Chitosan and \(N\)-Alkyl chitosan as a heterogeneous based catalyst in the transesterification reaction of used cooking oil

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Abstract. This paper explains the result of research on the use of chitosan and \(N\)-alkyl chitosan (\(N\)-methyl chitosan, \(N\)-isopropyl chitosan) as a heterogeneous base catalyst in the transesterification reaction of used cooking oil. \(N\)-methyl chitosan and \(N\)-isopropyl chitosan synthesized by reacting chitosan with formaldehyde and acetone successively forming Schiff bases were then reduced using NaBH\(_4\). Then chitosan, \(N\)-methyl chitosan, \(N\)-isopropyl chitosan are used as heterogeneous catalysts in the transesterification reaction of used cooking oil. The results show that inclusion of alkyl groups to the chitosan structure leads to increase the amount of base in which chitosan, \(N\)-methyl chitosan, and \(N\)-isopropyl chitosan are 0.066 mole.g\(^{-1}\), 0.0068 mole.g\(^{-1}\), 0.0070 mole.g\(^{-1}\) respectively. It is also evident from the increasing yield of methyl esters. \(N\)-isopropyl chitosan gives the greatest content of methyl esters yield.

1. Introduction
Chitosan and the derivatives are rarely used as a heterogeneous catalyst for transesterification reaction. It is usually used as supporting material of metal catalyst [1], enzyme [2] metal oxide catalyst [3].

Chitosan is a polysaccharide contain units of \(N\)-acetyl-D-glucosamine and D-glucosamine produced from the \(N\)-deacetylation of natural chitin polymers derived from the shells of marine animals, or fungi [4]. The high reactivity of free amine groups makes chitosan has potential as a Lewis base. The longer chain of chitosan gives more content of free amine groups so that the amount of base increase. Chitosan and the derivatives are expected to replace the homogeneous base catalysts used in transesterification processes such as NaOH and KOH. The amount of base chitosan amine group can be improved by incorporating the electron driving group to the amine group. One of the electron driving group is an alkyl functional group. The electron driving group will increase the stability of cation about the amine group that increases the amount of base [5].

This work reports the use of chitosan and \(N\)-alkyl chitosan (\(N\)-methyl chitosan and \(N\)-isopropyl chitosan) in transesterification reaction of used cooking oil and their amount of base evaluation.

2. Methods
2.1. Chemicals and Analysis Instruments
All chemicals were obtained from Merck, Germany. Chitosan was kindly donated by LIPI Yogyakarta. Used cooking oil was collected from “pecellele” food stalls around the campus of the Islamic University of Indonesia.

Methyl esters and functional group analysis were performed using Gas Chromatography (Agilent Technologies 6890 N), Mass Spectrometer (Agilent Technologies 5975 B), and Fourier Transform Infrared (FTIR) Spectrophotometer (Thermo Nicolet Avatar 360).
2.2. Synthesis of N-methyl chitosan
Synthesized chitosan derivative refers to the study of Kim and Choi (2001) was made of chitosan solution of 1% w/v by dissolving 5 grams of chitosan into glacial acetic acid 1% v/v of 500 mL. Furthermore, 1.6683 mL of formaldehyde 10% was added to the chitosan solution at room temperature and stirred using a magnetic stirrer at 500 rpm. After one hour, the pH of the solution was conditioned to 4.5 with NaOH 1M solution was added. Then this solution was added to the NaBH$_4$ solution of 10% w/v in 3.17 mL of water and the solution mixture was stirred for 1.5 hours. N-methyl chitosan produced subsequently precipitated at the pH 10. Precipitated material was washed with distilled water to neutralize the product. The precipitate was then dried at a temperature of 35 °C for several days to obtain dry N-methyl chitosan. Products were then characterized using FTIR spectrophotometer [6].

2.3. Synthesis of N-isopropyl chitosan
Synthesized chitosan derivative refers to the study of Kim and Choi (2001) was made of chitosan solution of 1% w/v by dissolving 5 grams of chitosan into glacial acetic acid 1% v/v of 500 mL. Furthermore, 4.411 mL of acetone 10% was added to the chitosan solution at room temperature and stirred using a magnetic stirrer at 500 rpm. After one hour, the pH of the solution was conditioned to 4.5 with 1M NaOH solution was added. Then this solution was added to the NaBH$_4$ solution of 10% w/v in 3.17 mL of water and the solution mixture was stirred for 1.5 hours. N-isopropyl chitosan produced subsequently precipitated by conditioning the pH 10. The material precipitate was washed with distilled water to neutralize the product. The precipitate was then dried at a temperature of 35 °C for several days to obtain dry N-isopropyl chitosan. Products were then characterized using FTIR spectrophotometer [6].

2.4. Amount of base determination of chitosan and N-alkyl chitosan
A total of 0.5 grams of chitosan or N-alkyl chitosan dissolved in 60 mL of HCl 0.0782 N. Few drops of phenolphthalein indicators incorporated into the solution. The solution was titrated using 0.108 N NaOH, and the volumes are noted to know the volume of HCl remaining. Moles of HCl determine the level of the amount of base chitosan and N-alkyl chitosan.

2.5. Treatment of used cooking oil
Used cooking oil was filtered through filter paper to remove solid particles ballpark. Then the filtrate is cleaned by using adsorbents of activated charcoal

2.6. Transesterification reaction of used cooking oil
Transesterification reaction was carried out in a two-neck round bottom flask of 250 mL capacity that has equipped with a hot plate, thermometer, magnetic stirrer, and condenser. One gram of chitosan inserted into a two-neck round bottom flask and then coupled with the condenser. The amount of filtered used cooking oil and methanol is added to the flask with a mole ratio of oil: methanol is 1:12 and refluxed for 2 hours at a temperature of 60 °C. After 2 hours, the reflux was stopped, and the mixture formed was poured into a test tube. The methyl esters were taken, weighed, and calculated the yield of methyl esters. Transesterification process above is repeated for the other catalysts, N-methyl chitosan, and N-isopropyl chitosan

3. Result and Discussion
3.1. Synthesis and characterization of chitosan and N-alkyl chitosan
Chitosan, N-methyl chitosan, and N-isopropyl chitosan synthesized by reacting chitosan with formaldehyde and acetone successively forming Schiff bases were then reduced using NaBH$_4$. 
N-methyl chitosan was produced by weighing 4.35 grams of pure chitosan weight used 5 grams. While the N-isopropyl chitosan products produced weighing 4.26 grams of pure chitosan weight of 5 grams. N-methyl chitosan and N-isopropyl chitosan were then characterized using FTIR and FTIR results were compared with the data of chitosan. FTIR spectra of chitosan, N-methyl chitosan, and N-isopropyl chitosan is shown in Figure 1.

FTIR spectra of chitosan in Figure 4(A) showed that $3444 \text{ cm}^{-1}$ is the absorption of hydrogen bonded to hydroxyl groups. The absorption band at 1020 - 1155 cm$^{-1}$ showed the C-O vibration of chitosan. The absorption band at $2919 \text{ cm}^{-1}$ shows alkanes and also gives absorption at $1457 \text{ cm}^{-1}$ that indicates the type CH$_2$ - group of alkanes. Absorption in the region $1580 - 1650 \text{ cm}^{-1}$ (2 peaks) showed primary amine NH$_2$. The difference between the absorption of chitosan and chitosan N-methyl group is located on NH absorption. NH$_2$ on chitosan occurred in the $1580 - 1650 \text{ cm}^{-1}$ with two peaks while the N-methyl chitosan is only formed one peak which means the NH$_2$ group has been transformed into NH. Furthermore, to know that there has been a methyl group on chitosan (N-methyl chitosan) can be identified by the presence of absorption at $1381 \text{ cm}^{-1}$. Uptake of NH with -CH$_3$ CN formed at $1250 \text{ cm}^{-1}$. FTIR spectra of N-isopropyl chitosan in Figure 1(C) has an absorption at ~ $1380-1400 \text{ cm}^{-1}$ (2 peaks ) with a high intensity. It indicates that there is isopropyl group in the N-isopropyl chitosan catalysts.

### 3.2. Amount of base of chitosan and N-alkyl chitosan

Determination of amount of base of chitosan and N-alkyl chitosan showed that inclusion of alkyl groups to the chitosan structure leads to increase of base that is shown in Table 1.

| Catalyst              | Amount of base mole.g$^{-1}$ |
|-----------------------|------------------------------|
| Chitosan              | 0.066                        |
| N-methyl chitosan     | 0.068                        |
| N-isopropyl chitosan  | 0.070                        |

Amine group in D-glucosamine unit of chitosan is the weak base. The amount of base chitosan amine group can be improved by incorporating the electron driving group to the amine group. Alkyl functional group will increase the stability of cation about the amine group, so that increase the amount of base.
Figure 1. FTIR Spectra of (A) chitosan, (B) N-methyl chitosan, (C) N-isopropyl chitosan
3.3. **Transesterification of used cooking oil**

Transesterification reaction gave unsatisfaction result of methyl ester yield. Transesterification using chitosan catalyst only gave 2.0% of methyl ester. Catalyst $N$-methyl chitosan and $N$-isopropyl chitosan gave 3.1% and 8.6% methyl ester yield, respectively.

When compared with homogeneous catalysts, the results obtained are very low. According to Lee et al. (2009), the synthesis of methyl esters (biodiesel) in laboratory scale is influenced by some factors. The factors are the type of catalyst (acid/base), the mole ratio of methanol to oil, the content of impurities (usually free fatty acids and water) and the reaction temperature [7].

Methyl palmitate and methyl oleate are the main compounds of methyl esters. The peak area of chromatogram showed that methyl esters yield increased with the use of catalysts (Figure 2).

![Figure 2](image-url)  
**Figure 2.** The methyl esters yield of methyl palmitate and methyl oleate with variation of chitosan and $N$-alkyl chitosan as a catalyst for the transesterification reaction.

The results above showed the increasing of the amount of base enhanced the methyl ester yield of methyl palmitate and methyl oleate.

4. **Conclusion**

The inclusion of alkyl groups to the chitosan structure increases the amount of base in which increasing the methyl ester yield of methyl palmitate and methyl oleate.

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