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### Modified Chitosan Into Chitosan Sulfonate Bead For Heterogeneous Catalyst Applications

Riniati, H.N. Chamidy and E. Widiastuti

Chemical Engineering Department, Politeknik Negeri Bandung, 40012, Bandung, Indonesia

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#### ABSTRACT

**Background:** Chitosan is a natural polymer found in many insects, marine invertebrates, fungi, and yeast. The presence of functional groups of -OH and -NH<sub>2</sub> in chitosan allows it can be converted into chitosan sulfonate. Chitosan Sulfonate can be applied as a heterogeneous acid catalyst in the esterification of oleic acid, especially in the manufacture of biodiesel. **Objectives:** Chitosan sulfonate was produced by crosslinked chitosan using sulfosuccinic acid and glutaraldehyde followed by soaking it into H<sub>2</sub>SO<sub>4</sub> for activation. Sodium hydroxide was used to produce chitosan sulfonate beads. Bead form was chosen for the chitosan sulfonate instead of thin film. Chitosan sulfonate beads should have a characteristic as a heterogeneous acid catalyst. The study was making a heterogeneous catalysts in the form of chitosan sulfonate bead. **Results:** The characteristics of chitosan sulfonate beads which made of 2% chitosan solution with a concentration of 8 mmol sulfosuccinic acid, 8M sodium hydroxide and 2.5% glutaraldehyde. FTIR characterization indicates the presence of functional groups of SO<sub>3</sub>H at 1118.71cm<sup>-1</sup> wave number, with IEC value of 1.265 mmol/g, the degree of development in the water by 55.43% and by 5.32% in methanol, and the surface area of 1.181 m<sup>2</sup>/g. **Conclusion:** The resulting chitosan sulfonate bead having a physical form as well as the characterization of functional groups, IEC and Ds quite as good as a solid heterogeneous catalyst, so it has potential to be applied in the manufacture of biodiesel esterification reaction with the substrate methanol and free fatty acids.

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#### INTRODUCTION

Chitosan is a natural polymer found in many insects, marine invertebrates, fungi, and yeast, which are classified as highly functional biopolymer. The existence of -OH and -NH<sub>2</sub> functional groups in chitosan allows a wide variety of chemical modifications (Ma Jia, Yogeshwar Sahai, 2013). By modifying its functional groups, a chitosan can be used for a variety of application purposes, one of which is used as an acid catalyst in the esterification process.

Homogeneous catalysts such as sulfuric acid are commonly used for the manufacture of biodiesel esterification reaction. In this case, the catalyst is at the same phase as the mixture, which is liquid. On the other side, heterogeneous catalyst having a better characteristic than homogeneous catalysts, such as environmentally friendly, non-corrosive, easily separated from the product by filtration, and can be used repeatedly in the long term. In addition, heterogeneous catalysts can improve product purity due to its capability to eliminate the side reactions.

Modification of the chitosan structure has been done by some researchers, such as by using a method of cross-linking with sulfosuccinic acid, glutaraldehyde (Wan, Y., 2006), sulfuric acid (Mukoma, P., 2004b) and propane sultone (Tsai, H., 2010) as cross-linking agents. Sulfonated chitosan mostly produced to form a chitosan network as an ion exchange film by using a mixture of sulfosuccinic acid and glutaraldehyde (Basuki, 2009; Dastimoghadam, E., 2010) as a cross-linking agent. Chitosan sulfonate production was formed as a thin film which was applied as a catalyst in the manufacture of biodiesel from oleic acid using methanol (Caetano, C.S., 2013).

This research designed to develop a heterogeneous catalyst chitosan sulfonate in the form of beads. Beads making refers to the manufacture of hybrid gel alginate-chitosan (Gotoh, T., 2003) bead. The advantages of a catalyst in a bead form is easier in the separation as well as more effective in surface contact between the catalyst and the substrate.

**Corresponding Author:** Riniati, H.N. Chamidy, Chemical Engineering Department, Politeknik Negeri Bandung, 40012, Bandung, Indonesia.  
E-mail: riniati.wahib@yahoo.com

### Methodology:

The industrial grade of chitosan which has a degree of deacetylation of 84.39% was used as a raw material, in this study. In the process of sulfonation of chitosan into chitosan sulfonate, crosslinking reagents used were sulfosuccinic acid p.a. and glutaraldehyde p.a. To produce bead and to activate the chitosan sulfonate, NaOH and H<sub>2</sub>SO<sub>4</sub> solutions were used.

The first stage among three stages on the making of chitosan sulfonate bead was the reaction of a 2% solution of chitosan with 2% acetic acid through constant stirring and heating at a temperature of 30-40 °C for ± 2 hours. The second stage was the sulfonation process of the chitosan solution through crosslinking reaction by using sulfosuccinic acid reagent (at various concentration of 5, 6, 7, 8 and 10 mmol). The third stage was the manufacture of sulfonate chitosan beads by dropping method in NaOH solution (at various concentration of 4, 6, 8, and 10 M). Sulfonate chitosan beads were washed with distilled water and dried at 60 °C for 2 hours. Further, the beads were crosslinked with glutaraldehyde then washed and dried again. Activation of the sulfonate group was done by soaking chitosan sulfonate bead into 2.5% H<sub>2</sub>SO<sub>4</sub> solution.

Characterization of chitosan sulfonate bead includes FTIR spectroscopy, structural morphology with SEM-EDX, the determination of the degree of development (Ds) in water and methanol, Ion Exchange Capacity (IEC) and surface area.

### Characterization of functional groups by FTIR:

The modification of chemical structure of chitosan into chitosan sulfonate was analyzed by Fourier Transform Infrared (FTIR) spectrometer (Shimadzu 8400). Spectrum was measured in the wavelength range of 4000-500 / cm.

### Characterization of the structure morphology by SEM-EDX:

Surface morphology and microstructure of chitosan sulfonate bead done by JSM-35 C Scanning electron microscope - energy dispersive X-ray (SEM-EDX).

### Degree of Swelling (Ds):

Analysis of the degree of swelling was done by soaking the chitosan sulfonate bead into water and into methanol at 25 °C for 24 hours. It was then dried with a tissue paper. Chitosan sulfonate was weighed before and after soaking. The water uptake (W) was then calculated from the following equation,  

$$Ds (\%) = [(W_{wet} - W_{dry}) / W_{dry}] \times 100$$
 Where W<sub>dry</sub> and W<sub>wet</sub> are the weights of dry and water swollen beads, respectively.

### Ion Exchange Capacity (IEC):

IEC analysis was done by immersing 100 mg chitosan sulfonate beads into 15 mL of 0.1 M NaCl and stirred for 24 hours at room temperature. Homogeneous solution was titrated with 0.1 M NaOH. IEC value was calculated based on the volume of NaOH required for titration.

$$IEC = M_{NaOH} / W_{dry}$$

Where M<sub>NaOH</sub>, is the mol equivalent (mequiv) of NaOH and W<sub>dry</sub>, the weight of the dry beads.

### Surface Area (SA):

Surface area analysis was done by using Quantachrome NovaWin surface area analyzer. The analysis includes surface area, pore volume and pore diameter.

## RESULTS AND DISCUSSION

The reaction between 2% chitosan solution with 8 mmol sulfosuccinic acid, 8M NaOH, and 2.5% glutaraldehyde resulting chitosan sulfonate bead with the most irregular shape and highest hardness. The chitosan sulfonate bead with 1-1.5 mm in diameter shown in Figure 1.



Fig. 1: Chitosan sulfonate beads

### Characterization of functional groups by FTIR:

Characterization of chitosan sulfonate bead using FTIR is shown in Figure 3.

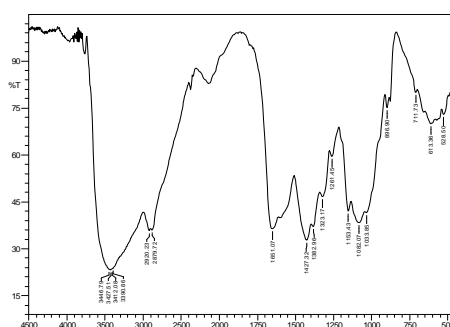


Fig. 2: FTIR Spectrum of Chitosan.

Figure 3 shows the IR spectrum which having widening peaks at wave number of 1118 cm<sup>-1</sup> and 1381 cm<sup>-1</sup>. This spectrum indicates a sulfonate group (-HSO<sub>3</sub>) on chitosan sulfonate bead. It proves the successful crosslink-reaction between chitosan with

sulfosuccinic acid which correspond to the reaction equation as Figure 4.

There is also a peak at the wave number 1730-1735  $\text{cm}^{-1}$  indicating ester functional groups. The esters itself resulting from the esterification reaction between -OH groups on chitosan with a carboxylic group of sulfosuccinic acid. The ester functional groups also reinforces the notion that the chitosan undergo sulfonation by sulfosuccinic acid.

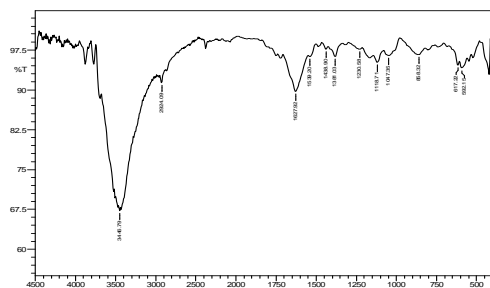


Fig. 3: FTIR Spectrum of Chitosan Sulfonate.

In addition, there is also a peak at wave number 1760  $\text{cm}^{-1}$ , which reported an imine bond,  $\text{N}=\text{C}$  [3]. Imine bond is the result of forming / bonding between the amine of the chitosan with the aldehyde of glutaraldehyde. Other IR spectra of chitosan sulfonate is NH peaks in the region 3310-3500  $\text{cm}^{-1}$  wave which is an amine group. Then the wave region 2853-2962  $\text{cm}^{-1}$  which is a CH group which is  $\text{CH}_3$  group of chitosan.

#### Spectrum SEM – EDX:

The SEM photographs of the chitosan sulfonate bead surfaces is shown in Figure 5. It was observed that the porosity of the chitosan sulfonate bead after activation were homogeneously dispersed in the bead, leading to the fact that sulfonate groups were able to interact to the chitosan. As the porous diameter getting bigger the more sulfonate group in the chitosan. The porous diameter of chitosan sulfonate bead was 0.5  $\mu\text{m}$  in average.

Moreover, the SEM-EDX observation provide information about the elements present on the surface of chitosan sulfonate bead. As depicted in Figure 6, it can be seen that the main component in the matrix structure of the membrane is the carbon and nitrogen. A high presence of  $\text{SO}_3$  in the chitosan sulfonate resulting a succesfull cross linked reaction of chitosan and sulfosuccinic acid.

#### Ion Exchane Capacity, (IEC):

One of important factors in measuring the performance of a heterogeneous acid catalyst is the value of Ion Exchange Capacity (IEC). It stating the amount of  $\text{H}^+$  ions contained in 1 gram samples of polymer which can be determined by acid-base titration method.  $\text{H}^+$  ions in  $\text{SO}_3\text{H}^+$  are replaced by  $\text{Na}^+$  in NaCl, forming  $\text{SO}_3\text{Na}$  and HCl. HCl formed will be titrated with NaOH through Phenofltalein

indicator. The amount of NaOH required is directly proportional to the volume of  $\text{H}^+$  originating from  $\text{SO}_3\text{H}^+$  on chitosan sulfonate.

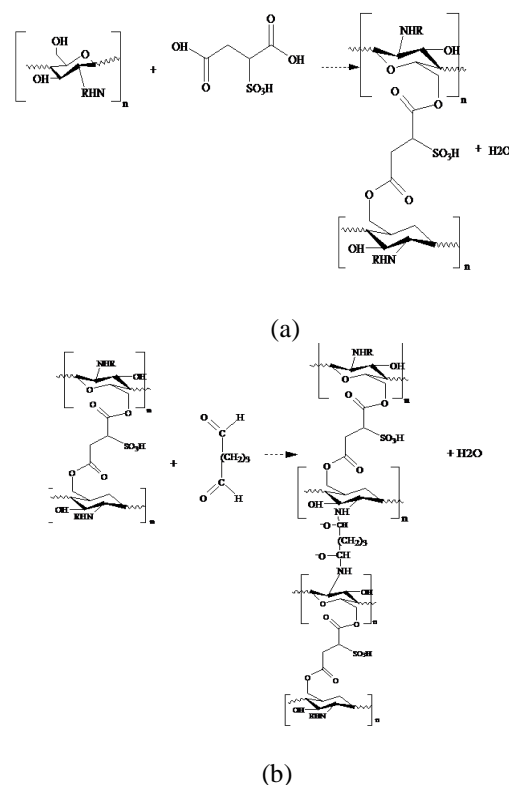


Fig. 4: The crosslinked reaction of chitosan with sulfosuccinic acid (a) and glutaraldehyde (b).

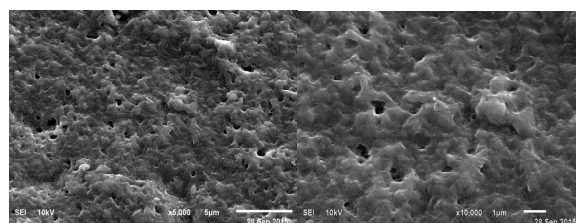


Fig. 5: Top surface SEM Photograph of Chitosan Sulfonate Bead.

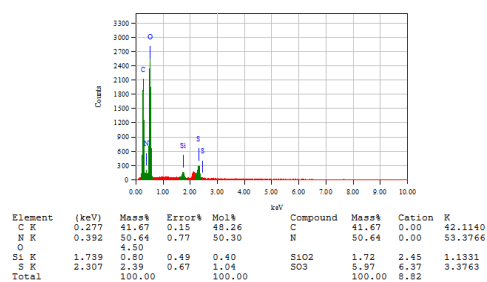


Fig. 6: EDX Spectrum of Chitosan sulfonate bead.

IEC value increases as the increasing presence of sulfonate groups (Figure 7).. The hydroxy groups on chitosan which is more difficult to remove the proton replaced with sulfonate groups which is easier to remove the proton. The higher the sulfonate groups from sulfosuccinic acid attach to the chitosan, the higher its IEC value (Caetano, C.S., 2013). The highest value of IEC achieved at 1.265 mmol/g with the concentration value of sulfosuccinic acid at 8 mmol.

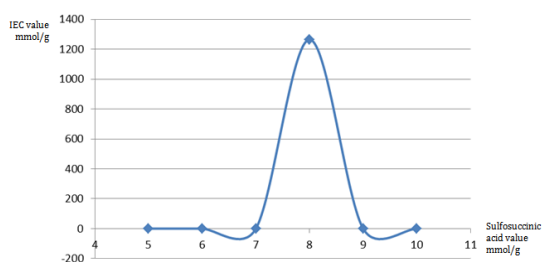


Fig. 7. IEC value of Chitosan sulfonate bead

#### Degree of Swelling (Ds):

The determination of Ds was done by soaking chitosan in a solvent during a certain time frame. The solvent used were water and methanol. The higher number of  $\text{SO}_3\text{H}^+$  in chitosan sulfonate makes it more hydrophilic which increasingly attracts

water. It was observed that the Degree of swelling of the chitosan sulfonate bead in methanol found smaller than in water (Figure 8). This is because the nature of methanol which can draw water from chitosan sulfonate. Degree of swelling of a catalyst is said to be good if it has low value.

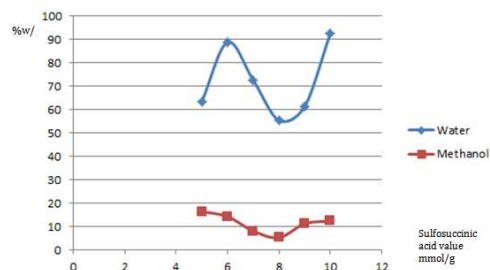


Fig. 8: Degree of swelling of Chitosan sulfonate bead.

#### Surface Area Determination:

The surface area, pore diameter and pore volume are important parameters in the catalytic process. The larger the surface area of a catalyst, the greater the contact between the substrate and the active part of the catalyst. The value of surface area, pore volume, and pore diameter is shown in Table 1.

Table 1: Surface Area of Chitosan Sulfonate bead.

Surface Area ( $\text{m}^2/\text{g}$ )	1.181
Pore Volume ( $\text{cc}/\text{g}$ )	0.001
Pore Diameter ( $\text{\AA}$ )	48.82

#### Conclusion:

Chitosan sulfonate bead prepared from 2% chitosan solution reacted with 8 mmol sulfosuccinic acid, 8M sodium hydroxide has a stable physical properties of the granules and high hardness.

Chitosan sulfonate has an IEC value of 1.265 mmol/g, the degree of development in the water was 55.43% and 5.32% in methanol. The surface area was  $1.181 \text{ m}^2/\text{g}$ , pore diameter of  $48.82 \text{ \AA}$  and a pore volume of  $0.001 \text{ cc}/\text{g}$ . In general, the resulting chitosan sulfonate beads having a good physical form and characterization as a solid heterogeneous catalysts. Hence, it is very potential to be applied in the manufacture of biodiesel esterification reaction with the substrate methanol and free fatty acids.

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