The Use of Heterogeneous Catalysts of Chitosan Sulfonate Bead on the Esterification Reaction of Oleic Acid and Methanol

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Abstract. Biodiesel is one of the ester compounds with physical properties closer to a biodiesel which can be produced by the esterification reaction between methanol and oleic acid (one of major components present in Palm Fatty Acid Distillate, PFAD). The purpose of this study was to obtain an optimum condition of esterification reaction by using chitosan sulfonate bead as heterogeneous catalysts. Chitosan sulfonate bead was made from chitosan undergo sulfonation process using acidic reagents cross-linked with sulfosalicylic and glutaraldehyde with a high enough value of ion exchange capacity. The stage of esterification reactions was carried by varying the amount of catalyst being added (4, 6, 8, 10, 12% by oleic acid), the operating temperature was varied of 40, 50 and 60 °C, and the reaction time of 1, 2, 3, 4 and 5 hours. Conversion determination of the products was done by analysing the free fatty acids content in each sample. Having obtained from the optimum amount of catalyst being added, temperature, and time, it was found that the catalyst was at 8%, 50 °C, during 5 hours in operation. The maximum conversion of oleic acid into biodiesel was 73.12%.

Keywords : catalysts, chitosan, sulfonate, oleic acid, methanol

1. Introduction
Chitosan is a long chain of beta polymeric glucose constructed of (2-acetamido-2-deoxy-ß-D-glucose-(N-acetylglucosamine)) (Figure 1) derived from chitin, a natural polysaccharide usually obtained from carapaces of the marine crustaceans such as crabs and shrimps [19]. It is cheaper to use Chitosan since chitin is the second most abundant biopolymer in nature next to cellulose [10].

![Chitosan structure](Thate, 2004)

Figure 1. Chitosan structure (Thate, 2004)

Chitosan is the most attractive choice of immobilization since it offers several advantages such as versatility of available physical forms (flakes, porous beads, gel, fiber and membrane); low biodegradability; ease of handling; high affinity for proteins and, above all, non-toxicity (Felse and
Panda, 1999). Chitosan may have been applied in various fields such as biotechnology, pharmaceutical, waste water treatment, agriculture and food. To increase the use of chitosan, it was synthesized and sulfonated to produce an insoluble acid chitosan sulfonate bead [2].

![Figure 2. Chitosan derived from chitin (Thate, 2004)](image_url)

Oleic acid, representing free fatty acid (FFA), is the second largest component present in the Palm Fatty Acid Distillate (PFAD) [1]. PFAD is a waste (a by-product of the refining process) produced during cooking oil production with a high free fatty acid content. The major components in PFAD are lauric acid (0.1%-1.7%), myristic acid (1.0%-1.8%), palmitic acid (46.4%-51.2%), stearic acid (3.7%-5.1%), oleic acid (33.0%-37.7%) and linoleic acid (7.8%-9.6%) [15]

Esterification of FFA with low-molecular-weight of alcohols using acid or base catalysts will produce biodiesel and water [18]. Homogeneous catalyst is a commonly used for acid catalyst [12]. However, homogeneous catalysts are corrosive; contaminate the product and causing environmental problems. The use of heterogeneous catalysts that are more environmentally friendly will partly solve these problems. It has an advantage of easily separated from its liquid with a low percentage loss of the catalyst.

![Figure 3. Esterification of FFA](image_url)

The existence of -OH and -NH₂ functional groups in chitosan allows a wide variety of chemical modifications that are classified as highly functional chitosan biopolymer. These groups can be used as an acid catalyst through sulfonation reaction [3]. Sulfonation could occur by chemically attaching sulfonate groups to chitosan using various methods and conditions [9]. N-sulfonated chitosan is attaching sulfonate groups into NH site, whereas O-sulfonated is attaching sulfonate groups into OH site. Propane sultone [20] is the example of N-sulfonated reaction. 5-sulfoisalicylic acid, and glutaraldehyde, SO₃ or chlorosulfonic acid reagents and dimethylformamide which has been patented by Hayashi (1993) are the example of O-sulfonated reaction. This method will improve the proton conductivity.

Chitosan which activated by -SO₃H group called chitosan sulfonate, could be applied as a catalyst in the process of esterification for biodiesel production [3]. In 2013, Castanheiro et al. have done a heterogeneous catalyst preparation of sulfonate-based biopolymer chitosan by reacting chitosan and sulfosuccinic acid. He produces a heterogeneous catalyst in a sheet form. Heterogeneous catalyst could be prepared by dissolving chitosan in a 2% acetic acid to form poly-cation. Sulfoisalicylic acid then be cross-linked to the functional groups -OH so that the chitosan has a sulfonate group (SO₃H⁻).
The -OH functional group is easier to remove proton ions (Figure 4) rather than –NH2. Sulfosalicylic acid as sulfonate group is a hydrophilic in which easier to remove proton ions at -OH groups. The production of chitosan sulfonate bead using sulfosalicylic acid was an electrophilic substitution, where SO$_3^-$ being attacked by a pair of free electrons of oxygen and nitrogen. The sulfonation can occur in two functional groups, namely the hydroxy and amine groups.

However, hydroxy group was the most likely sulfonated as the acidic atmosphere will protonated amine groups. The oxygen atom was more electronegative than nitrogen in the amine group so that when there was a free proton, the electron pair of the oxygen atom at the hydroxy group will attack it [2].

**Figure 4.** Cross-linked reaction of chitosan and sulfosalicylic acid

**Figure 5.** Chitosan sulfonate production

### 2. Experimental Method

Industrial grade chitosan with a degree of deacetylation of 84.39% was obtained from Biotech Surindo. 5-sulfosalicylic acid and glutaraldehyde were obtained from Merck. NaOH, H$_2$SO$_4$, a pure oleic acid, and methanol were obtained from commercial sources.

The chitosan sulfonate bead were prepared by dissolving 2 gram of chitosan in a 2 wt.% acetic acid solution (100 mL) to make a 2% in concentration and stirred in 30-40 °C for 2 hours. After complete dissolution of the chitosan flakes, the solution was added with sulfosalicylic varied at 17, 18, 20, and 22 mmol per liter of chitosan. Stirring was continued at ambient temperature for another 24 hours. The beads were formed by dripping the bubble-free mixture through a disposable plastic syringe with 2 mm outlet diameter into 200 mL, 8M NaOH solution for 30 minutes. The beads formed were then filtered and neutralized using aquadest. Cross-linking was done again by soaking the chitosan beads into 200 mL of 2.5% glutaraldehyde solution at ambient temperature for 24 hours. After filtering and washing, the beads were then soaked again in 200 mL of 2.5% acetic acid for another 24 hours. The
chitosan sulfonate beads were then filtered, neutralized, and dried at 60 °C for 3 hours and stored in a desiccator for 1 hour.

On the esterification reaction, the amount of catalyst was varied at 4, 6, 8, 10, and 12 wt% of oleic acid. The reaction was carried at ambient temperature. The optimum result will then be used for further esterification reactions by varying the reaction time at 1, 2, 3, 4 and 5 hours and also varying the operating temperature at 40, 50 and 60 °C.

Characterisation was done by determining the ion-exchange capacity (IEC) of chitosan sulfonate beads. IEC indicates the number of mili-equivalents of ions in 1 g of dry polymer. In brief, required amount of chitosan sulfonate bead sample was soaked in 50 mL of 3M sodium chloride (NaCl) solution for 24 h. Nearly 10 mL of the above solution was titrated against 0.01N sodium hydroxide (NaOH) solution using phenolphthalein as the indicator. By measuring the amount of NaOH consumed in the titration, the molar quantity of the sulfonic acid groups contained in the chitosan sulfonate sample was determined. By using this value, IEC was estimated by Equation (1).

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\text{IEC} = \frac{\text{Vol of NaOH consumed} \times \text{Normality of NaOH}}{\text{Dry weight of Chitosan sulfonate}} \quad \text{(meq/g)}
\]

FTIR Shimadzu 8400 was used to analyze a known amount of chitosan sulfonate bead for sulfonate group existence. Degree of conversion of oleic acid to become biodiesel was done by analyzing the free fatty acids content in each sample.

3. Results and Discussion

Dried chitosan sulfonate bead which has been produced have a diameter of 1-1.5 mm (Figure 6). The important factor of the resulting catalyst quality was the value of Ion Exchange Capacity (IEC), particularly regarding with the existing number of H⁺ ions. As the amount of sulfosalicylic acid rises, the IEC value rises. It was found that a harder bead indicating a higher IEC. In certain high amount of sulfosalicylic acid, the bead becomes soft, and will decrease the IEC.

IEC could be used as proton conductivity estimation indirectly on the ion exchangeable groups present in a bead for proton conduction [13]. Figure 7 shows that IEC was directly related to degree of sulfonation. IEC of chitosan sulfonate bead was varied between 0.14 and 0.34 mmol/g. The IEC was low because of the low reactivity of the aromatic rings directly attached to the sulfone groups.
The ability of the catalyst to perform an ion exchange was strongly influenced by the condition of the parent charged ions in the polymer chain, it was the existence of -HSO$_3^-$ group. A higher IEC value of sulfonate chitosan beads, indirectly indicating that cross-link was occurred.

The presence of sulfonate groups that resulted from crosslinking reaction in the sulfonation process can be observed from FTIR spectra of the chitosan sulfonate. The FTIR spectra of chitosan sulfonate shows in Figure 8. The peak at 1118 cm$^{-1}$ is the characteristic absorption bands of OH group in sulfonic acid. Meanwhile, the peak at 1124.50 cm$^{-1}$ could be ascribed as the stretching vibration of sulfoxide in sulfonic acid. The result suggests that the crosslinking between sulfsalicylic acid and chitosan was successful and chitosan was sulfonated. From the FTIR analysis, the results suggest that crosslinking reaction was successful and chitosan was sulfonated.

The chitosan sulfonate used as a heterogeneous catalyst in the esterification of oleic acid was the highest IEC achieved, which was using 20 mmol/g addition of sulfsalicylic acid. At ambient temperature, the conversion of oleic acid into biodiesel increases as the amount of catalyst increases from 6% into 8% by weight of oleic acid used. The highest oleic acid conversion was achieved during addition of 8% chitosan sulfonate bead.
Figure 9. FFA Conversion by Catalyst Concentrations

To continue the esterification, the reaction condition was varied by varying the temperature and time taken using 8% addition of the catalyst. The highest value of conversions was achieved on hour-5 at the reaction temperature of 50 °C (Figure 10). The maximum conversion of oleic acid into biodiesel was 73.12%.

Figure 10. Conversion degree of FFA by varying time and temperature

4. Conclusion
The chitosan sulfonate bead as heterogeneous catalyst produced has the highest IEC value of 0.34 mmol/gram by addition 20 mmol/L sulfosalicylic acid. The optimum conditions were 8% of chitosan sulfonate concentration in esterification reaction of oleic acid and methanol with a temperature of 50 °C for 5 hours which resulted in the conversion of oleic acid to form biodiesel up to 73.10%. It is expected these conditions can be applied to the manufacture of biodiesel using oleic acid.

5. References
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