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RESEARCH ARTICLE

Catalyst Effect on Steryl Glucosides Concentration in Palm-Based Biodiesel During Transesterification Process

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ABSTRACT - In this study, biodiesel was synthesized from crude palm oil through a double-step transesterification process using a $CaO\text{-}SiO_2$ bi-catalyst. The catalyst was designed to serve dual purposes: facilitating the transesterification reaction and removing steryl glucosides (SGs), a critical impurity in biodiesel. The process optimization was carried out using Central Composite Design to achieve maximum fatty acid methyl ester conversion. The synthesized biodiesel was characterized for density (0.863 g/cm³), viscosity (5 mPa·s), iodine value (19.572 g/100g), acid value (0.437 mg KOH/g), and conversion efficiency (81.71%), confirming its compliance with biodiesel standards. Catalyst characterization through SEM, XRD, BET, and FTIR analyses revealed an amorphous structure, high surface area (86.81 m²/g), and functional groups suitable for SG removal and catalytic activity. UV-visible spectroscopy confirmed an SG removal efficiency of 79.15 %. This study demonstrates the effectiveness of the $CaO\text{-}SiO_2$ bi-catalyst in integrating biodiesel synthesis and impurity removal in a single reaction, offering a simplified and efficient approach to biodiesel production.

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1. INTRODUCTION

Biodiesel, a renewable and sustainable alternative to fossil fuels, has gained considerable attention as an environmentally friendly energy source due to its potential to reduce greenhouse gas emissions and reliance on non-renewable resources. It is primarily produced through the transesterification of vegetable oils, such as crude palm oil (CPO), where catalysts are used to convert triglycerides into fatty acid methyl esters (FAMEs), the key component of biodiesel. However, despite its promising advantages, biodiesel production faces significant challenges, particularly related to the presence of impurities like steryl glucosides (SGs). SGs, which are minor constituents of CPO, exhibit low solubility in biodiesel and can precipitate over time during storage and transportation. This leads to the formation of sediments, compromising the quality, stability, and overall performance of biodiesel in engines. Therefore, removing SGs from biodiesel is crucial to meet the stringent quality standards required for its commercialization and widespread adoption.

Recent advancements in catalytic systems have shown promise in both improving biodiesel yield and addressing the challenge of impurity removal. Among these catalysts, calcium oxide (CaO) has emerged as a widely used base catalyst due to its high catalytic efficiency, cost-effectiveness, and ability to facilitate the transesterification reaction. However, its performance can be limited by issues such as leaching and insufficient impurity adsorption capacity. To overcome these limitations, the integration of silica (SiO_2) with CaO has been proposed, creating a bi-functional catalyst system that not only enhances the catalytic efficiency but also provides the necessary surface area and adsorption properties for effective impurity removal, including SGs.

This study explores the impact of a $CaO\text{-}SiO_2$ bi-catalyst on the concentration of SGs in palm-based biodiesel during the transesterification process. The research aims to examine both the catalytic performance and the efficiency of SG removal, providing valuable insights into the role of advanced catalysts in improving biodiesel quality. The combined effects of CaO and SiO_2 not only optimize biodiesel production but also reduce the need for post-production purification steps, thus offering a more efficient and cost-effective approach to biodiesel synthesis. Previous studies, such as those by Asif et al [1] and Liu et al [2] have demonstrated the effectiveness of similar bi-catalysts in enhancing biodiesel purity and reducing impurities, supporting the significance of this research. The findings of this study are expected to contribute to the development of more effective catalytic systems for biodiesel production, ensuring higher fuel purity, better storage stability, and compliance with international fuel standards. Ultimately, this work addresses key technical challenges in biodiesel processing, contributing to global efforts to promote cleaner, more sustainable energy solutions.

The study has two main objectives. Firstly, preparing biodiesel from crude palm oil using a bi-catalyst in transesterification, and secondly, examining the catalyst's impact on steryl glucosides concentration in palm-based biodiesel. The use of a bi-catalyst aims to enhance transesterification efficiency and reduce steryl glucosides levels, contributing insights for improved quality and performance of biodiesel derived from crude palm oil.

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2. METHODS AND MATERIAL

2.1 Material

Crude palm oil was collected from a palm oil refining plant in Kuantan. Calcium oxide (CaO), methanol, and silica (SiO_2) were purchased from Sigma-Aldrich. Standard sterol glucoside was obtained from Cayman Chemical, USA.

2.2 Transesterification

Following Maniam et al [3] with minor adjustment, a three-neck flask was filled with 50 g of refined crude palm oil. Methanol was added at a ratio of 1:24 (oil to methanol) and heated while stirring. After reaching 30 °C, 1% sulfuric acid was added as a catalyst. The temperature was maintained between 60 and 65 °C for 1 hour and 45 minutes. Afterward, the mixture was let sit for 24 hours to separate into layers. The bottom layer was then collected for the transesterification process. A three-neck flask was filled with 30.0 g of crude palm oil and mixed with methanol in a 1:9 ratio. Different amounts of a catalyst (CaO/SiO_2) were added at 1%, 2%, and 3%. The mixture was heated to 65 °C, stirred at 300 rpm, and refluxed for three hours. Afterward, it was transferred to a separatory funnel and allowed to sit for 24 hours to separate into layers. The upper layer, containing the biodiesel or methyl ester, was then collected for analysis. The acid value is an important factor in determining the quality of oil and biodiesel. We measured it using the titration method according to ASTM standards. The iodine value, which shows how unsaturated the oil is, was determined using the Wijs method. We measured the density, important for quality control and storage, with a calibrated density meter for crude palm oil. Viscosity, which affects how the oil flows, was measured with a rheometer. Lower acid values indicate higher quality oil or biodiesel. Overall, the assessments of iodine value, density, and viscosity help ensure quality, blending, and processing in biodiesel production from crude palm oil.

2.3 Methyl Ester Conversion

Using a gas chromatography-mass spectrophotometer (GC-MS) (Shimadzu 2010 plus, Japan) and DB-WAX capillary column (30 m × 0.320 mm × 0.25 m, Agilent, USA), the fatty acid methyl ester (FAME) concentration in the palm oil biodiesel was analyzed. Methyl heptadecanoic acid (C17:0) served as the internal standard. FAME's composition was evaluated by contrasting it with a conventional FAME reference mixture. Equation (1), where A_{total} is the total area of the methyl area peak, ASTD is the area of the internal standard, C_{STD} is the concentration of the internal standard, V_{STD} is the volume of the internal standard, and M_{sample} is the mass of the sample (mg), was used to calculate the palm oil to biodiesel conversion rate both before and after the adsorption treatment.

$$conversion = \frac{\mathrm{A_{total}} - \mathrm{A_{STD}}}{\mathrm{A_{STD}}} \times \frac{\mathrm{C_{STD}} \times \mathrm{V_{STD}}}{\mathrm{M_{sample}}} \times 100\% \tag{1}$$

2.4 Extraction of Sterol Glucoside

Following the approach of Tremblay and Montpetit [4] with some adjustments, a 30 mL solution of fatty acid methyl esters (FAME) and n-hexane in a 1:1 volume ratio was prepared. Ten microliters of hydrochloric acid (HCl) were added to the mixture, which was then vortexed and frozen for 16 hours at -26 °C, forming waxy solids. After centrifugation at 28 °C and 6000 rpm for 45 minutes, the pellet was dissolved in a chloroform/methanol mixture (2:1, v/v) along with 1 mL of 0.9 wt % sodium chloride (NaCl). Following the removal of the aqueous phase, the organic phase was dried, and nitrogen was used to eliminate any remaining water droplets. Rinsing with n-hexane and subsequent centrifugation at 6000 rpm for 20 minutes produced a distinct pellet, which was then dried after removing the supernatant.

2.5 Experimental Design

To study sterol glucoside (SG) removal using a Central Composite Design (CCD) methodology, two independent variables, catalyst load (%) and reaction time (min), were chosen, with the response variables being methyl ester conversion (%) and SG removal (%). The experimental design included factorial points, axial points, and center points to capture the linear, interaction, and quadratic effects of the factors. Factor levels were coded as low (-1), high (+1), and center (0), with axial points extending beyond the factorial levels (±α, where α= √2 for two factors) to ensure rotatability. Table 1 shows the Factors and their level for central composite design (CCD).

Table 1: Factors and their level for central composite design (CCD)

Factor	Notation	Level				
		- α	-1	0	+1	+ α
Catalyst Loads (%)	X_1	0.59	1	2	3	3.41
Reaction time (min)	X_2	138	150	180	210	222

3. RESULTS AND DISCUSSION

3.1 Physical Properties of Biodiesel

Table 2 compares characteristics of methyl esters from crude palm oil synthesized with CaO mixed SiO_2 catalyst against ASTM D6751 and EN 14214:2003 standards. The acid value of the synthesized methyl ester is 0.437 mg KOH/g, meeting the ASTM D6751 standard (maximum 0.5 mg KOH/g). Decreased acid number indicates successful transesterification of free fatty acids, preventing corrosion. The iodine value, reflecting unsaturation, decreases from crude palm oil (56.781 g/100g) to biodiesel (19.572 g/100g) during transesterification, aligning with biodiesel quality criteria. Biodiesel density, measured at 0.863 g/cm^3 at 15 °C, falls within the recommended range. A higher density ensures lower volatility but may cause incomplete combustion [5]. The viscosity of synthesized methyl ester is 5 mPa/s, contrasting with crude palm oil (70 mPa/s), confirming successful synthesis. The viscosity aligns with biodiesel standards (3.5 - 5 mPa/s), indicating its potential as biodiesel with improved fuel characteristics.

Table 2. Physical properties of crude palm oil and palm biodiesel

Properties	Crude Palm Oil	Palm Biodiesel	ASTM Standard
Acid value (mg KOH/g)	5.318	0.437	Max 0.5
Iodine value (g/100g)	56.781	19.572	Max 120
Density (g/cm^3) at 15ºC	0.901	0.863	0.860-0.900
Viscosity (mPa/s)	70	5	3.5-5.0

Biodiesel conversion serves as a quantitative approach for assessing the Fatty Acid Methyl Ester (FAME) content. Depicted in Figure 6 is the Gas Chromatography-Mass Spectrometry (GC-MS) spectrum of palm oil biodiesel. By employing a library search for the identification and quantification of the methyl esters' percentage area in the biodiesel, the derived conversion percentage from crude palm oil is determined to be 81.71 % FAME.

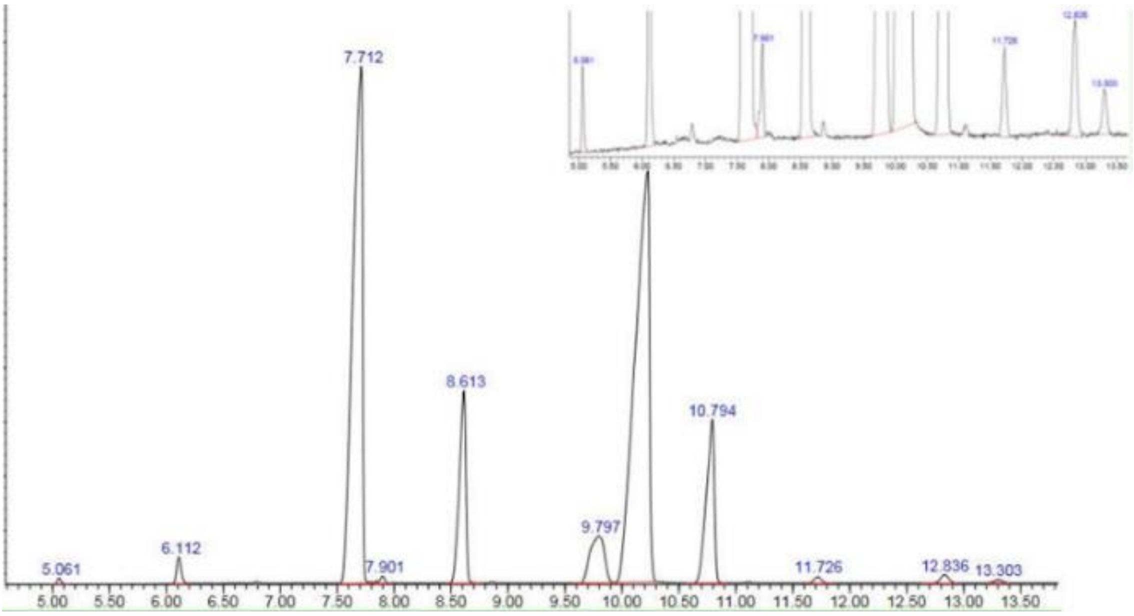

Figure 1. GCMS chromatogram for biodiesel

3.2 Fatty Acid Methyl Ester Composition

Table 3 provides insights into the fatty acid composition of palm oil biodiesel, revealing a balance between saturated and unsaturated fatty acids. Oleic acid (18:1) dominates unsaturated fatty acids at 40.58%, while palmitic acid (16:0) is the main saturated acid at 34.75%. The overall composition comprises 49.40% saturated and 50.60% unsaturated fatty acids, indicating successful transesterification using CaO mixed SiO_2 catalyst.

Saturated fatty acids, like palmitic acid, contribute to biodiesel's oxidative stability, extending its shelf life by resisting oxidation. However, higher saturation levels may lead to increased cloud points and reduced cold-flow performance in colder climates. Conversely, unsaturated fatty acids, like oleic acid, enhance biodiesel's cold-flow characteristics, making it more suitable for colder regions. Yet, high unsaturation increases the risk of oxidation, impacting stability. Achieving an optimal balance between saturated and unsaturated fatty acids is crucial for biodiesel, ensuring a harmonious mix of stability and low-temperature operability, making it versatile for various climates and conditions.

Table 3. Fatty acid composition of biodiesel from palm oil

Fatty acid	Structure	Composition (%)
Lauric	12:0	0.17
Myristic	14:0	0.88
Palmitic	16:0	34.75
Palmitoleic	16:1	0.26
Margaric	17:0	8.61
Stearic	18:0	4.73
Oleic	18:1	40.58
Linoleic	18:2	9.20
Linolenic	18:3	0.32
Eicosanoic	20:0	0.50
Total saturated fatty acid	-	49.40

3.3 Statistical Analysis

The experiments followed a statistically planned strategy, and Table 4 indicates the results of the conversion biodiesel under various conditions. Table 4 presents the fit statistics of the model. To assess the goodness of fit of the regression model, R^2 was evaluated using analysis of variance (ANOVA). The R^2 value was determined to be 0.8810, indicating that 88.10 % of the total variation fits the regression model. R^2 is defined as the extent to which a model can account for the expected response. The model in this study has been proven to fit the experimental data due to the high value of R^2 obtained. Additionally, the adjusted determination coefficient is also notably high at 0.7959. Adequate precision, which measures the signal-to noise ratio, is deemed satisfactory when exceeding a ratio of 4. With the model's ratio at 9.2279, it attests to an adequate signal. Therefore, it can be concluded that the model is well-suited for exploring the design space.

Table 4. Percentage of conversion and SGs removal of biodiesel

Treatment	Adsorption Loading (%), X_1	Reaction Time (min), X_2	Methyl Ester Conversion (%)	SGs Removal (%)
1	2 (0)	180 (0)	81.71	0.329
2	1 (-1)	210 (1)	65.33	0.651
3	3 (1)	210 (1)	65.24	0.587
4	2 (0)	180 (0)	81.71	0.329
5	3.41 (+α)	180 (0)	68.39	0.468
6	2 (0)	138 (-α)	75.84	0.240
7	2 (0)	180 (0)	81.71	0.329
8	2 (0)	180 (0)	81.71	0.329
9	2 (0)	180 (0)	81.71	0.329
10	1 (-1)	150 (-1)	70.28	0.546
11	2 (0)	222 (+α)	49.51	0.260
12	3 (1)	150 (-1)	70.33	0.307
13	0.59 (-α)	180 (0)	81.71	0.329

The conversion of methyl ester in transesterification reactions is often higher with an increased load of catalyst or adsorbent due to enhanced catalytic activity. A higher catalyst or adsorbent load provides more active sites for the reaction to occur, facilitating the conversion of triglycerides in palm oil to methyl esters. The catalyst promotes the breakdown of triglycerides into glycerol and fatty acid methyl esters more efficiently, leading to a higher overall conversion. However, it is essential to optimize the catalyst concentration to avoid potential issues such as increased costs, side reactions, or catalyst poisoning.

Insufficient or excessively prolonged transesterification times can lead to lower conversion of palm oil to biodiesel [6]. Too little time may not allow for complete reaction of triglycerides with the alcohol and catalyst, resulting in unconverted triglycerides and reduced biodiesel yield [7]. Conversely, excessively long reaction times may lead to side reactions, such as soap formation or the breakdown of biodiesel into undesired byproducts. Optimizing the reaction time is crucial for achieving a balance between complete conversion and avoiding undesirable reactions, ensuring the efficient production of biodiesel from palm oil. The accuracy of the model can be assessed by comparing the F-value, a ratio between the mean square of the regression model and the residual error. As shown in Table 5, a significant model is not indicated by the model's F-value of 10.36. The probability that an F-value this large could be the result of noise is only 0.39 %. This demonstrated that the experimental date could be accurately described by the model. Additionally, the model's p-value (p-value = 0.0039) being less than 0.05 indicates significance at the 95 % confidence level. Consequently, the regression model can be utilized to predict the correlation between independent factors, which is the adsorption loading and time reaction.

Table 1. Fit statistic of regression model

Parameter	Fit statistics
Std deviation	4.45
Mean	73.48
C.V %	6.06
R_2	0.8810
Adjusted R_2	0.7959
Predicted R_2	0.1535
Adequate precision	9.2279

Moreover, Table 6 also provide data of the significance of the parameter that was assessed using the p-value. The p-value below 0.05 was defined as signifying a highly significant impact of the corresponding coefficient on % conversion of biodiesel within a 95 % confidence interval. The findings revealed that, within a 95 % confidence interval, the quadratic terms associated with adsorption loading (X_1) and time reaction (X_2) had more pronounced effects on % conversion compared to methanol to oil molar ratio (X_3). The highest % conversion of biodiesel from the actual data is achieved under the conditions of 2 % adsorption loading and 180 minutes of time reaction as depicted in Table 4.

Table 2. ANOVA analysis for model of % conversion biodiesel

Source	DF	Sum of square	Mean square	F-value	P-value	Significant
Model	5	1028.02	205.60	10.36	0.0039	Significant
X_1	1	44.54	44.54	2.24	0.1777	Significant
X_2	1	279.38	279.38	14.08	0.0071	Significant
X_1X_2	1	0.0049	0.0049	0.0002	0.9879	Significant
X_1^2	1	90.00	90.00	4.53	0.0707	Significant
X_2^2	1	665.98	665.97	33.56	0.0007	Significant
Residual	7	138.90	19.84	-	-	-
Lack of Fit	3	138.90	46.30	-	-	-
Pure Error	4	0.00	0.00	-	-	-
Cor Total	12	1166.92	-		-	-

Based on the coded parameters, the quadratic regression model with determined coefficients were given in as follows:

$$\text{Methyl Ester} = 81.71 + -2.36\,(X_1) + -5.91\,(X_2) + -0.0350\,(X_1X_2) + -3.60\,(X_1^2) + -9.78\,(X_2^2) \quad (2)$$

The coefficient estimate represents the expected change in response per unit change in factor value when all remaining factors are held constant. According to the estimated coefficients exhibited in Equation (2), adsorption loading of SG has a positive effect on the yield. It means increase in the adsorption loading of SG accelerates the speed of the transesterification reaction.

4. CONCLUSION

In conclusion, this research presents a significant advancement in biodiesel production by effectively utilizing a CaO/SiO_2 catalyst for the transesterification of crude palm oil. The properties of the synthesized biodiesel are noteworthy: a density of 0.863 g/cm³, viscosity measuring 5 mPa/s, an iodine value of 19.572 g, and an acid value of 0.437 mg KOH/g of methyl ester, which collectively underline the quality of the resultant biodiesel. The transesterification process achieved a remarkable 81.71% conversion to fatty acid methyl esters (FAME), underscoring the efficacy of the catalyst employed. Furthermore, the reduction of steryl glucoside by 79.15% as demonstrated by UV-visible spectroscopy highlights the catalyst's ability to effectively mitigate impurities, enhancing the overall sustainability and performance of biodiesel. These findings not only contribute to the fields of renewable energy and sustainable fuels but also open avenues for further research into optimizing biodiesel production techniques through innovative catalyst development.

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CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest associated with this research. All experiments, analyses, and interpretations were conducted impartially and without any financial, personal, or professional influences that could have affected the outcomes or conclusions of the study.

AUTHORS CONTRIBUTION

All authors have significantly contributed to the completion of this research and the preparation of the manuscript.

F. K. Azmi (Conducted the laboratory experiments, collected data, and performed data analysis.)

M. N. F. Abd Malek (Conceptualization; Investigation; Supervision)

G. P. Maniam (Investigation; Resources; Funding acquisition)

REFERENCES

[1] M. Asif, F. Javed, M. Younas, M. A. Gillani, W. B. Zimmerman and F. Rehman, "Investigating biodiesel production from Chicken fat oil using bi-functional catalysts and microbubble mediated mass transfer," *Fuel*, vol. 358, p. 130125, 2024.

[2] J. Liu, T. Lin, S. Niu, J. Zhu, Z. Yang, J. Geng, et al., "Transesterification of acidic palm oil using solid waste/CaO as a bifunctional catalyst," *Fuel*, vol. 362, p. 130913, 2024.

[3] G. P. Maniam, N. Hindryawati, I. Nurfitri, R. Jose, M. H. A. Rahim, F. A. Dahalan, et al., "Decanter cake as a feedstock for biodiesel production: A first report," *Energy Conversion and Management*, vol. 76, pp. 527-532, 2013.

[4] A. Montpetit and A. Y. Tremblay, "A quantitative method of analysis for sterol glycosides in biodiesel and FAME using GC-FID," *Journal of the American Oil Chemists' Society*, vol. 93, no. 4, pp. 479-487, 2016.

[5] S. B. Lee, K. H. Han, J. D. Lee and I. K. Hong, "Optimum process and energy density analysis of canola oil biodiesel synthesis," *Journal of Industrial and Engineering Chemistry*, vol. 16, no. 6, pp. 1006-1010, 2010.

[6] S. M. Farouk, A. M. Tayeb, S. M. S. Abdel-Hamid and R. M. Osman, "Recent advances in transesterification for sustainable biodiesel production, challenges, and prospects: A comprehensive review," *Environmental Science and Pollution Research*, vol. 31, no. 9, pp. 12722-12747, 2024.

[7] R. Kasirajan, "Biodiesel production by two step processes from an energy source of Chrysophyllum albidum oil using homogeneous catalyst," *South African Journal of Chemical Engineering*, vol. 37, pp. 161-166, 2021.