

Synthesis of Biodiesel from Waste Cooking Oil Using the Sulfated Montmorillonite

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Abstract—One of the important factors in biodiesel production is a catalyst. The purpose of this research is to characterize sulfated montmorillonite and its application as catalyst for synthesis of biodiesel from waste cooking oil. Synthesis of sulfated montmorillonite using sulfuric acid as activator and its characterization were performed by using X-Ray Diffraction (XRD), and FTIR analysis. Biodiesel synthesis was carried out by reacting methanol and waste cooking oil with a molar ratio (1: 9) and 1.74 g of catalyst at 65oC for 2 hours. The percentage of methyl ester was analyzed by Gas Chromatography-Mass Spectrometer (GC-MS). Based on XRD analysis data, the addition of sulfuric acid (H₂SO₄) to montmorillonite does not change the basal spacing d001 on the diffractogram but occurs slight shift toward higher angle (2θ). The FTIR analysis results of sulfated montmorillonite show that the sulfated montmorillonite has functional groups, namely –OH, ≡Si-O-Si≡, Al-Al-OH in the tetrahedral and octahedral sheet structures which are the constituents of the mineral montmorillonite. The percentage of methyl ester produced by sulfated montmorillonite were 6.83% methyl palmitate and 24.17% methyl oleate. Based on the results, it can be concluded that sulfated montmorillonite can be used as catalyst for synthesis of biodiesel.

Keywords—sulfated montmorillonite, bentonite, catalyst, biodiesel

I. INTRODUCTION

Energy supply should be increased with the increasing population and the population of the industrial sector in Indonesia in order to avoid an energy crisis. To overcome the energy crisis needed the alternative natural resources that can be renewed as a substitute for petroleum fuels, including biodiesel development. The synthesis of biodiesel as an alternative source to petroleum fuels for development of renewable energy and is conducive to environmental protection [1]. Biodiesel is a fuel substitute produced from plant and animal oils use alcohol via transesterification and esterification reaction in the presence of a catalyst [2]. The advantages of biodiesel to petroleum fuels are biodegradability, bio-renewable nature, very low sulfur content and toxicity, low volatility or flammability, good transport and storage

properties, higher cetane number, and its salutary atmospheric CO₂ balance for production [3].

The synthesis of biodiesel from vegetable oil is carried out through esterification, transesterification or pyrolysis reactions. Esterification reaction is a reaction between fatty acids and alcohols using an acid catalyst which produces ester compounds [4]. Meanwhile transesterification is a chemical process to produce alkyl esters from fatty acid and glycerol by reacting a triglyceride with alcohol in the presence of an acid or base catalyst [5].

The existence of a catalyst also plays an important role in biodiesel production [2]. Catalyst is a substance that plays an important role in the chemical industry where catalysts are used to increase the rate of reaction in chemical processes [2]. In general, biodiesel is produced conventionally using a homogeneous catalyst, such as a strong acid or strong base, but the separation of the product with a catalyst was very difficult [6]. Therefore, research on heterogeneous catalysts has been developed as a substitute for homogeneous catalysts in the production of biodiesel such as clay [7], pillared clay [8], and activated clay [6]. Heterogeneous catalysts have several advantages including stable, high selectivity, reusable, purification processes was simply, safely, and environment friendly.

Based on previous research, it is known that several heterogeneous catalysts used in the synthesis of biodiesel from waste cooking oil include clamshells at temperature 338 K with a molar ratio of 1 ; 2.5 [2], natural zeolite 2% at temperature 333 K with a molar ratio of 6: 1 [9], cengar clay 20% at temperature 333 K with a molar ratio of 6: 1 [6], and Bagasse (Si-alumina) 1% at temperature 330 K with a molar ratio of 6: 1 [10].

Clay is a group of minerals from the phyllosilicate smectite family smectite group has a layered structure and crystalline. The type of clay that has attracted the most attention is bentonite. The main component of bentonite is montmorillonite minerals (85%) [11,12]. Some chemical reactions using montmorillonite as catalysts or catalyst supports such as reaction the hydrogenation reaction of benzene [13], the

reaction hydrocracking plant oils into biodiesel [14], and the esterification reaction of catalyzed acid [4,12,13].

The catalytic performance of clays can be improved by modification through activation using strong acids such as sulfuric acid (H_2SO_4), hydrochloric acid (HCl), phosphoric acid (H_3PO_4), and nitric acid (HNO_3). The acidity of montmorillonite can be increased by acid activation for the formation of large pores in montmorillonite. Acid activation can increase the number of protons (H^+) in the montmorillonite layer because of acid activation, which can leach cations in the octahedral and tetrahedral layers, dissolve impurities, and replace cations in the space between layers with hydrogen ions (H^+). These results can increase the surface area, pore diameter, and the acid site on the catalyst surface.

II. METHODS

The sample of bentonite used in the research comes from Aceh Tamiang, Aceh (Indonesia) in August 2018 and the chemicals used in this research were H_2SO_4 and methanol in pro-analytical grade which were purchased from E. Merck.

A. Catalyst Preparation

The bentonite is crushed and sieved using a 250-mesh sieve. A powder of bentonite (50 g) was put into the ultrasonic bath for 15 minutes. The solution is filtered, and the resulting sludge is called fraction 1. The filtrate results from stage I is stirred 3 times, left for 3 days and filtered to produce a precipitate called fraction 2. Furthermore, the filtrate produced in stage II is stirred 3 times, left for 7 days and filtered until the sediment or fraction is obtained. 3. The filtrate produced in the final stage is evaporated to produce fraction 4. Bentonite is activated using H_2SO_4 2 M with a molar ratio (1:50) slowly and stirred for 24 hours at room temperature [12].

B. Catalyst Characterization

The mineral constituents of montmorillonite and sulfated montmorillonite were analyzed using X-Ray Diffraction (XRD). The X-Ray Diffraction data were obtained by XRD Multiflex Rigaku with Ni-filtered Copper $K\alpha$ radiation of wavelength 1.5406 Å, operated at 40 kV and 30 mA. The presence of functional groups of materials was characterized by FTIR analysis at wave number 400-4000 cm^{-1} using KBr plate.

C. Synthesis of Biodiesel from Waste Cooking Oil

The waste cooking oil is added with methanol (molar ratio 1:9) and 1.74 grams of catalyst in a three-bottom flask. The reaction process was carried out at 65°C for 2 hours [1]. Biodiesel is separated from glycerol. The resulting biodiesel was determined by the percentage of methyl ester using Gas Chromatography-Mass Spectrometer (GC-MS).

III. RESULTS AND DISCUSSIONS

A. The Physicochemical Properties of Sulfated Montmorillonite

1) *X-Ray of sulfated montmorillonite*: XRD analysis of sulfated montmorillonite aims to determine the content of minerals contained in sulfated montmorillonite and see the diffraction pattern at a value of 2θ and the basal spacing of the crystalline lattice. The results of XRD analysis of the sulfated Montmorillonite are shown in Figure 1. Based on the diffractogram in Figure 1, it can be seen that there are diffraction peaks that are typical of Montmorillonite, namely in the area $2\theta = 19.7^\circ$ ($d_{002} = 4.48 \text{ \AA}$), 20.7° and 26.5° . The diffraction peaks in the 2θ region, namely 19.7° (68%) and 20.7° (44%), indicate that the sample contains montmorillonite minerals. In addition, a peak in the area of $2\theta 26.5^\circ$ in the diffractogram pattern indicated the peak of quartz mineral (SiO_2). The diffraction peaks of this quartz mineral have a high level of reflection intensity. Based on XRD analysis data, it shows that bentonite contains the main components of montmorillonite and quartz (SiO_2). The addition of sulfuric acid (H_2SO_4) to montmorillonite did not change the basal spacing d_{001} significantly on the diffractogram. The acid-activated montmorillonite diffractogram in Figure 2 shows angle (2θ) shift and the distance between planes becomes larger (slight shift toward higher angle (2θ)). This shift is due to the reaction between montmorillonite and acid, which results in a decrease in the pore size of acid-activated montmorillonite. This occurs due to a change in the layer arrangement in montmorillonite from a delamination structure (house to card) to a more regular arrangement (face-to-face arrangement) after the activation of sulfuric acid causing the pore size of montmorillonite to decrease after the acid activation process.

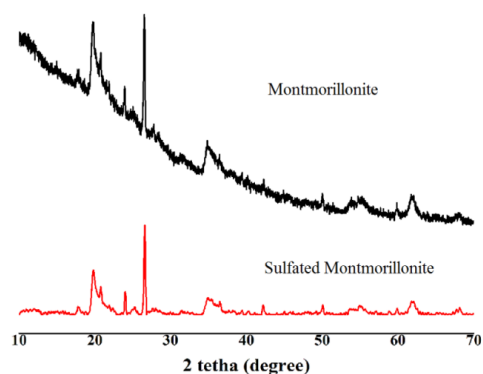


Fig. 1. Diffraction of X-Ray (a) Montmorillonite (b) Sulfated Montmorillonite.

2) *The functional groups of sulfated montmorillonite*: Infrared spectra of montmorillonite and sulfated montmorillonite at a wave number between 4000-400 cm^{-1}

are presented in Figure 2. Figure 2 showed that the activation process of montmorillonite using H₂SO₄ not produced a significant change in the absorption of the characteristic wave number of the functional groups in montmorillonite, namely –OH derived from the bentonite framework and water molecules, Si-O-Si, and Al-Al-OH which is the structure in the octahedral sheet and tetrahedral in bentonite (Table 1).

Figure 2 also showed the absorption intensity of bending –OH on sulfated montmorillonite is higher than montmorillonite. It indicates that the activation H₂SO₄ of montmorillonite is higher compared to montmorillonite before activated. Because of activation process with H₂SO₄ will be dissolve impurities found on the montmorillonite lattice and surface and could be increase acid sites Brønsted and Lewis in the montmorillonite surface. In the activation process, cations such as Na⁺, K⁺ Ca²⁺ were found in the interlayer of bentonite could be exchange with H⁺ from H₂SO₄ [14]. Based on the results, the surface of montmorillonite will become more acidic, more pore size and increase the ability of catalysis.

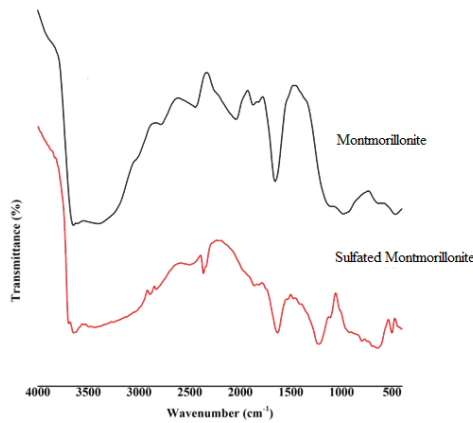


Fig. 2. Spectra of FTIR (a) montmorillonite; (b) sulfated montmorillonite.

TABLE I. THE CHARACTERISTIC OF ADSORPTION PEAK MONTMORILLONITE AND SULFATED MONTMORILLONITE

No	Wave Number (cm ⁻¹)		Functional Groups
	Montmorillonite	Sulfated Montmorillonite	
1	3645.46	3693.84	O-H Streching
2	3606.89	3646.58	O-H Streching
3	1654.95	1631.85	O-H Bending (H ₂ O)
4	1103.28	1113.94	Si-O-Si Streching
5	979.84	920.08	Al-Al-OH Bending
6	632.65	645.22	Si-O Streching (SiO ₂ /quartz)
7	466.77	501.51	Si-O-Si Bending

3) *The percentage of methyl ester from biodiesel:* The GC-MS analysis of biodiesel (Figure 3) which was synthesized

using a sulfated bentonite catalyst are shown in Figure 3. The percentage of methyl ester biodiesel from waste cooking oil is shown in Table 2.



Fig. 3. Biodiesel from Waste Cooking Oil.

TABLE II. THE COMPARISON OF COMPOSITION METHYL ESTER FROM BIODIESEL WASTE COOKING OIL

Composition of methyl ester	Biodiesel	Biodiesel Comparison (Yulanda <i>et al.</i> , 2018)
Methyl Palmitate	6.83%	54.49%
Methyl Linoleat	-	4.98%
Methyl Oleat	24.17%	2.86%

Based on Table 2, it can be seen that the dominant methyl ester composition in biodiesel from waste cooking oil produced using sulfated montmorillonite catalyst is methyl oleate. This is supported by research conducted by Taufiqurrahmi *et al.* [15], reported that the composition of fatty acids in waste cooking oil from the smallest to the largest percentage was linolenic acid (1.59%), myristic acid (3.21%), stearic acid (13%), linoleic acid (13.58%), palmitic acid (21.47%), and oleic acid (28.64%) respectively. This composition is in accordance with the fatty acid composition of waste cooking oil from palm oil, so it can be concluded that the use of sulfated montmorillonite catalysts has been converted fatty acids into biodiesel was successfully. The GC-MS results also showed that there is no free fatty acid content in biodiesel, so it can be stated that sulfated montmorillonite also functions as an adsorbent in absorbing impurities in the synthesis of biodiesel.

IV. CONCLUSION

Biodiesel has been successfully synthesized from used cooking oil using sulfated montmorillonite as catalyst. Based on XRD analysis data, it shows that bentonite contains the main components of montmorillonite and quartz (SiO₂). The addition of sulfuric acid (H₂SO₄) to montmorillonite does not change the basal spacing d₀₀₁ on the diffractogram but occurs slight shift toward higher angle (2θ) that indicating decrease in the pore size of montmorillonite after activation process. The FTIR analysis results of sulfated montmorillonite showed that the sulfated montmorillonite has functional groups, namely octahedral –OH stretching vibration, water molecule –OH stretching vibration, ≡Si-O-Si≡ bending vibration, ≡Si-O symmetric stretching vibration of (≡Si-O -Si≡), and the bending vibration of the –OH group from Al-Al-OH in the tetrahedral and octahedral sheet structures which are the

constituents of the mineral montmorillonite. The results of GC-MS biodiesel analysis represented that the composition of the methyl ester is palmitic acid 6.83% and oleic acid 24.17%. Based on the results, it can be concluded that the sulfated montmorillonite catalyst has succeeded in converting fatty acids into biodiesel.

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