

Green CaO-based composite catalyst for biodiesel synthesis simultaneously: Effect of free fatty acids (FFAs) toward its stability

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Abstract

Solid catalyst has been known to be material that can increase the reaction rate of biodiesel synthesis through esterification and/or transesterification that has better stability than liquid catalyst. The CaO-based solid catalyst is prepared from chicken eggshells impregnated with KOH solution and loaded by TiO₂/H to form CaO/K₂O-TiO₂/H composite. This composite is used as solid catalyst for the conversion of used cooking oil (UCO) into biodiesel in simultaneous esterification-transesterification reaction. The composite catalyst is tested for its stability by adding various concentrations of oleic acid in the UCO (0.5 to 2.5 wt). The results showed that the catalyst stability were obtained by adding 1.5% oleic acid. H-NMR and FT-IR analysis showed that the chemical compounds of biodiesel were methyl esters, with a specific functional group of CH₃-O at chemical shift of 3.63 ppm and at wave number of 756.13 cm⁻¹. Herein, we can conclude that the catalyst stability for biodiesel synthesis is influenced by the presence of FFAs.

Keywords: Biodiesel, CaO/K₂O-TiO₂/H composite, solid catalyst, oleic acid, free fatty acids

Introduction

Calcium oxide (CaO) is a good solid catalyst for transesterification reaction in biodiesel synthesis. CaO has many advantages including high activity, insoluble in methanol, relatively longer usage time, and economical [1]. CaO can be sourced from clamshell [2], CaO in dolomite [3], CaO from eggshell [4], and pure synthetic CaO [5, 6]. Currently, eggshells are widely utilized for applications on an industrial scale [4, 7]. Eggshells contain CaO as the main constituent, which can be used as a potential candidate for composite synthesis, so that the disadvantages of CaO that can be hydrated, easily carbonated at room temperature, and easily form a paste when mixed with liquid can be minimized [8].

Improving the stability of CaO to form a bifunctional catalyst (unity of catalyst properties for two functions) can be modified through the addition of KOH and acid-activated TiO₂ to form acidity and surface basicity at once. The combined catalyst properties make it possible to support simultaneous esterification-transesterification reaction in the synthesis of biodiesel from used cooking oil (UCO). However, the stability of the combined catalyst properties is also strongly influenced by the content of free fatty acids (FFAs) in UCO [9].

Solid catalysts for biodiesel production have been developed by previous researchers, including: K/TiO₂ solid catalyst for the canola oil esterification reaction [10]; Istadi *et al.* (2015), studied K₂O/CaO-ZnO catalyst for soybean oil transesterification [11]; Carlucci *et al.* (2019), reported that a suitable solid catalyst developed for esterification reaction is sulfated TiO₂ [12]; and He *et al.* (2016) and Carlucci *et al.* (2019), mentioned that the SO₄/TiO₂ compound is said to be a super acid that is good for esterification reaction and has good stability [12, 13]. However, all of these solid catalysts have not been utilized for simultaneous esterification-transesterification reaction. Besides, the SO₄/TiO₂ used is made from pure nanoparticles, making the catalyst separation process difficult and the operational costs relatively high. Therefore, the application of CaO-based

solid catalyst prepared from waste chicken eggshell to form CaO/K₂O-TiO₂/H composite functional properties in the simultaneous synthesis of biodiesel from UCO. Furthermore, the stability study of the catalyst was conducted in the presence of increased FFAs content and increased water content on biodiesel yield.

Materials and Methods

Materials

The materials that were used in these experiments, namely waste chicken eggshell as a source of CaO and UCO (FFAs content of 3.05%) from Gianyar-Bali, KOH (pro analysis), and TiO₂ (purity: ≥ 98%).

Methods

Preparation of CaO/K₂O-TiO₂/H composite bifunctional catalyst. CaO/K₂O was modified with TiO₂/H by solid state reaction. CaO/K₂O was mixed evenly with TiO₂/H in a porcelain cup with a weight ratio of 3:1, then calcinated at 550°C for 3 h. The synthesized catalyst was coded as CaO/K₂O-TiO₂/H.

Stability testing of catalyst in biodiesel synthesis. The UCO was filtered first to remove impurities. Heating the UCO is done to evaporate the water at 110°C for 30 min. After the heating process, the UCO is then allowed to cool down to 50-55°C [14]. Simultaneous esterification-transesterification reaction in biodiesel production was conducted with 5% CaO/K₂O-TiO₂/H catalyst, 9:1 methanol/oil mole ratio, and 60 min reaction time at 65°C [15]. The solid catalyst was tested stability for the conversion of UCO into biodiesel toward the addition of 0.5; 1.0; 1.5; 2.0; and 2.5% wt oleic acid [9]. The synthesized biodiesel is calculated as mass yield of

$$\frac{\text{mass of synthesized biodiesel}}{\text{mass of oil}} \times 100$$

and FFAs conversion percent calculated as

$$\frac{\text{FFAs of oil} - \text{FFAs of synthesized biodiesel}}{\text{FFAs of oil}} \times 100$$

, respectively [8, 16, 17].

Results and Discussion

Data in determination of biodiesel yield, FFAs conversion, and acid value in various adding oleic acid concentrations in UCO are presented in Fig. 1.

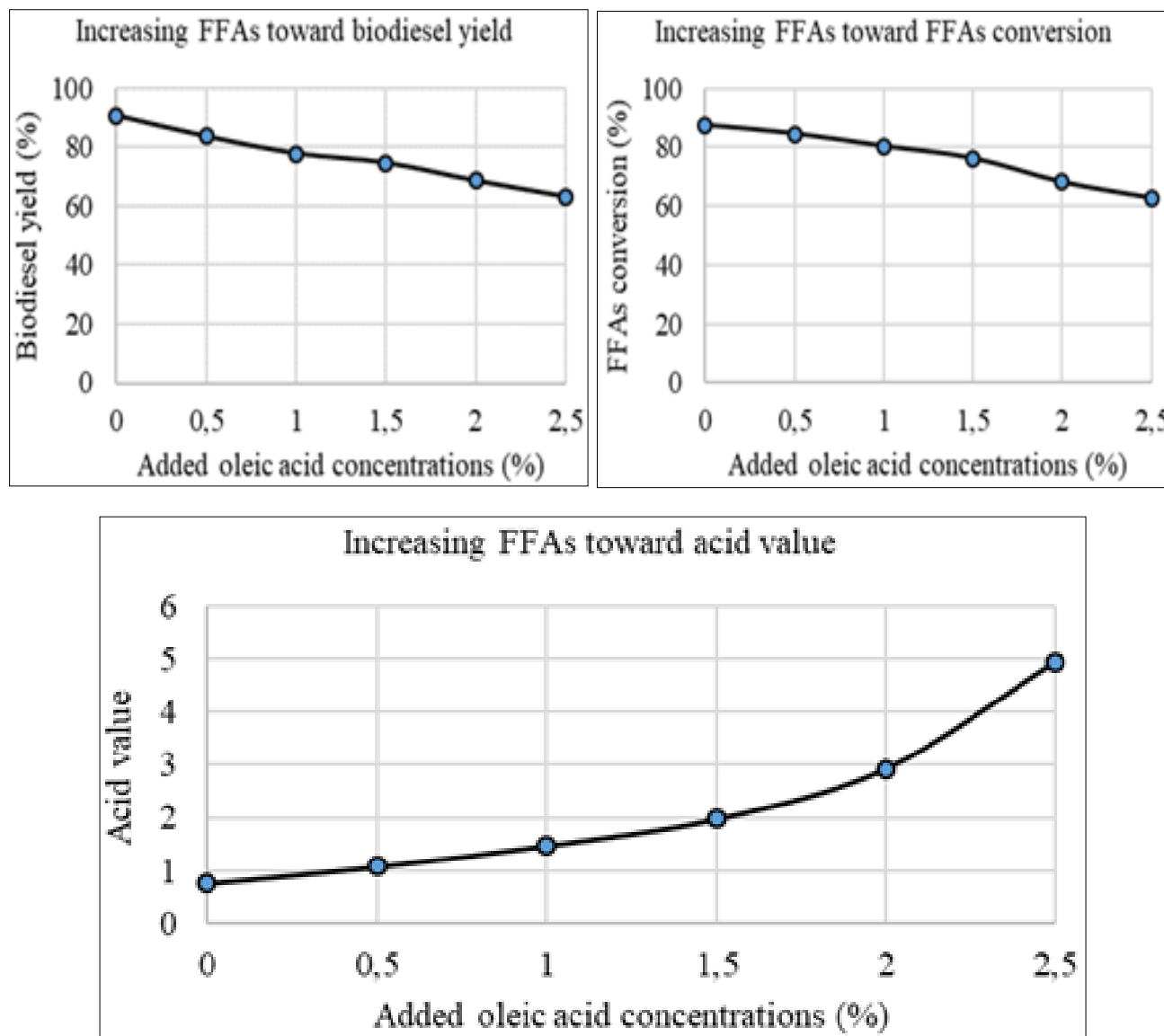


Fig 1: Biodiesel yield, FFAs conversion, and acid value in various adding oleic acid concentrations in UCO

Based on the Fig. 1, it was found that increasing the concentration of FFAs in the UCO can cause a decrease in biodiesel mass yield. The decrease in biodiesel mass yield is thought to be caused by the reduction of acidic sites and basic sites on the catalyst surface due to the reaction with FFAs in the UCO (3.05%) and due to the addition of oleic acid. However, the addition of oleic acid at concentrations of 0.5 to 1.5% caused the percent conversion of FFAs to increase relatively less than the biodiesel yield. Meanwhile, the addition of 2.0 to 2.5% oleic acid concentrations decreased the percent conversion of FFAs. This is due to the fact that the addition of oleic acid at concentrations of 0.5 to 1.5% resulted in maximum conversion into biodiesel. The addition of 2.0 to 2.5% oleic acid concentrations have seen the formation of soap due to the reaction between FFAs and the base sites of the catalyst, so that the produced biodiesel yield has decreased. This is in line with the results of Nasreen *et al.* (2015) [9], who utilized solid catalysts made from pure La/Mn oxide for the conversion of soybean oil

into biodiesel, with the addition of FFAs up to 1.5%, the triglyceride conversion results were still stable, but when the addition of FFAs above 1.5%, it decreased drastically due to soap formation.

H-NMR analysis

The determination of the chemical compound content of biodiesel was analyzed by proton H nuclear magnetic resonance (H-NMR). The result of H-NMR analysis of biodiesel at 1.5% oleic acid addition is presented on Fig. 2 and the spectra of standard oleic acid presented on Fig. 3. The results of biodiesel analysis have provided a specific indication of ester compounds (methoxide groups, O-CH₃) occurring at a chemical shift (δ) of H protons in the round of 3.63 ppm, which is a specific group of methyl esters (biodiesel) [18]. This means that the oleic acid has been converted into methyl esters. Meanwhile, when compared with the H-NMR spectra of oleic acid as a blending acid in UCO, it showed that the chemical shift does not appear.

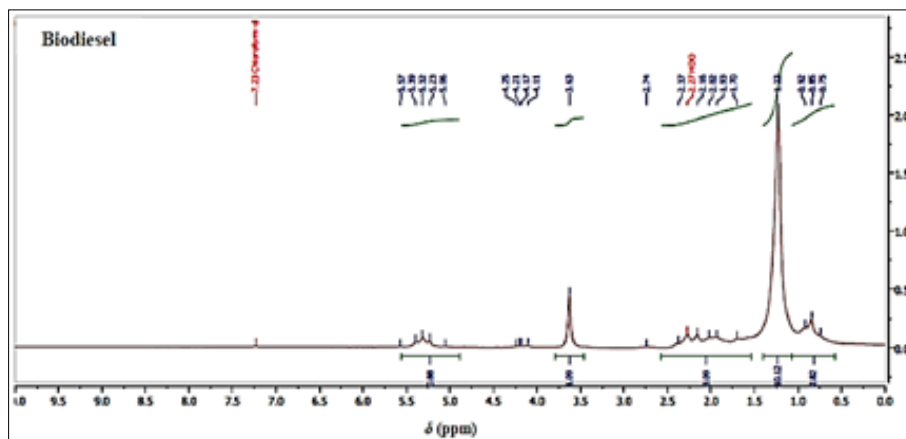


Fig 2: H-NMR spectra of biodiesel on adding 1.5% oleic acid

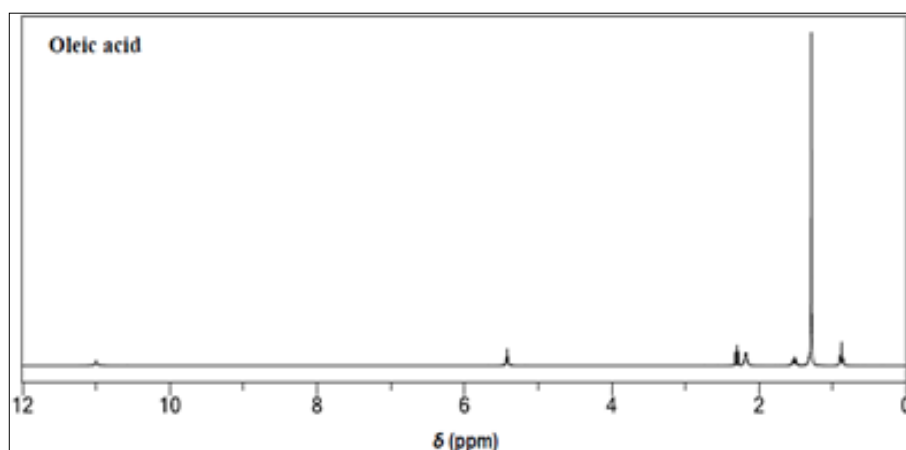


Fig 3: H-NMR spectra of oleic acid standard

FT-IR analysis

The results of FT-IR analysis of biodiesel at the optimum addition of 1.5% oleic acid are presented in Fig. 4. The result showed strong and broad vibration peaks of the hydroxyl group (O-H) at wave numbers 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 1400-1500 cm^{-1} in both samples.

Specific functional groups in wave numbers around 1250-1350 cm^{-1} as O-C=O or O-CH₃ stretching, wave numbers around 1500 as the presence of CH₃ groups and C-O as well as O-CH₃ bending functional groups in the 700-800 cm^{-1} absorption region [19, 20, 21]. The specific functional groups of O-CH₃ are appearing in wave numbers 1320.33 cm^{-1} stretching and 756.13 cm^{-1} bending. These peaks do not appear in the FT-IR results of oleic acid. This is because oleic acid does not contain these functional groups.

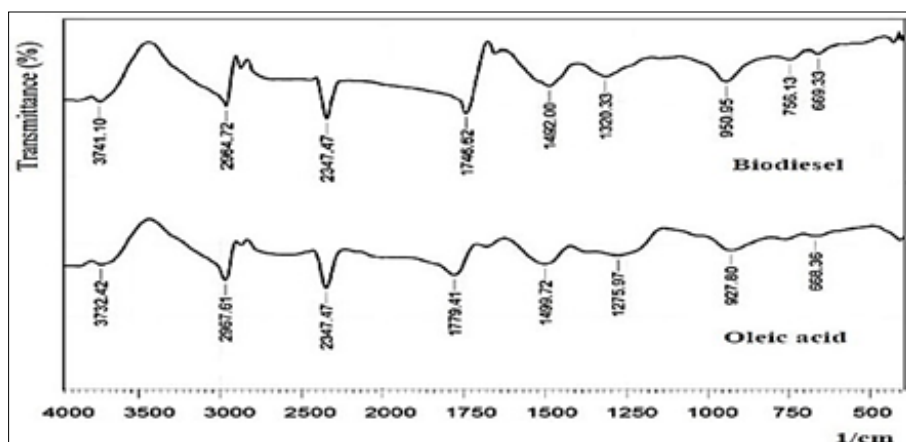


Fig 4: FT-IR spectra of biodiesel on adding 1.5% oleic acid

Conclusions

The catalyst stability toward oleic acid addition was obtained up to 1.5% and 2.0%, respectively. Increasing the

addition of oleic acid caused the biodiesel yield and FFAs conversion decreasing, with the acid value increasing. The results of FT-IR and H-NMR analysis at 1.5% oleic acid

addition showed that the chemical compounds content of biodiesel was methyl esters, with a specific methoxide group (CH₃-O) at a chemical shift of 3.63 ppm and functional groups of CH₃-O stretching and bending at wave numbers of 1320.33 cm⁻¹ and 756.13 cm⁻¹, respectively. The conclusion that the catalyst stability for biodiesel synthesis can be influenced by the presence of FFAs in the oil.

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