

PHYSICAL CHARACTERISTICS AND CATALYTIC ACTIVITY OF SULFATED SUGARCANE BAGASSE SILICA ($\text{SiO}_2/\text{SO}_3\text{H}^+$) FOR COCONUT OIL TRANSESTERIFICATION

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ABSTRACT

In this study, silica extracted from sugarcane bagasse was converted into sulfated silica $\text{SiO}_2/\text{SO}_3\text{H}^+$ by impregnating the silica with sulfuric acid to produce sulfated silica. The sulfated silica was then subjected to calcination at varied temperatures, and subsequently analyzed using Fourier Transform Infrared, Scanning Electron Microscope, and X-Ray Diffraction. The catalytic activity of the sulfated silica was tested for transesterification of coconut oil, and the reaction product was analyzed using Gas Chromatography-Mass Spectroscopy. The Fourier Transform Infrared results indicate the presence of absorption band at of 1126.43 cm^{-1} , which is associated with S=O group, in sulfated silica spectrum, while in the original silica, this band is not detected. This difference between the spectra confirms that the silica was successfully converted into sulfated form. The silica and sulfated silica were found to have similar X-ray diffractograms and fit very well with the X-ray diffractogram of standard amorphous silica (JCPDS No. 29-0085), confirming the existence silica and sulfated silica as amorphous materials. Characterization using SEM shows the presence of irregular granules on the surface, which is in agreement with amorphous structure as seen by the XRD. Analysis of the transesterification product using GC-MS reveals that the product is composed of methyl esters of the fatty acids composing coconut oil commonly reported, suggesting that the sulfated silica produced possess catalytic activity as expected.

Keywords: Silica, Sulfated Silica, Sugarcane Bagasse, Transesterification, Coconut oil

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INTRODUCTION

The catalysts generally applied in esterification are strong acids such as H_2SO_4 , p-toluensulfonic acid, and HF, but these catalysts are hampered by several drawbacks such as corrosive nature and relatively high price¹. In previous study^{2,3}, the production cost for biodiesel production using homogenous and heterogeneous catalyst was compared and it was reported that production costs is lower using heterogeneous catalysts, primarily due to reduction of final process and refinement. In addition, heterogeneous catalysts also suppress the corrosion problem⁴.

Acknowledging the advantages they offer, development of heterogeneous catalyst has become one of the research interests to improve biodiesel process^{5,6}. In this respect, silica has attracted particular interest since this material is known as amorphous material with high thermal and chemical stability, and insoluble in water as well as organic solvents. To take advantage of such excellent properties, silica has been used as a support for various metal oxides to synthesize heterogeneous catalysts, such as $\text{TiO}_2/\text{SiO}_2$ ⁷, NiO/SiO_2 ⁸, MgO/SiO_2 ⁹, and CaO/SiO_2 ¹⁰. Another approach to modify the surface of silica is based on the presence of silanol (Si-OH) group, which can be converted into Si-OM, where M is species other than

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hydrogen¹¹. This approach has been used to increase the acidity by impregnating the silica with acid. A typical example is impregnation of silica with sulfuric acid to produce sulfated silica ($\text{SiO}_2/\text{SO}_3\text{H}^+$). Large surface area provided by the silica and increased acidity of the surface due to SO_3H^+ are expected to enhance the catalytic activity of the sulfated silica. Conversion of silica in to sulfated form and its uses as catalyst has been reported by others.^{12,13}

The present study aimed to synthesize sulfated sugarcane bagasse silica ($\text{SiO}_2/\text{SO}_3\text{H}^+$) and to examine the potential of the ($\text{SiO}_2/\text{SO}_3\text{H}^+$) produced as catalyst for transesterification of coconut oil. Sugarcane bagasse silica was selected in recognizing the presence of sugarcane bagasse as agroindustrial residue abundantly available in Indonesia, including the Province of Lampung. In sugar industry, sugarcane bagasse is generally used as fuel for boiler, resulting the ash which consists of 71% SiO_2 and some other metal oxides¹⁴⁻¹⁶. This composition reflects that sugarcane bagasse ash is a potential source of silica.

EXPERIMENTAL

$\text{SiO}_2/\text{SO}_3\text{H}^+$ catalysts were prepared by the sol gel method. Sugarcane bagasse was cleaned from physical impurities, then heated in a furnace at 700°C for 6 hours to produce sugarcane bagasse ash. The ash was washed with distilled and filtered with Whatman 42, then oven dried for 2 hours at 100°C. A sample of 6 grams of sugarcane bagasse ash was dissolved in 200 mL of 1 M NaOH while stirring and heated to boiling for 1 hour. The solution was left overnight and then filtered with Whatman 42 paper. The resulting filtrate was acidified by dropwise addition of 0.6 M HCl to bring the solution into pH of 7.0, and then allowed to stand for 1 day to form hydrogel. An aliquot of 30 mL of distilled water was slowly added into the gel under stirring for 10 minutes. The gel was then separated using Whatman 42 and oven dried at 100°C for 6 hours, and the resulted solid silica was ground into powder.

To synthesize $\text{SiO}_2/\text{SO}_3\text{H}^+$, the silica (6.6 g) was transferred into a flask and then 40 mL methyl alcohol and 18 mL distilled water were added to the silica. The mixture was magnetically stirred, followed by dropwise addition of 100 mL of 0.1 N H_2SO_4 solution. The mixture was then refluxed at 65 °C for 24 hours under continuous stirring. After the completion of the experiment, the sulfated silica was filtered and then heated for eight hours at 100, 400, 600, and 800 °C

To examine the potential of the $\text{SiO}_2/\text{SO}_3\text{H}^+$ as catalyst, the sample calcined at 400°C was used for transesterification of coconut oil using methyl alcohol. The transesterification experiment was conducted with oil to methyl alcohol mole ratio of 1: 6 (taking molecular weight of coconut oil is 680 g/mole) and the catalyst used was 1% of the total mass of oil and methyl alcohol. The alcohol and catalyst were placed in a three-neck flask and then refluxed for 30 minutes under magnetic stirring. The preheated oil (45°C) was transferred slowly to the flask and then refluxed at a temperature of 60-65° C under magnetic stirring at 600 rpm for 2 hours. After the completion of the process, biodiesel and glycerol was separated using separating funnel. The biodiesel was evaporated and washed with hot distilled water to remove the remaining alcohol and glycerol. The water was removed from biodiesel using anhydrous Na_2SO_4 , and then the biodiesel was analyzed using GC-MS.

RESULTS AND DISCUSSION

To examine whether the formation of sulfated silica has been achieved, the samples of original and impregnated silica were characterized using FTIR spectroscopy, and the spectra of the samples were compiled in Fig.-1. The -OH functional group is evidently indicated by the absorption peak in the wavenumber range of 3200-3680 cm^{-1} , commonly assigned to silanol moiety in the silica and the contribution of absorbed water molecules¹⁴. The presence of this functional group is supported by the band at 1654 cm^{-1} , commonly assigned to bending vibration of water molecule O-H. The relative intensity of these two bands was found to gradually decrease with increasing calcination temperatures, suggesting the release of adsorbed water and the release of water from silanol group in silica when the sample was subjected to high temperature. The Si-O functional group of silica was indicated by the absorption bands located at wavenumber of 1070 cm^{-1} and 945 cm^{-1} , associated with Si-O stretching vibration and band at a wavenumber of 460 cm^{-1} , associated with Si-O bending vibration¹⁵. The attachment of sulfate group to silica matrix is indicated by the absorption band at around 1126.43 cm^{-1} ¹⁶ which is observed in the spectra of impregnated samples but not in the spectrum of the original silica.

This particular band is commonly assigned to the S=O group, suggesting that formation of sulfated silica has been achieved, although it should be acknowledged that the relative intensity of the peak is relatively low, most likely due to low concentration of the sulfuric acid used or insufficient impregnation time applied.

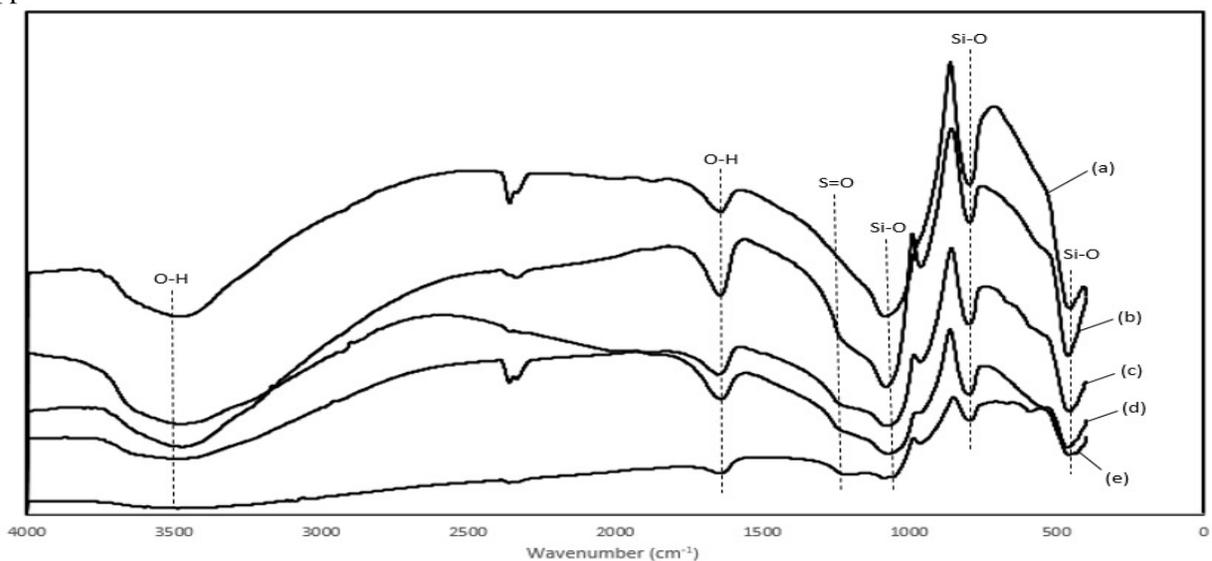


Fig-1: FT-IR spectra of different samples: original SiO_2 (a) and $\text{SiO}_2/\text{SO}_3\text{H}^+$ calcined at temperature of 100 (b), 400 (c) 600 (d), and 800 °C (e)

The -OH functional group is evidently indicated by the absorption peak in the wavenumber range of $3200\text{--}3680\text{ cm}^{-1}$, commonly assigned to silanol moiety in the silica and the contribution of adsorbed water molecules¹⁴. The presence of this functional group is supported by the band at 1654 cm^{-1} , commonly assigned to bending vibration of water molecule O-H. The relative intensity of these two bands was found to gradually decrease with increasing calcination temperatures, suggesting the release of adsorbed water and the release of water from silanol group in silica when the sample was subjected to high temperature.

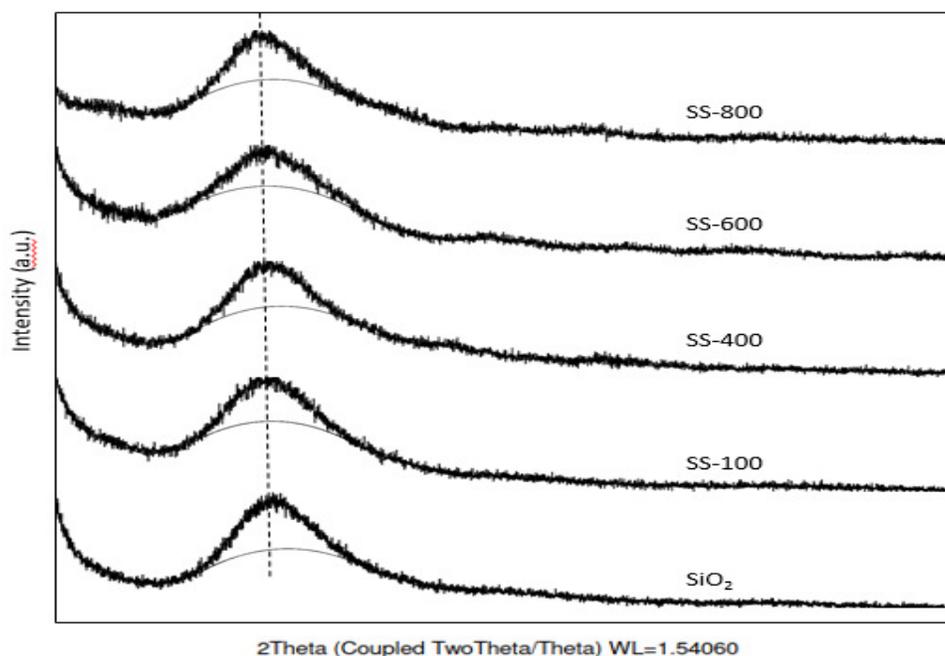


Fig-2: The X-Ray Diffractograms of Original SiO_2 and $\text{SiO}_2/\text{SO}_3\text{H}^+$ (SS)

The Si-O functional group of silica was indicated by the absorption bands located at wavenumber of 1070 cm^{-1} and 945 cm^{-1} , associated with Si-O stretching vibration and band at a wavenumber of 460 cm^{-1} , associated with Si-O bending vibration¹⁵. The attachment of sulfate group to silica matrix is indicated by the absorption band at around 1126.43 cm^{-1} ¹⁶ which is observed in the spectra of impregnated samples but not in the spectrum of the original silica. This particular band is commonly assigned to the S=O group, suggesting that formation of sulfated silica has been achieved, although it should be acknowledged that the relative intensity of the peak is relatively low, most likely due to low concentration of the sulfuric acid used or insufficient impregnation time applied.

Silica and sulfated silica subjected to different calcination temperatures were characterized using XRD, and compiled diffractograms of the samples are shown in Fig.-2. Silica and sulfated silica have similar x-ray diffractograms and they are in agreement with that of the standard silica listed in JCPDS No. 29-0085 file. The existence of the samples as amorphous materials is evidently displayed by the existence of broad peak at around $21\text{-}23^\circ$, which is a characteristic x-ray diffractogram of amorphous silica reported by others¹⁷.

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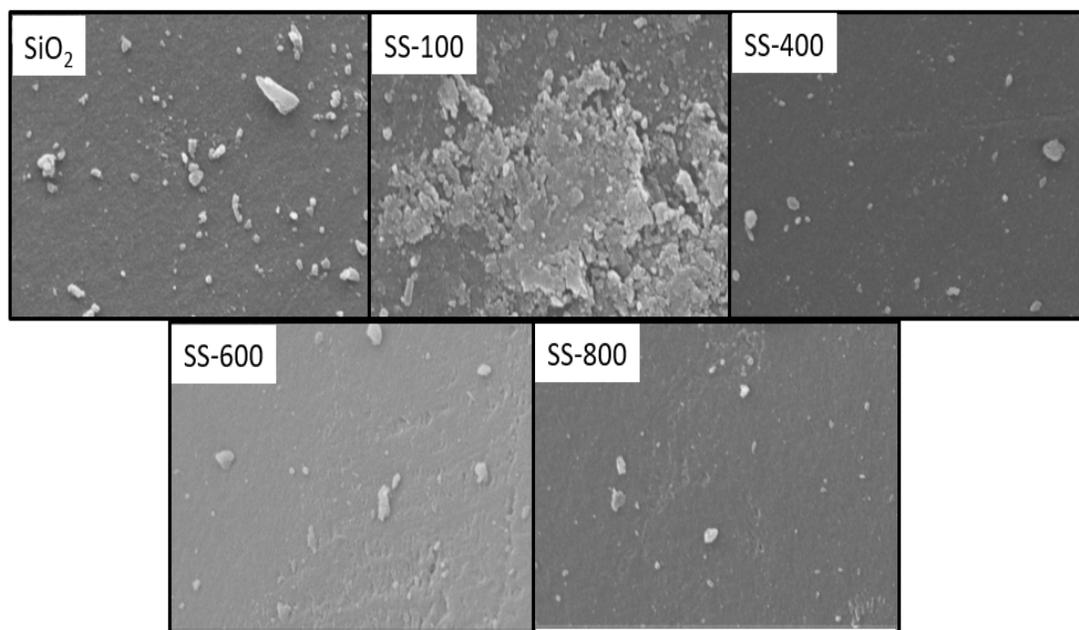


Fig.-3: SEM Images of SiO_2 and $\text{SiO}_2/\text{SO}_3\text{H}^+$ (SS)

To evaluate surface morphology, silica and sulfated silica calcined at different temperatures were characterized using SEM, and the micrographs obtained are presented in Figure 3. SEM images of silica and sulfated silica show irregular granules, without specific shape and size, supporting the existence of the samples as amorphous materials as indicated by the XRD results. In the samples subjected to calcination treatments, the difference between the samples that can be noted is the existence of clusters on the surface of the sample heated at 100°C , while in the samples subjected to higher temperatures, most of the clusters were disappear. The presence of clusters in the sample heated at 100°C (SS-100) is most likely due to loosely adsorbed sulfuric acid molecules on the surface of the samples, and most of these molecules evaporated when the samples were heated at higher temperatures.

To test the catalytic activity of the sulfated silica, the sample subjected to calcination temperature at 400°C was selected as a representative. This catalyst was utilized for coconut oil transesterification of and it

was found that a 89% conversion of the oil was achieved, suggesting that the catalyst used exhibit high activity for conversion of coconut oil. To identify the chemical components of the transesterification product, the sample was analyzed using GC-MS technique. The GC chromatogram obtained is presented in Fig.-4 and the identified compounds comprise the product are listed in Table-1.

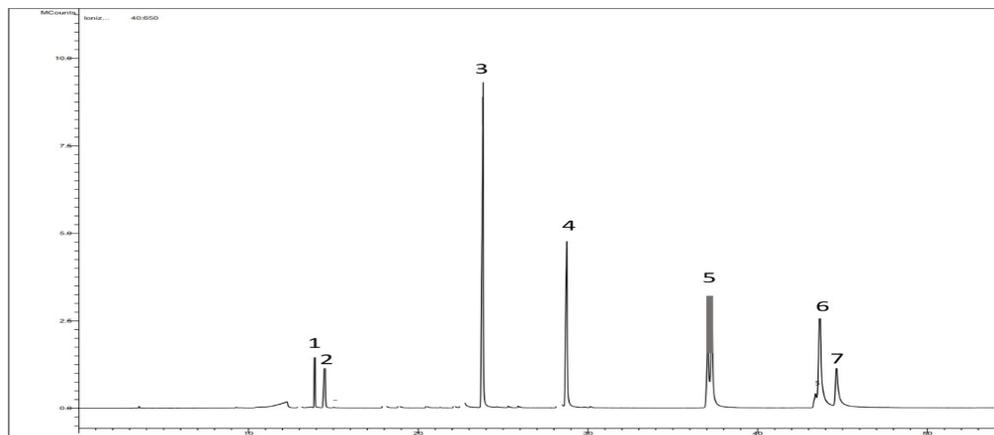


Fig.-4: GC-Chromatogram of the Product of Coconut Oil Transesterification

Table-1: Methyl Esters Data

Peak	Retention Time	%Area	Compound
1	14.502	6.36	C ₁₁ H ₂₂ O ₂ (Me- caprate)
2	15.032	5.37	C ₉ H ₁₈ O ₂ (Me- caprylate)
3	22.645	38.29	C ₁₃ H ₂₆ O ₂ (Me- laureate)
4	28.754	21.39	C ₁₅ H ₃₀ O ₂ (Me- myristate)
5	37.313	13.13	C ₁₇ H ₃₄ O ₂ (Me- palmitate)
6	43.661	10.63	C ₁₉ H ₃₆ O ₂ (Me- oleate)
7	44.647	4.83	C ₁₉ H ₃₈ O ₂ (Me- stearate)

As can be seen in the chromatogram (Fig.-4), seven peaks were observed, suggesting the existence of seven chemical substances in the samples. With the aid of MS library systems, the compounds were identified as methyl esters (Table-1), practically known as biodiesel. In addition, the methyl esters identified correspond with the fatty acids of coconut oil commonly reported¹⁸, demonstrating that the sulfated silica used possess the ability to convert any types of fatty acid presence in the oil into their corresponding methyl esters. This result implies that sulfated silica synthesized possess considerable activity for biodiesel production. It is also observed that the component of biodiesel with the highest relative percentage is Methyl laureate, which is in accordance with the existence of lauric acid as the most prominent component of coconut oil.

CONCLUSION

The results of FT-IR showed that the impregnation of sulfate into silica was successfully carried out which was shown by the emergence of a new band with a wavenumber of 1126.43 cm⁻¹ in sulfated silica which is a characteristic of the S=O group. The sulfated silica and silica have similar diffractograms and are very compatible with the diffractogram of standard amorphous silica (JCPDS No. 29-0085). The existence of the samples as amorphous materials are also supported by the results of SEM characterization. The results of GC-MS analysis of the product of coconut oil transesterification demonstrates that the sulfated silica produced possess the promising performance as solid catalyst for production of biodiesel.

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