Abstract

Biodiesel is a prominent alternative for diesel fuel, and for the development of alkaline catalysts for cost efficiency in excessive catalyst use. This study used a mixture of an oxide catalyst, CaO-TiO₂, with the wet impregnation method, which was successfully synthesized as a heterogeneous catalyst to convert waste frying oil (WFO) into biodiesel. The heterogeneous catalysts characterized were with EDX, XRD, FT-IR, BET, and SEM for the identification of catalyst characteristics and their morphology. The activity and catalytic performance of CaO-TiO₂ depend on the concentration (η), catalyst (n), methanol to oil molar ratio (m), reaction temperature, and (t) reaction time. The highest biodiesel yield of 94% was obtained using the following optimum reaction parameters: catalyst weight of 5wt%, and methanol-oil molar ratio of 6:1, at 65 °C, for 4 hours. Biodiesel was analyzed by gas chromatography-mass spectrometry (GC-MS). The Mixed-mixed oxide catalyst CaO-TiO₂ shows demonstrated good potential in biodiesel production from waste frying oil, which remained stable after being the used four times in the transesterification reaction.

1. Introduction

Current world energy demand continues to increase due to the rapidly increasing population growth, upsurging transportation needs, and industries that use fuel in carrying out activities. However, environmental pollution caused by the excessive use of fuel is a primary concern for developed and developing countries. One of the solutions offered is the production of environmentally friendly energy fuel, such as biodiesel. Biodiesel is a better alternative fuel compared to others, because it has similar characteristics to the diesel fuel produced by mining industries. It is also known as to be highly biodegradable, and non-toxic, and contributes to low carbon dioxide (CO₂) emissions [1].

Biodiesel production typically uses a catalyst such as a homogeneous catalyst and a heterogeneous catalyst through a transesterification reaction [1]. The advantages of heterogeneous catalysts are that they are being environmentally friendly, reducing waste problems, are easily separating separable from products, having higher activity and selectivity, and being reusable for transesterification reactions [2,3]. For this reason, over the last decades, researchers consider that the benefits of heterogeneous catalysts have become an essential subject in biodiesel production applications, such as using alkaline materials as solid catalysts [4].

One example of the heterogeneous solid base catalyst is CaO, which belongs to a type of metal oxides. Based on the related literature studies, metal oxides are often used in biodiesel production such as MgO, ZnO, SnO₂, and CaO, for the application of the transesterification reaction of triglycerides to glycerides [5]. A heterogeneous base catalyst, namely, calcium oxide (CaO), is a solid catalyst that has potential for biodiesel applications with significant quantity and efficiency of use [6]. Additionally, it is cheap and readily available, is in abundant abundance and its price is also cheap [7]. However, the problem is that CaO is unstable due to the washing process, which interferes with the transesterification process's catalytic activity [8]. Nowadays, research on applying various catalytic aids for CaO has been increasing for overcoming this problem has been increasing [9,10]. So, the solution is to modify CaO to stabilize the catalyst in repeated use, for example, such as modification with TiO₂ metal (titanium).

Titanium is one of the catalytic supports that has been heavily investigated based on several considerations such as its high surface area, high structural strength, strong chemical structure, good thermal stability, and non-toxic properties [11]. TiO₂ also has a small crystal size and high adsorption power [12]. Due to these the aforementioned advantages, several studies on the use of TiO₂ metal with other metal modifications have been conducted. For example, included Li was impregnated with TiO₂ as a heterogeneous catalyst for biodiesel production with a product yield of 98% in [13]. Also, Arghyadeep De and Siddhartha Sankar Boxi investigated Cu impregnated TiO₂ to produce biodiesel, with a result achieving of 90.93% at 45 °C and a ratio of methanol to oil 20:1 for 45 minutes [14]. Then, Mohammad suggested the modification of TiO₂ with CaO by the Ti
ion substitution process in the Ca lattice. The Whereas, Ti ion has a higher valence (IV) than the Ca(II) ion, resulting in defects and stable catalytic activity [1,15]. Therefore, TiO₂ is suitable for modifying CaO in which whereby the catalytic activity can be more steady rather than in the method using CaO only alone. Thus, the search for heterogeneous catalysts can produce satisfying products with the characteristics of short reaction times, lower temperatures and pressures, selling points, and high-quality measurement standards in the manufacture of biodiesel are attractive for the industry [16].

This study aims to develop heterogeneous catalysts in the transesterification process by exploring CaO from limestone supported by TiO₂. This involves the Modification modification of a CaO-TiO₂ catalyst for biodiesel synthesis from used cooking oil by studying the effect of methanol/oil ratio, amount of catalyst, and temperature as parameters for optimal catalytic conditions. Besides, catalyst reuse is also studied as a solution to the problem of reducing biodiesel production costs. Furthermore, the characterization of the catalyst has also been carried out to determine its properties.

2. Materials and Method

2.1 Material

The Waste Frying oil (WFO) can be obtained from traders who sell fried foods in the Padang area. The Limestone was obtained from the Lintau Bu community in West Sumatra. TiO₂, CH₃OH, and n-hexane were obtained from Merck in Indonesia. All those of the chemicals were utilized as they are received without further purification.

2.2 Catalyst Preparation

A total of 10 grams of sieved limestone with a size of 90 µm was prepared and washed with water, and dried at 105 °C for 3 h. After that, the sample was crushed and calcined at 900 °C for 5 h, to produce CaO. In this study, the transesterification reaction used utilized a catalyst prepared with by the wet impregnation method [17]. CaO was mixed homogeneously with TiO₂ at a weight ratio of 1:1. It was then dried by heating it up for 2 hours at 100 °C for 2 h, and calcined in a furnace at 600 °C for 5 h. The sample was cooled and stored in a desiccator.

2.3 Characterization

Elemental compositions were analyzed using X-ray spectroscopy (EDX) combined with SEM. Evaluation of catalyst crystallography was carried out using a Pan Analytical Expert Pro X-ray diffractometer (XRD) diffractometer equipped with Cu Kα radiation. The FTIR spectrum was analyzed using a Bruker Tensor 27 in the range 400-500 cm⁻¹ to determine the catalyst's functional groups. BET analysis was conducted to determine the surface area (SA) and pore distribution with N₂ adsorption at 77 K using Autosorb 1C made by Quantachrome. Catalyst surface morphology was analyzed using Scanning electron microscopy (SEM) and JEOL energy scattering (JSM-6290LV). Gas Chromatography-Mass spectrometry (GC-MS) of FAEEs was applied to the Bruker GC-45 X with the Scion MS system.

2.4 Transesterification of used cooking oil

The experiment was carried out in a 500 mL round bottom three-neck flask, equipped with a condenser and magnetic stirrer. The flask was immersed in an oil bath to control the reaction temperature, until it reached 35-75 °C. The catalyst was loaded with variations (1-7 % of oil weight). After that, methanol and oil are mixed with a variation of the methanol/oil mole ratio (3:1 to 12:1) at a speed of 850 rpm, during a variation of time (for 2-8 h) at variations in- at a temperature range (55-70 °C). The oil used in the transesterification reaction is waste frying oil in a hot state of 50 °C was used for the transesterification reaction. After that, the transesterification reaction of biodiesel was separated from the glycerol using a separating funnel. The results obtained were analyzed using GC-MS to determine the amount of methyl ester compounds, and calculated by the following equation used:

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\text{Yield of biodiesel (\%) = } \frac{\text{Area Gc Biodiesel x Weight of product}}{\text{weight of Waste Frying Oil}} \times 100\%.
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3. Results and Discussion

3.1 EDX analysis

Figure 1A shows the EDX results of the CaO-TiO₂ catalyst before the transesterification reaction. Furthermore, the EDX results indicate the presence of Ca and Ti atoms in the sample. Meanwhile, Figure 1B shows the CaO/TiO₂ catalyst after the reaction, which shows the presence of Ca and Ti atoms present. However, there was a change in composition, namely, a decrease in the number of Ca and Ti atoms from the catalyst's surface. This case