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Optimizing process parameter for biodiesel production from avocado peel oil using chicken eggshell biocatalysts using central composite design (CCD)

Yigezu Mekonnen Bayisa[1] · Tafere Aga Bullo[1] · Ketema Beyecha Hundie[1]

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Abstract
In this study, we investigated the application of waste avocado peel oil (WAPO) as a convenient and abundant source for biodiesel production using calcium oxide (CaO) biocatalysts derived from waste chicken eggshell via transesterification process. Likewise the functional group of extracted waste avocado peel oil and the structure of synthesized CaO biocatalyst were performed by using FT-IR (Fourier Transform Infrared Spectroscopy) and X-ray diffractometer analysis respectively. The physicochemical properties of the avocado peel oil and properties of biodiesel such as flash point, kinematic viscosity, density, cetane number, and acid number were also determined according to international standards. The optimum conditions were at a reaction temperature of 65 °C, a reaction time of 3 h, a catalytic load of 1.2 g, and a ratio of methanol to oil of 5:1 was achieved 94.45% with the desirability of 1 and the corresponding optimized biodiesel yield of 94.89%. The physicochemical properties of the avocado peel oil and the produced biodiesel were characterized using GC–MS to identify the composition of oil and biodiesel compound. The results represented that avocado peel oil can be used as a renewable feedstock source to produce biodiesel.

Keywords Biodiesel · Waste avocado peel oil · Calcium oxide biocatalysts · Waste chicken eggshell · Transesterification reaction · Optimization

Introduction

Currently, increasing global warming and consumption of fossil fuels are causing problems for social and economic growth [1, 2]. The influence of global warming is not limited on the economic growth and causes the environmental pollution. Since the main priority of all the biggest concerns of the world is to provide energy

✉ Tafere Aga Bullo
tafereaga@gmail.com

[1] School of Chemical Engineering, Jimma University Institute of Technology, Jimma University, P.O. Box 378, Oromia, Ethiopia

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for all sectors from transportation to communication, and health delivery systems, many scholars are focusing on the exploring the development of renewable energy resources due to sustainable and eco-friendly energy [3, 4].

The rapid rising of the world population and environmental pollution would ultimately lead to rising high energy demand by the usage of standard fuels and depletion of fossil fuels intended for the experts to analysis on the identification of further nonrenewable energy resources like fossil-based fuels [5, 6]. In addition, when compared to other fuels, biodiesel is significant over nonrenewable energy sources due to its, higher biodegradability, renewability, non-toxicity, environmentally eco-friend, high flash point, and emits less CO_2 and NOx emissions and has less sulfur or free to the atmosphere [7–10]. The primary renewable sources in the production of biodiesel are animal fats and vegetable oils. The most important supply of biodiesel feedstock's is soya bean oil, rapeseed, canola, palm, cottonseed, microalgae, sunflower, waste oils, peanut, and other non-edible oils like Karanja [11]. However, the feedstock's prices and availability of edible oil are serious problems for biodiesel production, because they compete with feed oils, and might compete through food sources and better use of non-edible vegetable oil sources and waste products of edible oil as the feedstock for biodiesel production [12]. Therefore, the majority of current and future research is to lower the cost of biodiesel production from low-cost, non-edible, and biomass sources. So, 60 to 80 percent of the overall cost of producing biodiesel is related to raw materials from edible oils raising the price of the fuel [13].

The average annual increase in fossil fuel consumption would have reached 1.5 percent, leading to an increase in the price of biodiesel [14]. Ethiopia is agro-ecologically diverse and the world's tenth-largest producer and sixth largest consumer in the world. Avocados are Ethiopia's second-largest total production next to bananas and popular fruits in Ethiopia, and consequently an increase in the generation of waste avocado peels. Avocado peels are a waste that many people discard away after using the pulp. From a waste management perspective, the production of biodiesel from the waste oil of avocado peels is environmentally friendly and reduces the CO_2 in terms of performance, which is the main cause of global warming and climate change due to the increase in the use of fossil fuels. Consequently, fossil fuels gained dominance as a source of energy, and recently covering 48% of the world's energy demand, and the excessive use of fossil fuels has facing challenges such as dwindling global reserves, continual environmental pollution, and market instability had increased fuel or biodiesel production [15]. Biodiesel production is being investigated as an alternative to petrodiesel production due to the availability of recoverable agricultural resources, environmental difficulties caused by fossil fuel consumption, and the dramatic influence on the total economy [16]. Biodiesel, on the other hand, is made from vegetable oils and animal fats, which may have no long-term implications for the food supply. The search for an inedible oil source as a raw material for biodiesel manufacturing has recently a lot of attention. Avocado peel oil is used as a biodiesel production replacement and an alternative source of biodiesel feedstocks. Recently biodiesel production from renewable energy sources received a lot of attention since renewable energy resources are only 11% of the world's total energy consumption [2].

Biodiesel is produced through a chemical reaction called the transesterification method, which is a progression of replacing the organic group of an ester with the organic group of alcohols in the presence of a catalyst which influences the efficiency of biodiesel yields [17]. Numerous acid catalysts (sulfonic acid, hydrochloric acid, sulfuric acid), alkaline catalysts (potassium hydroxide, sodium hydroxide, potassium methoxide), and enzymatic agents can be used in the biodiesel manufacturing process. Among the stated catalysts, acid and alkali catalysts need less reaction time than enzymatic catalysts. However, homogeneous catalysts cannot be recovered, and their separation as well as the refining of biodiesel produced using homogeneous catalysts is very difficult and requires a great deal of water, time, and heat increasing the cost of the product as well as polluting the environment. Calcium oxide is one of the environmentally benign substances utilized as heterogeneous catalysts in the production of biodiesel. Cao is now recovered from waste materials such as eggshells, shellfish, scallops, crab shells, and shrimp shells to lower the price of catalysts. Cao has been used as a solid base catalyst in the biodiesel production process. This substance has a high catalytic activity and is easily prepared [18]. However, Heterogeneous catalysts are less corrosive, more cost-effective, easier to recover and reuse, and easier to separate from the products (reaction mixture). It is available and can be used as a biosynthetic process and they could be intended to give a higher selectivity and longer catalyst lifetimes, so it can be effective for numerous industrial applications [4, 7, 18]. The heterogeneous solid calcium oxide catalysts prepared from waste chicken eggshells depend primarily on numerous operating independent parameters such as the ratio of methanol to oil, reaction temperature, and reaction time. The experiments were designed using the response surface methodology (RSM) via central composite (CCD) to investigate the effects of numerous independent operating variables on the produced biodiesel from the inedible avocado peel oil [8, 18].

The objective of this study is to produce and optimize biodiesel from waste avocado peel oil and investigate the effects of independent process variables (i.e. methanol/oil ratio, temperature, reaction time, and catalyst concentration) affecting the production of biodiesel (methyl ester) yield through the transesterification process to attain optimal conditions using response surface methodology (RSM) by central composite design (CCD) to investigate the interaction between the process variables. FT-IR and XRD investigations were used to assess the catalyst surface properties. The physical characteristics of biodiesel were calculated and compared to international standards, including pour point, kinematic viscosity, density, flash point, cloud point, acid number, cetane number, water content, and distillation point. FT-IR and GC–MS were used to identify the functional groups and as determine the composition of the methyl ester of avocado peel oil respectively.

Materials and methods

Materials

Waste avocado peel and chicken eggshell used for this study were obtained from Jimma University student cafeteria, Oromia, Ethiopia. All chemicals used in this

study were pure analytical grade. The chemical n-hexane (99%), methanol (99.5%), and sulfuric acid (98%) used for different purposes were purchased from Chem-Supply Kirkos Ltd. in Addis Ababa, Ethiopia.

Collection and preparation of oil extraction

The collected avocado peels were washed to remove the dirt and impurities contained in the peels (skins). Consequently, dried at 105 °C for 3 h in an oven to remove any unwanted water to determine the moisture contents of avocado peel and extract oil by Soxhlet extractor with n-hexane as a solvent [19, 20]. The oil yield extracted by Soxhlet extraction was calculated in percentage using Eq. (1).

$$Avocado\ peeloil\ yield\ (\mathrm{APO})(\%) = \frac{Mass\ of\ \mathrm{APO\ extracted\ (g)}}{Mass\ of\ \mathrm{avocado\ peel\ used\ (g)}} \quad (1)$$

The extracted crude oil was kept in a water bath at 70 °C using a rotary evaporator until the solvent n-hexane was recovered, and the collected oil was refined to remove solid impurities remaining in the crude oil. As shown in Table 3, the percent oil yield and characterization based on the standard methods of ASTM D6751 were achieved the physicochemical properties of APO such as density, viscosity, acid value, iodine value, and saponification value.

Preparation of catalyst

The chicken eggshell leftover was collected from Jimma institute of Technology staff lunches, and they were washed repeatedly with distilled water to remove any unnecessary substances and dried in a hot air oven at 105 °C for 12 h. Next, it was grounded and crushed in a mortar, and the size of the eggshell powder was adjusted to a constant size of 250 µm. Calcination was carried out at a temperature of 1000 °C for 2 h in a muffle furnace under static air at a heating rate of 2 °C/min until the temperature was reached [3, 22]. Finally, the collected samples of the Calcination Eggshell (CES) catalyst were stored in a closed jar before use to avoid reaction with carbon dioxide (CO_2) and humidity.

Characterization of catalysts

Calcined egg shells (CES) catalysts were characterized by using an X-ray diffractometer (XRD-7000) and Fourier Transform Infrared spectroscopy, FTIR (PerkinElmer, Spectrum two) which is used with the help of IR correlation charts, and the spectra were recorded in the range of wavenumber from 4000 to 500 cm^{-1} [23]. Fourier Transform Infrared (FTIR) spectroscopy was used to confirm the existence of a functional group in a CaO resulting from calcinated eggshell discarded. To approve the effective synthesis of Calcined Egg Shells (CES) the XRD analysis for the crystal structure of the catalysts was investigated using a Darwell XRD 7000, with K_α

(3 kW) X-ray diffractometer. The analysis was conducted in a range of 10–800 at a scanning speed of 2° min^{-1}.

Transesterification process

The transesterification reaction is performed in a Chemical Engineering laboratory, followed by the appropriate volume of methanol with an appropriate amount of a heterogeneous solid catalytic (CaO) solution whose concentration is adjusted with a condenser and magnetic stirrer on an electric heater. Calcium methoxide was then added to the avocado peel oil preheated or heated to 50 °C and the reaction system was sealed to avoid alcohol loss [24]. By incorporating independent operating variables such as temperature 45–65 °C, the ratio of methanol to oil of 5:1–7:1, a reaction time of 3–5 h, and catalyst load of (0.8–1.2 g) to ensure the optimum mixing for biodiesel production. When the reaction was complete, the solution was transferred to a separator funnel, cooled and the mixture was allowed to settle for 24 h to form layers. The upper layer is the biodiesel yield and the lower layer is glycerin with excess alcohol and undissolved catalyst as by-products [12]. While collecting the crude biodiesel was washed 3–4 times with water, and dried the remaining water from biodiesel by heating at 100 °C for 10 min [25]. The percent yield of biodiesel obtained based on 10 g of oil was calculated using Eq. 2 and the samples were characterized using FT-IR analysis, and gas chromatography-mass spectrometry (GC–MS).

$$\%\ yield\ (\%\mathrm{Y}) = \frac{Mass\ of\ \text{obtained biodiesel (g)}}{Mass\ of\ \text{oil used}} \tag{2}$$

Characterization of catalyst, oil, and biodiesel

The acid and saponification values of the oil were determined using standard titration methods. Density at 15 °C was measured with a densimeter [7]. The kinematic viscosity was measured using a viscometer, at 40 °C. Fourier transform infrared spectroscopy (FT-IR) analysis was performed to determine the catalyst under consideration and the functional groups of the oil, and biodiesel produced. FT-IR analysis was performed in the range of 500–4000 cm^{-1}. To measure the functional groups in the catalyst, 1 mg of catalyst powder was first mixed with completely dry potassium bromide (KBr). Next, a tiny amount of it was poured into a special metal and compressed with a hydraulic press to obtain a transparent tablet. Similarly, we performed an FTIR analysis to measure the functional group in the extracted oil, and biodiesel was poured onto a KBr plate to create a thin film, which was then used to quantify the functional group in the oil and biodiesel. The second plate was then positioned on top of the first plate (sandwich mode) [13, 26].

Table 1 Coded levels of independent operating variables in the experimental design

Variables	Symbols	Units	Coded factor levels		
			Low (-)	Mid-level	High (+)
Methanol-to-oil ratio (v/v)	A	(mL/mL)	5:1	6:1	7:1
Reaction temperature	B	°C	50	60	70
Reaction time	C	h	3	4	5
Catalyst load	D	g	0.8	1	1.2

Table 2 Constraints for optimization

Variables	Goal	Lower limit	Upper limit	Lower weight	Upper weight	Importance
ratio of methanol to oil (mL/mL)	In range	5	7	1	1	3
Reaction temperature (°C)	In range	45	65	1	1	3
Reaction time (h)	In range	3	5	1	1	3
Catalyst load (g)	In range	0.8	1.2	1	1	3
Yield	Maximize	69.1928	94.45	1	1	3

Experimental design

The statistical analysis was performed with the help of Design-Expert version 13.0, which is used to predict the yield of the response obtained at the design points and determine the optimal process operating parameter for biodiesel production by chemical transesterification process from avocado peel oil. Based on a statistical analysis of variance (ANOVA), a response surface methodology (RSM) is used to identify the effects of operating independent factors that significantly influence the yield of biodiesel through the transesterification process. In this study, a 4-factor, 5-level central composite design (CCD) was used to generate 29 experimental runs that were performed in a randomized order based on the experimental design.

Table 1 shows the selected independent process variables to investigate the effects of reaction-independent variables, reaction temperature (°C), reaction time (h), the ratio of methanol to oil (mL), and catalytic loading (g) at high and low levels to optimize biodiesel yields [19–21, 27].

The optimization of process parameters such as reaction temperature, reaction time, the ratio of methanol to oil, and catalyst load was analyzed using CCD. As shown in Table 2, the main criteria for maximizing the process parameters of biodiesel yield and keeping the values of the factors in range.

Results and discussion

Characterization of oil and biodiesel

Table 3 summarizes the physicochemical parameters of avocado peel oil and biodiesel standards, which meet the specifications compared to ASTM D6751 and EN 14214 [2, 28].

Analysis of calcined eggshells

The prepared calcined chicken eggshell (CES) was characterized by FTIR, and XRD spectroscopy to determine its functional groups of various compounds that occur in calcinated eggshells, and structure respectively. As shown in Fig. 1, Fourier transform infrared spectroscopy (FTIR) of the IR spectrum of calcined chicken eggshell (CaO) prepared from chicken eggshell wastes found in the range of 500–4000 cm^{-1}. Therefore, the bands observed between the highest peak at 3650 cm^{-1} and the lowest peak near 3120 cm^{-1} indicate that both are in the single bond region of the calcinated eggshell are associated with functional hydroxyl (OH) and carbonyl groups, while the weak bands in the 2920 cm^{-1} dispensed to asymmetric C-H stretching. On the other hand, the peaks observed in the region from 1700 to 1490 cm^{-1} were assigned to the pyrone C=C and C=O to the carboxyl group. In addition, C-O functional groups of compounds such as carbonyls, ketones, aldehydes, or ester groups were observed at 1,632 cm^{-1} in the aromatic region. The peak in the 1200–900 cm^{-1} region is also associated with the expansion and contraction of Si–O or C–O in alcohol and ether.

Table 3 Physicochemical properties of the obtained avocado peel oil, and biodiesel standards in the United States (ASTM D-67510 and Europe (EN 14214)

Property	Avocado peel oil	Biodiesel	EN 14214	ASTM D-6751	References
PH	6.75	7.65	5–6.7	7–9	[2, 7, 10, 26, 29]
Density at 15 °C, kg/m^3	900	890	860–900		
Specific gravity	0.91	0.89	0.86–0.9		
kinematic viscosity at 40 °C, cSt	4.85	4.95	3.5–5.0	1.9–6.0	
Flashpoint (°C)		135	> 120	> 130	
Yield %	38	94.45			
Iodine value, g I_2/100 g	82	114.21	< 120		
Cetane number		52.5	> 51	> 47	
Acid value, mg NaOH/g	8.8	0.4		< 0.5	
Free fatty acids		0.2		< 0.24	
Molecular weight (g/mol)	880				
Saponification value (gKOH/g)	200				

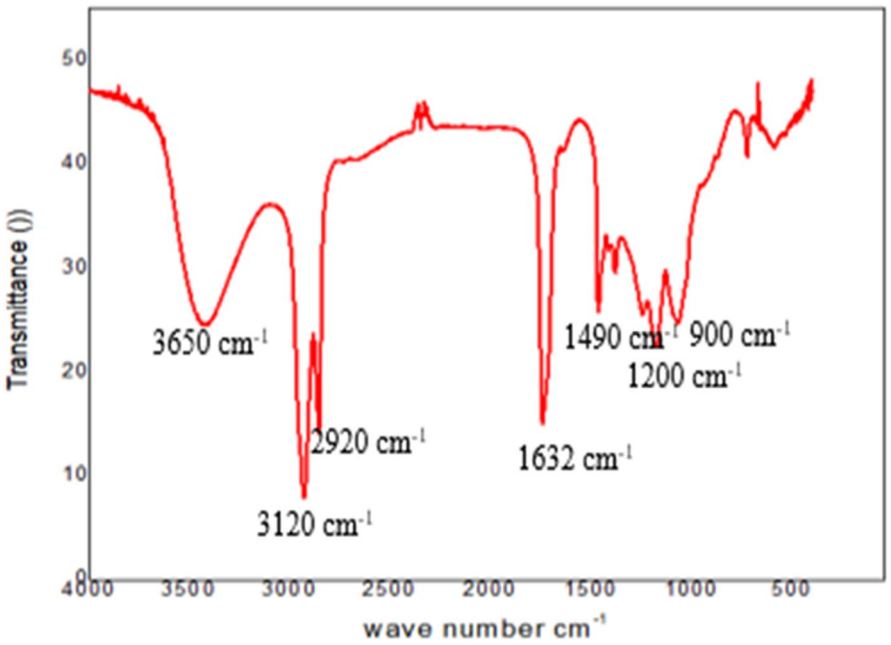

Fig. 1 Fourier Transform Infrared spectra of Calcined chicken eggshell

The XRD pattern for CES is shown in Fig. 2. The analysis was performed on calcined chicken eggshells (CES) to confirm the formation of CES produced as a heterogeneous catalyst for biodiesel production. The X-ray diffraction pattern of the main peak of the chicken eggshell, observed at $2\theta = 21.04°$, 24.19°, 25.48°, 26.8°, 31.12°, 50.26°, corresponds to the reflective surfaces of (102), (110), (040), (101), (100), and (105) confirm the presence of a fully crystallized pure amorphous phase. The peak at $2\theta = 26.8°$ is due to the amorphous phase CES, and the peak at 50.26° indicates the presence of the brookite phase [30, 31].

Characterization of oil and biodiesel by FT-IR analysis

Fig. 3 shows the results of the FT-IR analysis of avocado peel oil (APO) and the biodiesel produced. For APO, the absorption peak is observed at 3429 cm^{-1}. This is due to the stretching vibration of the -OH bond of the water molecule. In addition, an absorption peak is seen at 3083 cm^{-1}, which characterizes the vibration of the C-H bond in the CH_2 and CH_3 groups. Due to the stretching vibration of the C–O bond in the structure of the APO, vibrations of various intensities were observed along the absorption spectrum of the APO at various wave numbers in the range of 1168 to 1462 cm^{-1}. The presence of triglycerides and esters composition of the produced biodiesel, and APO was comparable by its FT-IR spectrum. The FT-IR spectrum of the produced biodiesel was observed at 3430 cm^{-1}, which

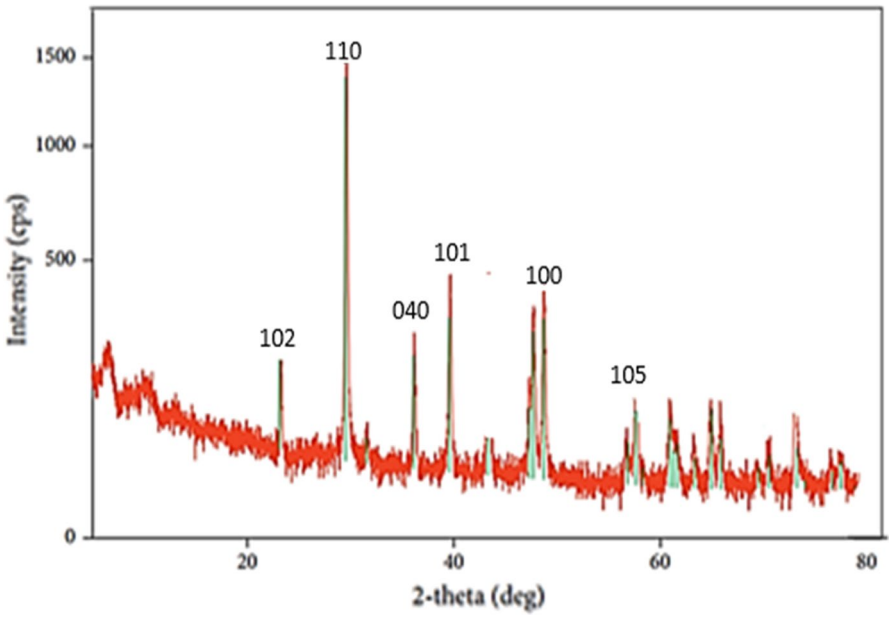

Fig. 2 XRD diffraction patterns of calcined chicken eggshell

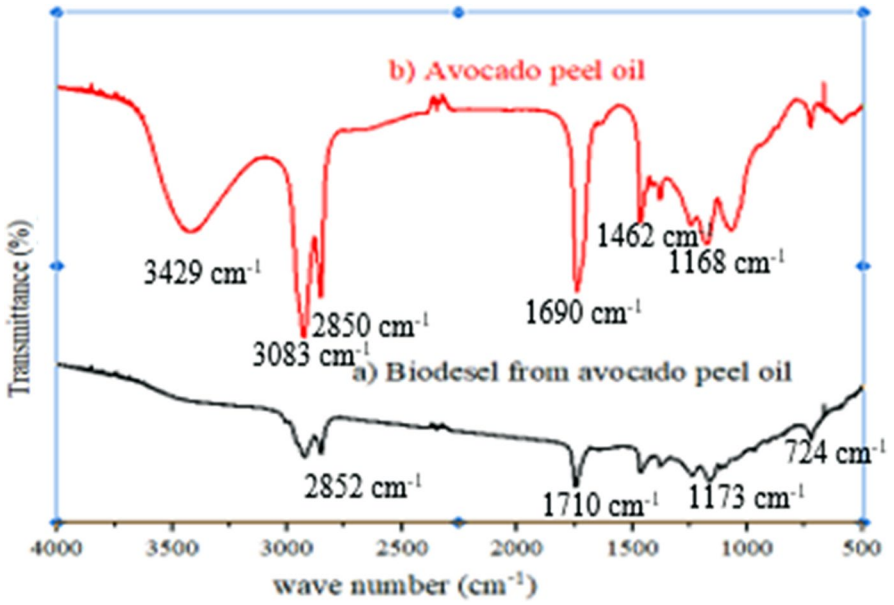

Fig. 3 FT-IR analysis of the extracted APO and produced biodiesel

is a very low-intensity absorption peak. This peak is related to the expansion and contraction vibration of the –OH group of the water molecule, confirming that the water content of biodiesel is low. After the biodiesel production process, the area and intensity of the peaks along the FT-IR spectrum changed from those of APO due to the transesterification process and ester production. After biodiesel production from APO, new absorption peaks appear at 2852, 1173, and 724 cm^{-1} to show biodiesel production from APO. The absorption peak of 1173 cm^{-1} along the FT-IR spectrum of biodiesel generated from APO can be assigned to the $–OCH_3$ group of generated biodiesels.

GC–MS analysis of biodiesel obtained from avocado peel oil

Gas chromatography-mass spectrometry (GCMS) was performed to determine the composition of the methyl ester or identify the biodiesel compounds produced from avocado peel oil. When using GC–MS, we should always consider two important pieces of information: retention time (RT) and peak area (PA). However, due to the unique physical properties of the sample, RT should remain constant as long as the analytical method is the same. It is also important to understand the elution sequence of the compounds in the mixture before GC–MS analysis of the sample. The elution sequence also ensures that the method descends to a height sufficient for the compound to elute from the column and shows an accurate retention time [31]. Analysis of the fatty acid ester mixture by GC–MS composed of four different peak area esters with retention times of 26.89, 27.85, 29.85, and 31.8 min as shown in Fig. 4 (Table 4). Since the GC–MS are recorded simultaneously so that the observed retention time can be compared to the sample MS data with a computer-embedded database, the esters

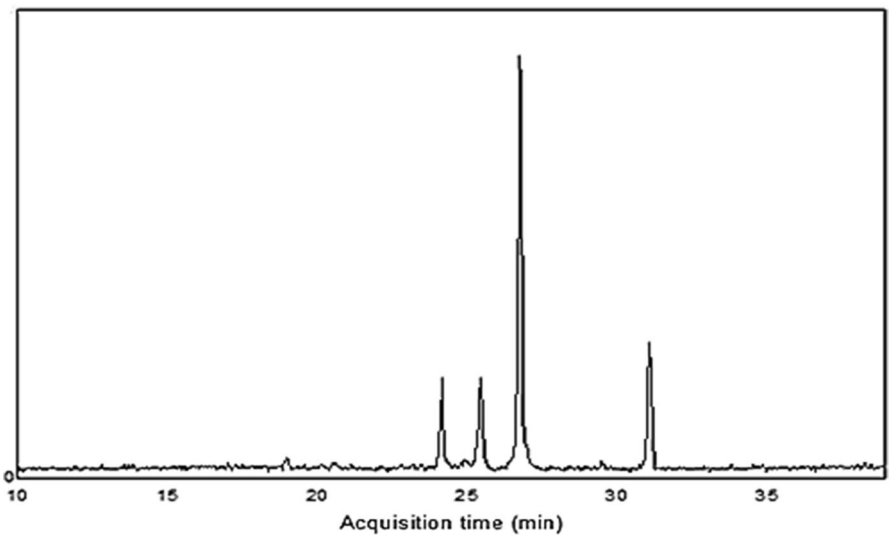

Fig. 4 The GC–MS chromatography of biodiesel produced from avocado peel oil

Table 4 Retention time (RT) and composition (%) of FAMEs of the major compounds in biodiesel produced from avocado peel oil

No	Compound	RT (min)	Approximate composition (%)
1	Methyl ester palmitic acid	27.85	11.0
2	Methyl ester linoleic acid	25.89	54.9
3	Methyl ester oleic acid	31.8	23.1
4	Methyl ester stearic acid	24.32	11.0

were identified as methyl esters of palmitic acid, linolenic acid, oleic acid, and linolenic acid as summarized in Table 4. If there is no match in the database, we can use the online compound identification database to see the relative ions and their relative abundance. Table 4 shows the RT of various esters of fatty acids from avocado peel oil and their corresponding molecular weights.

The results of GC–MS analysis show the four methyl ester substances. The percentage composition of methyl ester linoleic acid was found to be the most abundant at 54.9%. Similarly, the percentage composition of the fatty acid oleic acid methyl ester was 23.1%, and fatty acid palmitic acid and stearic acid methyl ester were equal to 11.0%.

Statistical analysis of the experimental results

Analysis of parameters that significantly affect biodiesel yield through the transesterification process is based on analysis of variance (ANOVA). Table 5 shows the significance of each regression coefficient was determined using the p-value (probability error values) as a tool. A model F-value of 62.80 means that the model is significant, there is only a 0.01% chance that such a high F-value will occur due to noise. A P-value of less than 0.0500 indicates a model term is significant. In this case, all factors (A, B, C, D, AB, AC, AD, and BD) are significant, and values above 0.1000 indicate that the model terms are not significant, and the Lack of Fit F-value

Table 5 ANOVA for biodiesel yield based on independent operating variables

Source	Sum of squares	Df	Mean square	F-value	P-value	
Model	930.55	14	66.47	62.80	< 0.0001	Significant
A-molar ratio of methanol to oil (A)	24.78	1	24.78	23.41	0.0003	
B-reaction temperature (B)	45.94	1	45.94	43.40	< 0.0001	
C-Reaction time (C)	19.45	1	19.45	18.37	0.0008	
D-catalyst Load (D)	31.28	1	31.28	29.55	< 0.0001	
AB	376.26	1	376.26	355.47	< 0.0001	
AC	10.33	1	10.33	9.76	0.0075	
AD	62.36	1	62.36	58.92	< 0.0001	
BD	246.97	1	246.97	233.32	< 0.0001	

of 0.27 implies the Lack of Fit is not significant relative to the pure error. There is a 95.93% chance that such a big lack of Fit F-value is due to noise.

Regression model development

The quadratic model proved to be the best of all other approximate models because of the higher-order polynomials with significant additional terms. The model equation from RSM software is based on the coded value of the linear variable. The positive symbol before the term represents an increase in FAME yields, and the negative sign represents a decrease in FAME yield. Equation 3, shows that the positive coefficients are A, B, A^2, B^2, C^2, and AB, and the negative coefficients are C, AC, and BC. The analysis was done in coded units. Coefficient estimates represent the expected change in response per unit change in factor values given that all remaining factors remain constant.

Final equation in terms of coded factors

$$\begin{aligned} Yield = {} & +84.34 + 1.17\,A + 1.53\,B - 0.9985\,C + 1.27\,D - 5.17\,AB \\ & + 0.8560\,AC + 2.10\,AD + 0.1057\,BC + 3.99\,BD - 0.4452\,CD \\ & + 0.0471\,A^2 - 0.1961\,B^2 + 0.0148\,C^2 - 0.1952\,D^2 \end{aligned} \tag{3}$$

Here A is the molar ratio of methanol to oil, B is reaction temperature, Cis reaction time, and D is catalyst load.

Equation 3 in terms of coded factors can be used to make predictions about the response for given levels of each factor. High levels of the components are coded as + 1, whereas low levels are represented as − 1. The coded equation is useful for identifying the relative impact of the factors by comparing the factor coefficients.

Final equation in terms of actual factors

$$\begin{aligned} \mathbf{Yield} = {} & 73.99052 + 15.07807\,A + 1.43085\,B - 4.60802\,C - 147.83675\,D \\ & - 0.516545\,AB + 0.855964\,AC + 10.51474\,AD + 0.01057\,BC + 1.99536\,BD \\ & - 2.22599\,CD + 0.047066\,A^2 - 0.001961\,B^2 + 0.014792\,C^2 - 4.8802\,D^2 \end{aligned} \tag{4}$$

Equation 4 in terms of actual factors can be used also to make predictions about the response for given levels of each factor. Here, the levels should be specified in the original units for each factor. This equation should not be used to determine the relative impact of each factor because the coefficients are scaled to accommodate the units of each factor and the intercept is not at the center of the design space.

From Fig. S1a as shown, the normal probability diagram shows the residuals that follow a normal distribution. The quadratic polynomial model meets the assumptions of analysis of variance (ANOVA). In other words, the error distribution is almost normal. According to the model shown in Fig. S1b, the residuals should not be structural. In particular, it should be independent of other variables, including the expected response. The plot of residuals and increasing predicted response values

test the assumption of constant variance. Fig. S1 shows a random spread that does not guarantee changes to minimize personal errors.

Factors affecting the production of biodiesel

In this study, the key operating process parameters affecting the heterogeneous-catalyzed transesterification process are methanol to oil molar ratio, reaction temperature, reaction time, and amount of catalyst. The molar ratio of alcohol (methanol) to oil is one of the key factors that have a significant impact on the yield of biodiesel. Transesterification reaction requires the involvement of excess alcohol to shift the reaction towards the product. However, too much alcohol makes it difficult to recover glycerin and is needed to accelerate the reaction to the product, so the ideal molar ratio of alcohol to oil must be determined empirically. As shown in Fig. S2a, the results show that a more favorable ratio of methanol to oil at 5:1 gives an optimum yield of 94.45% at a reaction temperature of 65 °C, a reaction time of 3 h, and a catalyst load of 1.2 g. The higher the molar ratio, the higher the transesterification rate in a short time [32]. After the reaction reaches maximum yield, the alcohol content begins to tend to decrease. This is due to the diluting effect of alcohol, which slightly affects the yield of FAME. In addition, too much methanol slows the separation of the methyl ester and glycerol phases.

The reaction temperatures are strongly influenced by the rate of transesterification reactions and the percentage yield of biodiesel. The influence of varying the temperature from 45 to 65 °C was studied. As indicated in the results in Fig. S2b, the obtained value showed that an increase in temperature usually takes place near the boiling point of the alcohol (methanol) favors an increase in percentage yield of biodiesel. At a reaction time of 3 h, 5:1 of methanol to oil molar ratio, and 1.2 g of catalyst load was found to be the maximum percentage yield of biodiesel obtained at 65 °C is 94.45%. Generally, the produced biodiesel increases with increasing temperature. However, raising the temperature above the boiling point of methanol can burn and affect the saponification response of triglycerides. However, the obtained yields are going to be decreased after 65 °C due to evaporation of the methanol, especially under supercritical conditions, which had a positive effect on the yield of transesterification.

The result shown in Fig. S2c by varying the response time from 3 to 5 h and adjusting the ratio of methanol to oil to 5: 1, catalyst load of 1.2 g, and the reaction temperature to 65 °C was determined to the utmost yields of 94.45% were obtained in 3 h. In the initial stage of the transesterification reaction, the production of methyl esters gradually increased and the rate decreased and eventually began to decrease after about 3 h. This is because the transesterification reaction between oil and alcohol forms soap due to the reversible reaction when the response time increases. The effect of catalyst concentration on the conversion of methyl ester is provided as shown in Fig. S2d. In this process, a 5:1, methyl alcohol to oil ratio, reaction temperature of 60 °C, and reaction time of 3 h were kept constant. The maximum methyl ester conversion efficiency was obtained at a 1.2 g catalyst concentration. The biodiesel conversion efficiency decreased at low catalyst concentrations, the

amount of catalyst is lacking to complete the reaction and at higher catalyst concentrations, the catalyst reacts with free fatty acids in the oil to form soap and causes a decrease in the efficiency of methyl ester. Beyond the optimized amount, adding more will reduce production and is not economically effective [32].

Interaction effects of process parameters on biodiesel yield

3D surface (Fig. S3), shows the relationships between dependent and independent process variables of the developed model. Each 3D presented the effect of two variables on the methyl ester yield, holding the third variable at a constant level. The third variable is held at zero level. However, the interaction factor also must be considered, as the individual effect plot does not give information regarding the significant interaction involved. Remarkable the interaction between the independent variables could be observed if the contour plots had an elliptical profile. In general, at a sufficient contact time of 3–5 h, reaction temperature of 45–65 °C, a molar ratio of methanol to oil of 5:1 to 7:1, and catalyst load from 0.8 to 1.2 g increase the yield of produced biodiesel from 69.1928% to 94.45%. Fig. S3 shows that the yield (in percent) rises as the concentration of the catalyst CaO. This has reached the maximum avocado peel oil methyl ester yield of 94.45% at 65 °C reaction temperature, 5:1 methanol to oil molar ratio, 3 h reaction time, and 1.2 g concentration of NaOH [33].

Optimization of the Effect of process variables

The Design Expert 13.0 is familiar with optimizing process parameters using RSM through CCD techniques and used to examine and decide optimal conditions for biodiesel production from APO in the presence of CaO catalyst. The outcomes are displayed in Fig. 5. This study was conducted to determine the optimized independent operating process parameters for producing biodiesel with methanol to oil molar ratio, catalyst loading, reaction temperature, and reaction time.

The maximum conversion of biodiesel yield from waste avocado peel was found to be 94.45% at a reaction time of 3 h, a reaction temperature of 65 °C, a

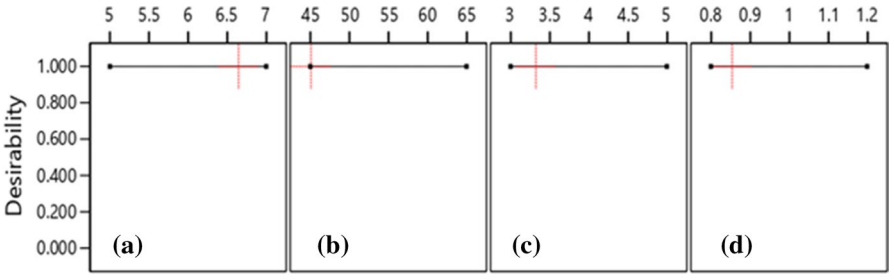

Fig. 5 Constraint's solutions; **a** desirability vs molar ratio (mL), **b** desirability vs reaction temperature (°C), **c** desirability vs reaction time (h), and **d** desirability vs catalyst load (g)

Table 6 Analysis of variance and summary fit

Source	DF	Sum of squares	Mean square	F–ratio
Model	14	930.55	66.47	62.80
Error	4	8.90	2.22	Prob > F
C. Total	28	945.37		< 0.0001
Summary of fit				
R-squared			0.9843	
R-squared adj			0.9686	
R-squared			0.9471	
Mean of response			84.21	
Model precision			35.1133	

methanol-to-oil ratio of 5:1, and a catalyst dosage of 1.2 g. To examine the predicted optimal conditions, biodiesel production was conducted in the laboratory under the optimal conditions. Experimentally, a maximum biodiesel production yield of 94.49% was attained under these ideal circumstances. This means that the experimental values obtained are very close to the predicted values calculated from the model (0.44% of error). It can be concluded that the generated model had reasonable predictability and accuracy for biodiesel yields under the experimental conditions used.

As it shown in Table 6, the adjusted R^2 of 0.9686 is reasonably close to the Predicted R^2 of 0.9471; i.e. the difference is less than 0.2. The predicted R^2 indicates that the error value used to estimate the current model value and the sum of the squares is defined by the sum of the squares and the numerical value differs between 0 and 1. The closer the number is to 1, the more valid the proposed model. The R-squared value in this study was 0.9843, demonstrating the strength and high adaptability of the proposed model for producing biodiesel using calcined chicken eggshells as a heterogeneous catalyst. The maximum biodiesel yield was 94.4666% at the maximum level of initial process independent parameters (5.1:1 of methanol to oil molar ratio, 3.08119 h of reaction time, 64.9923 °C reaction temperature, and 1.19681 g of catalyst load.

Numerical optimization of process parameters such as reaction temperature, reaction time, the molar ratio of methanol to oil, and catalyst load using response surface methodology by CCD offers 100 different solutions. Therefore, the numerical optimization considering the desirability function gives the optimum point of the independent variable that can maximize the response solution with 100% desirability and selects the optimum value for the optimum condition. Therefore, CCD chose optimal conditions at a reaction temperature of 65 °C, a reaction time of 3 h, a catalytic load of 1.2 g, and a molar ratio of 5:1 methanol to oil, resulting in a yield of 94.89% is an optimization option provided at Run 1 from Design Expert Software.

Table 7 Performance analysis of the yield of biodiesel produced used with various catalysts at different operating variables

Ref.	Yield (%) of B biodiesel conversion	Alcohol: oil ratio	Time (h)	Temperature (°C)	Amount of catalyst (wt%)	Catalyst
[13]	96	8:1	1.5	50	1	CaO
	88	6:1	3	65	3	Ba/CaO
	92.1	15:1	3	80	3	4Mn-6Zr/CaO
	96.33	9.05	1.28	57.31	0.99	KOH
	98.37	16.7:1	7.08	69.37	4.571	CaO@MgO
[18, 34]	99	0.69 w/w	200 min	70	4	MgO/K_2CO_3/HAp
[35]	96.33	9.05	1.28	57.31	0.99	KOH
[36]	97.45	2.25:1	0.223	65	8.1	KOH/Clinoptilolite
This study	94.45	5:1	3	65	1.2	CaO (*Calcined chicken eggshell*)

Performance analysis of the results with the previous studies

In this study comparing the produced biodiesel conversion yield with the previous studies or results are presented in Table 7. The CaO catalyst was used in this study to produce the biodiesel yield (94.45%); this shows a good result when compared to the other research as indicated in the table below.

Summary

This study investigated the influence of operating process parameters to achieve optimal biodiesel performance from avocado peel oil as raw material and CaO (calcined chicken eggshell) as a heterogeneous biocatalyst. Optimizing the biodiesel yield through the transesterification process by central composite design (CCD) was utilized to investigate the effect of different parameters such as methanol -to- oil molar ratio (5:1–7:1), reaction temperature (45–65 °C), reaction time (3–5 h), and catalyst (0.8–1.2 g) as independent operating variables and considering the constant stirring speed of 500 rpm. The results showed that the maximum yield of biodiesel production from waste avocado peel oils (94.45%) was achieved with a heterogeneous Cao-catalyzed at a temperature of 65 °C, oil—alcohol molar ratio of 1:5, a reaction time of 3 h, and 1.2 g catalyst load. This is the best yield of biodiesel obtained from waste non-edible avocado peel oil. The result puts forward avocado peel oil potentially used as a renewable material for

the feedstock of biodiesel production due to its non-edible vegetable oil sources. A comparison between the predicted values and the actual value with a small percentage error indicates that the regression model is reliable in predicting the conversion to all conditions within the range. The physicochemical properties of the produced biodiesel were characterized by GC–MS and fulfill the requirements in the ASTM D6751 and EN 14214 standards.

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Data availability All data generated or analyzed during this study are included in this article and its supplementary files.

Declarations

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

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