Utilization of Modified Coal Fly Ash (CFA) as a Catalyst for Production of Biodiesel from Coconut Oil_ Part 1 - Characteristics of the Catalyst

by Arif Hidayat

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Utilization of Modified Coal Fly Ash (CFA) as a Catalyst for Production of Biodiesel from Coconut Oil: Part 1 - Characteristics of the Catalyst

ARIF Hidayat[1], ACHMAD Chafidz[1,2,a*], BACHRUN Sutrisno[1]

[1]Chemical Engineering Department, Universitas Islam Indonesia, Yogyakarta 55584, Indonesia

[2]Study Center for Material Science and Technology, Chemical Engineering Department, Universitas Islam Indonesia, Yogyakarta 55584, Indonesia

[a]achmad.chafidz@uii.ac.id

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Abstract. The current research studied about the utilization of modified coal fly ash (CFA) as catalyst for biodiesel production from coconut oil. Coal Fly ash (CFA) is a solid waste that is abundantly available in the coal-based power plant. Coal Fly Ash is a type of material that has high content of oxide minerals, e.g. silicates and silicate alumina. With proper physical/chemical treatment, the coal fly ash can be converted into a heterogeneous catalyst. In this work, the coal fly ash was modified with HCl and $Ca(NO_3)_2{\cdot}4H_2O$ and used as catalyst for biodiesel production from coconut oil. This paper will focus only on the characteristics of the prepared modified CFA-based catalyst. The modified CFA-based catalyst was characterized for its crystallinity using X-Ray Diffraction (XRD), determined its surface area and pore size distribution using Surface Area Analyzer, and its functional groups by Fourier Transform – Infra Red (FT-IR). The specific surface area of the catalyst (modified CFA) decreased from 28.08 m^2/g to 17.54 m^2/g after impregnation process of calcium oxide in the raw coal fly ash. This decrease was also accompanied by a decrease in the average pore network from 32.59 Å to 20.31 Å. Additionally, based on the XRD pattern shown, the raw CFA is composed of mostly quartz (SiO_2) and mullite ($3Al_2O_3.2SiO_2$) minerals, and a small portion of hematite.

Introduction

Biodiesel is an alternative fuel for diesel engine that can be made from vegetable and animal oils that are environmentally friendly. They have the advantage of not containing sulfur and benzene which are carcinogenic. Biodiesel is made from triglycerides and fatty acids from vegetable and animal oils with a chemical reaction called transesterification and esterification. In this process oil is reacted with alcohol with the help of catalysts, both acidic and basic catalysts [1, 2]. One of the raw materials for making biodiesel is coconut. Coconut is the result of plantations in Indonesia that are available throughout the year. Coconut meat contains 40-60% oil [3]. The production of biodiesel from coconut oil is carried out by transesterification reaction. Transesterification is a chemical process that brings together an alkoxy group in an ester group with alcohol [4]. Transesterification is an alcohol transfer reaction from esters by other alcohols that is related to three sequential reversible reactions. Biodiesel synthesis through the transesterification reaction between oil and alcohol takes place according to Fig. 1.

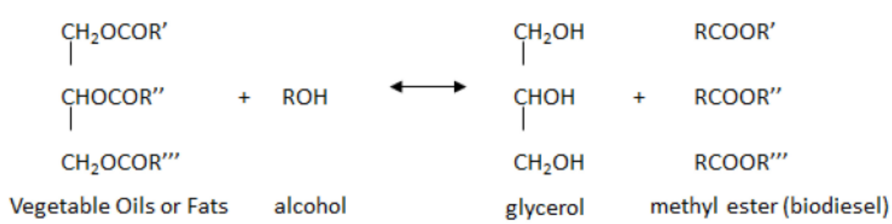

Fig. 1. Triglyceride transesterification reaction with alcohol.

Where R ', R' ', and R' " are fatty acid alkyl clusters. The constituent fatty acids can be saturated fatty acids and unsaturated fatty acids. Unsaturated fatty acids are fatty acids that have double bonds on carbon bonds, for example oleic acid, linoleic acid. Saturated fatty acids are fatty acids that do not contain carbon bonds in their carbon bonds [5]. There are three conditions for carrying out a transesterification reaction, namely an acid catalyzed reaction, an alkaline catalyzed reaction, or an enzyme catalyzed reaction [6]. Processes that use enzymes as catalysts require a much longer reaction time than other processes. There are three kinds of transesterification processes that are commonly carried out to make biodiesel from vegetable oils, which are: (1) transesterification with basic catalysts, (2) transesterification with direct acid catalysts, (3) conversion of vegetable oils / fats to fatty acids proceed to biodiesel [7]. Almost all biodiesel is produced by the transesterification method using a basic catalyst because it is an economical process and only requires low temperatures and pressures. Transesterification reactions are often carried out using basic catalysts because they produce a reaction rate that is much higher than acidic catalysts. Commonly used catalysts are hydroxide bases such as NaOH and KOH.

So far, the synthesis of biodiesel using a homogeneous catalyst. This catalyst has several disadvantages in its use such as the difficulty of separating the product from the catalyst, resulting in hazardous waste to the environment because the remaining catalyst cannot be reused, and the difficulty of handling and storage. An alternative that can be used is the use of solid (heterogeneous) catalysts. Heterogeneous catalysts have advantages in terms of the separation process after an easier reaction, high activity, can be used repeatedly and a high lifetime, and more environmentally friendly. Coal Fly ash (CFA) is a solid waste that is abundantly available in the coal-based power plant. Coal Fly Ash is a type of material that has high content of oxide minerals, e.g. silicates and silicate alumina. With a proper physical/chemical treatment it can be converted into zeolite-like materials [8, 9].

There have been numerous research studies about modified CFA used as catalyst for biodiesel production. Bhandari, et al. [10] investigated about preparation of mesoporous catalyst made of CFA for soybean oil transesterification. They synthesized waste CFA into different kinds of zeolites. It was reported that the zeolites have size of averagely 2-5 μm with maximum surface area of 727.2 m^2/g. Similarly, Manique, et al. [11] also reported about transesterification process for biodiesel production from soy oil using CFA-based sodalite (zeolite) as heterogenenous catalyst. The zeolite type sodalite was prepared via hydrothermal process in alkali medium. Xiang, et al. [12] studied about utilization of modified CFA as a catalyst for biodiesel production from waste cooking oil. In the current research study, modified coal fly ash was utilized as catalyst for synthesis of methyl ester from coconut oil. The CFA was modified using sodium sulphate and sodium hydroxide. The synthesized catalyst was characterized by X-Ray Diffraction (XRD), Fourier Transform-Infra Red (FT-IR), and Surface Area Analyzer.

Experimental

Materials and methods. The coal fly ash obtained from the PLTU was first carried out by grinding and screening to obtain a uniform particle size. The activation process is then carried out by mixing coal fly ash with 3N HCl solution, where the number of components in the reflux system is 50 g of coal fly ash and 500 mL mixture of 3N HCl solution. Reflux is carried out at reflux temperature for 4 hours. Refluxed coal fly ash is then neutralized by adding distilled water to neutral pH. After neutral pH, the fly ash is then roasted for about 2 hours. Then impregnation of Calcium metal is carried out into the activated fly ash material. The impregnation process is by mixing activation fly ash with precursors of $Ca(NO_3)_2 \cdot 4H_2O$ salt solution. The loading process is carried out at reflux temperature for 8 hours and followed by a drying process to evaporate the solvent. After drying, the fly ash material is then calcined in the furnace at a temperature of 500 °C for 4 hours. The synthesized catalyst (i.e. modified CFA) was then characterized by measuring crystallinity using X-Ray Diffraction (XRD), determining surface area and pore size distribution with Surface Area Analyzer and functional groups by Fourier Transform Infra Red (FTIR).

Results and Discussion

X-Ray Diffraction (XRD) characterization. The results of X-ray diffraction pattern analysis for coal ash are shown in Fig. 2. Based on the XRD pattern shown, raw coal ash is composed of mostly quartz (SiO_2) and mullite ($3Al_2O_3.2SiO_2$) minerals, and a small portion of hematite. The quartz diffraction pattern is shown at 2θ = 20.86°, 26.65° and 36.5°, while the diffraction peak at 2θ = 26.3°; 39.4° and 64.9° show the existence ofullite. The formation of mullite is related to the process of burning coal at a power plant at temperatures above 1050 °C. XRD analysis of the catalyst showed a characteristic peak at 2θ = 29.0°; 32.5°; 47.5°; and 54.0° which indicates the presence of calcium oxide (CaO).

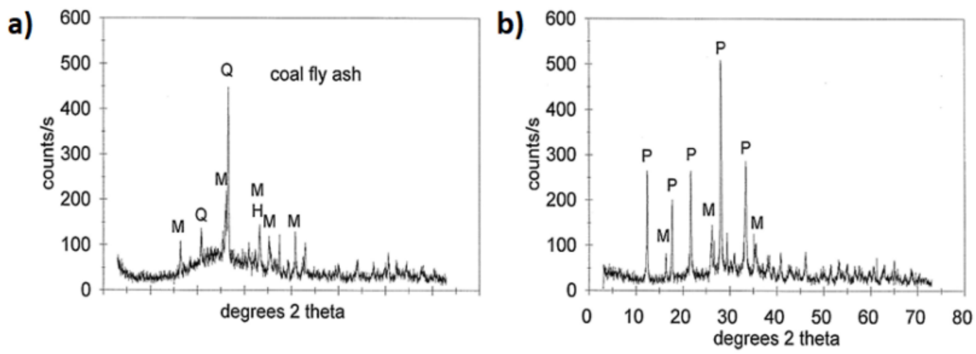

Fig. 2. XRD Analysis Results: (a) fly ash; and (b) catalyst.

Fourier Transform-Infra Red (FT-IR) analysis. To strengthen the results of the analysis of fly ash material characteristics, an analysis was carried out using FT-IR. Spectroscopically, fly ash can be observed in the range of wave numbers 300-1300 cm^{-1}. The wavelength is the main area of tetrahedral bond uptake of the main components making up fly ash, namely SiO_4 and AlO_4. While the results of infra-red spectra analysis for raw fly ash can be seen in Fig. 3. For raw fly ash spectra, it can be seen that the absorption at wave number of 3450 cm^{-1} is characteristic for stretching OH octahedral (OH) strain) of H_2O which is amplified by absorption at wave number of 1641 cm^{-1} which is the deformation absorption of H_2O (OH buckling). Uptake at wave numbers 1047 and and 795 cm^{-1} are asymmetric and asymmetrical strain absorption of external O-Si-O or O-Al-O. Uptake at wave number 461 cm^{-1} is characteristic of Al-O and Si-O bonding.

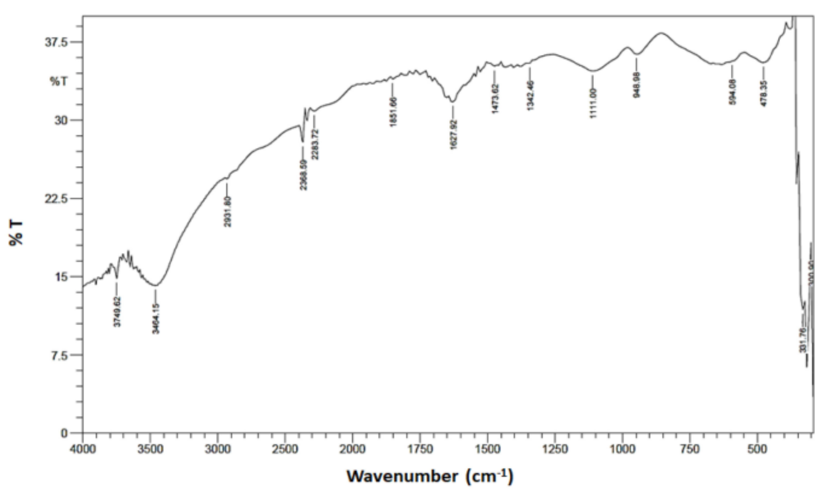

Fig. 3. FT-IR Spectra for Coal Fly Ash (CFA)

Furthermore, to see the effect of acid treatment on the characteristics of functional groups on the surface of the material, a spectral analysis of the activated fly ash is carried out, the results of which can be seen in Fig. 4. From the figure, it can be observed that there is no significant difference in the results of functional group analysis of modified and raw CFA. To facilitate comparison, the results of the IR spectra analysis of the two samples are presented in Table 1.

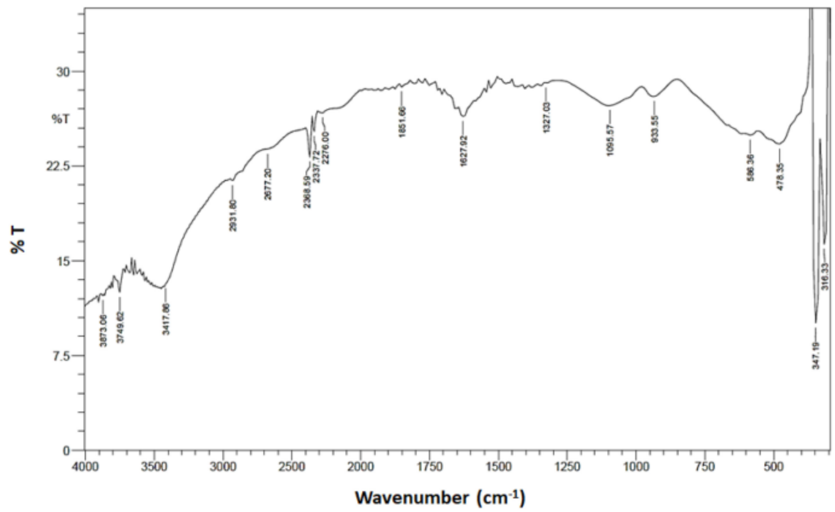

Fig. 4. FT-IR Spectra for Modified Coal Fly Ash (CFA)

Table 1. Comparison of Functional Group Uptake of Raw Ashes and Activated Ashes.

Wavenumber (cm^{-1})		Absorbed functional groups
Raw CFA	Modified CFA	
3450 dan 1641	3450 dan 1639	OH stretch from OH octahedral and or H2O
1047	1059	Internal asymmetrical strain O-T-O, (T = Si and Al)
795	795	O-T-O external symmetry strain, (T = Si and Al)
461	463	vibrational buckling of T-O-T (T = Si)

From the results of the FTIR analysis it appears that there is no significant difference between raw fly ash and fly ash after acid activation indicating no change in functional groups due to acid activation process. In the Al-O and Si-O vibrations there are no significant changes in wave numbers. This indicates that the acid activation process does not damage the Al-O and Si-O bonds.

Specific Surface Area of Solid. The data on the specific surface area of solids, pore volume, average pore network lines are presented in Table 2.

Table 2. Specific Surface Area Analysis Data.

Characteristics	**Modified CFA (catalyst)**	**Raw CFA**
Specific surface area (m^2/g)	17.542	28.075
Pore volume (cm^3/g)	0.2005	0.2316
Average pore radius (Å)	32.59	20.31

The decrease in specific surface area occurred after the process of impregnation of Calcium metal in fly ash from 28.08 m^2/g to 17.54 m^2/g. This decrease in specific surface area is accompanied by a decrease in pore network average from 32.59 Å to 20.31 Å. This shows that the Calcium metal impregnation process causes an increase in the distribution of mineral pore sizes in the mesoporous range as a result of deficiencies in impurities. However, the total volume of pore solids showed an increase. This further supports the assumption of new mesopores formed by the activation process.

Conclusion

The modified coal fly ash (CFA)-based catalyst has been successfully synthesized for the triglyceride transesterification reaction (i.e. biodiesel production) of coconut oil. Modification of the CFA was carried out using sulfuric acid treatment and calcium metal (Ca) treatment. This treatment/modification has improved the physicochemical character of fly ash, which was indicated by the formation of mesopores on the catalyst and the presence of Calcium metal content on the surface of the catalyst which is an active group for the benefit of biodiesel synthesis. The prepared catalyst has the following characteristics. The specific surface area of the catalyst (modified CFA) decreased from 28.08 m^2/g to 17.54 m^2/g after impregnation process of Calcium metal in the raw coal fly ash. This decrease was also accompanied by a decrease in the average pore network from 32.59 Å to 20.31 Å. Additionally, based on the XRD pattern shown, the raw CFA is composed of mostly quartz (SiO_2) and mullite ($3Al_2O_3.2SiO_2$) minerals, and a small portion of hematite.

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