

The Effects of Montmorillonite and Cane Sugar Composition on The Properties of Montmorillonite-Carbon Sulfonate Catalyst

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The influence of montmorillonite and cane sugar mixture with composition of 1:3, 1:2, 1:1, 2:1, and 3:1 to the characteristics of the synthesized montmorillonite-carbon sulfonate composite catalyst had been investigated. The mixture of montmorillonite and cane sugar was carbonized at 400 °C for 15 hours and then sulfonated using sulfuric acid at 175 °C for 15 hours. The presence of sulfonate group was detected using FT-IR and the surface topology of the catalyst was characterized using SEM-EDX. FT-IR spectra showed the existence of sulfonate group at wave number of 1095 cm⁻¹. SEM-EDX analysis showed that the catalyst with the montmorillonite and cane sugar ratio of 1:2 consisted of 1.06% sulfur. The catalyst activity was examined using an esterification reaction between acetic acid and ethanol, and the reaction products were characterized using GC-MS. The chromatogram peak at $m/z = 88$ confirmed that the product was ethyl acetate. Catalyst with the montmorillonite and cane sugar ratio of 1:2 was shown to have the highest acidity and gave the highest esterification product with 76.97% conversion.

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1 Introduction

Inline with the population growth and technological advances, the use of fuels, especially petroleum, continues to increase so that fuel reserves from petroleum are decreasing. Various attempts has been made to overcome dependence on petroleum fuels, including the use of biodiesel. Biodiesel is used as an alternative fuel for diesel engines. Biodiesel is produced through the alcoholysis process (transesterification) between triglycerides and methanol or ethanol with the help of a catalyst to become alkyl esters and glycerol. Biodiesel can also be produced by esterification of fatty acids (free) with methanol or ethanol with the help of an acid catalyst to become an alkyl ester compound and water¹.

The catalysts for esterification and transesterification reactions in biodiesel production that are often used today are homogeneous catalysts including KOH, NaOH and H₂SO₄. Homogeneous catalysts have the same phase as the reagents and can accelerate the reaction by forming activated complexes with reactants.

However, homogeneous catalysts have several disadvantages as they can lead to equipment corrosion, difficulties in handling and separation of the product from the catalyst². Another weakness of the homogeneous catalyst is that the process is still relatively expensive, the conversion is still low, and there are by-products in the form of acid or alkaline waste which can pollute the environment³. Seeing these conditions, another way is needed to overcome this problem, namely by using a heterogeneous catalyst in the form of sulfonated carbon⁴. Based on research, sulfonated carbon can qualify as a heterogeneous catalyst because it has a large surface area and a sulfonate group. Furthermore, the morphological structure of the catalyst is more exposed than an activated carbon after the sulfonation process⁴. Solid acid (heterogeneous) catalysts have unique advantages in esterification reactions and transesterification reactions. This is because it can increase the high fatty acid value to be used as a raw material for biodiesel synthesis⁵.

Sulfonated carbon can be made by using cane sugar as a base material. The sugar is converted into polyaromatic hydrocarbons, which still have -OH groups, through an imperfect carbonization process at temperatures between 300 – 500 °C. The carbon produced from the carbonization process is then sulfonated using

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Table 1 Comparison of cane sugar with montmorillonite

No	Montmorillonite (g)	cane sugar (g)	Water (mL)
1	33	100	500
2	50	100	500
3	100	100	500
4	200	100	500
5	300	100	500
6	-	100	-

sulfuric acid. The polyaromatic hydrocarbon structure, which has an –OH group, binds the sulfonic groups of sulfuric acid in the sulfonation process. The result is carbon sulfonate, and the sulfonate group is expected to be the active site of the catalyst⁶. Carbon generally has a low specific gravity, so the homogeneity of the catalyst in the reaction is also low. Therefore, carbon density needs to be increased by using a support material that is both catalyst and has a large density.

The formation of montmorillonite-sulfonated carbon composites is made through the adsorption process of cane sugar on montmorillonite, followed by carbonization and sulfonation processes to obtain carbon sulfonate that can improve its catalytic properties. Previous research had carried out the formation of sulfonated carbon using cellulose, glucose, starch and lignin. In this study, cane sugar (sucrose) was selected as the raw material because it is easy to obtain and is easily dissolved in water, making it easier to combine with montmorillonite.

The catalyst activity was examined through the esterification reaction of acetic acid with ethanol. The esterification reaction of glacial acetic acid with ethanol is the simplest esterification reaction model and is often used to test the activity of freshly made catalysts before they are applied to biodiesel production⁷. Based on the description above, the effects of the composition of cane sugar and montmorillonite to the catalyst properties of carbon sulfonate montmorillonite composites were investigated in this work.

2 Methodology

2.1 Instrumentations and materials

Materials used in this work were natural montmorillonite, cane sugar, nitrogen gas, sulfuric acid 99% (Merck), sodium hydroxide (Merck), hydrochloric acid (Merck), and anhydrous calcium chloride. The instrumentations used were Scanning Electron Microscope (JEOL JSM-6300), FT-IR spectrophotometer, and GC-MS (Shimadzu) installed at Sriwijaya University.

2.2 Montmorillonite and cane sugar mixture preparation

Montmorillonite was crushed with porcelain mortar and sieved with a 200-mesh sieve. The obtained montmorillonite is then washed using Demin water and dried at 120 °C for 24 hours.

A solution of 20% cane sugar was prepared with volume variations as listed in the Table 1. To each of these solutions, montmorillonite is added according to the amount listed in the Table 1. These data refer to the research conducted by Lu et.al⁸. The mixture was then stirred at 80 °C in a 1 L beaker until it became dry.

**Figure 1** Carbonization results of monmorillonite-cane sugar composite.

After further drying at 120 °C, the mixture is then crushed and carbonized for 15 hours between a temperature of 350–500 °C with N₂ gas flowing at 2 mL s⁻¹. The result of this carbonization is then called montmorillonite-carbon composite. Likewise, pure cane sugar was given the same treatment with the five samples during the carbonization process⁹.

2.3 Montmorillonite-carbon composite sulfonation

For each mixture ratio, 20 g of the montmorillonite-carbon composites was taken and added with 100 mL concentrated H₂SO₄. The mixture was refluxed at 175 °C for 15 hours. Then it was washed with hot water at 80 °C to remove any remaining sulfuric acid. The mixture was then dried at 120 °C for 24 hours. This product is then called a montmorillonite-carbon sulfonate composite.

2.4 Determination of acid number

For each mixture ratio, 1 g of montmorillonite-carbon sulfonate was taken, and then immersed in 100 mL of NaOH 0.49 M for 4 hours. The suspension was then centrifuged, and titrated with 0.1 M HCl to determine the amount of acid present¹⁰.

2.5 Identification of functional groups of montmorillonite-carbon sulfonate composites

The identification of the functional groups in montmorillonite-carbon sulfonate composite was carried out using FT-IR. The sample pellet was made by hand-press from the mixture of 0.5 mg sample with 100 mg KBr.

2.6 Characterization of catalyst surface

Montmorillonite-carbon sulfonate composite with selected ratio was analyzed using SEM-EDX. The sample was ground and sieved prior to the analysis. Samples were cleaned using a hand blower to remove impurities. Cleaning with a hand blower also serves to strengthen the adhesion of the test object to the specimen holder. The sample was coated with a gold-palladium coating system (Au = 80% and Pd = 20%) using the Ion Sputter JFC-1100 machine, with a voltage of 1.2 kV, an electric current of 6-7.5 mA, and a vacuum of 0.2 torr. It took 4 minutes to obtain a layer thickness of 400 Å before the analysis was carried out.

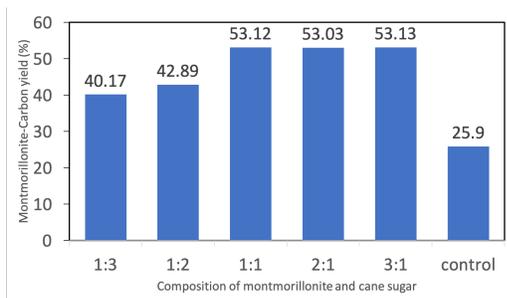


Figure 2 The % yield of montmorillonite-carbon as a function of montmorillonite and cane sugar composition.

2.7 Catalyst activity in esterification reaction

A mixture of 150 mL of ethanol and 50 mL of glacial acetic acid was placed in a round base boiling flask, and 3 g of montmorillonite-carbon sulfonate was added. The mixture was refluxed for 240 minutes at 77.1 °C. The mixture was then distilled to separate ester product from the residue. The residual acid and water that possibly remain in the ester product were removed by adding 20% Na₂CO₃ solution and anhydrous CaCl₂, respectively.

3 Results and discussion

3.1 Montmorillonite and cane sugar composite preparation

The mixture of montmorillonite and dried cane sugar was carbonized for 15 hours to produce hydrocarbon polyaromatics with imperfect carbonization process at a temperature of 350–500 °C. Temperatures of 400 °C and carbonization time of 15 hours were chosen because they are the optimum conditions for carbonization. The resulting solid is shown in Figure 1. This carbonization result has a black appearance, indicating that it has been transformed into a hydrocarbon polyaromatic that coats the montmorillonite as shown in Figure 1.

The carbonization % yield was determined and its dependence to the composition is shown in Figure 2. The percentage of carbon montmorillonite yield shows that the process of carbonization of montmorillonite and cane sugar mixture produces an increasing amount of carbon yield. Cane sugar coupled with montmorillonite produces a higher percentage of carbon contents as montmorillonite was added. Composite with 3:1 ratio has a high percentage of carbon yield of 53.13%, while pure cane sugar as a control has smaller carbon yield at 25.9%.

3.2 Montmorillonite-carbon composite sulfonation

The purpose of this sulfonation is to attach the –HSO₃ groups into the montmorillonite-carbon composite. The results of the sulfonation reaction was washed with water to remove the remaining sulphuric acid, so that only the –HSO₃ groups bound to the polyaromatic structure of hydrocarbons remained. The –HSO₃ groups are bound to the position of ortho or para on hydrocarbon polyaromatic structure. This sulfonate group is expected to be the active site of the montmorillonite-carbon sulfonate composite as a catalyst.

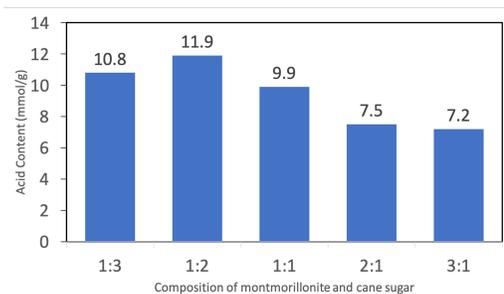


Figure 3 The acid contents in montmorillonite-carbon sulfonate composites.

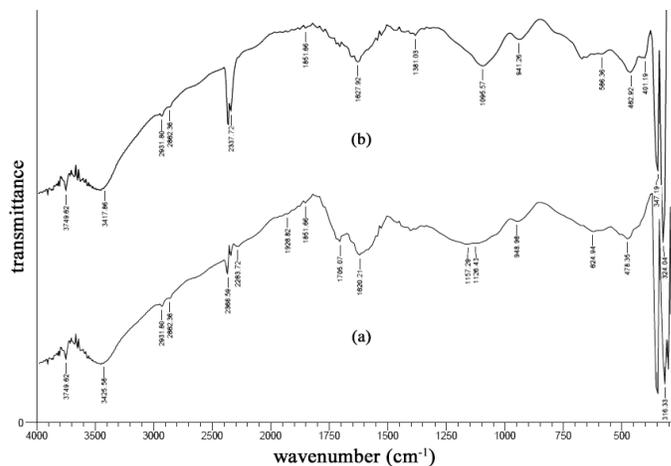


Figure 4 FT-IR spectra of (a) sulfonate carbon catalyst (b) montmorillonite-carbon sulfonate composite catalyst with 1:2 ratio.

3.3 Acidity test and the number of sulfonate groups

The numbers of sulfonate group in the composite catalyst at different montmorillonite and cane sugar ratios are shown in Figure 3. The number of sulfonate group is represented by the acid H⁺ content. The highest acid content, 11.9 mmol g⁻¹, was found in the composite with 1:2 ratio. This amount is higher than those synthesized from oil palm trunk and sugarcane¹¹, or from coconut shells using active carbon¹², or from activated carbon¹³. While composite with 1:3 ratio is expected to have more carbon atoms to which the sulfonate groups are bound, the fact that composite with 1:2 ratio showed higher acidity may be attributed to the optimum condition where more surface area containing sulfonate groups can be exposed. In case of the ratio of 1:1, 2:1 and 3:1, the acidity decreases along with the decrease of cane sugar as a source of carbon where the sulfonate groups are bound. This result is further supported by the FT-IR and SEM EDX analysis, as will be discussed in the following subsection.

3.4 FT-IR analysis of montmorillonite-carbon sulfonate composite catalysts

FT-IR spectra of composite with 1:2 ratio can be seen in Figure 4. The absorption of the –SO₃H group is expected to be observed with the wavenumber range of 1037–1200 cm⁻¹. The peak at wavenumber 1095 cm⁻¹ shows the presence of sulfonate groups (–SO₃H), but the addition of montmorillonite raises a

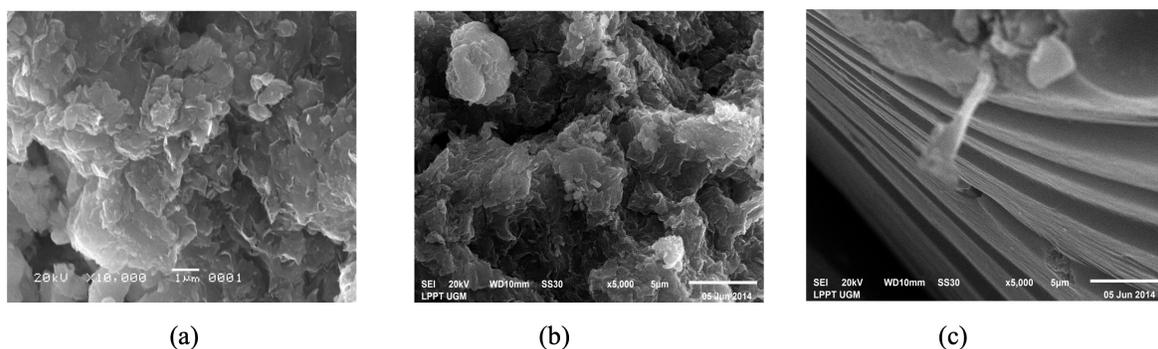


Figure 5 SEM images of (a) natural montmorillonite, (b) montmorillonite-carbon sulfonate composite with 1:2 ratio, and (c) carbon sulfonate catalyst.

broad peak from Si-O group within $830 - 1110 \text{ cm}^{-1}$ ¹⁴. Another peak at 3417 cm^{-1} is estimated from the -OH group of hydrocarbon polyaromatic compounds that were formed from the imperfectly carbonized cane sugar¹³.

3.5 SEM-EDX analysis for surface topology and sulfur content

The surface topologies of natural montmorillonite, montmorillonite-carbon sulfonate with 1:2 ratio, and carbon sulfonate catalyst were examined using SEM and the results at magnification of 5000 times can be seen in Figure 5. The montmorillonite-carbon sulfonate composite was shown to have a layered surface structure, similar to natural montmorillonite, coated with carbon that filled inbetween layers. On the other hand, carbon sulfonate catalyst has a multi-layered surface area with a wide gap between layers. Unlike carbon sulfonate catalyst, however, the montmorillonite composite catalyst has a multi-layered surface where the interlayers are filled with carbon, so that its density is greater than that of carbon sulfonate catalyst.

Quantitative analysis of sulfur content was carried out using EDX and the results are shown in Figure 6. The sulfur contents in the composite of montmorillonite-carbon sulfonate with 1:2 ratio and in the carbon sulfonate catalyst were found to be 1.06% and 1.03%, respectively. These results are inline with the presence of sulfonate clusters shown by the FT-IR results. Sulfur was not detected in natural montmorillonite.

3.6 Effects of montmorillonite-carbon sulfonate composition on catalytic activity

The catalytic activity of montmorillonite-carbon sulfonate composite was examined through the esterification reaction between acetic acid and ethanol. The reaction was carried out by refluxing the mixture with montmorillonite-carbon sulfonate composite at $77.1 \text{ }^\circ\text{C}$ for 4 hours. The products were obtained by distillation and then subjected to GC-MS analysis to determine the % yield of ethyl acetate.

The chromatogram depicted in Figure 7 shows the appearance of two different peaks with retention times of 2.077 minute for ethanol and 2.728 minute for ethyl acetate. The latter peak has a larger area that is proportional to the concentration of ethyl

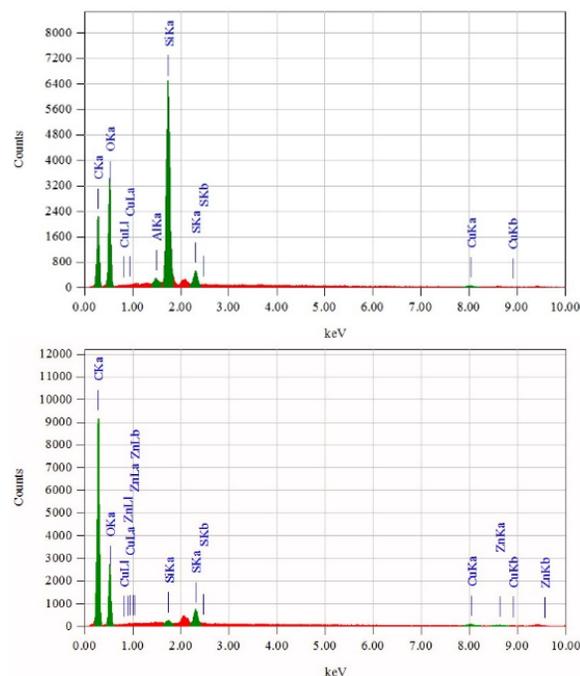


Figure 6 EDX analysis of (top) montmorillonite-carbon sulfonate with 1:2 ratio, and (bottom) carbon sulfonate catalyst.

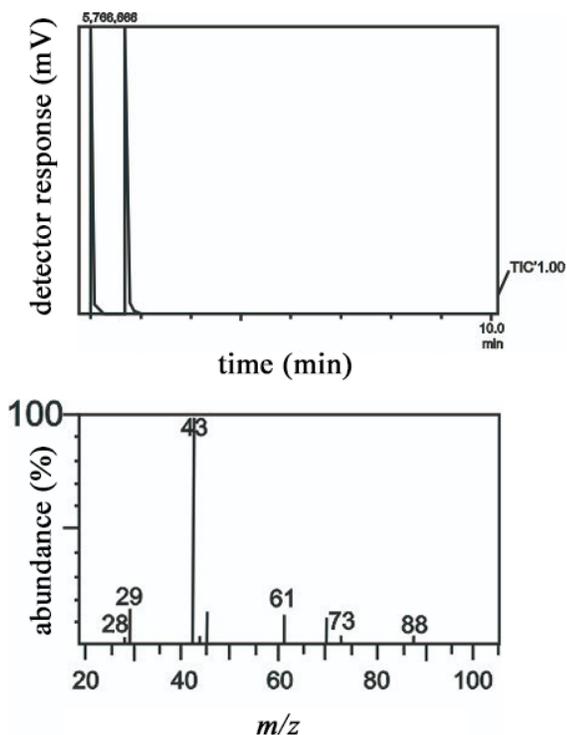


Figure 7 Chromatogram (top) and mass spectra (bottom) of the esterification products.

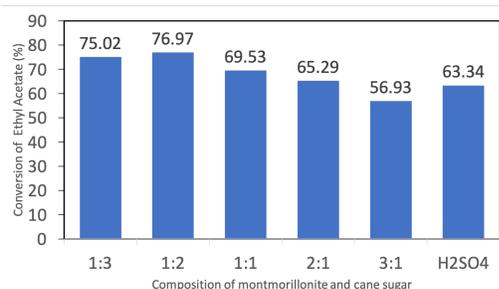


Figure 8 Catalyst activity of montmorillonite-carbon sulfonate composite at various montmorillonite and cane sugar composition.

acetate. The latter peak also corresponds to $m/z = 88$, which is inline with the molar mass of ethyl acetate, and the base peak is shown at $m/z = 43$ as an evidence for compounds from ethyl acetate fragmented into CH_3CO^+ and $\text{CH}_3\text{CH}_2\text{O}^-$ which corresponds to $m/z = 45$.

The effects of montmorillonite-carbon sulfonate composition on catalytic activity are shown in Figure 8. The percent yield of ethyl acetate conversion was found to be the highest, at 76.97%, for the montmorillonite-carbon sulfonate catalyst with 1:2 ratio. As a comparison, the yield on ethyl acetate conversion using H_2SO_4 catalyst was only 63.34%, lower than that produced by using the montmorillonite-carbon sulfonate composite catalyst. This shows the montmorillonite-carbon sulfonate composite is more effective as a catalyst compared to the conventional H_2SO_4 catalysts for the esterification reaction.

4 Conclusions

Montmorillonite-carbon sulfonate composite with montmorillonite and cane sugar of 1:2 ratio was shown to have the highest acidity value of 11.9 mmol g^{-1} . The presence of sulfonate group ($-\text{SO}_3\text{H}$) was confirmed by FT-IR with the appearance of a peak at wavenumber of 1095 cm^{-1} , and SEM-EDX analysis showed that the sulfur content was 1.06% for the composite with montmorillonite and cane sugar of 1:2 ratio. The activity of montmorillonite-carbon sulfonate composite as a catalyst was examined from the esterification reaction between glacial acetic acid with ethanol. The esterification product was identified using GC-MS spectrometry and the chromatogram at $m/z = 88$ corresponded to ethyl acetate compound. It was further observed that the composite with montmorillonite and cane sugar ratio of 1:2 gave the highest % conversion of ethyl acetate at 76.97%.

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