Synthesis and Characterization of CaO Limestone from Lintau Buo Supported by TiO_2 as a Heterogeneous Catalyst in the Production of Biodiesel

Vivi Sisca[1,2], Aju Deska[1], Syukri[1], Zilfa[1], and Novesar Jamarun[1*]

[1] *Department of Chemistry, University of Andalas, Limau Manis, Padang 25163, West Sumatera, Indonesia*

[2] *Department of Biology Education, Institute of Education YPM Bangko, Jendral Sudirman St. 2,*
Meranging, Jambi 37313, Indonesia

* ***Corresponding author:***

tel: +62-751-71671
email: novesarjamarun@sci.unand.ac.id

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Abstract: *Biodiesel constitutes an alternative to diesel fuel, developing a base catalyst in cost efficiency and reducing the impact on the environment due to toxic waste and excessive chemicals. This study employed a mixture of an oxide catalyst, CaO/TiO_2, which was ably synthesized as a heterogeneous catalyst to convert waste frying oil (WFO) into biodiesel. Heterogeneous catalysts have been characterized by XRD, FT-IR, TEM, SEM-EDX, and BET to identify their crystal type, morphology, composition, and surface area. Catalytic activity was affected by the amount, oil/methanol ratio, reaction temperature, and duration. A 94% biodiesel yield was achieved by optimizing the following reaction parameters: 5wt.%, 6:1 methanol: oil, 65 °C, for 4 h. The addition of TiO_2 to CaO improves the catalyst stability and transforms the reactants into products. The structure and characteristics of TiO_2 maintained stability and supported CaO well. Its repeated biodiesel fuel production demonstrated the catalyst stability from WFO throughout the transesterification reaction.*

Keywords: *CaO/TiO_2; heterogeneous catalyst; WFO; transesterification; biodiesel*

INTRODUCTION

The global energy demand continues to increase with the rapidly growing population, transportation needs, and industries that use fuel in carrying out activities. However, environmental damage due to excessive fuel use is a significant concern for developed and developing countries. Among the solutions offered is producing an environmentally-friendly energy fuel such as biodiesel. It is a better alternative fuel than others since it has similar characteristics to diesel fuel produced by the mining industry. Well-known to be highly biodegradable and non-toxic and contributes to low carbon dioxide (CO_2) emissions into the environment [1]. Biodiesel production typically uses homogeneous and heterogeneous catalysts through transesterification reactions [1-2]. The advantages of heterogeneous catalysts are that they are environmentally friendly, reduce waste problems, are easily separable from glycerol, have higher activity and selectivity, and are reusable in transesterification reactions [3-4]. Therefore, over the past decade, heterogeneous catalysts have become an essential subject in biodiesel production applications, such as using alkaline materials as solid catalysts [5-6].

Based on the related literature, metal oxides are often applied in biodiesel production at transesterification reaction of triglycerides to biodiesel [7-8]. CaO is a cheap and abundant [9] heterogeneous base catalyst with a significant quantity and efficiency in biodiesel applications [10]. However, the main problem is that CaO is unstable due to leaching during the transesterification process, which interferes with the catalytic activity [11]. Therefore, current research concentrating on applying various catalytic aids to overcome this problem has increased [12-13]. The solution is to modify CaO to stabilize the catalyst in repeated use, such as modification with TiO_2.

TiO_2 is among the catalytic supports heavily investigated based on several benefits such as its high porosity, better structural power, solid molecular structure, reliable thermal properties, and non-toxicity [14]. Additionally, TiO_2 possesses a small crystal size and high adsorption power [15]. Due to the advantages mentioned earlier, numerous studies on the application of TiO_2 with other metal modifications have been carried out. For example, lithium was impregnated with TiO_2 catalyst for biodiesel production with a product yield of 98% [16]. De and Boxi [17] investigated Cu impregnated TiO_2 to produce biodiesel, achieving 90.93% at 45 °C and methanol to oil ratio of 20:1 for 45 min. Mohammad et al. suggested the modification of TiO_2 with CaO by the Ti ion substitution process in the Ca lattice. The Ti(IV) ion has a higher valence than the Ca(II) ion, resulting in defects and stable catalytic results [1]. Consequently, TiO_2 is reliable in modifying CaO, allowing the catalytic activity to be more consistent than the CaO-only method. Thus, the search for heterogeneous catalysts can produce satisfying products with short reaction times, lower temperature and pressure, selling points, and high-quality measurement standards in biodiesel manufacturing [18-19].

This study aims to develop heterogeneous catalysts in the transesterification process by exploring CaO from limestone supported by TiO_2. The CaO/TiO_2 catalyst modification process was employed to synthesize biodiesel from WFO by examining the effect of methanol/oil ratio, catalyst weight, and temperature as test parameters. Additionally, the repeated use of catalysts has been investigated to solve production costs for manufacturing biodiesel. Furthermore, the characterization of the catalyst is to determine the characteristics of the material properties.

■ EXPERIMENTAL SECTION

Materials

Waste Frying oil (WFO) was obtained from traders who sell fried foods in Indonesia's Padang area. The limestone was obtained from the Lintau Buo area of West Sumatra, Indonesia. TiO_2, CH_3OH, and n-hexane were obtained from Merck, Indonesia. Most of the chemicals were received without further purification.

Instrumentation

Evaluation of catalyst crystallography was carried out using a PANalytical Expert Pro X-ray diffractometer (XRD) diffractometer equipped with Cu-Kα radiation. The elemental compositions were analyzed using X-ray Spectroscopy (EDX) combined with SEM. The FTIR spectrum was analyzed by utilizing a Bruker Tensor 27 in the wavelength of 4000–500 cm^{-1} to determine the catalyst's functional groups. The BET technique was employed to assess the surface area (SA) and pore distribution with N_2 adsorption at 77 K using Quantachrome's Autosorb 1C. Catalyst surface morphology was then examined using (TEM) and scanning electron microscopy (SEM), JEOL energy scattering (JSM-6290LV). Gas Chromatography-Mass Spectroscopy (GC-MS) of FAAEs was performed on the Bruker GC-45 X applying the Scion MS system.

Procedure

Catalyst preparation

Preparation of CaO. A total of 10 g of sieved limestone with 90 μm was prepared, washed with water, and allowed to dry for 3 h at 105 °C. The sample was then crushed and calcined at 900 °C for 5 h to produce CaO.

Preparation of CaO/TiO_2. In designing the catalyst, the composition of CaO dopants on the TiO_2 support matrix is crucial. Therefore, CaO and TiO_2 were varied (0.25:1, 0.5:1, 0.75:1, 1:1, and 1.25:1 mol/mol). The CaO/TiO_2 catalyst was prepared by the wet impregnation method [20]. CaO was mixed with 100 mL of distilled water to dilute the solution before adding TiO_2. The solution was then stirred for 4 h at 50 °C and dried for 2 h at 100 °C. Next, it was calcined for 5 h in a furnace at 600 °C. Finally, the sample was cooled and stored in a desiccator. A catalyst is used in the transesterification reaction to study the catalytic activity. The CaO/TiO_2 (1:1 mol/mol ratio) with the most optimal activity was used as a catalyst for further process.

Catalytic activity test

The catalytic activity was determined by using a catalyst in the transesterification reaction. An investigation was carried out inside a 500 mL three-neck flask outfitted with a condenser and magnetic stirrer. In the initial stage, 5 wt.% catalyst was filled into a flask. After that, methanol and WFO were mixed at a ratio of

6:1(methanol:oil) at a speed of 850 rpm, at 65 °C for 4 h. After the reaction is complete, transfer to a separatory funnel to separate the product from the glycerol. To see the parameters that affect the catalytic activity carried out under the following conditions and variables: the amount of catalyst (1, 3, 5, 7 wt.%), methanol:oil ratio (3:1, 6:1, 9:1, 12:1), reaction temperature (55, 60, 65, and 70 °C), reaction time (2, 4, 6, and 8 h), and stability (1, 2, 3, 4). Each product obtained was analyzed using GC-MS to determine the amount of methyl ester compound. The following equation is used:

$$\text{Yield of biodiesel (\%)} = \frac{\text{weight of biodiesel}}{\text{weight of oil}} \times 100\% \quad [21]$$

■ RESULTS AND DISCUSSION

XRD Analysis

In this study, characterization was carried out on CaO/TiO_2 1:1 catalyst at optimal reaction conditions. XRD analysis determines the crystallinity of fresh and used CaO/TiO_2 catalyst, as depicted in Fig. 1. Phase identification of the X-ray diffraction pattern was carried out using Highscore Plus software, using the search match method, and refinement was performed using the Rietveld method. The CaO/TiO_2 catalyst demonstrated peaks of CaO at 2θ = 32.43, 37.62, 54.24, 64.65, and 67.90°; and peaks of $Ca(OH)_2$ at 2θ = 18.07, 28.72, 34.15, 47.21, 50.89, 54.45, 62.72, and 64.39°. TiO_2 anatase is confirmed by the diffraction at 2θ = 25.32, 36.99, 37.86, 38.59, 48.05, 53.96, 55.079, 62.736 and 75.12°. The presence of CaO peaks is the result of limestone calcination [22]. When exposed to air and hydrated, peaks of $CaCO_3$ and $Ca(OH)_2$ appear [23-24]. The diffraction of CaO/TiO_2 is a combination of the peak of TiO_2 and CaO [25-26]. In addition, $CaTiO_3$ peaks were observed at 2θ = 32.88, 33.12, 33.29, 47.49, 47.59, 58.86, 59.38, and 69.50°, which were formed due to the interaction between CaO and TiO_2 on the catalyst surface [27]. The XRD results also follow SEM and TEM analysis, showing that the CaO catalyst was successfully supported using TiO_2 to improve catalyst activity. After being used for the reaction, XRD results of CaO/TiO_2 showed peaks of $Ca(OH)_2$ at 2θ = 18.09, 34.15, 47.21, and 50.89°. Characteristic of $CaCO_3$ was observed at 2θ = 29.37, 35.95, 39.39, 43.14, 47.48, 48.48°, while the TiO_2 was at 2θ = 25.32, 37.85, 48.05, 53.96, 55.08, and 75.12°. The presence of $CaTiO_3$ can be confirmed from the diffraction at 2θ = 32.86, 33.06, 33.23, 47.43, 47.48, 59.27, and 69.37°. The XRD pattern of before and after used in a transesterification were different since the interaction between the catalyst and WFO affects the active site and causing the changes in the catalytic activity.

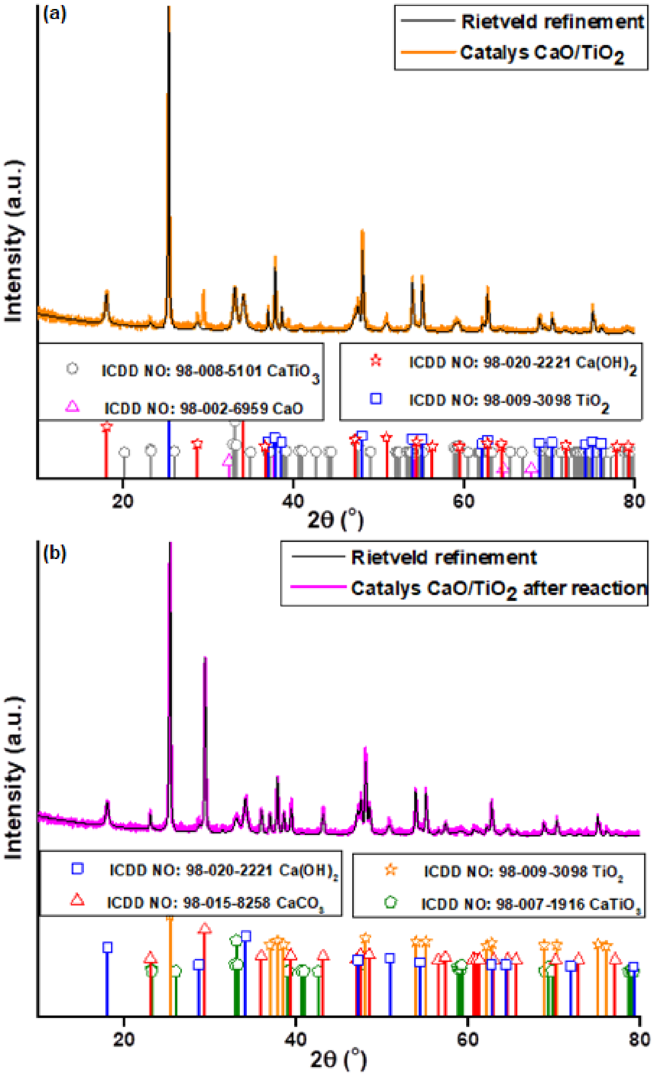


Fig 1. XRD pattern of CaO/TiO_2 (a) before and (b) after transesterification

FTIR Analysis

FTIR analysis was carried out to determine the functional groups of CaO/TiO_2 catalysts before and after use (shown in Fig. 2). The FTIR spectrum of the catalysts

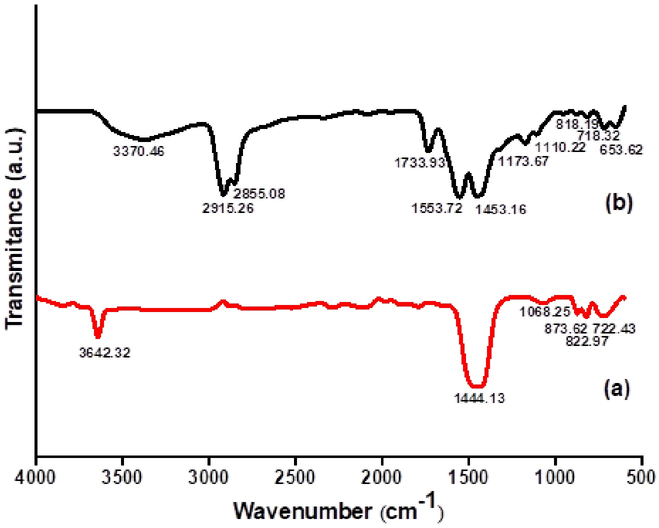


Fig 2. FTIR spectra of CaO/TiO_2 (a) before and (b) after transesterification

before used has two sharp and broad peaks at the wavenumber of 3642 cm^{-1}, associated with the -OH vibration [7]. Identical CaO bonds are observed at the wavenumbers of 1444.13 cm^{-1} and 873.62 cm^{-1} [26-28]. An absorption at 722.43 cm^{-1} is associated with the vibration of the Ti–O bond [29-30]. The new phase of $CaTiO_3$ is found at a wavenumber of 1068.25 cm^{-1} [13].

For the used sample, the catalyst showed a peak at a wavenumber of 3370.46 cm^{-1}, which was associated with –OH vibrations [31]. Wavenumbers of 2855.08 cm^{-1} and 2915.26 cm^{-1} were attributable to the stretching vibration of the C-H bond. The strain characteristic of the carbonate ion C=O was observed at 1733.93 cm^{-1} [16], while absorption at 1553.72 cm^{-1} was associated with the $–CH_2$ groups [32]. A new phase of $CaTiO_3$ observed at 1110.22 cm^{-1} and 718.32 cm^{-1} was related to Ti–O vibrations [7,33]. The existence of C–H and $–CH_2$ stretching vibrations suggesting the presence of organic compounds on the catalyst, as can be seen in the morphological analysis.

Morphological Analysis with SEM and TEM

The morphology of the CaO/TiO_2 catalyst before and after the reaction analyzed using SEM and TEM are shown in Fig. 3. Analysis of CaO/TiO_2 using TEM (Fig. 3(a)) and SEM (Fig. 3(b)) shows agglomeration in various particle shapes. It was seen on the TEM image that the refined grains were scattered on the spherical particles. This phenomenon indicates that the sample consists of two mixed oxides. According to EDX results,

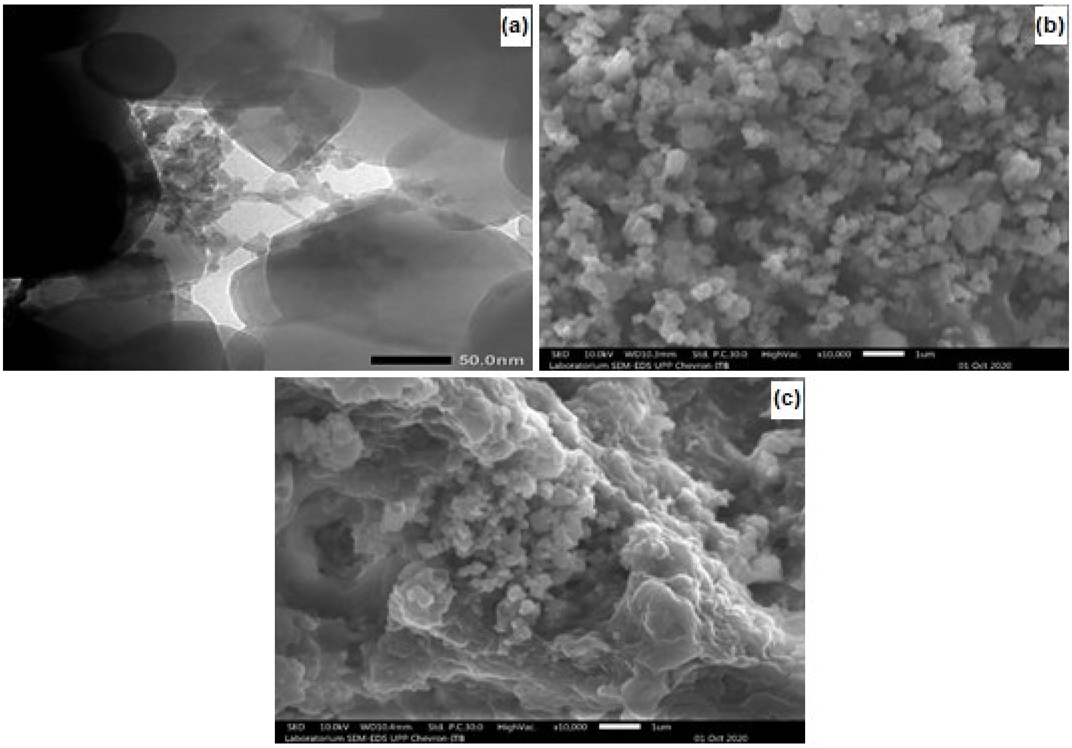


Fig 3. (a) TEM image of CaO/TiO_2 and SEM images of CaO/TiO_2 (b) before and (c) after a reaction

the catalyst consists of Ca, and Ti confirmed that CaO is dispersed in the TiO_2 support matrix. The results of the analysis are in agreement with those in Ref. [33]. CaO combined with TiO_2 causes an increase in catalyst stability, primarily due to the interaction between the two metal oxides, as evidenced by the presence of $CaTiO_3$ on XRD. TiO_2 support can maintain the catalytic activity of CaO, which can avoid leaching in the reaction medium [34]. After transesterification, the morphology of the catalyst shows that the sample had agglomeration and accumulation of glycerol on the active surface. It is assumed that the adsorption of fatty acids or glycerol in the pores inhibits further transesterification between the reactants and the active site of the pores [35].

EDX Analysis

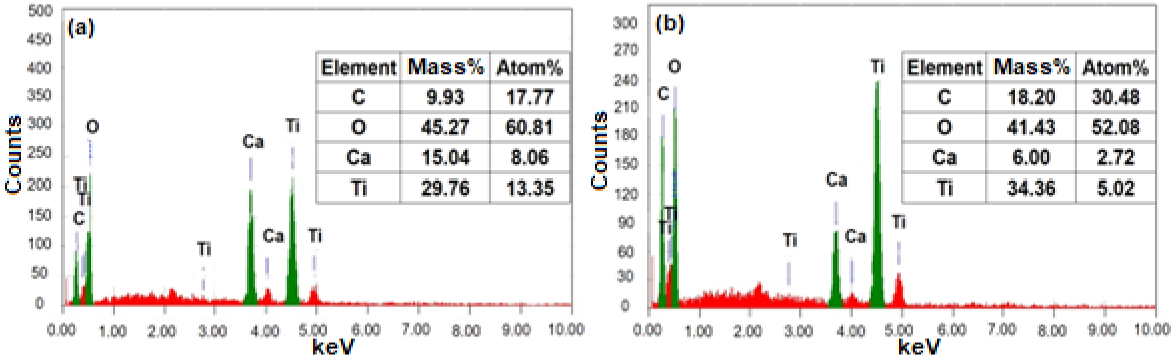
EDX was used to determine the CaO/TiO_2 catalyst components before and after use, as shown in Fig. 4. The EDX results show that Ca and Ti elements were the components of the CaO/TiO_2 catalyst. Meanwhile, the catalyst was used also contains the same elements. However, there was a change in composition, namely, a decrease in the amount of Ca and Ti on the catalyst's surface. Therefore, this case produces fewer CaO particles [12]. The availability of Ca and Ti indicates that the catalyst has good catalytic activity in converting reactants into products due to the cooperation between the dopant and the support matrix.

Catalyst Surface Area

The surface area directly affects the catalytic activity. Higher catalytic activity is gained from a larger surface area [1]. The surface area of CaO/TiO_2 of 136 m^2/g, and this larger surface area was associated with the addition of TiO_2 (Table 1). A high interaction of TiO_2 with CaO provides an increase in the surface area of the catalyst, which reduces the surface diffusion of CaO. Aside from that, it results in sintering and a stable crystalline structure of CaO/TiO_2 [36]. After the catalyst was used, the surface area was enhanced to 252 m^2/g. Increasing the surface area can maintain the catalytic activity upon reuse [19].

Comparison of Biodiesel Yield Using CaO and TiO_2 Catalyst

The catalytic test for the CaO catalyst obtained a Fatty Acid Methyl Ester (FAME) yield of 86%, compared to the 61% yield by TiO_2 catalyst (carried out in our previous study) in (Fig. 5). This indicates that the difference in the amount of product is probably affected by the strength of the catalyst interacting with the surface. However, CaO can only be used twice with the highest yield. The 3rd and 4th repetitions experienced decreased activity and the number of FAME products [37]. Therefore, we are interested in improving the catalytic activity of CaO with the support of TiO_2.



(a)

Element	Mass%	Atom%
C	9.93	17.77
O	45.27	60.81
Ca	15.04	8.06
Ti	29.76	13.35

(b)

Element	Mass%	Atom%
C	18.20	30.48
O	41.43	52.08
Ca	6.00	2.72
Ti	34.36	5.02

Fig 4. EDX analysis of CaO/TiO_2 (a) before and (b) after a reaction

Table 1. The surface area of CaO/TiO_2 before and after reaction

Catalyst	Surface area (m^2/g)	Pore volume (cc/g)	Pore size (Å)
CaO/TiO_2	136	0.389	20.27
CaO/TiO_2 after reaction	252	0.520	15.85

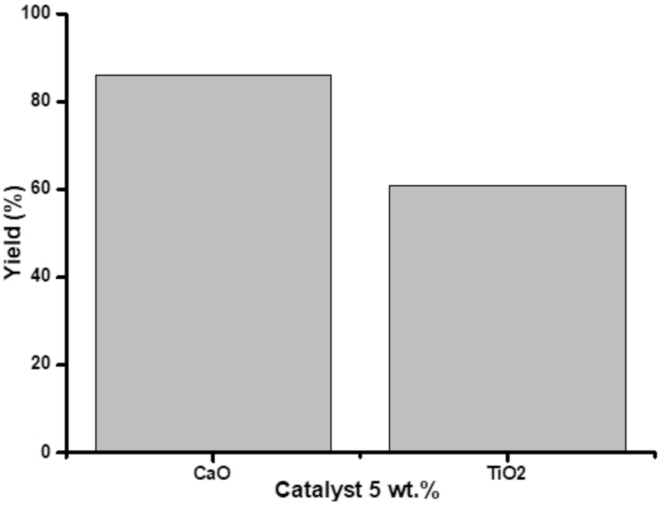


Fig 5. Yield product of biodiesel using (a) CaO and (b) TiO_2

Catalytic Activity Test

Effect of CaO/TiO_2 ratio

The transesterification reaction with different total weight ratios is shown in Fig. 6. This demonstrates the catalytic performance of a mixture of CaO/TiO_2 oxides with various Ca/Ti mol ratios. The FAME increases by increasing the CaO/TiO_2 ratio up to 1:1. However, it starts to decrease by increasing the ratio, possibly due to the destruction of the TiO_2 lattice structure at higher CaO concentrations because of the lattice mismatch, which inevitably causes structural instability within the material [38]. The changes in the material structure and catalytic properties were also disrupted, directly affecting biodiesel yield [17]. These results indicate that the optimum Ca/Ti ratio obtained is 1:1 at 94%. In other words, the Ca addition is the reason for obtaining the maximum amount of product.

Effect amount of catalyst

The impact of loading CaO/TiO_2 on biodiesel yield was investigated by assorting the catalyst weight 1, 3, 5, and 7 wt.%. The use of catalysts up to 5 wt.% gradually increased biodiesel production and achieved a maximum of 94%. However, the increase in yield is insignificant after attaining the optimum result. The addition of a catalyst can further reduce the biodiesel yield, primarily owing to the decreasing quantity of active sites that could swift the reaction rate [39]. In addition, the catalyst was used excessively, causing the reactants and their products to be absorbed by the catalyst powder. This results in aggregation and thus reducing the total active sites [40]. According to Wen et al. [19], the maximum yield was 85.3% within the following reaction conditions: methanol/oil 50:1, 10 wt.%, and 433 K. Meanwhile, Mguni et al. [25] reported that the maximum biodiesel yield was 84% under the reaction conditions: 225 °C, 1 h, methanol/oil 18:1, and 5 wt.% (Fig. 7).

Effect of methanol:oil molar ratio

The ratio of methanol:oil is an essential parameter

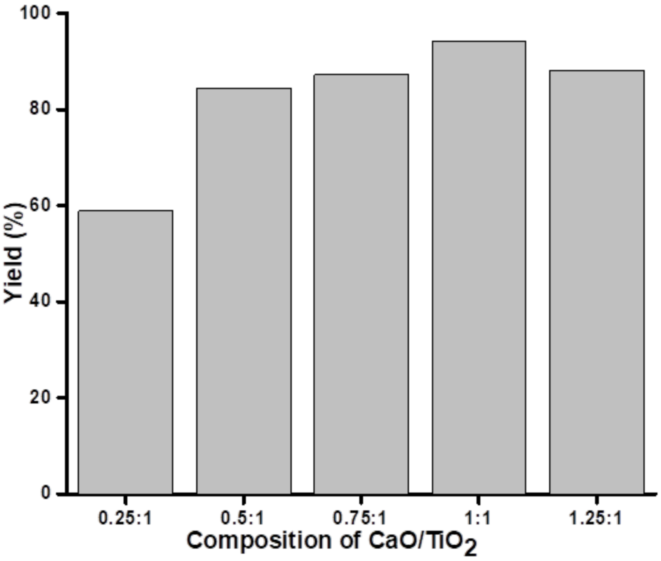


Fig 6. Effect of CaO/TiO_2 ratio on biodiesel yield

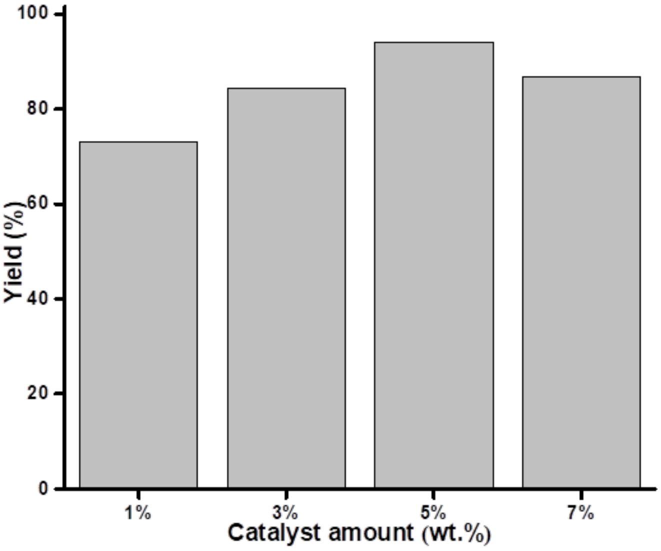


Fig 7. Effect of CaO/TiO_2 catalyst ratio on biodiesel yield

in transesterification to obtain the maximum biodiesel yield. Transesterification is a reversible reaction, and excessive methanol is intended to shift the equilibrium forward to obtain the optimal results [41]. In determining the optimal ratio of methanol:oil, the reactions implemented with different rates, 3:1, 6:1, 9:1, and 12:1. The yield of FAME products increases with a ratio up to 6:1. Nonetheless, a drop in the result was noticed when the ratio exceeded 6:1. This is because excessive alcohol consumption complicates the heating and elimination processes. To improve transesterification, the molar ratio of methanol:oil is retained [18]. Therefore, 6:1 was considered the optimal ratio for biodiesel yield. The results were not significantly different from Madhuvilakku and Piraman [18], which reported that the optimum conversion was 92.2% in 200 mg at 60 °C for 5 h with methanol:oil ratio of 6:1. Therefore, the ratio of 6:1 was considered the optimal ratio for biodiesel yield. The results were not significantly different from Suprapto et al. [42]; the optimum conversion was 56.13% in 1% of catalyst at 60 °C for 2 h, with methanol:oil ratio of 1:1 (Fig. 8).

Effect of reaction temperature

The reaction temperature has a crucial impact on the transesterification reaction. Transesterification was performed at 55, 60, 65, and 70 °C. The biodiesel yield improves with an increase in the temperature up to 65 °C, leading to a reduction. At a low temperature, the reaction is not totally done before, resulting in a low biodiesel yield. A moderate temperature of 65 °C can affect the reaction by increasing the kinetic energy, leading to a higher product [43]. At relatively high reaction temperatures, FAME with a low yield was acquired because the evaporation of methanol is in the vicinity of a similar temperature. During the reaction, methanol was lost and inhibited the transesterification [44]. Consequently, T = 65 °C was considered as the optimal temperature for biodiesel yield. The results obtained were similar to those of Mohammad et al. [1] mentioned that the optimum result was 93.33% in the following conditions: calcination at 600 °C, 0.5%, palm oil:methanol ratio of 3:5, reaction at 65 °C, 150 min, and ± 500 rpm. In the experiment by Moradi et al. [45], the optimum yield was 98.5% by using methanol:oil ratio of 16:1, 6 wt.%, at 60 °C, for 8 h (Fig. 9).

Effect of reaction time

Time is among the crucial variables for the reaction to obtain product selectivity. Therefore, the biodiesel production process was conducted at various durations to optimize the reaction's completion time. The procedure was repeated for 2, 4, 6, and 8 h. The interaction was slow for the first 2 h because there was insufficient time to increase the mixing and dispersion of the catalyst and methanol in WFO [46]. However, within

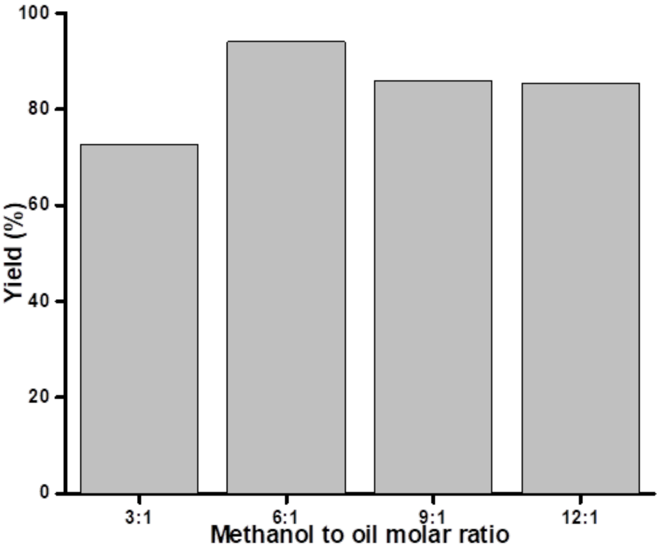


Fig 8. Effect of methanol/oil ratio on biodiesel yield

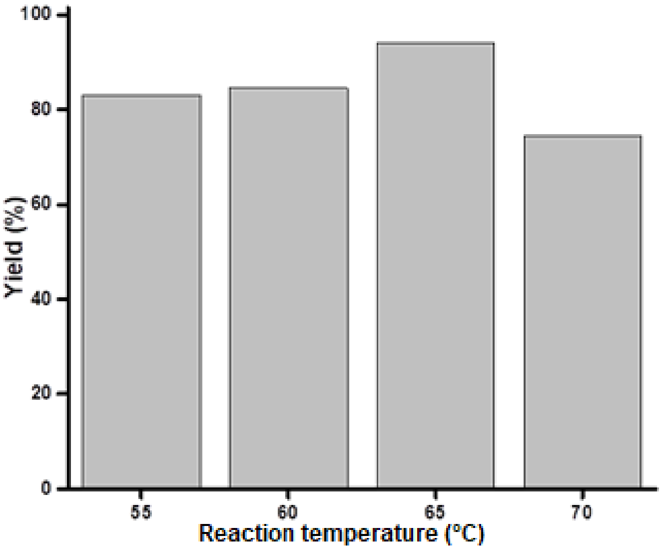


Fig 9. Effect of reaction temperature on biodiesel yield

4 h, the interaction between the reactants and products could increase the reaction rate. The amount of product tends to decrease when it exceeded the optimum time, as shown in Fig. 10. This could be explained by the possibility of a reversible reaction [46-47]. It is in line with the results by Sithole et al. [48], reporting that the optimum result of 100% was achieved using 20 wt.% catalysts and methanol:oil molar ratio of 18:1. Wong et al. [35] also obtained the optimum biodiesel yield of 95% using a catalyst weight of 5 wt.% and methanol:oil molar ratio of 12:1, at 65 °C, for 4 h.

Stability of Catalyst

Among the benefits of heterogeneous catalysts is that the former could be recycled during various reaction cycles. Therefore, catalyst stability is a prominent test in developing heterogeneous catalysts for transesterification, especially when there is a loss of active elements due to catalyst leaching, such as most previously reported solid catalysts [48]. Stability studies were conducted under optimal reaction conditions after each reaction process, namely, separating the catalyst, washing with methanol and n-hexane, and drying for reuse. Interestingly, this catalyst could be utilized repeatedly, as shown by the FAME results in Fig. 11. This catalyst was stable enough to be applied in biodiesel production. However, the fourth usage inflicts a decrease in the count of products, although the change was insignificant. One of the factors causing a decrease in selectivity was the damage to the surface of the active catalyst caused by the replacement of Ca ions [19], blockage of the active site by adsorbed products (such as monoglycerides, diglycerides, and glycerides), as well as moisture and CO_2 contamination in the air during the filtration process, triggering a decrease in catalytic activity [49]. Fig. 11 shows that the mixed oxide CaO/TiO_2 has a high probability of being used in large-scale biodiesel processes since reuse is a potential solution to overcome large waste generation and relatively low costs. Salinas et al. showed four reaction cycles, with no deactivation of the active species on the catalyst or leaching observed. A mean conversion of 81 ± 6% was achieved after four cycles using the same catalyst [50]. A study by Wen et al. reported that the FAME yield decreased from 92.3% to 81.2% as repeated 1–4 times [19], pointing out that this catalyst was stable for biodiesel production (Fig. 11.).

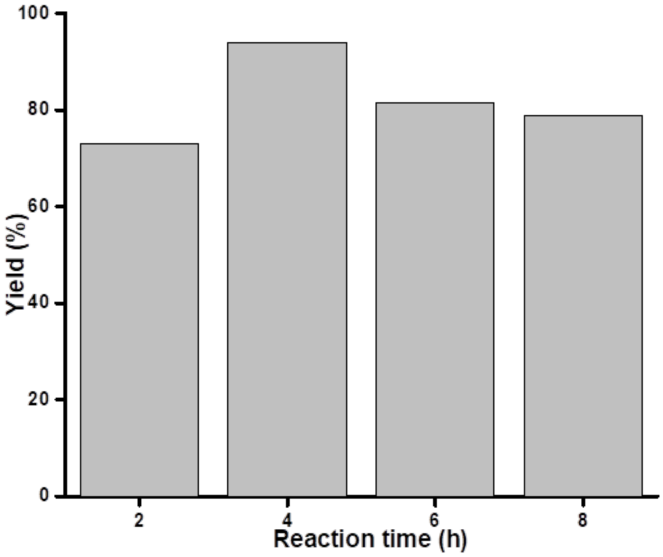


Fig 10. Effect of reaction time on biodiesel yield

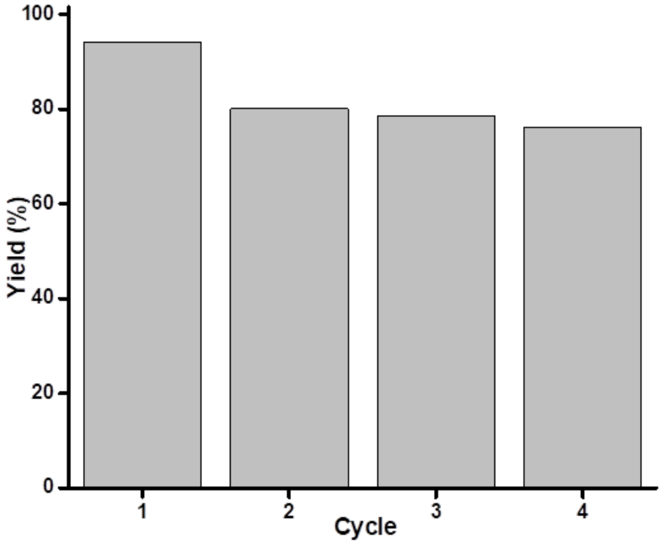


Fig 11. The differences in the amount of biodiesel and variations in reuse (1, 2, 3, and 4 cycles)

▪ CONCLUSION

Waste Frying Oil (WFO) is a promising raw material for biodiesel production cheaper than conventional vegetable oils. Additionally, WFO is environmentally friendly to use. CaO supported by TiO_2 can increase biodiesel yield since the TiO_2 catalyst is superior. The morphological analysis demonstrated that showed CaO particles were scattered on the surface of

TiO_2, which indicated mixed metal oxides interactions so that the surface of the active site was damaged. It is indicated by its low intensity and the formation of a new phase of $CaTiO_3$ in the XRD pattern, increasing stability and maintaining catalytic activity. The maximum biodiesel yield of 94% was obtained under 5 wt.% catalyst conditions and a 6:1 methanol:oil ratio, with a reaction temperature of 65 °C in 4 h. The high yield of biodiesel shows suitable good catalytic properties to be used for use in biodiesel production from WFO.

■ AUTHOR CONTRIBUTIONS

VS collected the experimental data, VS and AD drafted the manuscript, and SY, ZF, NJ developed the idea and corrected the manuscript. All authors read and approved the final manuscript.

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