Abstract

Biodiesel is a prominent~~a~~ 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-TiO_2~~,~~ ~~with~~ by 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-TiO_2 depend on the concentration ~~(i)~~, catalyst ~~(ii)~~, methanol to oil molar ratio ~~(iii)~~, reaction temperature~~,~~ and ~~(iv)~~ reaction time. The highest biodiesel yield of 94% was obtained ~~at~~ using the following optimum reaction parameters: ~~with~~ 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-TiO_2 ~~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~~ with ~~to~~ the rapidly increasing population growth, uprising 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~~ Among the solutions offered is the production of ~~environmentally~~ environmentally-friendly energy fuel~~,~~ such as biodiesel. Biodiesel is a better alternative fuel compared to others, ~~because~~ since 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 (CO_2) emission [1]. Biodiesel production ~~usually~~ typically uses a catalyst such as a homogeneous catalyst and a heterogeneous catalyst through a transesterification reaction [1]. The advantages of ~~Heterogeneous~~ heterogeneous catalysts are ~~have the advantages of~~ that they are ~~being environmentally~~ environmentally-friendly, ~~reducing~~ reduce waste problems, are easily ~~separating~~ separable from ~~products from~~ glycerol, ~~having~~ have higher activity and selectivity, and ~~being~~ are reusable for transesterification reactions [2,3]. For this reason, over the last decade~~s~~, ~~for 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~~ An example of ~~The~~ a heterogeneous solid base catalyst is CaO, which ~~belongs to~~ is ~~one~~ a type of metal oxide~~s~~. Based on the related literature ~~studies~~, metal oxides ~~is~~ are often ~~used~~ applied in biodiesel production such as MgO, ZnO, SnO_2, 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 ~~is~~ has potential ~~for~~ in biodiesel applications with significant quantity and efficiency of use [6]. Additionally, ~~and~~ it~~s~~ is cheap and readily ~~availability~~ 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~~ process's catalytic activity [8]. Nowadays, research on applying various catalytic aids for CaO ~~has been increasing in~~ for overcoming this problem has been increasing [9,10]. ~~So t~~The solution is to modify CaO to stabilize the catalyst in repeated use, ~~for example,~~ such as modification with TiO_2 metal ~~metal~~ (titanium).

Titanium is one of the catalytic supports that has been heavily investigated ~~studied~~ based on several considerations such as its high surface area, high structural strength, strong chemical structure, good thermal stability~~,~~ and non-toxic properties [11]. TiO_2 also has a small crystal size and high adsorption power [12]. Due to ~~these~~ the aforementioned advantages, several studies on the use of TiO_2 metal with other metal modifications have been conducted. For example, ~~include:~~ Li was impregnated with TiO_2 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 TiO_2 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,~~ M. Mohammad suggested the modification of TiO_2 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, TiO_2 is suitable for modifying CaO, ~~in which~~ whereby the catalytic activity can be ~~more~~ steady~~ier~~ ~~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 temperature~~s~~ and pressure~~s~~, 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 TiO_2. This involves the ~~Modification~~ modification of a CaO-TiO_2 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~~ was obtained from traders who sell fried foods in the Padang area. The Limestone ~~is~~ was obtained from the Lintau Buo area of West Sumatra. TiO_2, CH_3OH, and n-hexane ~~are~~ were obtained from Merck in Indonesia. All ~~those~~ of the chemicals ~~are~~ 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 hours. After that, the sample was crushed and calcined at 900 °C for 5 h, to produce CaO. ~~In this study, t~~The transesterification reaction ~~used~~ utilized a catalyst prepared ~~with~~ by the wet impregnation method [17]. CaO was mixed homogeneously with TiO_2 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 4000-500 cm^{-1} to determine the catalyst's functional groups. BET analysis was conducted to determine the surface area (SA) and pore distribution with N_2 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 spectroscopy (GC-MS) of FAAEs 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 ~~is~~ was immersed in an oil bath to control the reaction temperature, until it ~~reaches~~ reached ~~(~~35-75 °C~~)~~. The catalyst was loaded with variations (1-7 % of oil weight). After that, methanol and oil ~~are~~ were 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~~ours)~~ ~~at variations in~~ at a temperature range (55-70 °C~~)~~. ~~The oil used in the transesterification reaction is w~~Waste frying oil in a hot state of 50 ºC 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 was used~~s~~:

$$\text{Yield of biodiesel (\%)} = \frac{\%\text{Area Gc Biodiesel} \times \text{Weight of product}}{\text{weight of Waste Frying Oil}} \times 100\%$$

3. ~~Resul~~Results and Discussion

3.1 EDX analysis

Figure 1A shows the EDX results of the CaO-TiO_2 catalyst before the transesterification reaction. ~~Furthermore, t~~The EDX results indicate the presence of Ca and Ti atoms in the sample. Meanwhile, Figure 1B ~~is about a~~ shows the CaO/TiO_2 catalyst after the reaction, which ~~shows~~ indicates the presence of Ca and Ti atoms~~' presence~~. However, there was a change in composition, namely, a decrease in the number of Ca and Ti atoms from the catalyst's surface. ~~this~~ This case