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Regeneration study of CaO/K_2O-TiO_2/H composite catalyst used for biodiesel synthesis: The effect of desorption and calcination

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Abstract
Catalysts can enhance the reaction rate and make efforts in a certain direction into biodiesel synthesis. Solid catalysts have advantages compared with liquid catalysts, one of those can be regenerated. Catalyst regeneration can be carried out using desorption and calcination. The purpose of this study was to observe the effect of various solvents in desorption and temperature on calcination in regenerating the CaO/K_2O-TiO_2/H composite catalyst after it used for biodiesel synthesis from used cooking oil (UCO) in a one-step esterification and trans-esterification process. The catalyst was prepared by CaO prepared from eggshell which is impregnated by KOH and loading TiO_2/H to form a CaO/K_2O-TiO_2/H composite. The composite is used as a catalyst for converting UCO into biodiesel in a one-step process. Furthermore, the catalyst of the process was regenerated with ethanol and acetone desorbed and calcined at 400, 500, 600 and 700°C. The results showed that the acetone desorbed after using catalyst in cycle-3 was higher biodiesel yield of 65.32% than ethanol (60.47%). The calcination temperature also has an effect in increasing the conversion ability into biodiesel, the highest at 600°C of 84.86% biodiesel yield. The performance of catalyst for synthesizing biodiesel can be increased by solvent desorbed and calcination methods, so that it is important considered.

Keywords: biodiesel, calcination, CaO/K_2O-TiO_2/H composite catalyst, desorption, regeneration

Introduction

Potentially clean fuel biodiesel is primarily made by trans-esterifying vegetable oils, animal fats and waste oils with methanol and a catalyst. In addition to plants and animal fats, used cooking oil (UCO) can also be a promising and cost-effective feedstock for the production of biodiesel [1, 2]. One of the potential biofuel feedstocks for use in Indonesia is UCO, which contains free fatty acids (FFAs) over 1%. The most crucial step in creating a renewable energy source is the conversion of the UCO [3].

The solid catalysts were chosen to overcome properties weaknesses of the liquid catalyst. The strength of solid catalysts including the biodiesel synthesis process using only a few units of separation and product purification so it becomes more efficient [4, 5]. In addition, solid catalysts are also non-corrosive, environmentally friendly and can be regenerated, so that it can be reused [6]. Meanwhile, the advantage of a bifunctional solid catalyst has both surface acid and base sites of the catalyst, which can be function at the same time [2, 7]. The bifunctional solid catalyst makes it possible to catalyze the esterification and trans-esterification reactions continuously, so that the process of biodiesel synthesis from UCO with FFAs more than 1% can be simplified into one-step process [8].

Calcium oxide (CaO) is a good solid catalyst for transesterification reaction in biodiesel synthesis. CaO has many advantages including insoluble in methanol, high activity, relatively long shelf-life, and cheap [9]. However, when pure CaO is used, it still has weaknesses, namely it is quickly hydrated and easily carbonated at room temperature, and when mixed with methanol is quickly forming a paste, so the role of the catalyst becomes less stable. As a result, the conversion of oil into biodiesel decreases [10]. This weakness can be overcome by utilizing the CaO-matrix from culinary waste (green CaO), which is structurally more stable than pure CaO. Green CaO as an environmentally friendly matrix can be obtained from waste, including crab shells, bones, and eggshell. The high content of CaO in eggshell can be used as support of solid catalyst for biodiesel synthesis.

Increasing the stability of CaO and forming a bifunctional catalyst (the unity of catalyst properties for two in one functions) can be conducted by KOH impregnated and acid activated-TiO_2 to form a CaO/K_2O-TiO_2/H composite with both surface acidity and basicity [11]. The combined properties of this catalyst make it possible to continuously support esterification-transesterification reactions to form methyl esters (biodiesel). The catalyst regeneration process was carried out by a desorption method (removal of residual oil and methanol from the catalyst surface) and calcination (thermal decomposition of oil compounds to appear again pores and active sites on the catalyst surface). The method was chosen because it is easy to do, effective results obtained, and also efficient. Furthermore, to prove the effectiveness of the regeneration method, the performance test of the regenerated catalysts are carried out on the biodiesel yield and its characterization.

Materials and methods

Materials

In this the experiments were used chicken eggshell and UCO collected from culinary waste in Gianyar-Bali, KOH (99.8% purity), TiO_2 (98% purity), sulfuric acid (95-97% purity), methanol (99.9% purity), ethanol (95%) and acetone (95%).

Methods

Preparation of CaO/K_2O-TiO_2/H catalyst. (1) Green CaO is prepared from eggshell (in powder), by the decomposition of thermal. A hundred g of green CaO are mixed with 200

mL of distilled water and a solution of 1.25 mole/L KOH 25 mL and then stirred for 3 h. The component is repeatedly washed free of base residual, furthermore dried at 110°C for 5 h and calcinated at 600ºC for 5 h [12] as CaO/K_2O. (2) The prepared TiO_2/H, 10 g TiO_2 powder is impregnated with sulfuric acid solution of 200 mL of 0.5 mole/L and stirred, by the medium of stirring speed of a magnetic stirrer for 24 h. Then, it is repeatedly washed free of sulfate ions and filtered using Whatman 1 filter paper. Next, it was calcinated at 500ºC for 4 h [1, 11, 13]. (3) CaO/K_2O-TiO_2/H composite is prepared by physical mixing-calcination method. The TiO_2/H is mixed evenly with CaO/K_2O of 1:3 mass ratio in a porcelain dish and added distilled water in 1:2 ratio, then calcinated at 550ºC for 3 h [11].

Catalyst regeneration

After converting the UCO into biodiesel, 5 g CaO/K_2O-TiO_2/H bifunctional solid catalyst is desorped with 50 mL of ethanol and acetone, respectively, by stirring using a magnetic stirrer for 1 h. The desorption process is repeated for 3 times. After stirring for 1 h from each repetition, filtering is done with Whatman 1 filter paper, then dried in an oven at 110ºC for 3 h. Afterward, the desorbed catalysts are calcined at 400, 500, 600 and 700ºC for 3 h. The regenerated solid catalysts are characterized its physical and chemical properties, including surface acidity-basicity by acid-base titration method and specific surface area by surface area analyzer with N_2 sorption (Brunaurer-Emmett-Teller, BET method).

The regenerated CaO/K_2O-TiO_2/H activity testing into biodiesel synthesis

Synthesis of biodiesel in a one-step esterification and transesterification process is conducted using a solid catalyst of CaO/K_2O-TiO_2/H at catalyst concentrations to oil of 5%; mole ratios of oil/methanol of 1:9; and 60 min reaction times. This step is done at 65ºC and low scale mixing intensity [14]. Synthesized biodiesel is calculated as percent.

$$\text{yield} = \frac{\text{Amount of synthesized biodiesel}}{\text{Amount of sample oil used in the reaction}} \chi\, 100 \quad [15, 16, 17]$$

Functional groups and FFAs of biodiesel are analyzed by Fourier Transform Infrared (FT-IR) and acid-base titration method, respectively.

Results and discussion

Optimization of catalyst regeneration

Based on the Table 1, the regenerated catalyst by desorption using acetone relatively higher biodiesel yields is compared to using ethanol. The residue from a biodiesel synthesis process that is bound on the surface of the catalyst is more easily desorbed by acetone than ethanol. The residue bounding on the surface of the catalyst can be a mixture with oil, biodiesel, glycerol and methanol, so that the difference in the polarity of desorption agent greatly determines the cleaning (desorption) on the surface of the catalyst. The acetone, which is semi-polar compared to ethanol which is polar, is better able to clean on the surface of the catalyst from impurities.

Table 1: Biodiesel yield after catalyst desorbed with ethanol and acetone at a drying temperature of 110ºC

Cycle	Biodiesel yield (%) after catalyst desorbed with ethanol	Biodiesel yield (%) after catalyst desorbed with acetone
1	90.41	90.41
2	77.88	80.15
3	60.47	65.32

Increasing the calcination temperature in the catalyst regeneration process causes an increase in the yield of biodiesel (Table 2). The regenerated catalyst at 600ºC provided the highest biodiesel yield (21.52% increase) and relatively the same performance at 700ºC. This means that the catalyst regeneration process at 600ºC is optimized for biodiesel synthesis. At this temperature, there has been a maximum release of impurities that covering the pores and active sites on the surface of the catalyst, so that the performance of catalyst increases again compared to the calcination temperature of 400-500ºC.

Table 2: Biodiesel yield after catalyst desorbed with acetone at cycle-3 in various calcination temperature

Biodiesel yield (%) in various calcination temperature				
110ºC	400ºC	500ºC	600ºC	700ºC
65.32	75.43	82.64	84.86	84.58

Biodiesel characterization

The effect of calcination on catalyst after the desorption process (Table 3), gives an increase in the conversion of FFAs (from 6.07 initial content of acid value) into biodiesel and also has a linear effect on the acid value of biodiesel. The effect of calcination gives a significant value (increase of 8.56%) for the conversion of FFAs into biodiesel and 0.52 for the acid value of biodiesel.

Table 3: FFAs conversion into biodiesel synthesis with presence regenerated catalyst

Conversion of FFAs (%) on desorbed catalyst without and with calcination		Acid value of biodiesel on desorbed catalyst without and with calcination	
110ºC	600ºC	110ºC	600ºC
70.83	79.39	1.77	1.25

Based on Fig. 1 (a) and (b), the functional groups of biodiesel have been seen below the FT-IR spectra results. The result showed strong and broad vibration peaks of the hydroxyl group (O-H) at wavenumber around 3300-3700 cm^{-1}, C-H (methyl group) stretching of the alkane group at around 3000-2800 cm^{-1}, C-C at around 2345-2370 cm^{-1} and C=C aliphatic appeared at around 1500-2000 cm^{-1}. The carbonyl group (C=O) of the ester seen at around 1600-1700 cm-1 and COOH at around 1350-1400 cm^{-1} in both samples. The metoxy groups ($O-CH_3$) appeared at around 1250-1300 cm^{-1}, C-O-O of the carboxylate group asymmetry appeared at around 1100-1200 cm^{-1} and $-CH_2$ appeared at around 725-910 cm^{-1} [18, 19, 20]. However, the specific functional groups of $O-CH_3$ in both (a) samples vibration peaks at 1261-1263 cm^{-1} were lower intensity (41.67%) than (b) sample of intensity 42.52%.

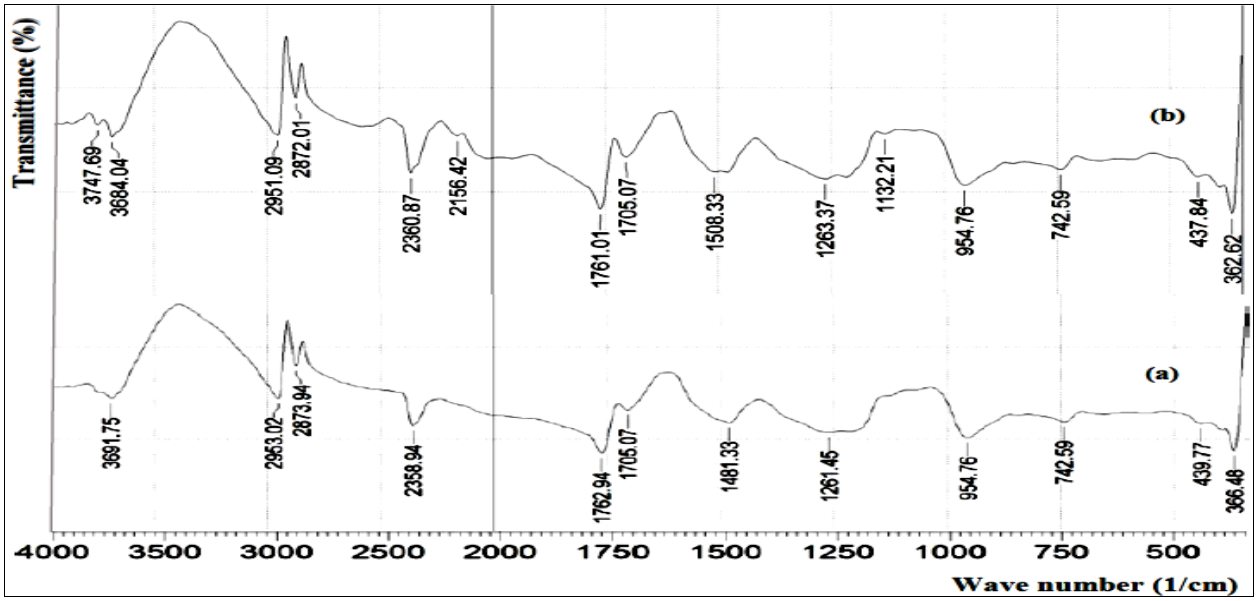

Fig 1: The functional groups of biodiesel on acetone desorbed catalyst: (a) without cacination and (b) with cacination

Catalyst characterization

The acidity-basicity characterization of the surface of catalyst due to calcination temperature at 600ºC increased significantly is compared to that without calcination (at 110ºC) (Table 4). The catalyst resulting from desorbed with acetone without calcination, the active sites on the surface of catalyst were covered with impurities. These impurities can be in the form of residual methanol, unconverted oil, as well as residual conversion products (biodiesel and glycerol). Meanwhile, the calcination process at 600ºC was able to remove impurities covering the active sites on the catalyst surface, resulting in a significant increase in surface acidity-basicity. It has a significant effect on the biodiesel yield (Table 3), that the increase in biodiesel yield is influenced by the specific surface area of catalyst and the number of surface-active sites (surface acidity-basicity of catalyst).

Table 4: Surface basicity-acidity of desorbed catalyst with acetone without and with calcination at 600ºC

Surface basicity (mmole/g) of desorbed catalyst with aceton without and with calcination		Surface acidity (mmole/g) of desorbed catalyst with acetone without and with calcination	
110ºC	600ºC	110ºC	600ºC
8.4430	14.5057	0.0000	0.0039

The specific surface area of catalyst by BET method (Table 5), showed that its value decreases after being used for conversion. After the regeneration process with acetone, there was an increase in the specific surface area when its calcination temperature carried out at 600ºC compared than without calcination (heating at 110ºC). This shows that the calcination process can evaporate and release impurities that cover the pores of the catalyst. According to Fertal et al. (2021), the calcination effect on catalyst over 500ºC occurred the evolution of H_2O- and CO_2-related species of organic matter formed upon exposure to air, so that following differences in the properties such as increasing specific surface area, surface species and its activity [21]. However, over 700ºC can reduce the properties of catalyst due to occurr agglomeration and covering surface active sites [22].

Table 5: Specific surface area of the fresh catalyst and the desorbed catalyst of acetone without and with Calcination

Catalyst type	Specific surface area (m^2/g)
Fresh catalyst	2.902
Desorbed catalyst without calcination (110ºC)	0.490
Desorbed catalyst without calcination (600ºC)	0.854

Conclusion

The acetone desorption ability on the 3-cycle catalyst was higher biodiesel yield (65.32%) compared to ethanol (60.47%). The calcination temperature on catalyst after desorbed with acetone also had an effect increasing its ability to convert into biodiesel, the highest at 600ºC (84.86% biodiesel yield). The characterization of the regenerated catalyst showed linear results with the conversion of oil into biodiesel.

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