



KINETICS STUDIES AND OPTIMIZATION OF BIODIESEL PRODUCTION FROM SHEA BUTTER AND CaO/TiO_2 AS CATALYST USING RESPONSE SURFACE METHODOLOGY

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ABSTRACT :

Global demand for clean and sustainable energy triggered by the negative environmental impacts and fossil fuels resource depletion has intensified the quest for alternative renewable energy sources. Biodiesel produced via transesterification of fat/oil with alcohol in the presence of catalyst has emerged as an eco-friendly and sustainable alternative of conventional diesel fuel. Shea butter/oil extracted from Shea seed using n-hexane was used for the production of biodiesel. The physico-chemical properties revealed the extracted oil has a pH of 7.36, specific gravity of 0.85, density of 831 kg/m³, acid value of 0.33 mgKOH/g, free fatty acid 0.17 mgKOH/g, peroxide value of 0.43 mEq/kg, iodine value of 32.33 gI₂/100g, flash point of 168 °C, pour point 7 °C and cloud point 11°C. The biodiesel production parameters including reaction time, catalyst loading and ethanol/oil molar ratio were optimized using Response surface methodology with central composite design at 65 °C. The experimental results obtained revealed a 98.50 % optimum biodiesel yield by transesterifying Shea seed oil with 0.5 g of calcium oxide impregnated with titanium dioxide catalyst and ethanol: oil molar ratio of 12:1 for 1 hr. The kinetic data from the experiment were fitted for zeroth-order, first-order, and second-order kinetics. The kinetics correlation coefficient obtained in this study for the three models increase linearly with the model sophistication, from $R^2 = 0.7897$ for the zeroth order, $R^2 = 0.9335$ for the first order, and to $R^2 = 0.9943$ for the second order kinetics. Therefore, the kinetic behavior of the transesterification followed second-order kinetics.

Key words: shea butter, biodiesel, optimization, response surface methodology, central composite design, kinetic studies.

1.1 INTRODUCTION

The increasing demand for energy due to increased activities in the industrial and transportation sector, combined with limited abundance and negative environmental impacts of fossil fuels has prompted the urgent need for sustainable alternative energy sources. Additionally, global demand for clean energy coupled with the rise in environmental pollution and climate change has driven some of the most significant scientific and technological discussion of the 21st century (Haruna *et al.*, 2023; Haruna *et al.*, 2026). The combustion of fossil fuels release great amount of greenhouse gases which accumulate in the atmosphere leading to climate change and air pollution (Demirbas, 2009; IPCC, 2013; Sorrel, 2015). These have become major global issues and various methods have been suggested to curtail the undesired effects of fossil fuel emission (Moyo *et al.*, 2020; Abubakar *et al.*, 2022). In addition the fossil fuels international market price volatility, resource depletion and the geographical tension around its reserves spotlight the need to reduce dependence on these conventional energy sources. Therefore, these problems facilitated research in renewable and cleaner alternative to mitigate environmental degradation caused by greenhouse gases emissions and consequently ensures global energy security (Pimentel and Patzek, 2005).

Interestingly among numerous promising sustainable alternatives, biodiesel emerged as the cleanest alternative to conventional diesel fuel (Knothe, 2010). Biodiesel, a monoalkyl ester of long chain fatty acid, produced via transesterification of vegetable oils, animal fat, or algal biomass presents various advantages including biodegradability, reduced particulate matter emission and low toxicity, releases less smoke, low carbon dioxide and hydrocarbon emission, high cetane number, good lubrication and can be used directly with or without modification in compression ignition engine (Ramadhas *et al.*, 2004; Encinar, 2007; Kumar and Kant, 2013). These exceptional properties positioned biodiesel as more sustainable and eco-friendly alternative.

The large-scale commercial production of biodiesel relies on homogeneous catalyst system, such as Potassium hydroxide or Sodium hydroxide. However, the use of homogeneous based catalyst for transesterification is faced with numerous disadvantages, among which are high separation and purification cost, high energy consumption as well as suppression of unwanted side reaction leading to formation of soap. These challenges necessitate the need to develop novel, easily recoverable, potent and eco-friendly solid state catalyst system that can replace conventional homogeneous catalyst. Interestingly, recent advances in the field of biodiesel suggested calcium oxide as potent heterogeneous catalyst for biodiesel production due to its high basicity, abundance, low cost, non-corrosive nature, and environmental compatibility (Boey *et al.*, 2011). However, the catalytic performance of CaO is affected by its relatively low surface area. The incorporation of CaO with titanium dioxide (TiO_2) improves the catalyst surface area, active site dispersion and resistant to leaching, thus providing catalyst with excellent reusability, performance and transesterification efficiency (Chouhan & Sama, 2011; Goh *et*

al., 2019).

Shea butter (SB) generally consists of more than 90% triglycerides (Honfo et al., 2014) of which 41.1% is saturated fatty acids, which is a good property for biodiesel production, because properties of biodiesel largely depend on the methyl esters of saturated fatty acids that make for a higher cloud point, cetane number and better biodiesel stability with good quality (Enweremadu and Alamu, 2010). Another advantage of biodiesel produced from SB is that it undergoes less oxidation reaction, because it contains natural anti-oxidants such as tocopherols and some phenolic compounds (Enweremadu and Alamu, 2010). Therefore, biodiesel produced from SB can

make a good alternative fuel in compression ignition engines. However, high consumption of catalysts, formation of soaps, and low yield due to the presence of high Free Fatty Acid (FFA > 1%) and moisture content more than 0.5% are the drawbacks in using SB for biodiesel production (Cardoso et al., 2008; Refaat et al., 2008; Saifuddin et al., 2009). This is because the transesterification of high FFAs vegetable

oil using alkaline catalyst readily leads to soaps formation due to unwanted saponification reaction that take place as side reaction (Choo, 2004; Pasias et al., 2006) and causes difficulties in the purification of biodiesel (Mathiyazhagan et al., 2011; Saifuddin et al., 2009), thereby increase the overall cost of biodiesel production (Saifuddin et al., 2009). Nevertheless, it is a suitable alternative to refined vegetable oil due to its abundant availability and low cost.

In order for SB to be suitable for biodiesel production by overcoming the mentioned challenges, the FFA must first be reduced to <1%, in an esterification reaction using acid catalyst by a reversible reaction between carboxylic acids and alcohol in the presence of a strong catalyst, resulting in the formation of water and at least one ester product (Viele et al., 2013). Thereafter, the transesterification reaction of the esterified shea butter (ESB) followed in the presence of base catalyst using excess alcohol to shift the equilibrium to favour production of SBD. Therefore, appropriate Methanol (MeOH): oil mole ratio, catalyst loading, adequate agitation with moderate temperature is required to achieve high %yield of biodiesel using high FFA SB through esterification and transesterification reactions, because excess methanol, temperature and too much agitation speed leads to waste of resources, while insufficient catalyst can cause incomplete conversion of feedstock and lower the yield of biodiesel; excess catalyst can also lead to soap formation thereby hampering the yield of the biodiesel (Jahirul et al., 2014). Hence, the need for optimisation studies using RSM.

RSM is an effective and important tool for statistical analysis to find the optimal conditions for different complex processes, which has been applied in the optimisation of multiple variables with a minimum number of experiments (Ajala et al., 2015c; Stroescu et al., 2013). Meanwhile, the CCD of RSM has been applied in the optimisation of several chemical and technological processes. The benefit of the CCD of RSM is in the reduction of experimental runs that would provide sufficient data to generate enough information for a statistically acceptable result. RSM has been successfully used for the optimisation of esterification and transesterification of beauty leaf (*Calophyllum inophyllum*) (Jahirul et al., 2014) and *Jatropha caucis* (Goyal et al., 2012) for biodiesel production, but it has not been reported for SB to produce biodiesel more abundantly.

This research aim at investigating the kinetic studies and optimization of parameters for biodiesel production using Response Surface Methodology (RSM) to maximize biodiesel yield and improve process efficiency.

MATERIALS AND METHOD

Muffle furnace (XMT4000), Soxhlet extractor set-up (KDM 1000), rotary shaker (iso-9001-2008 Coslab), water bath (XMTE-200), heating mantle (78-1 PEC medical USA) and Reflux condenser, separatory funnel and analytical balance (JT2003A PRT).

Sample Collection

Fresh shea seeds were collected within Abubakar Tafawa Balewa University, Bauchi State. The seeds were identified at the Department of Biological Sciences, Abubakar Tafawa Balewa University, Bauchi. The samples were washed three times with distilled water and then dried in the shade. The outer layer of the dried seed, the epicarp, was broken open and removed. The seed was then crushed using a mortar and pestle. The resulting powder was kept in a sealed container for future use.

Catalyst Preparation

The method of Abubakar *et al.* (2022) was used with little modifications. Eggshells were collected and washed carefully in warm water and then dried in an oven at 110 degrees Celsius for 2 hours. The sample was soaked in 0.05M hydrochloric acid and stirred for 2 hours to remove the cuticle layer, which helps lower the phosphorus content. The eggshells were dried again in the oven at 110 degrees Celsius for 1 hour and then crushed into fine powder. The powdered eggshell was heated in a muffle furnace at 700 °C for 4 hours. The CaTiO₃ catalyst was synthesized by calcining CaO obtained from eggshells with TiO₂ at ratio 1:1 (20.0 grams each) and ground in a mortar for 10 to 15 minutes. The mixture was then heated first at 550 °C for 3 hours and then at 1050 °C for 3.5 hours to form CaTiO₃ as a white powder. The synthesized catalyst was kept in a clean and dry container for future use.

Oil Extraction

A 500.00 gram sample of the shea seed powder was defatted using a Soxhlet apparatus. N-hexane was used as solvent for the extraction process, which was allowed to run for 6 hours. After the extraction, the solvent was removed using a rotary evaporator. The amount of oil collected was calculated as a percentage of the total oil present in the shea seed. The extracted oil was then stored in a clean container.

TRANSESTERIFICATION PHASE

The transesterification phase for biodiesel production followed the experimental conditions produced by design expert version 11 with central composite design. Each response was recorded as biodiesel yield and the biodiesel produced was characterized using FT-IR.

RESULT AND DISCUSSION

TABLE 1: The Range of Independent and Variables for Transesterification process

Name	Units	Type	Changes	Std. Dev.	Low	High
catalyst loading	G	Factor	Easy	0	0.1	0.5
molar ratio	v/v	Factor	Easy	0	9	15
Reaction time	Hrs	Factor	Easy	0	1	3
Yield	%	Response		1.06812	93.6	98.5

Table 1 shows the range of independent variables for the transesterification process. The independent variables are catalyst loading which ranged between 0.1-0.5 g, reaction time ranged between 1-3 hours and the oil:ethanol molar ratio ranged between 1:9-1:15. Collectively these ranges were used to generate 20 sets of experiments for the transesterification process as shown in table 2 using Design Expert software version 11 with central composite design. Each response obtained from these experiments were used to build a mathematical model that connects biodiesel yield with the independent variables in the process.

TABLE 2: Design Matrix of Experiments and their Respective Experimental Yields

Run	A: Catalyst loading	B: Molar ratio	C: Reaction time	Yield
	G	v/v	Hrs	%
1	0.3	12	2	97.8
2	0.3	12	0.318207	96.4
3	0.5	15	3	95.7
4	0.3	12	2	97.6
5	0.3	12	2	97.8
6	0.3	6.95462	2	94.3
7	0.636359	12	2	97.8
8	0.0363586	12	2	94.6
9	0.5	9	1	98.5
10	0.1	9	3	96.5
11	0.3	12	2	97.8
12	0.5	9	3	97.5
13	0.3	12	2	97.6
14	0.1	9	1	97
15	0.3	12	3.68179	95.3
16	0.3	17.0454	2	93.6

17	0.5	15	1	97
18	0.1	15	3	96
19	0.1	15	1	96.3
20	0.3	12	2	97.3

Design-Expert® Software

Factor Coding: Actual

Yield (%)

● Design points above predicted value

○ Design points below predicted value

93.6  98.5

X1 = A: catalyst loading

X2 = B: molar ratio

Actual Factor

C: Reaction time = 2

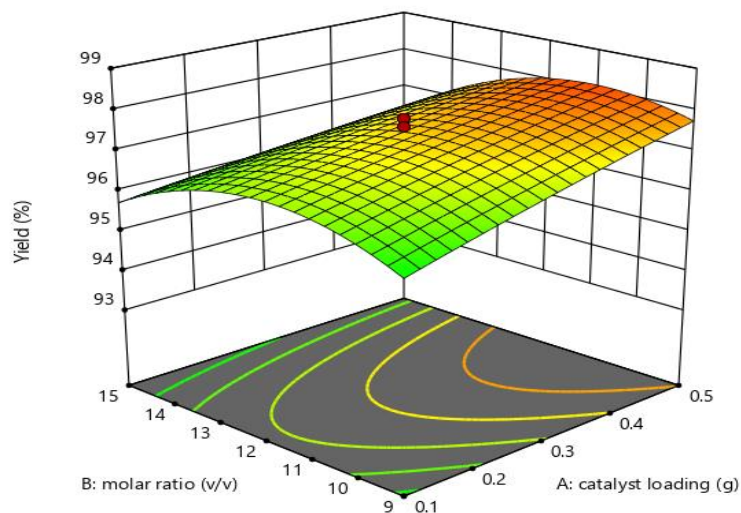


Fig. 1a: Shows the 3D plot for the effect of molar ratio and catalyst loading on biodiesel yield

Design-Expert® Software

Factor Coding: Actual

Yield (%)

● Design Points

93.6  98.5

X1 = A: catalyst loading

X2 = B: molar ratio

Actual Factor

C: Reaction time = 2

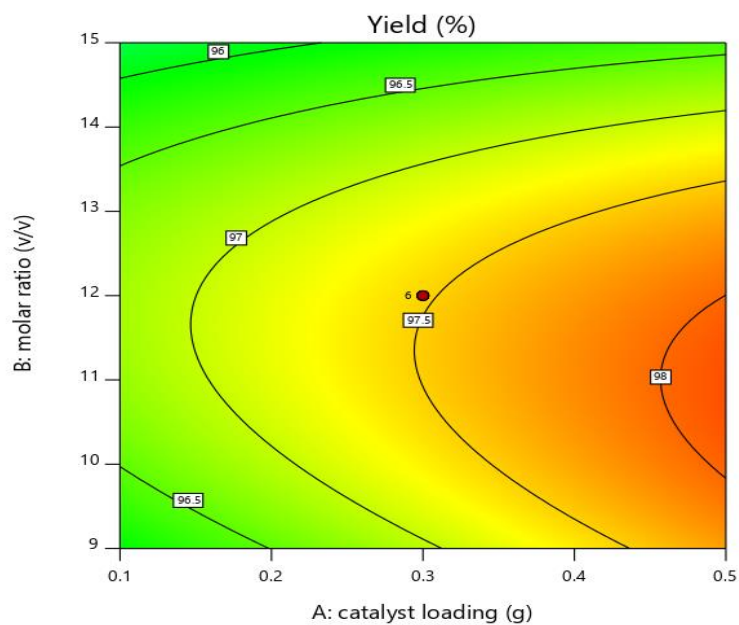


Fig 1b: Shows the contour plot for the effect of catalyst loading and molar ratio on biodiesel yield

Design-Expert® Software
Factor Coding: Actual

Yield (%)

● Design points above predicted value

○ Design points below predicted value

93.6 98.5

X1 = A: catalyst loading

X2 = C: Reaction time

Actual Factor

B: molar ratio = 12

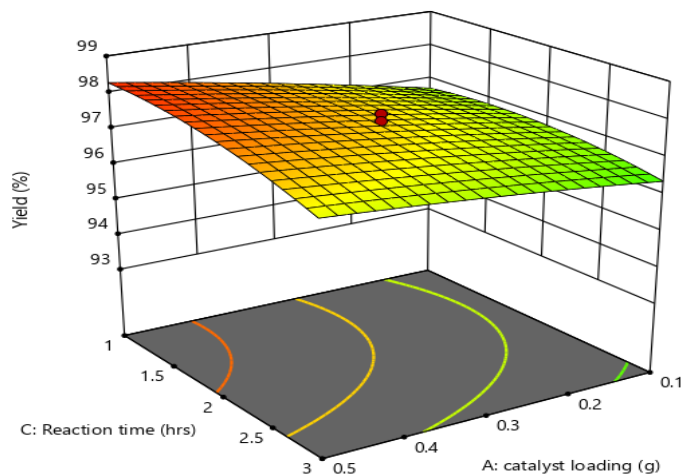


Fig. 2a: Shows the 3D plot for the effect of reaction time and catalyst loading on biodiesel yield

Design-Expert® Software
Factor Coding: Actual

Yield (%)

● Design Points

93.6 98.5

X1 = A: catalyst loading

X2 = C: Reaction time

Actual Factor

B: molar ratio = 12

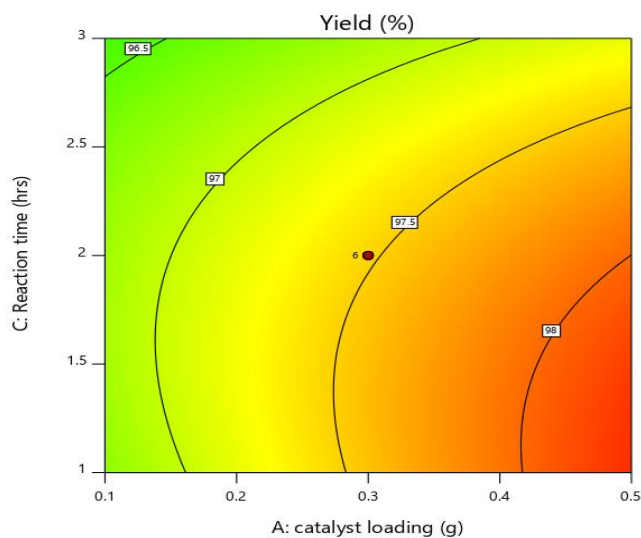


Fig 2b: shows the contour plot for the effect of catalyst loading and reaction time

Design-Expert® Software
Factor Coding: Actual

Yield (%)

● Design points above predicted value

○ Design points below predicted value

93.6 98.5

X1 = B: molar ratio

X2 = C: Reaction time

Actual Factor

A: catalyst loading = 0.3

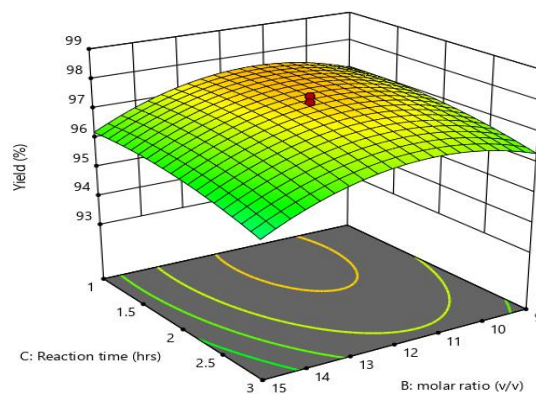


Fig. 3a: Shows the 3D plot effect of molar ratio and reaction time on the biodiesel yield

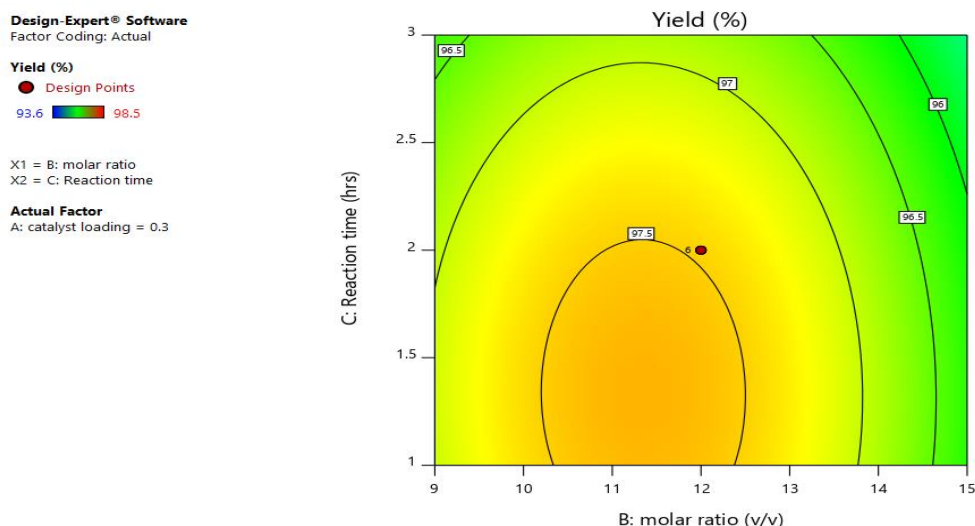


Fig 3b: Shows the Contour plot for the effect of molar ratio and reaction time on the biodiesel yield

Table 2 shows the full design matrix along with the experimental yield. From the table, the biodiesel yield ranges between 93.60-98.50%. The Response Surface Methodology (RSM) software generated several models that fit the response, and the one that matched best was chosen. The effect of each independent variable is presented as 3D plot, explaining how the variables affect the transesterification process.

Figures 1a shows a 3D plot that explain how the catalyst (A) and molar ratio (B) affect the transesterification process while temperature and time were kept the constant at 65 °C and 2 hours respectively throughout all the tests. In the 3D plot from Figure 1a, it is vividly shown that, the amount of biodiesel produced increases with an increase in amount of catalyst and decreased molar ratio. More catalyst and a lower molar ratio lead to better conversion of oil into biodiesel. When 0.50 g of catalyst and a molar ratio of 9 were used, the biodiesel yield reached 98.50%. However, when the molar ratio went up to 15, the conversion dropped to about 95.70%. This suggests that using more ethanol (which is part of the molar ratio) makes it harder to separate the biodiesel because it dissolves more glycerol into the product, which agree with report of Hamza *et al.* (2015).

Figures 2a shows the 3D for the interaction between reaction time and catalyst amount, while the molar ratio and temperature were kept constant. The plot shows that at 1 hour and 0.10 grams of catalyst, the biodiesel conversion was 96.5%. When the reaction time was increased to 3 hours, there was a slight decrease in conversion to 96%. This shows that using more catalyst helps increase the conversion, but only slightly and longer reaction time led to lower biodiesel conversion.

Figures 3a shows 3D plot that explain how reaction time and molar ratio affect biodiesel yield. This graph shows that as reaction time and molar ratio decrease, the biodiesel yield increases. When more ethanol is used, biodiesel conversion goes down, showing that ethanol has a strong effect on the process. Using excessive ethanol is harmful to biodiesel conversion, which agrees with Abubakar *et al.* (2022). Reaction time also has a negative effect on biodiesel yield because when time increases, a reversible reaction happens, causing less biodiesel production. This is seen in plot 2a, where lower reaction time lead to higher biodiesel yield. The transesterification is a reversible reaction, so with longer reaction time, some of the biodiesel turns back into esters, reducing the overall yield.

Table 3: Interaction effect of variance

Source	Sum of Squares	df	Mean Square	F-value	p-value
Model	22.86	9	2.54	2.23	0.1142 Significant
A-catalyst loading	4.18	1	4.18	3.66	0.0847
B-molar ratio	2.36	1	2.36	2.07	0.1809
C-Reaction time	1.79	1	1.79	1.57	0.2384
AB	0.5513	1	0.5513	0.4832	0.5028
AC	0.2813	1	0.2813	0.2465	0.6303
BC	0.0013	1	0.0013	0.0011	0.9742
A ²	0.0364	1	0.0364	0.0319	0.8617
B ²	12.85	1	12.85	11.27	0.0073

C ²	1.05	1	1.05	0.9225	0.3595
Residual	11.41	10	1.14		
Lack of Fit	11.21	5	2.24	57.51	0.0002 Not significant
Pure Error	0.1950	5	0.0390		
Cor Total	34.27	19			

Table 4: Physicochemical Properties of Shea Butter and its Biodiesel

PARAMETERS	SHEA BUTTER	BIODIESEL	ASTM STANDARD
Viscosity (mm ² /s)	44.70	4.26	1.9-6.0
pH	6.73	7.36	-
Specific gravity	0.91	0.85	0.90
Density (kg/m ³)	904	831	900
Acid Value (mgKOH/g)	2.16	0.33	0.00-0.90
Peroxide Value (mEq/kg)	1.86	0.43	-
Iodine Value (gI ₂ /100g)	54.07	32.33	-
Free Fatty Acid (mgKOH/g)	1.02	0.17	25.00
Flash Point (°C)	331	168	170
Pour Point (°C)	12.00	7.00	-15.00-10.00
Cloud Point	17.00	11.00	-3.00-12.00

Table 3 shows the results of physicochemical analysis of shea butter and its biodiesel. The tests looked at several properties including: density, acid value, specific gravity, iodine value, cloud point, flash point, peroxide value, saponification value, free fatty acid, pour point, and pH. Density shows how thick is the biodiesel, based on its mass compared to its volume. The biodiesel had a density of 831 kg/m³. This is within the range (575 – 900) set by ASTM D6751 and EN 14214, while the density of shea butter itself was 904 kg/m³, which is higher than density of *Jatropha curcas* oil (877 kg/m³) (Abubakar et al., 2022), while less than sun flower oil (910 kg/m³) (Kermakar et al., 2017). The specific gravity of the biodiesel was 0.85, which matches what Odisu et al. (2019) found when they made biodiesel from shea butter using acid-catalyzed transesterification, which was 0.852. The current result also fits with past results like 0.90 from Ejeh and Aderemi (2014) and with the standards from ASTM D6751 and EN 14214. The specific gravity of the oil is 0.91 which is less than Bebra seed oil (0.926) and Cashew nut oil (0.964) as reported by Aremu et al. (2006). Acid value which indicates the amount of potassium hydroxide needed in milligrams to neutralize one gram of the biodiesel and also shows the amount of free fatty acid in the sample. The shea biodiesel had an acid value of 0.33 mg KOH/g. This is within the acceptable limit of 0.5 mg KOH/g as set by ASTM D6751 and EN 14214, and also similar to 0.37 mg KOH/g reported by Datti et al. (2020). The acid value of the original shea oil was 0.47 mg KOH/g, which is less than T. mantaly seed oil (0.56 mg KOH/g) (Abubakar et al., 2020), Sun flower oil (0.5 mg KOH/g) (Hossain et al., 2007).

The iodine value of 32.32 gI₂/100g was obtained for the biodiesel, which is close to the 34.24 gI₂/100g reported by Datti et al. (2020) and much lower than the 76.14 gI₂/100g by Ejeh and Aderemi (2014). This value fits the standards set by ASTM D6751 and EN 14214. The iodine value of the oil is 54.07 gI₂/100g which is less than *Jatropha curcas* oil (86.88 gI₂/100g) (Abubakar et al., 2022) but higher than 53.99 gI₂/100g for Bitter kola (Aremu et al., 2006). The biodiesel had a cloud point of 11 °C while the oil had a cloud point of 17 °C which is within the range allowed by ASTM D6751 and EN 14214. In this study, the flash point of shea biodiesel was found to be 168 °C. Earlier studies by Ejeh and Aderemi (2014) and Datti et al. (2020) reported 110 °C and 96 °C. The values found in this research are very close to the minimum requirement of 93 °C specified by the international standards ASTM D6751 and EN 14214.

The peroxide value of the Shear butter was 1.86 mEq/kg which is lower than 12.45 mEq/kg Shear butter as reported by Bello and Mamman (2015), Shear butter (12.15 mEq/kg) (Enweremadu & Alamu, 2009), *Jatropha curcas* seed oil (6.55 mEq/kg) (Abubakar et al., 2022), *Terminalia catappa* (2.60 mEq/kg) as reported by (Abubakar et al., 2020). The peroxide value of the biodiesel is 0.43 mEq/kg which is lower than 0.84 mEq/kg as reported by Bello and Mamman (2015). The free fatty acid of the Shea butter was found to be 1.02 mg KOH/g which lower than 4.76 mg KOH/g for *Jatropha Curcas* (Abubakar et al., 2022), Shear butter (1.819 mg KOH/g) (Tulashie et al., 2018).

The pour point of the Shea butter was 12.00 °C which is higher than 6.00 °C as reported by Bello and Mamman (2015), *Citrus sinensis* seed oil (2.5 °C) (Adenkunle et al., 2019), while lower than Neem oil (25.00 °C) (Idris et al., 2018), *Jatropha curcas* (1.83 °C) (Abubakar et al., 2022). The pour point of the biodiesel was 7.00 °C which is in close agreement with 6.00 °C as published by Enweremadu & Alamu, (2009) and Bello and Mamman (2015). The cloud point of the Shea oil was 17.00 °C which is higher than 4.56 °C for *Jatropha curcas* as reported by Abubakar et al. (2022), 3.00 °C for shea butter as reported by Bello and Mamman (2015). The biodiesel cloud point was 11.00 °C which higher than 3.00 °C for shea butter biodiesel as reported by Bello and Mamman (2015), 6.00 °C for shea butter biodiesel (Enweremadu & Alamu, 2009), while less than 24.00 °C shea butter biodiesel as reported by Ejeh and Aderemi, (2014).

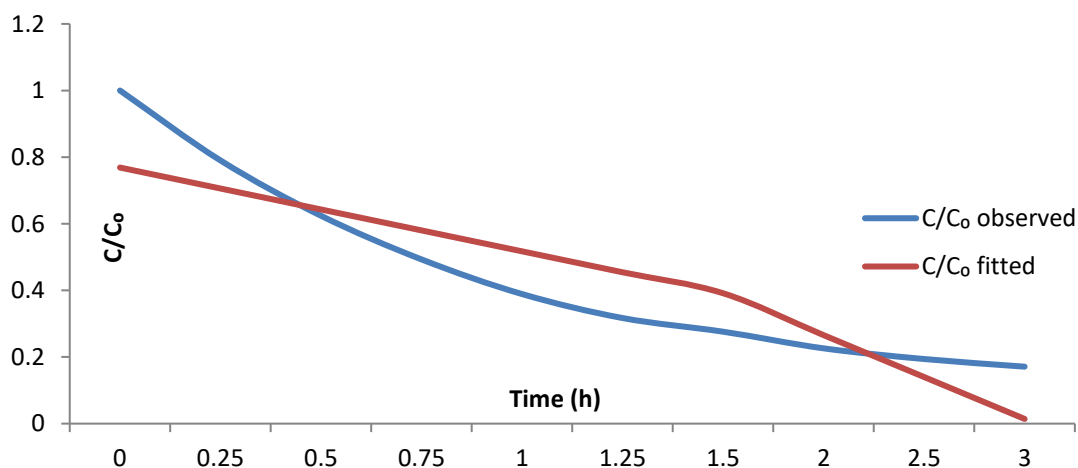
Table 5: Functional Groups Present in Shea Butter Biodiesel

Wave number (cm ⁻¹)	Type of Vibration	Functional Group
2920.40	C-H Stretching	Alkane
2849.50	C-H Stretching	Alkane
1738.80	C=O Stretching	Esters
1623.30	C=C Stretching	Alkene
1459.30	C-H Bending	Alkane
1164.80	C-O Stretching	Esters
1023.20	C-O-C Stretching	Ethers Esters
808.80	RCH=CHR	Methylene

The results from the FT-IR analysis of the biodiesel revealed the presence of C-H stretching between 2848.50 cm⁻¹ and 2920.40 cm⁻¹ shows the presence of alkanes. The C=O stretching at 1738.80 cm⁻¹ indicates the presence of esters. The C=C stretching at 1623.30 cm⁻¹ and C-H bending at 1459.30 cm⁻¹ also shows alkanes, while the peak at 1436.90 cm⁻¹ is due to the ethyl ester group. These results match with the findings of C-H stretching at 2853.21 cm⁻¹, C=O stretching at 1724.14 cm⁻¹, C-H bending at 1462.14 cm⁻¹, and the peak at 1435.32 cm⁻¹ which is as a result of ethyl ester group. The C-O bending and stretching at 1195.5 cm⁻¹, RCH=CHR bending at 993.43 cm⁻¹, and the peak at 892.218 cm⁻¹ indicate the presence of alkene, as reported by Abubakar et al. (2022). Similarly, the peak at 2923.40 cm⁻¹ shows alkyl group, the peak at 1722.68 cm⁻¹ shows a ketone, the peak at 1598.10 cm⁻¹ indicates alkenes, and the peak at 1374.83 cm⁻¹ shows methyl groups. These findings are also similar to what has been reported by Elkady et al. (2015), including peaks at 721 cm⁻¹ for CH₂ rocking, 1373.70 cm⁻¹ for bending vibrations of CH₂ groups, 1745 cm⁻¹ for C=O ester stretch, 1163 cm⁻¹ for C-O stretching, 1456 cm⁻¹ for bending vibrations of CH₂. Additional peaks include 1115.85 cm⁻¹ for -O-CH₂-C, 1117.75 cm⁻¹ for -O-CH₂-C, 1743.87 cm⁻¹ for C=O ester, 1742.07 cm⁻¹ for C=O ester, 1160.11 cm⁻¹ for C-O stretching, 1169.37 cm⁻¹ for C-O ester, 3005.44 cm⁻¹ for -CH, 2922.24 cm⁻¹ for -CH₂, 2922.41 cm⁻¹ for -CH₂, and 2853.43 cm⁻¹.

Table 6: Kinetic Model for Shear Butter Biodiesel

Model	Rate constant (k)	R ²	Qe Cal at final time (%)
Zeroth Order	0.251519078	0.789722396	98.58704
First Order	0.593979959	0.933540616	86.37729
Second Order	1.700234966	0.994330858	83.3338

**Fig 1: Zeroth order kinetic of Shea butter Biodiesel**

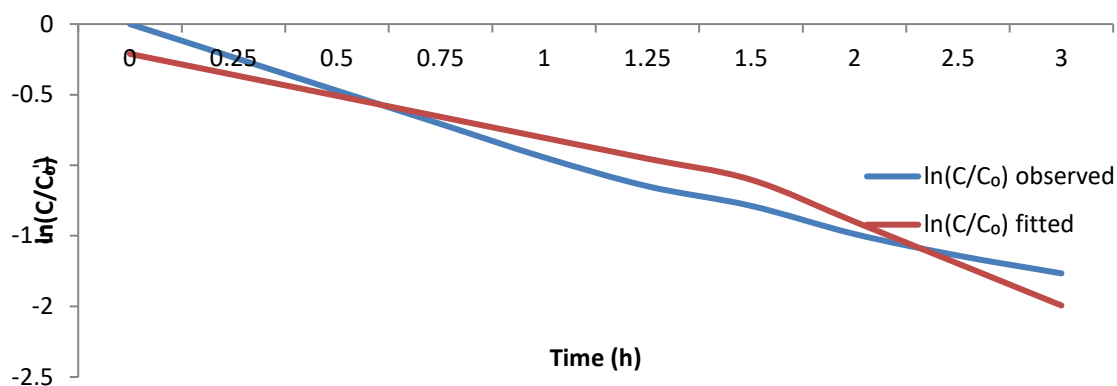


Fig 2: first order kinetics of Shea butter Biodiesel Produce

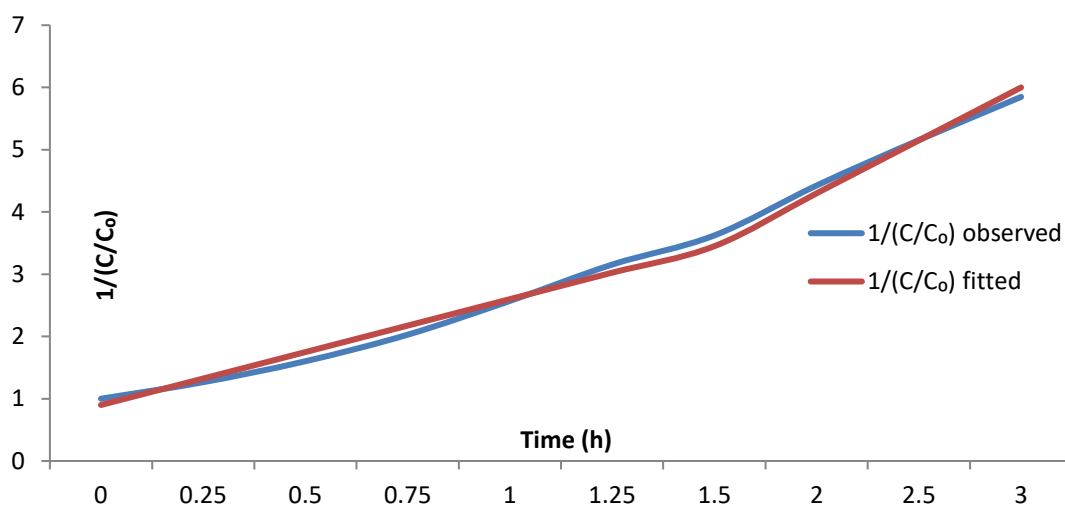


Fig 3: Second order kinetic of Shea butter Biodiesel

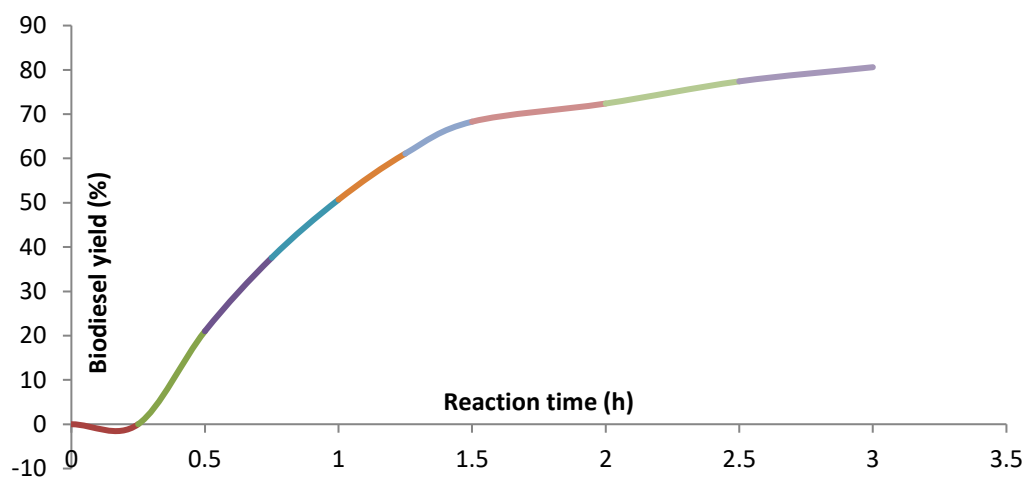


Fig 4: Biodiesel yield

The kinetics studies of biodiesel revealed relationship between the conversion of shea butter into biodiesel and the factors affecting the process. The kinetics correlation coefficient obtained in this study for the three models increase linearly with the model sophistication, from $R^2 = 0.7897$ for the zeroth order, $R^2 = 0.9335$ for the first order, and to $R^2 = 0.9943$ for the second order kinetics. Based on the value of the correlation coefficients obtained from the three models examined, the second-order model provide the highest correlation. The R^2 value of 0.9943 suggested a direct relationship between the obtained experimental data and the second-order kinetic model within reaction conditions. The result revealed that the second-order model describes the observed reaction pattern more closely than the zeroth-order and first-order models. This is consisted with numerous transesterification literature including Freedman *et al.* (1986) which reported that the forward reaction settles into a second order regime once an initial mass-transfer-controlled stage has

passed, with rate constants and activation energies extracted from that fit. A similar pattern was observed for jatropha oil, where Okullo and Temu (2015) fitted a second order rate law to methanolysis data and obtained a correlation coefficient of 0.999. Ezzati et al. (2021) reported that the kinetic behavior can change during the course of biodiesel transesterification reaction based on their developed theoretical kinetic framework. Their study demonstrated that a second-order model may explain the early stage of the reaction, while under excess alcohol condition, pseudo-first behavior occurs. This experimental observation provides scientific basis for interpreting the present second-order kinetics, while recognizing reaction conditions determine the model's applicability. The results presented in Table 1 indicated that the zeroth-order model produced a rate constant of 0.2515, the first-order model recorded a rate constant of 0.5940, and the second-order model generated a rate constant of 1.7002. The second-order model therefore provided the highest correlation with the experimental data among the three models examined.

Conclusion

In this research Shea seed oil was extracted from Shea nut dried powder using Soxhlet's extractor and n-hexane as solvent. The oil extracted and catalyst produced from calcined egg shells (CaO) impregnated with titanium dioxide were utilized as feed stock for the production of biodiesel. Response surface methodology (RSM) was employed to optimize the effect of transesterification process independent parameters namely; catalyst loading, molar ratio and reaction time biodiesel yield. Among the three parameters optimized, it was found that catalyst loading has direct relationship with the biodiesel yield whilst molar ratio and reaction time were inversely related at 65 °C. In addition, the study also revealed the optimal condition for transesterification using Shea oil and calcium oxide impregnated with titanium dioxide catalyst as, 0.5 g of catalyst and ethanol to oil molar ratio 12:1 for 1 hr at 65 °C and the optimized condition was validated with biodiesel yield of 98.50%. The result of Physicochemical properties of both Shea butter and its biodiesel revealed that the biodiesel produced satisfied standards of American society for testing materials (ASTM) and the parameters tested were viscosity, pH, density, specific gravity, acid value, peroxide value, saponification value, cloud point, pour point, flash point, Iodine value and free fatty acid value. The result of the physico-chemical analysis revealed the quality of the produced biodiesel is within the standard set by ASTM. The kinetics behavior of the process followed second-order kinetics.

Conflict of Interest

The authors declare no conflict of interest.

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