel purity. (C =8 wt.%, T=63 ºC, and R_{OM}=2 v/v), and (c) Effect of oil-to-methanol volume ratio and eggshell/(eggshell + biochar) on purity of biodiesel (C =8 wt.%, T=63 ºC, and t=90 min).

3.3. Biodiesel specification

Table 5 shows the physical properties of the biodiesel produced under the optimum conditions (t=90 min, R_{OM}=2 v/v, and EB=30 wt.%). These properties mostly align with the acceptable ranges defined by the ASTM D6751 standard.

Table 5. Properties of biodiesel under optimal conditions compared by ASTM D6751.

Physical property	Biodiesel	ASTM D6751
Density at 15 ºC, g/cm^3	0.88	0.86 to 0.90
Kinematic viscosity at 40 ºC, cSt	4.7	4 to 6
Pour point, ºC	5	-15 to 10
Cloud point, ºC	7	-3 to 12

3.4. Catalyst reusability

The catalyst was tested for reusability under optimal conditions (t=90 min, R_{OM}=2 v/v, and EB=30 wt.%) over six cycles. After each cycle, the catalyst was washed with methanol and then heated at 90°C with gentle stirring to remove any remaining methanol [47]. The results, shown in Figure 6, indicate that the FAME percentage decreased from 96.49% to 91.37% after seven uses. This reduction in efficiency is likely due to the blockage of active sites on the catalyst and the loss of active components from the catalyst surface.

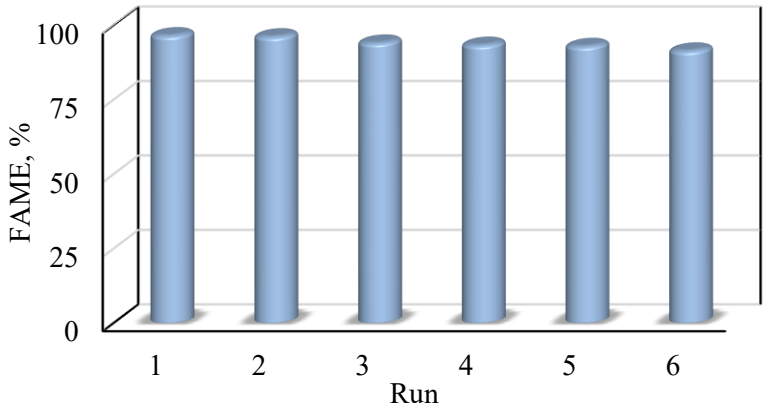

Fig. 6. Reusability of eggshell/biochar catalyst at optimal conditions (t=90 min, R_{OM}=2 v/v, and EB=30 wt.%).

4. Conclusion

In the present study, the production of biodiesel proceeds via the transesterification process of waste cooking oil using an eggshell catalyst in conjunction with hydrochar derived from pine fruit, all conducted

at a laboratory scale. In the present study, three independent variables were considered: reaction time (60, 90, and 120 minutes), oil-methanol volume ratio (1, 2, and 3 v/v), and catalyst-eggshell percentage (20, 30, and 40 wt.%). While reaction temperature was kept constant at 63ºC and catalyst loading was fixed at 8 wt.%, Response surface methodology was employed to predict the purity of biodiesel produced from this waste stream using a quadratic polynomial fit. The analysis of the experimental results showed that the optimum purity of the produced biodiesel was 96.83%. Further, from the optimization results obtained, the optimum oil-to-methanol volume ratio was determined to be 2.4 v/v. The Box-Behnken experimental design and modeling of the experiment, however, showed that the relationship of biodiesel purity vs. variables is given by a quadratic equation. Among the factors investigated, the linear and quadratic effects of reaction time, t and t^2, respectively, explained most of the biodiesel purity. For efficiency, the most important contribution was provided by the interaction of the oil-to-methanol volume ratio with the percentage of eggshell used in the catalyst, $R_{OM}.EB$.

Authors' contributions

Samira Rahmati Asl: Data curation, Writing- Original draft preparation, Investigation

Majid Mohadesi: Supervision, Methodology, Software, Writing- Reviewing and Editing

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Declaration of competing interest

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

Availability of data and materials

All data, models, or code generated or used during the study are available in a repository or online.

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