Baghdad Science Journal

Volume 22 | Issue 3

Article 9

2025

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Vivi Sisca

Research Center for Chemistry, National Research and Innovation Agency, B.J. Habibie Science and Techno Park, Serpong, South Tangerang, Banten, 15314, Indonesia, vivi009@brin.go.id

Syukri

Department of Chemistry, University of Andalas, Limau Manis, Padang, West Sumatra, Indonesia, syukri.darajat@yahoo.com

Zilfa

Department of Chemistry, University of Andalas, Limau Manis, Padang, West Sumatra, Indonesia, zilfa@sci.unand.ac.id

Novesar Jamarun Department of Chemistry, University of Andalas, Limau Manis, Padang, West Sumatra, Indonesia, novesarjamarun@sci.unand.ac.id

Denny Akbar Tanjung Department of Agrotechnology, University of Medan Area, Medan, Indonesia, Dennyakbartanjung@staff.uma.ac.id Follow this and additional works at: https://bsj.researchcommons.org/home

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Sisca, Vivi; Syukri; Zilfa; Jamarun, Novesar; Tanjung, Denny Akbar; Ritonga, Ahmad Hafizullah; Annas, Dicky; Khoiriah, Khoiriah; and Hariani, Poedji Loekitowati (2025) "Catalytic Innovation for Renewable Energy: TiO₂-Supported Precipitated Calcium Carbonate Catalyst for Eco-Friendly Biodiesel Synthesis," *Baghdad Science Journal*: Vol. 22: Iss. 3, Article 9. DOI: https://doi.org/10.21123/bsj.2024.11692

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Authors

Vivi Sisca, Syukri, Zilfa, Novesar Jamarun, Denny Akbar Tanjung, Ahmad Hafizullah Ritonga, Dicky Annas, Khoiriah Khoiriah, and Poedji Loekitowati Hariani

RESEARCH ARTICLE

Catalytic Innovation for Renewable Energy: TiO₂-Supported Precipitated Calcium Carbonate Catalyst for Eco-Friendly Biodiesel Synthesis

Vivi Sisca¹, Syukri², Zilfa², Novesar Jamarun², Denny Akbar Tanjung³, Ahmad Hafizullah Ritonga⁴, Dicky Annas¹, Khoiriah Khoiriah¹, Poedji Loekitowati Hariani⁵

¹ Research Center for Chemistry, National Research and Innovation Agency, B.J. Habibie Science and Techno Park, Serpong, South Tangerang, Banten, 15314, Indonesia

³ Department of Agrotechnology, University of Medan Area, Medan, Indonesia

⁵ Department of Chemistry, Sriwijaya University, Ogan Ilir 30662, Indonesia

ABSTRACT

Biodiesel produced through transesterification reactions with homogeneous and heterogeneous base catalysts is a promising alternative energy source. This study uses Precipitated Calcium Carbonate (PCC) enriched with TiO₂ to produce biodiesel from waste vegetable oil. The synthesized catalyst was comprehensively identified through XRD, XRF, SEM, BET, and FT-IR analyses and then applied in the transesterification reaction. The results showed that PCC enriched with TiO₂ is an effective catalyst, producing biodiesel with an efficiency of 95.09% under optimal conditions: 5 wt% catalyst, a methanol to oil ratio of 6:1, a reaction temperature of $65 \,^{\circ}$ C, and a reaction time of 4 hours. Enhancing catalytic properties, increased surface area, and strengthening of basic sites significantly improved biodiesel yield.

Keywords: Biodiesel, Heterogeneous catalyst, Precipitated calcium carbonate/TiO₂, Transesterification, Waste vegetable oil

Introduction

The search for renewable and environmentally friendly energy sources has become increasingly crucial amidst the global energy crisis and climate change. Biodiesel is a promising alternative fuel as it is renewable and more environmentally friendly compared to fossil fuels.^{1,2} However, conventional biodiesel production processes still need to overcome several challenges, including using homogeneous catalysts that are difficult to separate and can contaminate the final product.^{3,4} Biodiesel can be produced

from various feedstocks such as legumes, palm oil, sunflower, and coconut.⁵ However, the cost of these feedstocks is relatively high due to competition with food production needs. Therefore, this research uses waste vegetable oil as an alternative feedstock.⁶

Catalytic innovation is required to improve the efficiency and sustainability of biodiesel production. One promising approach is the development of heterogeneous catalysts based on titanium dioxide (TiO₂) supported by precipitated calcium carbonate (PCC). This combination has the potential to leverage the superior properties of both materials. PCC, derived from

Received 31 May 2024; revised 8 September 2024; accepted 10 September 2024. Available online 18 March 2025

* Corresponding author.

https://doi.org/10.21123/bsj.2024.11692

² Department of Chemistry, University of Andalas, Limau Manis, Padang, West Sumatra, Indonesia

⁴ Institut Kesehatan Medistra Lubuk Pakam, Deli Serdang-20512, Indonesia

E-mail addresses: vivi009@brin.go.id (V. Sisca), syukri.darajat@yahoo.com (Syukri), zilfa@sci.unand.ac.id (Zilfa), novesarjamarun@sci.unand.ac.id (N. Jamarun), Dennyakbartanjung@staff.uma.ac.id (D. A. Tanjung), ahmad.hafizullah.r@gmail.com (A. H. Ritonga), dick015@brin.go.id (D. Annas), khoi013@brin.go.id (K. Khoiriah), pujilukitowati@yahoo.com (P. L. Hariani).

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the abundant limestone of Lintau Buo, is inexpensive and has high activity.^{7–9} TiO_2 offers durability, antifungal properties, environmental friendliness, and cost efficiency.^{10,11}

Overall, the novelty of the PCC/TiO₂ catalyst lies in its innovative material combination, enhanced catalytic activity, high stability, and reusability, as well as its being environmentally friendly and sustainable. This study aims to investigate the effectiveness and stability of the PCC/TiO₂ catalyst in the transesterification reaction using waste vegetable oil for biodiesel production.

Materials and methods

Materials

This research uses limestone from Lintau Buo, West Sumatra, Indonesia. The oil used in the biodiesel synthesis is waste vegetable oil obtained from local food traders in the Padang area. Chemicals such as methanol, n-hexane, and TiO₂, all procured from Merck, Indonesia, are used in a pure and uncontaminated state.

Preparation of PCC

The PCC synthesis procedure follows the method described by Erdogan and Vivi.^{7,12} First, limestone is cleaned with distilled water and dried at 105 °C. The dried limestone is finely ground and then heated in a furnace at 900 °C for 5 hours to produce CaO. Second, 20 grams of CaO are dissolved in 300 ml of 2 M nitric acid (HNO₃). The mixture is stirred at 350 rpm for 30 minutes and filtered to separate the solution. The filtrate is heated to 60 °C, adjusted to pH 12 using concentrated ammonia (NH₄OH), and then filtered again. Third, CO₂ gas bubbles through the filtrate until the pH reaches 8, producing a white residue. This residue is filtered, rinsed, and then heated for 2 hours at a temperature between 100–115 °C.

Preparation of PCC/TiO₂

Before preparing the PCC/TiO₂, the PCC is activated by calcination at 900 °C for 5 hours. The preparation of PCC/TiO₂ is carried out using the solgel technique.^{13,14} First, 21.0 g of TiO₂ powder is dissolved in 600 mL of 1.5% NaOH. Second, 7.0 g of PCC is dissolved in 10 mL of HNO₃. The two solutions are mixed by slowly adding the PCC solution to the TiO₂ sol while stirring until the mixture transforms into a gel. The gel is then dried at 110 °C, ground into a powder, and calcined at 650 °C for 6 hours.

Biodiesel production

Biodiesel was produced through a transesterification reaction using the PCC/TiO₂ catalyst. The oil used in the transesterification reaction was waste vegetable oil. The experiment was conducted in a 500 mL three-neck flask with 5 wt. % of the catalyst added. Methanol and waste vegetable oil were mixed in a 6:1 ratio at 850 rpm and 65 °C for 4 hours. After the reaction, the mixture was transferred to a separating funnel to separate the product from the glycerol. The parameters affecting catalytic activity were examined under the following conditions and variables: catalyst amount 1, 3, 5, 7 wt. %, methanol-to-oil ratio 3:1, 6:1, 9:1, 12:1, reaction temperature 55, 60, 65, and 70 °C, and reaction time 2, 4, 6, and 8 hours. Each obtained product was analyzed using GC-MS to determine the amount of methyl ester compounds. The following Eq. (1) was used to determine the production yield: ¹⁵

Biodiesel yield (%) =
$$\frac{\text{Weight of Biodiesel}}{\text{weight of Oil}} \times 100\%$$
(1)

Reusability testing

For reusability, the catalyst was washed with nhexane and methanol and dried at 110 °C for 3 hours. The same catalyst was reused in the transesterification reaction for up to four repetitions.

Characterization

Various characterization techniques were employed in the study. The crystallinity of the catalyst was assessed using X-ray Diffraction (XRD) with a Pan Analytical Expert Pro X-ray instrument equipped with Cu K α radiation. Elemental analysis was conducted using X-ray Fluorescence (XRF) with an Epsilon PANalytical Model 3. The surface morphology of the catalyst was examined using Scanning Electron Microscopy (SEM) and JEOL Scattering Energy (JSM-6290LV). Finally, Fatty Acid Alkyl Ester (FAAE) composition was determined through Gas Chromatography-Mass Spectrometry (GC-MS) analysis using a Bruker GC-45 instrument.

Results and discussion

XRD analysis

XRD analysis, Fig. 1, was performed on the PCC/TiO_2 catalyst to determine its crystallinity in

Fransmitance (a.u)

3374.87

3641.02

4000

. 3500 2853.90

3000

Fig. 1. XRD pattern of PCC/TiO₂ catalyst (a) fresh (b) after use.

fresh and used states. In the fresh catalyst, the XRD pattern indicated the cubic phase of CaO at $2\theta =$ 37.32°, 53.81°, and 64.09°. Ca(OH)₂ was detected at $2\theta = 18.01^{\circ}$ and 34.10° . The pattern also showed TiO₂ in the anatase form at $2\theta = 25.33^{\circ}$, 37.84° , 48.07° , 53.95°, and 55.11°, and the perovskite phase of $CaTiO_3$ at $2\theta = 23.03^\circ$, 32.71° , 32.78° , 32.87° , 34.76° , 47.01°, 47.06°, 58.43°, 58.63°, and 68.71°. These XRD results are consistent with the existing literature. The CaO peaks are associated with the calcination of PCC, ¹⁶ while the Ca(OH)₂ indicates hydration and air contamination.¹⁷ The overlapping diffraction peaks of TiO₂ and CaO suggest that the PCC/TiO₂ catalyst integrates both elements.¹⁸ CaTiO₃ formation is due to the interaction between PCC and TiO₂ on the catalyst surface.¹⁹ These XRD findings are consistent with SEM and TEM analyses, confirming that TiO₂ supports PCC. The successful support of PCC by TiO₂ is expected to enhance the overall effectiveness of the catalyst.

After being used in the transesterification reaction, the XRD pattern changed, showing the presence of



Wavenumber(cm-1)

2000

2500

h

660.7

500

1434.94

450.45

1000

1500

Ca(OH)₂ at $2\theta = 18.04^{\circ}$, 34.12° , 50.85° , 59.23° , and 64.67° , TiO₂ at $2\theta = 25.32^{\circ}$, 29.42° , 37.83° , 48.19° , 53.94° , and 55.14° , and CaTiO₃ at $2\theta = 23.026^{\circ}$, 32.711° , 32.777° , 32.871° , 34.762° , 47.014° , 47.055° , 58.426° , 58.630° , and 68.708° . The variation in the XRD pattern before and after use indicates an interaction between the catalyst and waste vegetable oil, affecting the catalyst's active sites and overall catalytic activity.²⁰

FTIR analysis

(Fourier-Transform Infrared) FTIR analysis was performed to identify functional groups in the PCC/TiO₂ catalyst, Fig. 2, both in its fresh state and after use. The FTIR spectrum of the fresh catalyst shows several characteristic peaks, namely at 3641.02 cm⁻¹ (hydroxyl/OH stretching in the PCC molecule), 1430.45 cm^{-1} (CaO bond), 1077.65 cm⁻¹ (CaTiO₃ bond), and 743.87 cm⁻¹ (Ti-O bond vibration).²¹ After being used in the transesterification reaction, the FTIR spectrum reveals changes with peaks at 3374.87 cm⁻¹ (OH stretching), 2853.90 cm⁻¹ and 2913.65 cm⁻¹ (CH stretching vibrations), 1738.22 cm⁻¹ (carbonate ion C=O stretching), 1551.44 cm^{-1} (C=C stretching) vibration), 1434.94 cm⁻¹ (CH stretching vibration), 961.49 cm⁻¹ and 875.68 cm⁻¹ (CO stretching), $1100.19 \,\mathrm{cm}^{-1}$ (CaTiO₃ bond), and $660.72 \,\mathrm{cm}^{-1}$ (Ti-O bond). The presence of C=O, CH, and C=C absorption bands indicates the presence of organic compounds in the catalyst, consistent with morphological analysis. These FTIR results align with the findings reported by Putra and Lani in their research.^{19,22} The results are consistent with the XRD findings, highlighting the chemical changes in the catalyst before and after the esterification reaction.



| | Conc. | | | | | | | |
|--------|-------|---------|------|-----------|---------|-------------------|--|--|
| Sample | CaO | TiO_2 | MgO | Al_2O_3 | SiO_2 | Ag ₂ O | | |
| a | 41.49 | 55.07 | 0,38 | 0,40 | 0,37 | 0,7 | | |
| b | 41.32 | 55.0 | 0,89 | 0,43 | 0,35 | 0,66 | | |
| | | | | | | | | |

Table 1. XRF analysis of PCC/TiO₂ (a) fresh and (b) after use.

XRF analysis

The chemical composition of the fresh PCC/TiO₂ catalyst after the transesterification reaction was analyzed using XRF (X-ray Fluorescence), with the results presented in Table 1. Analysis of the fresh catalyst reveals the presence of critical elements, namely CaO and TiO₂, which are the main components of the catalyst. XRF analysis of the new catalyst confirms the synthesis's success and the impregnation method's effectiveness.²³ After the transesterification reaction, although CaO and TiO₂ remain present, their quantities have decreased due to the reaction process. Nevertheless, the consistent presence of these elements in the catalyst indicates that catalytic activity is maintained. XRF also shows that the catalyst's support matrix effectively retains the catalyst components and prevents leaching during the process, contributing to the stability and effectiveness of the catalyst.²⁴ This analysis confirms the suitability and stability of the PCC/TiO2 catalyst for the intended catalytic functions.

SEM analysis

SEM (Scanning Electron Microscopy) and TEM (Transmission Electron Microscopy) analyses were performed to assess the surface morphology of the PCC/TiO₂ catalyst, as shown in Fig. 3. SEM results for the fresh catalyst reveal the presence of agglomerates with various particle shapes. TEM shows fine particles distributed within spherical particles, indicating a combination of CaO and TiO₂ in the catalyst. These findings are consistent with XRF analysis, which identifies CaO and TiO₂ as the predominant elements, confirming that PCC is effectively dispersed within the TiO₂ matrix and contributes to the catalyst's stability.²⁵ The SEM results are in line with those reported by Mardiah Mohamad.²³ After the transesterification reaction, the catalyst shows aggregation and accumulation on its active surface, likely due to fatty acids or glycerol adsorption, which hinders further reactions.²⁶ These findings underscore the importance of understanding the surface morphology of the catalyst in evaluating its performance and interactions during the catalytic process.

BET analysis

BET (Brunauer-Emmett-Teller) analysis using nitrogen adsorption at 77 K provides information on the catalyst's surface area and pore volume, which affects catalytic activity. The fresh PCC/TiO₂ catalyst exhibits a high surface area of 73.567 m²/g. The addition of TiO₂ enhances the surface area, reduces PCC particle aggregation, and stabilizes the crystal structure. However, after being used in transesterification reactions, the catalyst's surface area significantly decreased to 40.249 m²/g, likely due to the formation of an oil layer on the catalyst's surface.¹⁹ This reduction in surface area indicates significant changes in catalytic activity and the interaction of the catalyst



Fig. 3. (a) TEM image of PCC/TiO₂ and SEM images of PCC/TiO₂ (b) fresh and (c) after use.

| Table 2. | The | surface | area | of F | PCC/TiO2 | (a) | fresh | (b) | after | use |
|----------|-----|---------|------|------|----------|-----|-------|-----|-------|-----|
|----------|-----|---------|------|------|----------|-----|-------|-----|-------|-----|

| Catalyst | Surface Area (m ² /g) | Porevolume (cc/g) | Pore Size A° |
|----------|----------------------------------|---|-----------------|
| a | 73.567 | $\begin{array}{l} 1.292 \times 10\text{-}1 \\ 8.741 \times 10\text{-}2 \end{array}$ | 30.393 |
| b | 40.249 | | 24.334 |

 Table 3. Physical and chemical properties of waste vegetable oil.

| Parameters | Waste vegetable oil |
|------------------------------|------------------------|
| Kinematic Viscosity at 40 °C | 15 mm ² /s |
| Density | 0,912Kg/m ³ |
| Acid Value | 4,07 mg KOH/g |
| Saponification Value | 152,24 mg KOH/g |
| Free Fatty Acid | 1,48% |

with reactants during the transesterification process. The BET analysis is summarized in Table 2.

Physical and chemical properties of waste vegetable oil

The physical and chemical properties of waste vegetable oil in Table 3, such as viscosity, density, acid value, saponification value, water content, and free fatty acid content, are generally consistent with the literature by Favour and Salima.^{27,28}

Catalytic activity

Influence of the amount of catalyst

In Fig. 4a, biodiesel yield gradually increases with a catalyst amount of 1%–3% by weight, reaching its peak at 5% by weight. However, at 7% by weight, a significant drop in biodiesel production occurs due to increased mass transfer resistance in the multiphase system.²⁹ Higher catalyst concentrations result in a more viscous mixture, hindering the reaction rate.³⁰ These findings are consistent with previous research, highlighting the importance of optimizing catalyst amounts to enhance biodiesel production and reduce mass transfer resistance.²⁹

Effect of methanol: oil

Fig. 4b shows that biodiesel yield is lower at a methanol-to-oil ratio 3:1 but peaks at 6:1, indicating the highest production efficiency. However, biodiesel yield decreases after this optimal point due to excessive methanol use, which can disrupt the process.³⁰ An optimal methanol-to-oil ratio is crucial for the efficiency of the transesterification reaction. This study maintains a 6:1 ratio for optimal reaction, supported by Madhuvilakku R, who reported a biodiesel conversion of 92.2% under similar conditions,³¹ and

consistent with the findings of Mohamad M, who showed an optimal yield of 76.67%. 11

Effect of reaction time

The results in Fig. 4c show that biodiesel production was slow during the first 2 hours of the reaction due to inadequate mixing and dispersion of the catalyst and methanol.³² Adequate mixing is crucial for the even distribution of reactants and catalysts. The reaction increased rapidly between 2 and 4 hours due to the longer mixing time. After 4 hours, the reaction reached equilibrium, and biodiesel production decreased due to reverse reactions and saponification.³³ Previous research showed optimal yields at 4 hours with 90.93%.¹⁰ This finding is supported by Salinas D, who achieved optimal FAME content with a reaction time of 4 hours, a methanol-to-oil ratio of 6:1, and a temperature of 55 °C.³⁴ This emphasizes the importance of selecting the appropriate reaction time for efficient biodiesel production and minimizing side reactions.

Effect of reaction temperature

Transesterification is an endothermic reaction and requires higher temperatures to improve ester conversion.¹ Fig. 4d shows that biodiesel yield increases with temperature up to 65°C, but conversion decreases at higher temperatures. The increase in temperature raises kinetic energy and mass transfer, but excessively high temperatures lead to methanol evaporation and reduced polarity, which decreases the availability of methanol and the concentration of methoxide.^{16,35} Research by Boonphayak P and Wilasinee indicates that optimal biodiesel yield, reaching 93%-97%, is achieved at 65°C, with a methanol-to-oil ratio of 12:1 and a reaction time of 4 hours, highlighting the importance of selecting the appropriate reaction temperature for maximum biodiesel yield. 26,36

Reuse

Fig. 4e shows a decrease in FAME production during the initial cycles due to glycerol accumulation on the catalyst surface. However, after the fourth cycle, there is an increase in biodiesel yield, indicating catalyst stability.²⁸ This stability may be attributed to the irregularity in the Ca lattice, which helps maintain the structural integrity of the catalyst.²² The catalyst can be used up to 12 to 14 times without significant loss of activity, as Youness and Vinicius reported.^{37,38} These findings underscore the importance of catalyst stability for repeated use and the viability of the biodiesel production process.



Fig. 4. Catalytic activity of PCC/TiO₂ on biodiesel yield (a) Influence of the amount of catalyst (b) Effect of methanol: oil (c) Effect of reaction time (d) Effect of reaction temperature (e) reuse.

Table 4 presents the performance of modified heterogeneous catalysts in biodiesel synthesis. The reaction conditions are also provided, as they influence the catalyst performance. PCC/TiO₂ yielded higher

biodiesel than the others due to its innovative material composition, high catalytic activity, stability, reusability, and environmentally friendly and sustainable properties.

| | | | Reactions Conditions | | | | | |
|--------------------------------------|------------------------------|----------------------------|----------------------|--------------------|----------|-------------|----------------------|-------------|
| Catalyst | Biodiesel feedstock (oil) | Catalyst Preparation | Methanol:oil | Catalyst (wt.%) | Temp(°C) | Time (h) | Product Y or C(%) | References |
| CaO/dolomite | Mongogo nut oil | Calcination | 9:1 | 6 | 65 | 3 | 90 (Y) | 39 |
| K-CaO/Al ₂ O ₃ | Palm oil | Wet impregnation | 12:1 | 10 | 65 | 3 | 88,8 (Y) | 40 |
| CaO/MgO | Soyben oil | Wet impregnation method | 12:1 | 1,5 | 60 | 2 | 92,28 (Y) | 41 |
| CaO/ZnO | sunflower oil | wetness impregnation | 9:1 | 20 | 65 | 3 | 82 (Y) | 42 |
| PCC-TiO ₂ | waste vegetable oil | sol-gel technique | 6:1 | 5 | 65 | 4 | 95.09 (Y) | In research |

Table 4. Presents the performance of modified heterogeneous catalysts in biodiesel synthesis.



Fig. 5. GC chromatogram of biodiesel synthesized from WVO.

Table 5. FAME composition of synthesized biodiesel.

| Rt time (mins) | Area% | Fatty Acids | Methyl ester | Chemical formulae |
|----------------|---------------------------|---|------------------|--|
| 13,738 | 0.59 | Tetradecanoic acid, methyl ester | Methyl myristate | C ₁₅ H ₃₀ O ₂ |
| 15,975 | 36.58 | Hexadecanoic acid, methyl ester | Methyl Palmitate | C ₁₇ H ₃₄ O ₂ |
| 17,990 | 3.77 | Octadecanoic acid, methyl ester | Methyl Stearate | C ₁₉ H ₃₈ O ₂ |
| 19,842 | 0.20 | Octadecanoic acid, methyl ester | Methyl Stearate | C ₂₁ H ₄₂ O ₂ |
| 17,786 | 41.14% 46.88 46.88% | Total Saturated fatty acids 9-Octadecenoic acid, methyl ester Total Saturated fatty acids | Methyl oleate | C ₁₉ H ₃₆ O ₂ |

GC-MS analysis

The chemical composition of biodiesel was analyzed using GC-MS, as shown in Fig. 5 and Table 5. The biodiesel obtained from transesterification contains fatty acids with carbon atoms ranging from C15 to C19. This composition aligns with Putra MD's findings that the oil source affects the types of fatty acids in biodiesel.¹⁹ Factors such as soil type, plant maturity, weather, and genetics influence the fatty acid composition. Biodiesel composition, inherited from the vegetable oil used, generally ranges from C15 to C24 and affects the oxidation rate.³⁸ GC-MS analysis identifies methyl palmitate as a saturated fatty acid and oleic acid as an unsaturated fatty acid. Biodiesel with higher levels of saturated fatty acids exhibits more excellent resistance to oxidation and higher cetane numbers. Understanding the fatty acid composition of biodiesel is crucial for assessing its performance, stability, and oxidation resistance.

| | | Biodiesel | | | | |
|-----------------------------|-------------------|-------------|-------------------------|--------|---------------|---------------|
| | | In research | 43 | 44 | | |
| Biodiesel Properties | Unit | PCC/TiO_2 | CeO ₂ -SBA15 | CaO | SNI 7182:2015 | Test Method |
| Specific gravity at 15 °C | g/cm ³ | 890 | 872 | 880 | 850 - 890 | ASTM D 4025 |
| Viscosity at 40 °C | cSt | 6,0 | 3.58 | - | 2,3 - 6,0 | ASTM D 445 |
| Flash point | °C, min | 162 | 42.5 | 160.00 | 100 | ASTM D 93 |
| Cloud Point | °C, max | 13 | - | 1.10 | 18 | ASTM D 2500 |
| Centane number | min | 57 | 52.07 | 89.06 | 51 | ASTM D 613 |
| Water and sediment | %volume, max | 0,05 | - | - | 0,05 | ASTM D 2709 |
| Sulfur | mg/kg, max | 0,08 | - | - | 50 | ASTM D 5453 |
| Phosphor | mg/kg, max | 2 | - | | 4 | AOCS Ca 12–55 |
| Iodine number | %massa, max | 108 | 102.50 | 60.00 | 115 | AOCS Cd 1-25 |
| Sulfated ash | %massa, max | 0,01 | - | - | 0,02 | ASTM D 874 |
| Carbon residue | %massa, max | 0,3 | - | - | 0,3 | ASTM D 4530 |
| Total Acid Number | mgKOH/g, max | 0,3730 | 0.40 | 0.30 | 0,5 | ASTM D 664 |
| Glycerol Free | %massa, max | 0,0146 | - | - | 0,02 | ASTM D 6584 |
| Total Glycerol | %massa, max | 0,1314 | - | - | 0,24 | ASTM D 6584 |

Table 6. Fuel properties of biodiesel.

Physicochemical properties of biodiesel

The PCC/TiO₂ catalyst offers significant advantages in biodiesel production. It produces a fuel with optimal density, viscosity, cloud point, cetane number, water and sediment, sulfur, phosphorus, iodine number, sulfate ash, carbon residue, total acid number, free glycerol, and total glycerol following SNI 7182:2015. Compared to other catalysts, as shown in Table 6, PCC/TiO₂ demonstrates higher efficiency and better biodiesel quality. Thus, this catalyst becomes attractive for environmentally friendly and sustainable biodiesel production industrial applications.

Conclusion

This study shows that the catalyst developed from precipitated calcium carbonate and titanium dioxide is an effective and sustainable solution for biodiesel production. The research highlights several key advantages of this catalyst, including high catalytic efficiency, good stability, and potential for reuse. The biodiesel produced, with a conversion rate of 95.09%, meets the quality standards of SNI 7182:2015, making it suitable for industrial applications. Using waste vegetable oil as a feedstock shows potential for reducing production costs and environmental impact. Overall, the PCC/TiO₂ catalyst offers an innovative solution to the challenges of conventional biodiesel production by enhancing efficiency, quality, and sustainability in the biodiesel production process.

Authors' declaration

- Conflicts of Interest: None.
- We hereby confirm that all the Figures and Tables in the manuscript are ours. Furthermore, any

Figures and images, that are not ours, have been included with the necessary permission for republication, which is attached to the manuscript.

- No animal studies are present in the manuscript.
- No human studies are present in the manuscript.
- No potentially identified images or data are present in the manuscript.
- Ethical Clearance: The project was approved by the local ethical committee at National Research and Innovation Agency (BRIN), Indonesia.

Authors' contribution statement

V.S: data curation; formal analysis; investigation; methodology; writing - original draft; writing - review & editing, S: supervision; validation; visualization, Z: supervision; validation; visualization, N.J: supervision; conceptualization; validation; visualization; review and editing, D.A.T: writing - review & editing, A.H.R: writing - review & editing, D.A: validation; visualization, KK: validation; visualization, P.L.H: review and editing.

References

- Haryono H, Safri I, Isy F. Synthesis and characterization of calcium oxide impregnated on silica from duck egg shells and rice husks as heterogeneous catalysts for biodiesel synthesis. Baghdad Sci J. 2023;20:1976–1984. https://doi.org/10. 21123/bsj.2023.7895.
- Vishnulal KS, Venkatasailanathan R, Srinivas S. Biodiesel synthesis using spent FCC catalyst and CaO from a mixture of sunflower oil and oleic acid. Bioresour Technol Rep. 2024;25:1–10. https://doi.org/10.1016/j.biteb.2023.101714.
- Widayat, Hantoro S, Prambudi WS, Dimas S, Luqman B, Hadiyanto H, *et al.* Preparation CaO/MgO/Fe₃O₄ magnetite catalyst and catalytic test for biodiesel production. Result Eng. 2024;22:1–7. https://doi.org/10.1016/j.rineng. 2024.102202.

- Shaige X, Junyu T, Yihua Z, Yanhui M, Chao C, Yongjie H, *et al.* Application of waste derived magnetic acid-base bifunctional CoFe/biochar/CaO as an efficient catalyst for biodiesel production from waste cooking oil. Chemosphere. 2024; 350:1–10. https://doi.org/10.1016/j.chemosphere.2023. 141104.
- Rabiah A, Ruba N, Azeem I, Hifza R, Dilawar H, Rehana K. An insight into the catalytic properties and process optimization of Fe, Ni doped eggshell derived CaO for a green biodiesel synthesis from waste chicken fat. Catal Commun. 2024;187:1– 8. https://doi.org/10.1016/j.catcom.2024.106848.
- Fekadu A, Zebene K, Sundramurthy VP, Belachew ZT, Venkatramanan V, Manivasagan R, *et al.* Biodiesel production from Argemone mexicana oil using chicken eggshell derived CaO catalyst. Fuel. 2023;332:1–15. https://doi.org/10.1016/ j.fuel.2022.126166.
- Natalia C, Donata KL. Utilization of gaseous carbon dioxide and industrial Ca-Rich waste for calcium carbonate precipitation: A review. Energies. 2020;13:1–25. https://doi.org/10. 3390/en13236239.
- Sri W, Rendy MI, Darjito D, Davina K, Shafira QA. Surface modification of precipitated calcium carbonate(PCC)-derived from Indonesia's limestone using sodium tripolyphosphate and sodium stearic. Biointerface Res Appl Chem. 2024;14:1– 12. https://doi.org/10.33263/BRIAC144.087.
- Niladri SS, Anweshan, Piyal M, Utpal B, Mihir KP. Synthesis of precipitated calcium carbonate from LD-slag using CO₂. Mater Today Commun. 2023;36:1–19. https://doi.org/ 10.1016/j.mtcomm.2023.106588.
- 10. De A, Boxi SS. Application of Cu impregnated TiO_2 as a heterogeneous nanocatalyst for the production of biodiesel from palm oil. Fuel. 2020;265:1–6. https://doi.org/10.1016/j.fuel. 2020.117019.
- Mohamad M, Ngadi N. Effect of TiO₂ mixed CaO catalyst in palm oil transesterification. Appl Mech Mater. 2014;695:319– 322. https://doi.org/10.4028/www.scientific.net/amm.695. 319.
- Sisca V, Tanjung DA, Jamarun N. Catalytic activity of precipitated calcium. Rasayan J Chem. 2021;14:1587–1593. http://doi.org/10.31788/RJC.2021.1436167.
- Abdelmoniem HAG, Hosam HA, Amina AM, Mohamed SE. Enhanced low-temperature production of biodiesel from waste cooking oil: Aluminum industrial waste as a precursor of efficient CaO/Al₂O₃ nano-catalyst. Fuel. 2023;351:1–18. https://doi.org/10.1016/j.fuel.2023.128897.
- Pandiangan KD, Satria H, Sembiring Z, Simanjuntak W, Alista DI, Bramanthio N, *et al.* High-Performance CaO/SiO₂ composite prepared from limestone and pumice silica as catalyst for rubber seed oil transesterification. Rasayan J Chem. 2024;17:14–20. http://doi.org/10.31788/RJC.2024. 1718684.
- Siregar AGA, Manurung R, Taslim T. Synthesis and characterization of sodium silicate produced from corncobs as a heterogeneous catalyst in biodiesel production. Indones J Chem. 2021;21:88–96. https://doi.org/10.22146/ijc.53057.
- 16. Farooq M, Ramli A, Naeem A, Mahmood T, Ahmad S, Humayun M, *et al.* Biodiesel production from date seed oil (Phoenix dactylifera L.) via egg shell derived heterogeneous catalyst. Chem Eng Res Des. 2018;132:644–651. https://doi. org/10.1016/j.cherd.2018.02.002.
- Konwar LJ, Boro J, Deka D. Activated carbon supported CaO from waste shells as a catalyst for biodiesel production energy sources part A: Recovery, utilization, and environmental effects. 2018;40:601–607. https://doi.org/10.1080/15567036. 2012.733483.

- Aghilinategh M, Barati M, Hamadanian M. Supercritical methanol for one put biodiesel production from chlorella vulgaris microalgae in the presence of CaO/TiO₂ nanophotocatalyst and subcritical water. Biomass Bioenerg. 2019;123:34–40. https://doi.org/10.1016/j.biombioe.2019. 02.011.
- Putra MD, Ristianingsih Y, Jelita R, Irawan C, Nata IF. Potential waste from palm empty fruit bunches and eggshells as a heterogeneous catalyst for biodiesel production. RSC Adv. 2017;7:55547–55554. https://doi.org/10.1039/c7ra11031f.
- Liu G, Yang J, Xu X. Synthesis of hydrotalcite-type mixed oxide catalysts from waste steel slag for transesterification of glycerol and dimethyl carbonate. Sci Rep. 2020;10:1–14. https://doi.org/10.1038/s41598-020-67357-z.
- Yatish K V, Lalithamba HS, Suresh R, Latha HKE. Ochrocarpus longifolius assisted green synthesis of CaTiO₃ nanoparticle for biodiesel production and its kinetic study. Renew Energy. 2020;147:310–321. https://doi.org/10.1016/j.renene. 2019.08.139.
- Lani NS, Ngadi N, Ibrahim MI. S New route for the synthesis of silica-supported calcium oxide catalyst in biodiesel production. Renew Energy. 2020;156:1266–1277. https://doi.org/ 10.1016/j.renene.2019.10.132.
- Mohamad M, Ngadi N, Wong S, Yahya NY, Inuwa IM, Lani NS. Synthesis and characterization of CaO-TiO₂ for transesterification of vegetable palm oil. Int J Eng Trans B Appl. 2018;31:1326–1333. https://doi.org/10.5829/ije. 2018.31.08b.22.
- 24. Rahman WU, Fatima A, Anwer AH, Athar M, Khan MZ, Khan NA, *et al.* Biodiesel synthesis from eucalyptus oil by utilizing waste egg shell derived calcium based metal oxide catalyst. Process Saf Environ Prot. 2019;3:13–19. https://doi.org/10. 1016/j.psep.2018.12.015.
- Bishwajit C, Chhangte V, Avinash PI, Rahul B, Samuel LR. Widely used catalysts in biodiesel production: A review. RSC Adv. 2020;10:41625-41679. https://doi.org/10.1039/ D0RA07931F.
- 26. Wilasinee K, Jirapa M, Khemmanich K, Sasikarn N, Kewalee N, Sudarat I, *et al.* Preparation of CaO@CeO solid base catalysts used for biodiesel production. Catalysts. 2024;14:1–15. https: //doi.org/10.3390/catal14040240.
- 27. Favour OI, Charles OO, Innocent UO, Chinemerem JC, Chidimma MN, Adebola OO, *et al.* Biodiesel synthesis from waste vegetableoil utilizing eggshell ash as an innovativeheterogeneous catalyst. Arch Adv Eng Sci. 2023;0:1–18. https: //doi.org/10.47852/bonviewAAES32021761.
- Salima KE, Mijan NA, Abdulkareem AG, Omar K, Yusop MR, Hadj M, *et al.* Optimization of the activity of Mo₇-Zn₃/CaO catalyst in the transesterification of waste cooking oil into sustainable biodiesel via response surface methodology. Energy Convers Manag. 2024;303:1–16. https://doi.org/10.1016/j. enconman.2024.118185.
- 29. Moradi G, Mohadesi M, Hojabri Z. Biodiesel production by CaO/SiO₂ catalyst synthesized by the sol–gel process. React Kinet Mech Catal. 2014;113:169–186. https://doi.org/10. 1007/s11144-014-0728-9.
- Bhatia SK, Gurav R, Choi TR, Kim HJ, Yang SY, Song HS, et al. Conversion of waste cooking oil into biodiesel using heterogenous catalyst derived from cork biochar. Bioresour Technol. 2020;302:1–6. https://doi.org/10.1016/j.biortech. 2020.122872.
- Madhuvilakku R, Piraman S. Biodiesel synthesis by TiO₂-ZnO mixed oxide nanocatalyst catalyzed palm oil transesterification process. Bioresour Technol. 2013;150:55–59. https://doi. org/10.1016/j.biortech.2013.09.087.

- Ibrahim MM, Amr ASA, Mahmoud OAE, Xuemin C, Abdelghaffar SD. Eco-friendly self-terminated process for preparation of CaO catalyst based on chitosan production wastes for biodiesel production. J Mater Res Technol. 2024;30:1217– 1227. https://doi.org/10.1016/j.jmrt.2024.03.091.
- 33. Victor SA. Modiied of CaO-Nanoparticle synthesized from waste oyster shells with tin tailings as a renewable catalyst for biodiesel production from waste cooking oil as a feedstock. Chem Afr. 2023;6:1025–1035 https://doi.org/10. 1007/s42250-022-00541-y.
- 34. Salinas D, Araya P, Guerrero S. Study of potassium-supported TiO₂ catalysts for the production of biodiesel. Appl Catal B Environ. 2012;117–118:260–267. https://doi.org/10.1016/j. apcatb.2012.01.016.
- 35. Nabilah AZ, Shangeetha G, Tuan SH, Wen DO, Hazwan H. A review on the utilization of calcium oxide as a base catalyst in biodiesel production. J Environ Chem Eng. 2021;9:1–23. https://doi.org/10.1016/j.jece.2021.105741.
- Boonphayak P, Khansumled S, Yatongchai C. Synthesis of CaO-SiO₂ catalyst from lime mud and kaolin residue for biodiesel production. Mater Lett. 2021;283;1–4. https://doi. org/10.1016/j.matlet.2020.128759.
- 37. Youness B, Said S, Hanane AO, Othmane A, Houda M, Mohamed Z, *et al.* Design and development of a highly efcient reusable zeolite impregnated ZnAl₂O₄ catalyst for biodiesel production. Environ Sci Pollut Res Int. 2023;30:86773– 86789. https://doi.org/10.1007/s11356-023-28551-4.
- Vinícius MM, Gabriela FF, Leonardo VF. Sustainable catalysts for biodiesel production: The potential of CaO supported on sugarcane bagasse biochar. Renew Sustain Energy Rev. 2024; 189:1–12. https://doi.org/10.1016/j.rser.2023.114042.

- 39. Mmusi K. C, Odisitse S, Nareetsile F. Comparison of CaO-NPs and chicken eggshell-derived CaO in the production of biodiesel from schinziophyton rautanenii (Mongongo) nut oil. J Chem. 2021;3:1–15. https://doi.org/10.1155/2021/6663722.
- 40. Narita C, Nattawadee M, Kanokwan N, Worapon K, Doonyapong W, Weerinda M, *et al.* Metal loading on CaO/Al₂O₃ pellet catalyst as a booster for transesterification in biodiesel production. Renew Energy. 2023; 218:1–12. https://doi.org/10.1016/j.renene.2023.119336.
- 41. Mingyue H, Jianglong P, Eika WQ, Hui W. Biodiesel production using MgO–CaO catalysts via transesterifcation of soybean oil: Efect of MgO addition and insights of catalyst deactivation. Bioenergy Res. 2023;16:2398–2410. https://doi.org/10.1007/s12155-023-10580-z.
- 42. Oguzhan İ. Study on kinetics and reaction parameters of biodiesel production from sunflower oil and methanol using zinc oxide supported calcium oxide. Period Polytech Chem Eng. 2022;66:261–268. https://doi.org/10.3311/PPch.19198.
- Ngomade SBL, Fotsop CG, Nguena KLT, Tchummegne IK, Ngueteu MLT, Tamo AK, *et al.* Catalytic performances of CeO₂-SBA-15 as nanostructured material for biodiesel production from Podocarpus falcatus oil. Chem Eng Res Des. 2023;194:789–800. https://doi.org/10.1016/j.cherd.2023. 05.010.
- Kedir W. M, Wondimu K. T, Weldegrum G. S. Optimization and characterization of biodiesel from waste cooking oil using modified CaO catalyst derived from snail shell. Heliyon. 2023;9:1–13. https://doi.org/10.1016/j.heliyon. 2023.e16475.

الابتكار التحفيزي للطاقة المتجددة: محفز كربونات الكالسيوم المترسب المدعوم بـ TiO2 لتخليق وقود الديزل الحيوي الصديق للبيئة

فيفي سيسكا ¹، سيوكري ²، زيلفا ²، نوفيسار جامارون ²، ديني أكبر تانجونج ³، أحمد هزيز الله ريتونجا ⁴، ديكي أناس ¹، خويرية خويرية ¹، بودجي لوكيتواتي هارياني ⁵

¹ مركز أبحاث الكيمياء، الوكالة الوطنية للبحث والابتكار، بي جي حبيبي للعلوم والتقنية، سيربونج، جنوب تانجير انج، بانتن، 15314، إندونيسيا.

² قسم الكيمياء، جامعة أندلاس، ليماو مانيس، بادانج، غرب سومطرة، إنّدونيسيا.

³ قسم التكنولوجيا الزراعية، جامعة منطقة ميدان، ميدان، إندونيسيا.

⁴ معهد كيسهاتان ميدستر الوبوك باكام، ديلي سير دانغ-20512، إندونيسيا.

⁵ قسم الكيمياء، جامعة سريويجايا، أوغان إلّير 30662، إندونيسيا.

الخلاصة

إن الوقود الحيوي المنتج من خلال تفاعلات الاسترة مع محفزات قاعدية متجانسة و غير متجانسة هو مصدر طاقة بديل واعد. تستخدم هذه الدراسة كربونات الكالسيوم المترسبة (PCC) المخصبة بثاني أكسيد التيتانيوم لإنتاج الوقود الحيوي من زيت نباتي مستعمل. تم التعرف على المحفز المصنّع بشكل شامل من خلال تحليلات XRD و XRF و SEM و BET و FT-IR متم تطبيقه في تفاعل الاسترة. أظهرت النتائج أن PCC المخصب بثاني أكسيد التيتانيوم هو محفز فعال، ينتج الوقود الحيوي بكفاءة 60.00% في ظل الطروف المتلى بالوزن، ونسبة الميثانول إلى الزيت 6: 1، ودرجة حرارة التفاعل 65 درجة مئوية، ووقت التفاعل 4 ساعات. أدى تحسين الخصائص الحفزية، وزيادة مساحة السطح، وتعزيز المواقع الأساسية إلى تحسين إنتاج الوقود الحيوي بشكل كبير.

ا**لكلمات المفتاحية:** وقود الديزل الحيوي، محفز غير متجانس، كربونات الكالسيوم المترسبة/ثاني أكسيد التيتانيوم، إعادة الاسترة، زيت نباتي مستهلك.