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Modification Of CaO Catalyst From Crab Shells With $AlCl_3$ Catalyst For Biodiesel Production Using Waste Cooking Oil As A Raw Material

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Abstract: The background is that in the biodiesel production process, the use of CaO catalyst can react with CO_2 and H_2O to form $Ca(OH)_2$ and $CaCO_3$ in the air, causing its catalytic activity to become less effective. Therefore, modification of the CaO catalyst is needed by using the method of impregnating the CaO catalyst with $AlCl_3$ catalyst. Modifying the CaO catalyst with the $AlCl_3$ catalyst using the impregnation method is necessary. This process can prevent deactivation, increase catalytic activity and surface area, and prevent soap formation during biodiesel production**. This study aims** to determine the presence of alkyl ester groups, the effectiveness and yield percentage of biodiesel in the resulting product. **The research method** begins purifying waste cooking oil through netralization and bleaching, impregnating CaO with $AlCl_3$, and synthesizing biodiesel through transesterification using the waste cooking oil as the raw material. The reaction was performed at 70 °C with a 3% catalyst concentration by weight of the oil. The products were identified using Fourier transform infrared spectroscopy (FTIR). **The results** showed the presence of ester groups with a biodiesel conversion value of 85,15%. **Conclusion** that biodiesel produced using the impregnated catalyst method is effective because the obtained value is close to the ASTM D6751 standard.

Keywords: Biodiesel, impregnation, CaO-$AlCl_3$ catalyst, transesterification, waste cooking oil

A. Introduction

Biodiesel is a renewable energy source for the future. Biodiesel is environmentally friendly, biodegradable, renewable and produces low carbon dioxide (CO2) emissions, making it one of the alternative replacements for fossil fuels such as diesel that can support sustainable energy in the future. Since 2014, the government has started implementing the use of B10 (a mixture of 10% biodiesel and 90% diesel) for use in vehicle diesel engines, showing good engine performance, fuel efficiency, and low carbon dioxide (CO2) emissions. In fact, the government currently plans to establish a new biodiesel mandate for the use of B50 by the end of the second semester of 2026 (Anonymous, 2024).

Biodiesel can be obtained through a transesterification reaction between vegetable oils, alcohol solvents, and catalysts. Several studies have used palm oil, rice bran oil, candlenut oil, and seaweed as raw materials for biodiesel production (Lestari, 2019). However, the large demand for extensive land can impact local resources and affect biodiesel production costs. Used cooking oil can be utilized as a raw material for biodiesel production. Used cooking oil can be produced in large quantities from households, restaurants, and the food industry. Used cooking oil is a waste product that is carcinogenic, so improper disposal can cause environmental pollution, such as waterway blockages and ecosystem disruption, necessitating measures to prevent such pollution. Research in Europe found that the transesterification process using used cooking oil provides a product efficiency of up to 90% (Bossio, 2025). The used cooking oil employed is oil that has been previously refined through neutralization and bleaching processes to reduce the free fatty acid (FFA) content to less than 0.05%. High FFA content in the raw material can cause saponification (soap formation) with the catalyst used, leading to a lower yield of biodiesel produced (Suhendi, et al., 2021).

Generally, the catalysts used in biodiesel production are homogeneous catalysts such as NaOH and KOH because they react quickly at low temperatures. However, homogeneous catalysts have several drawbacks, such as the occurrence of saponification reactions that make the catalyst difficult to separate from the biodiesel product and can reduce biodiesel yield, are corrosive, and are more expensive compared to heterogeneous catalysts (Puspitasari et al., 2024). Calcium oxide (CaO) is a heterogeneous catalyst that is more stable, easy to separate, cost-effective, and environmentally friendly. CaO catalysts can be obtained from waste shells, eggshells, and animal bones (Hariono et al., 2018; Macheli et al., 2025). Using CaO catalysts sourced from waste offers significant economic value because it can reduce waste management costs. However, in its use, CaO catalyst can react with CO2 and water (H2O) in the air to form CaCO3 and Ca(OH)2, which can lead to a decrease in catalytic activity and the quality of the biodiesel produced (Kesic, et al., 2016). The addition of active substances to CaO can enhance its catalytic activity, increase biodiesel efficiency and yield, accelerate the reaction, and reduce activation energy, making the biodiesel production process shorter.

Several studies have used a combination of CaO catalysts with other active substances such as CaO-K_2O, CaO-ZnO, CaO-Al_2O_3 in the biodiesel production process (Anindita et al., 2023). However, there are some drawbacks to these catalyst combinations, such as their hygroscopic properties, ease of absorbing water from the air, ZnO potentially covering CaO active sites and thus reducing biodiesel conversion, and the possibility of catalyst pores being clogged by oil residues or soap, which lowers catalyst performance (Hashmi et al. 2016). Aluminum chloride (AlCl3) is a Lewis acid catalyst that is effective for biodiesel production using low-quality cooking oil feedstock with high FFA content, such as used cooking oil. It achieves a fairly high conversion rate of 98% at 110 °C. $AlCl_3$ catalysts can also be obtained from waste generated from aluminum foil usage (Youssef et al. 2024). The $AlCl_3$ catalyst can be used as an active substance by combining CaO with $AlCl_3$ using the CaO-AlCl3 impregnation method to increase its catalytic activity. Until now, CaO-AlCl3 catalysts have been very minimally used as catalysts in biodiesel production, so this study is expected to produce a high biodiesel yield with characteristics that comply with the American Society for Testing Materials (ASTM).

B. Materials and Methods

Materials

The materials used are waste cooking oil, rice husk ash, crab shell, $AlCl_3$ catalyst, methanol, ethanol, KOH, NaOH, phenolphthalein indicatoopr, oxilic acid, Whatman filter paper, Na_2SO_4 anhydrous, n-hexane.

Methods

Refining of Used Cooking Oil

The refining of waste cooking oil was carried out through neutralization and bleaching process. The neutralization was carried out by heating the oil with water until it reached a temperature of 35°C and adding 4 mL of 6% NaOH solution for every 100 mL of waste cooking oil. This oil mixture was then stirred for 10 minutes at a temperature of 40°C and subsequently cooled and filtered to separate impurities present in the used cooking oil. The oil obtained from neutralization was then subjected to the bleaching process by heating it to 70°C and adding rice husk ash in a ratio of 6.25 g for every 100 g of oil. This oil was then stirred using a magnetic stirrer for 60 minutes while increasing the temperature to 100°C. The oil mixture was then filtered to remove any remaining impurities in the oil.

CaO-$AlCl_3$ Catalyst Impregnation

The CaO catalyst is obtained through the calcination of crab shells at a temperature of 900 °C for 3 hours. The resulting CaO catalyst is then modified using the impregnation method with an $AlCl_3$ catalyst. CaO and $AlCl_3$ catalysts (in a 1:1 ratio) are dissolved in methanol and stirred for 3 hours. The solution is then filtered using a vacuum pump while being washed with n-hexane and distilled water until the filtrate is clear. The resulting residue is then oven-dried for 2 hours and subsequently furnace-treated for 1.5 hours at a temperature of 500 °C.

Biodiesel Synthesis

30 g of waste cooking oil is placed in a three-neck flask and heated to 70°C. After that, methanol, which has previously been mixed with CaO-$AlCl_3$ catalyst (3% of the oil weight) in a molar ratio of 12:1 with the used cooking oil, is added and refluxed for 4 hours at 65°C. The mixture is then poured into a separatory funnel and left to stand for one day. Three phases form in the mixture: the upper and middle phases consist of methyl esters and glycerol, while the lower phase consists of the catalyst. The lower phase is then separated from the mixture, and the upper phase is extracted with distilled water. Two phases form in this mixture: the upper phase consists of methyl esters, and the lower phase consists of glycerol mixed with methanol. The upper phase is then added with anhydrous Na_2SO_4 and allowed to stand overnight. The obtained methyl ester is then filtered and heated at 90°C for one hour to obtain pure methyl ester (biodiesel).

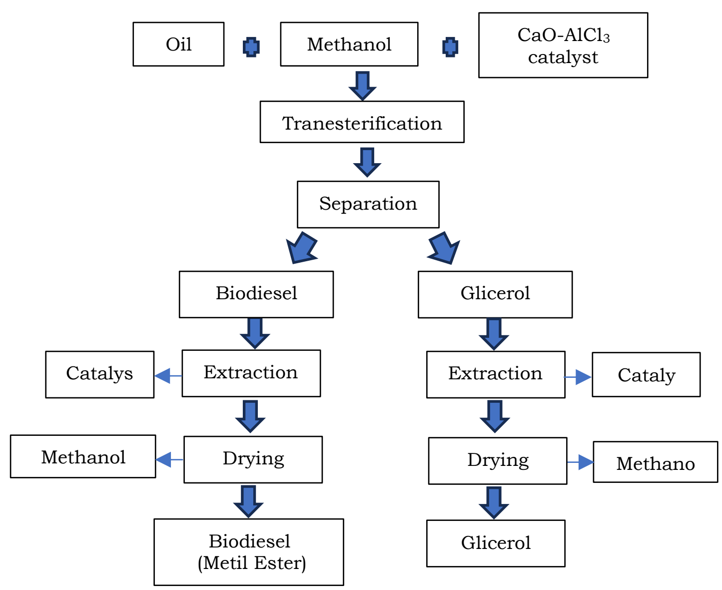

Fig 1. Diagram of Transesterification Process

Characteristic Test of Biodiesel Physical Property

Density Analysis

The empty pycnometer, which has been cleaned and dried, was weighed using an analytical balance. Distilled water that had been heated to 40 ^{o}C was poured into the pycnometer until full, and its temperature was recorded. The outer walls of the pycnometer were dried and weighed, and the weight was noted. Next, the distilled water was replaced with biodiesel that had been heated to 40-43 ^{o}C and weighed. The weighing results were recorded in grams. This procedure was carried out twice.

Water Content Analysis

The determination of water content is carried out by heating the sample in an oven at a temperature of 105-110 °C. First, a heat-resistant container is placed in the oven at 105–110 °C for 30 minutes and then placed in a desiccator. After cooling, the container is weighed to obtain the weight of the empty container. Then, 0.5 grams of used cooking oil is added to the container and it is placed in the oven at 105–110 °C for one hour. The container containing the sample is cooled in a desiccator and then weighed until a constant weight is obtained. This procedure is repeated twice.

Free Fatty Acid Analysis

A total of 0.2 g of biodiesel was placed in an L-shaped Erlenmeyer flask, 5 mL of 95% neutral alcohol was added, and then heated in a water bath until a homogeneous solution was formed. After cooling, it was titrated with 0.1N KOH using phenolphthalein as an indicator. The free fatty acid content was then calculated.

$$yield\ biodiesel = \frac{weight\ bioidesel}{weight\ oil} x\ 100\%$$

Result and Discussion

Refining of Waste Cooking Oil

The process of refining waste cooking oil aims to improve the quality of the used oil by removing impurities still bound to it, such as food particles, FFA content, soap, and colored pigments that can negatively affect the production process and biodiesel quality. The process involves steps from despicing, neutralization, to bleaching to reduce the FFA content in the waste cooking oil.

The acid number content obtained in used cooking oil after neutralization and bleaching is 139.3838 mgKOH/kg and 194.8575 mgKOH/g. This value exceeds the limit set by ASTM, which is a maximum of 0.8 mgKOH/g. This is due to the very high acid content in the used cooking oil, so it still requires special treatment to lower the acid number value to comply with ASTM standards.

CaO-$AlCl_3$ Catalyst Impregnation

The impregnation reaction of CaO with the Lewis acid AlCl3 can improve the efficiency of CaO catalysts in biodiesel production by increasing the surface area of CaO. The high catalytic activity of the CaO-AlCl3 catalyst is demonstrated by the high biodiesel yield (Table 1) and the short reaction time. The diffraction pattern data obtained using a Shimadzu XRD-700 Maxima XRD instrument show significant values compared to the Joint Committee on Powder Diffraction Standards (JCPDS) 37-1497, as shown in Figure 2.

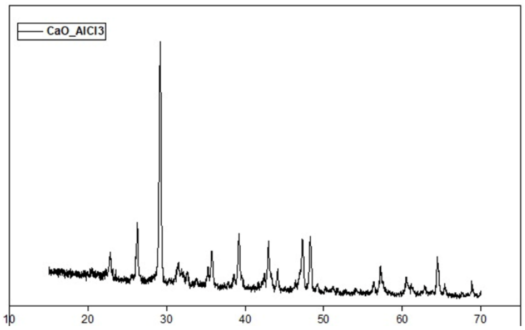

Fig 2. XRD Pattern of CaO-$AlCl_3$ catalyst

Identification Functional Group of Biodiesel

The produced biodiesel was analyzed using Fourier Transform Infrared (FTIR) to identify the presence of ester groups in the produced biodiesel. The FTIR test results of the biodiesel are illustrated in Figure 3.

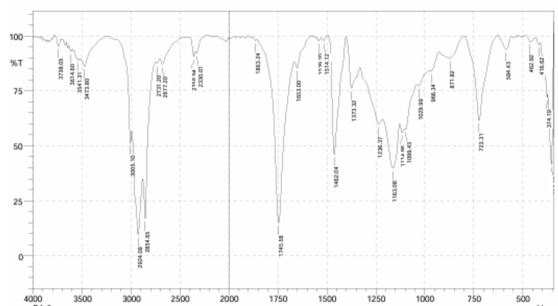

Fig 3. FTIR spectrum of biodiesel

Figure 3 shows the results of the FTIR testing with a wavelength range of 500-4000 cm^{-1}. Based on Figure 3, the IR spectrum with wavelengths of 2924.09 and 2854.6 cm^{-1} indicates the presence of C-H stretching in the CH_2 and CH_3 groups. The CH stretching occurs in the absorption region of 2800-3000 cm^{-1}. Referring to the research by Puspitasari et al., (2024), the ester functional group (C=O) is shown at 1745.58 cm^{-1} and the methyl functional group at 1458.18 cm^{-1}. The presence of methyl ester groups, as demonstrated by the FTIR test, shows that the production of biodiesel from used cooking oil using a CaO-$AlCl_3$ catalyst has been successfully carried out.

Characterization Test of Biodiesel

Table 1. Characterization test of biodiesel

Test	Biodiesel	ASTM D6751
Yield Ester (%)	85,15	
Water content (%)	0,0032	Max 0,05
Dencity (g/mL)	0,9037	0,82-0,86
Acid number (mg KOH/kg)	0,1394	Max 0,8

Table 1 shown the results of the characterization test of the biodiesel, which are still not fully in accordance with the established ASTM standards. This is likely caused by the high acid number content in the raw materials used. The acid value is crucial for ensuring the quality and performance of biodiesel, as it can affect its compatibility with diesel engines and its environmental impact.

Conclusion

The impregnation method using CaO-AlCl3 catalyst resulted in a high biodiesel yield of 85.15% with biodiesel characteristic test values in accordance with ASTM D6751.

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