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Catalytic Innovation for Renewable Energy: TiO_2-Supported Precipitated Calcium Carbonate Catalyst for Eco-Friendly Biodiesel Synthesis

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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 TiO_2 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 TiO_2 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°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/TiO_2, 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 (TiO_2) supported by precipitated calcium carbonate (PCC). This combination has the potential to leverage the superior properties of both materials. PCC, derived from 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/TiO_2 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/TiO_2 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 TiO_2, 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 2M nitric acid (HNO_3). 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 (NH_4OH), and then filtered again. Third, CO_2 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/TiO_2

Before preparing the PCC/TiO_2, the PCC is activated by calcination at 900°C for 5 hours. The preparation of PCC/TiO_2 is carried out using the sol-gel technique[13, 14]. First, 21.0 g of TiO_2 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 TiO_2 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/TiO_2 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]:

$$\text{Biodiesel yield (\%)} = \frac{\textbf{Weight of Biodiesel}}{\textbf{weight of Oil}} \text{x } 100\% \;\ldots.1$$

Reusability Testing

For reusability, the catalyst was washed with n-hexane 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

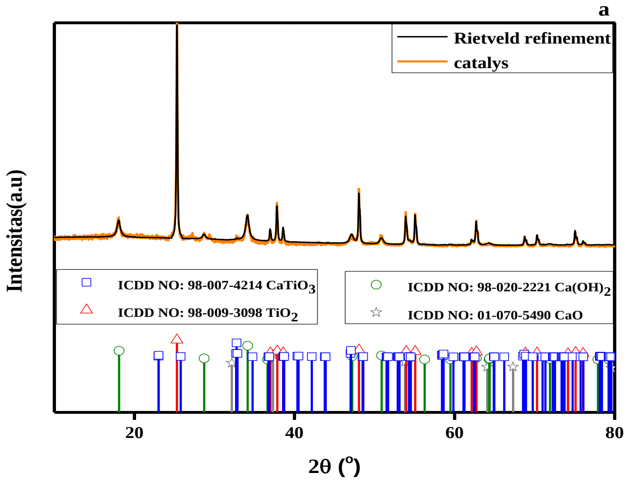
Various characterization techniques were employed in the study. The crystallinity of the catalyst was assessed using X-ray Diffraction (XRD) with a Pan Analytical Expert Pro X-ray instrument equipped with Cu Kα radiation. Elemental analysis was conducted using X-ray Fluorescence (XRF) with an Epsilon 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 fresh and used states. In the fresh catalyst, the XRD pattern indicated the cubic phase of CaO at 2θ = 37.32°, 53.81°, and 64.09°. $Ca(OH)_2$ was detected at 2θ = 18.01° and 34.10°. The pattern also showed TiO_2 in the anatase form at 2θ = 25.33°, 37.84°, 48.07°, 53.95°, and 55.11°, and the perovskite phase of $CaTiO_3$ at 2θ = 23.03°, 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 TiO_2 and CaO suggest that the PCC/TiO_2 catalyst integrates both elements[18]. $CaTiO_3$ formation is due to the interaction between PCC and TiO_2 on the catalyst surface[19]. These XRD findings are consistent with SEM and TEM analyses, confirming that TiO_2 supports PCC. The successful support of PCC by TiO_2 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 $Ca(OH)_2$ at 2θ = 18.04°, 34.12°, 50.85°, 59.23°, and 64.67°, TiO_2 at 2θ = 25.32°, 29.42°, 37.83°, 48.19°, 53.94°, and 55.14°, and $CaTiO_3$ at 2θ = 23.026°, 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].



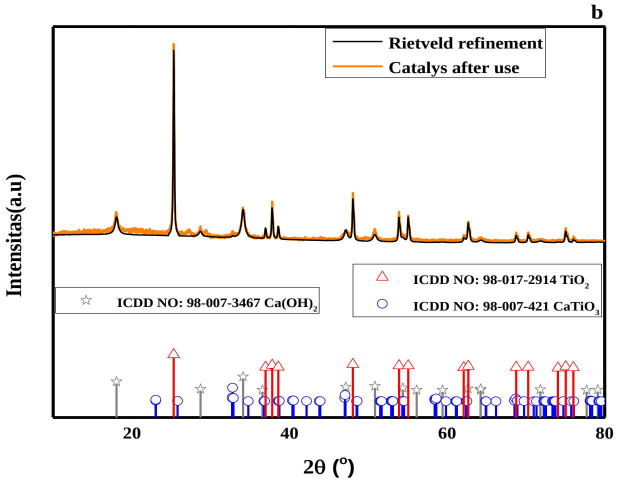


Figure 1. XRD pattern of PCC/TiO_2 catalyst (a) fresh (b) after use

FTIR Analysis

FTIR (Fourier-Transform Infrared) analysis was performed to identify functional groups in the PCC/TiO_2 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} ($CaTiO_3$ 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 cm^{-1} ($CaTiO_3$ bond), and 660.72 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.

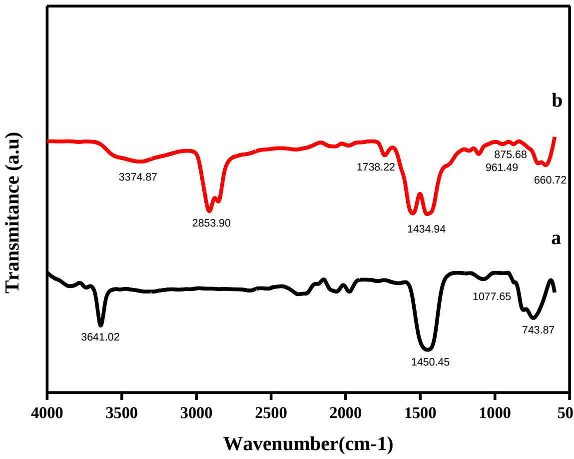


Figure 2. FTIR spectra of PCC/TiO_2 catalyst (a) fresh (b) after use

XRF analysis

The chemical composition of the fresh PCC/TiO_2 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 TiO_2, 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 TiO_2 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/TiO_2 catalyst for the intended catalytic functions.

Table 1. XRF analysis of PCC/TiO_2(a) fresh and (b) after use

Sample	Conc.					
	CaO	TiO_2	MgO	Al_2O_3	SiO_2	Ag_2O
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

SEM Analysis

SEM (Scanning Electron Microscopy) and TEM (Transmission Electron Microscopy) analyses were performed to assess the surface morphology of the PCC/TiO_2 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 TiO_2 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 TiO_2 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.

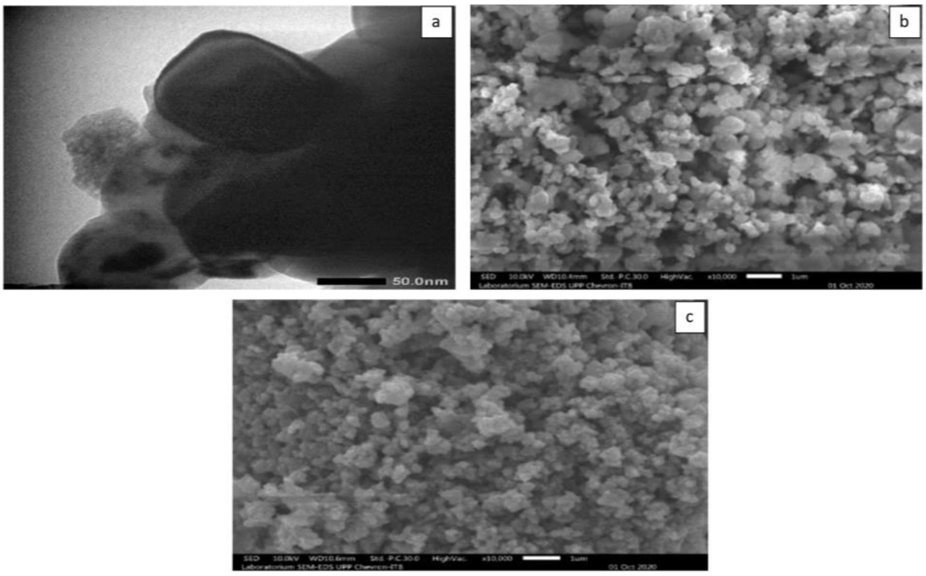


Figure 3. (a) TEM image of PCC/TiO_2 and SEM images of PCC/TiO_2(b) fresh and (c) after use

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/TiO_2 catalyst exhibits a high surface area of 73.567 m²/g. The addition of TiO_2 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 with reactants during the transesterification process. The BET analysis is summarized in Table 2.

Table 2. The surface area of PCC/TiO_2 (a) fresh (b) after use

catalyst	Surface Area (m^2/g)	Porevolume (cc/g)	Pore Size A◦
a	73.567	1.292 x 10-1	30.393
b	40.249	8.741 x 10-2	24.334

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].

Table 3. Physical and chemical properties of waste vegetable oil

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

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

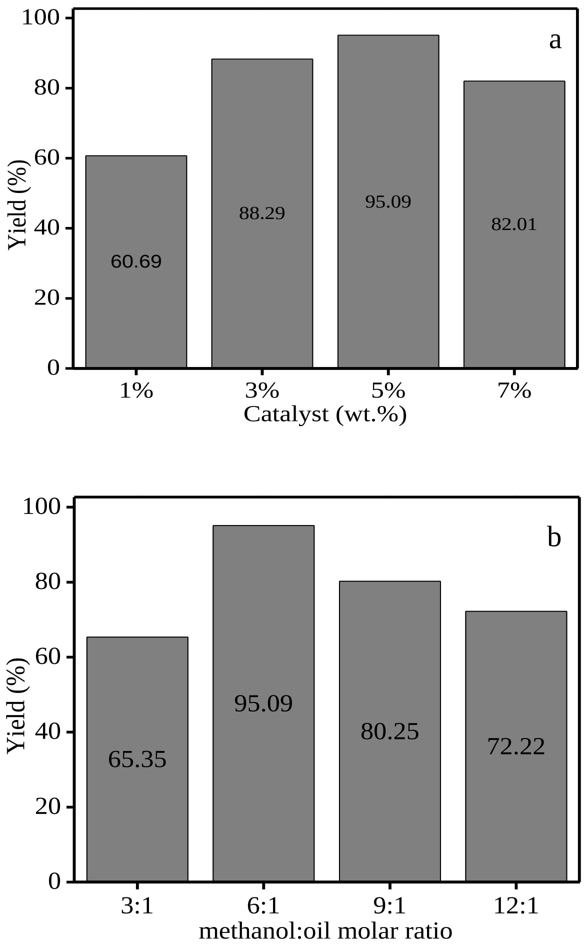
The results in Fig. 4c show that biodiesel production was slow during the first 2 hours of the reaction due to inadequate mixing and dispersion of the catalyst and methanol[32]. Adequate mixing is crucial for the even distribution of reactants and catalysts. The reaction increased rapidly between 2 and 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.



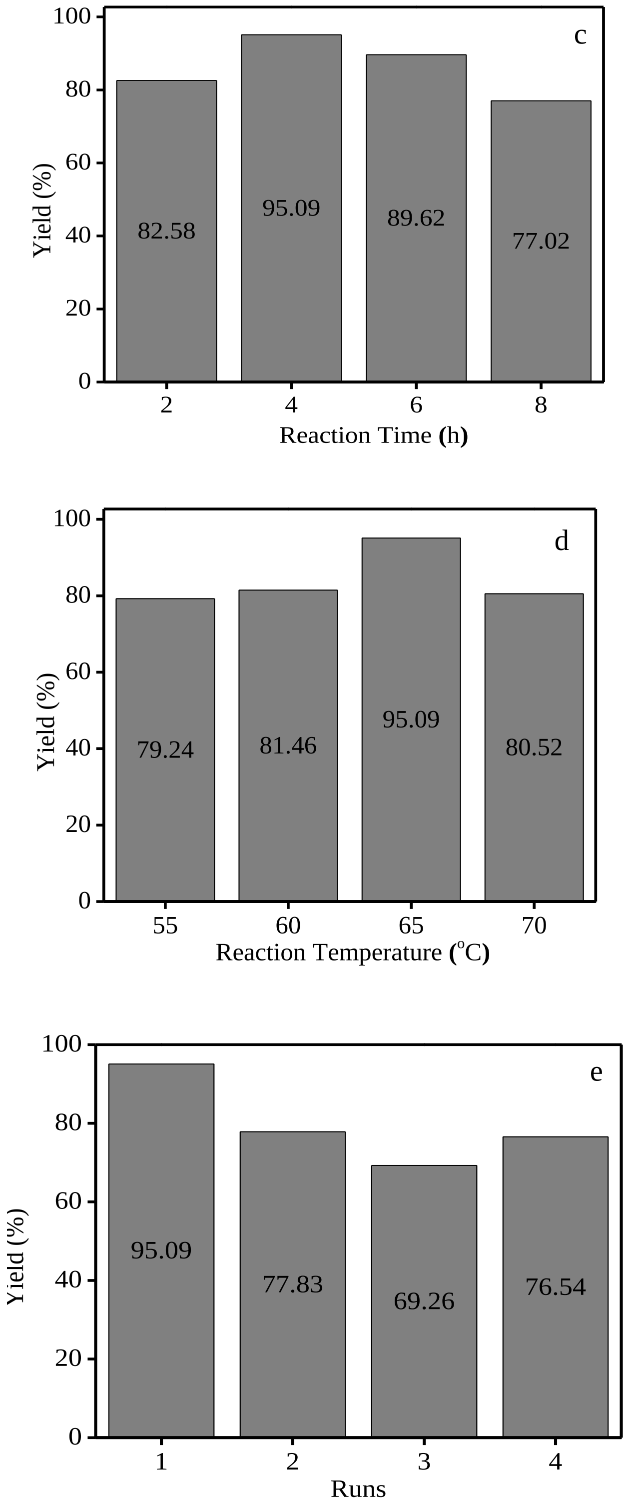


Figure 4. Catalytic activity of PCC/TiO_2 on biodiesel yield (a) Influence of the amount of catalyst (b) Effect of methanol: oil (c) Effect of reaction time (d) Effect of reaction temperature (e) reuse

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

Catalyst	Biodiesel feedstock (oil)	Catalyst Preparation	Reactions Conditions					References
			Methanol:oil	Catalyst (wt.%)	Temp(°C)	Time (h)	Product Y or C(%)	
CaO/dolomite	Mongogo nut oil	Calcination	9:1	6	65	3	90 (Y)	[39]
K-CaO/Al_2O_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. The reaction conditions are also provided, as they influence the catalyst performance. PCC/TiO_2 yielded higher biodiesel than the others due to its innovative material composition, high catalytic activity, stability, reusability, and environmentally friendly and sustainable properties.

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.

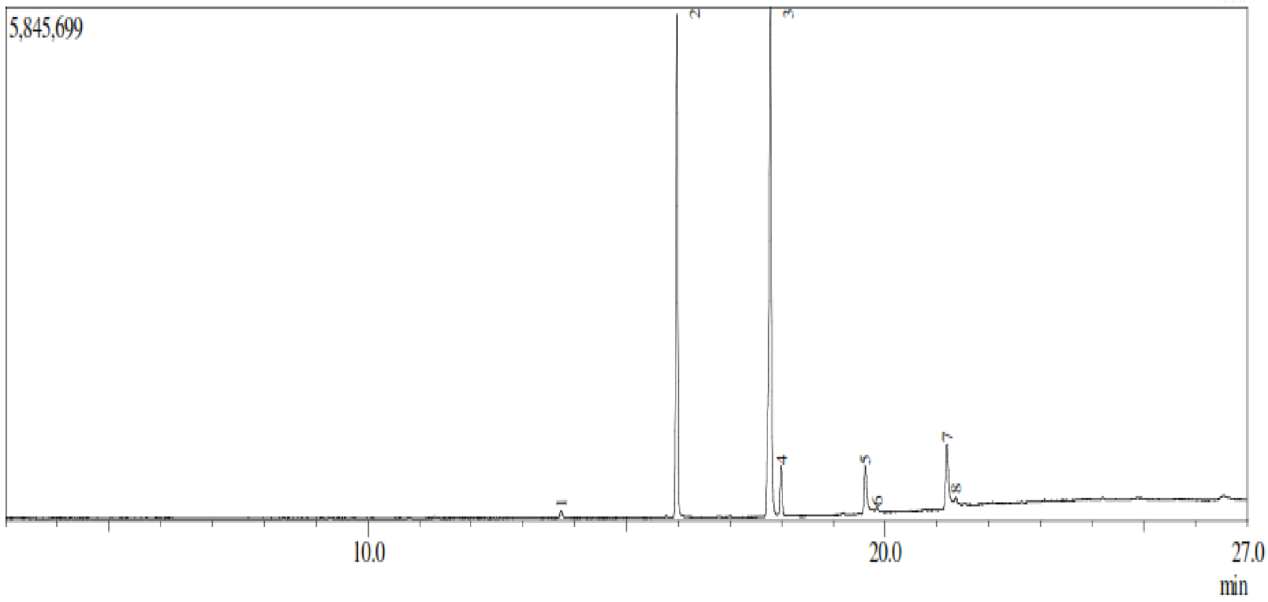


Figure 5. GC chromatogram of biodiesel synthesized from WVO

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	$C_{21} H_{42} O_2$
	41.14%	Total Saturated fatty acids		
17,786	46.88	9-Octadecenoic acid, methyl ester	Methyl oleate	$C_{19} H_{36} O_2$
	46.88%	Total Saturated fatty acids		

Physicochemical Properties of Biodiesel

The PCC/TiO_2 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/TiO_2 demonstrates higher efficiency and better biodiesel quality. Thus, this catalyst becomes attractive for environmentally friendly and sustainable biodiesel production industrial applications.

Table 6. Fuel properties of biodiesel.

			Biodiesel			
Biodiesel Properties	Unit	In research	[43]	[44]	SNI 7182:2015	Test Method
		PCC/TiO_2	CeO_2-SBA15	CaO		
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

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/TiO_2 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 re-publication, 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.

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

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الخلاصة

إن الوقود الحيوي المنتج من خلال تفاعلات الاسترة مع محفزات قاعدية متجانسة وغير متجانسة هو مصدر طاقة بديل واحد. 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 XRFو SEMو BETو FT-IRثم تم تطبيقه في تفاعل الاسترة. أظهرت النتائج أن PCC المخصب بثاني أكسيد التيتانيوم هو محفز فعال، ينتج الوقود الحيوي بكفاءة 95.09٪ في ظل الظروف المثلى: محفز 5٪ 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.

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