Synthesis, characterization and biodiesel conversion of monodispersed sulfonated-silica nanoparticles

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Abstract. The enhancing need of energy followed by increasing of human population to be main factors in fuels depleting. This motivated researcher over the world to solve and to utilize natural resources as bioenergy for human sustainability in future. Today, there are numerous research related to bioconversion and bioprocessing of natural resources as well as optimizing catalyst in biodiesel conversion. Design of suitable catalyst for biodiesel conversion to be a challenge in this research area. In this paper, we report of preparation, characterization and biodiesel conversion ability of heterogeneous catalyst, so called monodispersion sulfonated-silica nanoparticles (MSN). This nanoparticles was characterized by FTIR, TEM, SEM and SEM-EDAX as well as N2 adsorption-desorption. The result revealed that the catalyst prepared through CTAB templating technique has been successfully synthesized with high monodispersion nano-size. Moreover, its ability in biodiesel conversion up to 13.33\% for purity percentage.

1. Introduction
Biodiesel is a fuel that can be derived from biomass sources and can substitute conventional fuel that taken from petroleum sources [1,2]. Biodiesel is one of alternative fuel because it is biodegradable, non-toxic, free of sulfur and organic compound [3,4]. Biodiesel can reduce gas pollution significantly, such as carbon monoxide gas (CO) decrease 4-16\%, carbon dioxide gas (CO\textsubscript{2}) decrease 50-80\% and SOx gas decrease 100\% [5]. Basically, biodiesel is produced through transesterification reaction with methanol by alkali catalyst and this step require vegetable oil that contain very low free fatty acid (FFA) [6]. Biodiesel with high FFA, produce through 2 steps reactions, there are esterification and transesterification reaction using homogeneous or heterogeneous catalyst [7].

Homogeneous catalyst is used for oil that contain free fatty acid less than 1\%, and heterogeneous catalyst is used for oil that contain free fatty acid more than 1\% [7,8]. Using of H\textsubscript{2}SO\textsubscript{4} and KOH as catalyst for Biodiesel production from Ceiba pentandra oil produce biodiesel product yield 99.5\% [9]. Using of H\textsubscript{2}SO\textsubscript{4} and KOH (1.5\% : 2\%) as catalyst in biodiesel production from castor oil (Karanja) has been reported that has yield 85\% [10]. Biodiesel production of crude palm oil with the presence of H\textsubscript{2}SO\textsubscript{4} as acid catalyst produce biodiesel product with yield 97\% [11]. The weakness of homogenous catalyst is hard to separate from the product and lack of reuseability [12]. Homogeneous acid catalyst can caused environmental problems [13-16]. So heterogeneous catalyst is solution for that problem. That issues have be an trending topic to develop the ideas. Some researcher have synthesis some of
heterogeneous catalyst but the main problem is how to enhanced the yield of biodiesel and reuseability.

Mesoporous material can describe as porous separation media without interparticular void [17]. The strength of monolithic are easy to separate, easy to surface modified, and high permeability. Mesoporous catalyst is effective for gas-liquid-solid reaction catalytic. Mesoporous catalyst has high surface area, high efficiency transfer mass and can separate easily [18]. Some researcher have synthesis MSN as catalyst. So in this paper have synthesized successfully MSN material that modified with sulfonate material to enhanced yield of biodiesel.

2. Experimental

2.1. Materials
The employed materials in this research were commercially available from Merck and Aldrich and used without purification except mentioned. The silica sources were tetra ethyl ortho silicate (TEOS, Aldrich). Organosilane functional compound was 3-(trimethoxysilyl)propyl methacrylate (TMPMA, Aldrich). The sulfonate monomer was Sodium-4-vinylbenzene sulfonate (VBS, Aldrich).

2.2. Synthesized of mesoporous silica nanoparticle (MSN)
For synthesized Mesoporous Silica Nanoparticle, 0.789 gram CTAB dilute in 21.6 mL aquades, 3.42 mL ethanol and 0.04 mL ammonium hydroxide solution. The solution stirred 30 minutes in 60°C, 4.83 mL TEOS dropped into solution in 6 minutes and mixed it for 2 hours. The solution has centrifuged and washed by ethanol. The solid phase was dilute in 20 mL methanol and 1.44 mL HCl, stirred for 8 hours in 60°C. The solution has centrifuged and washed by ethanol and dried in 60°C for one night. The powder mention as mesoporous silica nanoparticle (MSN).

2.3. Funcionalized of mesoporous silica nanoparticle (MSN)
Funcionalized of MSN by sulfonate function group, 0.5 gram MSN was added into 2.5 mL TMPMA, 10 mL aquadest and 10 mL ethanol solution. The solution was sonication for 20 minutes, stirred in 110°C for 12 hours. Sulfonate functional group, 0.17 gram VBS and 0.0002 gram BPO as initiator agent was diluted into 10 mL DMF and added into the solution. The solution was stirred 120°C for 20 hours and dried in 60°C for one night. The powder mention as Mesoporous silica nanoparticle sulfonation (sMSN).

2.4. Catalytic Activity
Activity catalytic of sMSN for conversion of palm oil to biodiesel is carried out using the reflux method. Palm oil, methanol and sMSN catalyst are put into a three neck flask with a palm oil: methanol ratio of 1:15. The amount of catalyst used is 5% w / w of palm oil. The mixture is stirred at a stirring speed of 400 rpm in 140 °C for 2 and 4 hours. The formed products were then analysis using GC-MS.

3. Result and Discussion

3.1. Chemical Interaction of MSN Synthesize
Infra-red spectroscopy is one of the simple techniques that can be used to analyze the success of a synthesis that can be seen from the shift, disappear or appearance of a new peak of a functional group. Figure 1 is an infra-red spectra of TEOS precursors and MSN synthesis products. Based on these spectra, MSN has successfully formed which is characterized by the appearance of hydroxyl absorption (-OH) in the region of wave numbers 3500 cm⁻¹. In addition, the disappear of -CH stretching peak in area about 2900-2800 cm⁻¹ strengthens the suspicion of the formation of MSN products.
Figure 1. FTIR Spectra of TEOS and MSN.

The chemical illustration of MSN formation is shown in Figure 2.

Figure 2. Chemical reaction mechanism of MSN.

The same characterization was also carried out to determine the success of MSN surface modification with sulfonate compounds. Based on the infra-red spectra shown in Figure 3, it can be seen that the appearance of absorbance in the wave number 1690 cm\(^{-1}\) which is characteristic of the \(\text{C} = \text{O}\) group indicates that the TMPMA compound has been successfully attached to the surface of the MSN. In addition, it has also been found that wide absorption in the wave number 1100-1000 cm\(^{-1}\) is a sulfonate vibration that overlaps with a Si-O-Si vibration. Based on these data it can be concluded that surface modification has been successful whose chemical reaction mechanism is shown in Figure 4.

Figure 3. FTIR spectra of MSN and sMSN
3.2. Morphology Analysis

Morphological analysis by SEM imaging can be used to evaluate and observe the morphological form of the sample. Figure 5a is the SEM morphology of MSN. It is clearly seen that from the morphological structure MSN has a structure similar to a mesoporous, which is a pore that is interconnected. However, after modification with sulfonate compounds, the morphology of the MSN shown in Figure 5b undergoes the union that is made possible by the existence of cross-linking so that one particle with another particle is connected to form a more bulky structure.

The presence of sulfonate groups on the surface of MSN can be proof by electron mapping and EDX techniques. Figure 6a is an electron mapping of the sMSN sample that the imaging results can conclude the S atom (sulfur, yellow) has distributed on the surface of MSN. The atomic composition of the sMSN is shown in Figures 6b. The S element on the surface of sMSN has a proportion of 1%, while other elements such as C, O, Si and Na are 44.3%, 39.9%, 14.5% and 0.2%, respectively.
The imaging of nanostructures from MSN was evaluated by TEM. Figure 6c shows that the homogeneity of the nano-particle size distribution of MSN can be said to be evenly distributed. This happened because of the assistance from CTAB which was used as a template in the MSN synthesis process. In Figure 6c, it is clear that one nano-particle is connected to another. In the previous discussion, it has been explained that surface modification causes the structure of MSN to become more bulky, which is possible the connection of MSN particles through TMPMA and sulfonate compounds. The sMSN samples have particle sizes of less than 100 nm, so they can be categorized as nano-materials.

**Table 1.** Data summaries of physical properties of MSN and sMSN.

| Materials | Surface area (m²·g⁻¹) | Pore volume (cm³·g⁻¹) | Average pore radius (nm) |
|-----------|-----------------------|-----------------------|-------------------------|
| MSN       | 474.105               | 8.54 x 10⁻¹           | 3.60                    |
| sMSN      | 27.278                | 8.46 x 10⁻²           | 6.20                    |

Figure 7 show profile N2 adsorption-desorption of MSN and sMSN. It shown that MSN has mesoporous isotherm profile. Isotherm graph of sMSN shown that it has mesoporous isotherm profile. Figure 8 show pore radius and pore volume of MSN and sMSN. It show that MSN and sMSN have same range pore volume is around 8.00 x10⁻¹ – 9.00 x 10⁻¹ cm³g⁻¹. Summary of surface area, pore volume, pore radius can be seen in Table 1. Surface area of MSN is higher than sMSN. It caused
sulfonate has been attached into surface of MSN. Modification sulfonate into MSN make MSN surface is covered by sulfonate that caused decreasing surface area of MSN.

![Graph showing N2 adsorption-desorption of MSN and sMSN.]

**Figure 7.** N2 adsorption-desorption of MSN and sMSN.

![Graph showing pore radius distribution of MSN and sMSN.]

**Figure 8.** Pore radius distribution of MSN and sMSN.

2. **Catalyst Activity of sMSN**

Products from the esterification and transesterification process of CPO using sMSN catalyst were analyzed using GC-MS. Figure 9 shows the GC profile of the esterification and transesterification products. FAME product is divided into two products, namely hexadecanoic acid methyl ester (FAME 1) and octadec-9-enoic acid methyl ester (FAME 2), each appearing at a retention time of 16 minutes and 17.8 minutes. In addition to FAME products in the GC profile, free fatty acids and
triglycerides were detected. This indicates that biodiesel conversion cannot be done 100%. By setting aside free fatty acid products, it was obtained that the conversion of FAME to triglycerides was 13.33%.

Figure 9. GC chromatogram of biodiesel product.

Figure 10 show the summary of schematic FAME contain in biodiesel product. Result of GC-MS analysis shows that the biodiesel contain of 5 peaks of FAME. Those are hexadecanoic acid methyl ester that change become hentriacontan-16-one if the reaction continuous, octadec-9-enoi acid methyl ester that change become octadec-9-enal if the reaction continuous, and Hexadecanoic acid-2-hexadecanoyloxy-3-hydroxy-propylester (see table 2). Formed of ketone and aldehyde can be caused of reduction reaction from FAME.

Figure 10. Schematic of FAME that contained in biodiesel product.
Table 2. List of product from crude palm oil esterification.

| No | Compounds                                           | Yields  |
|----|-----------------------------------------------------|---------|
| 1  | Hexadecanoic acid methyl ester                      | 6.02%   |
| 2  | Octadec-9-enoic acid methyl ester                   | 7.31%   |
| 3  | Octadec-9-enal                                      | 6.56%   |
| 4  | Hexadecanoic acid-2-hexadecanoyloxy-3-hydroxy-prorylester | 8.74%   |
| 5  | Hentriacontan-16-one                                | 72.37%  |

4. Conclusion

Biodiesel is renewable fuel that can be produced from biomaterial. The important thing to make biodiesel is transesterification reaction. The reaction is needed base catalyst. The MSN catalyst has been successfully synthesized and modified using sulfonate functional groups. MSN catalysts have a 13.33% conversion activity from palm oil to biodiesel which consists of FAME 1 and FAME 2.

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