

## CHITOSAN AND N-ALKYL CHITOSAN AS A HETEROGENEOUS BASE CATALYST IN THE TRANSESTERIFICATION REACTION OF USED COOKING OIL

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### Abstract

It has conducted 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.

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<sub>4</sub>. Then chitosan, *N*-methyl chitosan, *N*-isopropyl chitosan are used as heterogeneous catalysts in the transesterification reaction of used cooking oil.

The results showed that inclusion of alkyl groups to the chitosan structure leads to increase in the level of alkalinity in which chitosan, *N*-methyl chitosan, and *N*-isopropyl chitosan respectively are 0.066 mol/g, 0.0068 mol/g, 0.0070 mol/g. It is also evident from the increase in the area of methyl palmitate and methyl oleate. The use of *N*-isopropyl chitosan gave the greatest methyl ester yield results is about 8.6%.

**Keywords:** chitosan, N-alkyl chitosan, methyl ester, transesterification, used cooking oil

### INTRODUCTION

Biodiesel is a promising alternative fuel that can be derived from plant oils, animal fats or used oil through transesterification with alcohol. Biodiesel provides less pollution than petroleum fuels. In addition it can be used without diesel engine re-modification.

Biodiesel production methods commonly used today is through the process of transesterification of vegetable oils using alkaline catalyst. In this reaction, the alcohol in the form of methanol and ethanol, added to the triglyceride using homogeneous alkaline catalysts such as NaOH, KOH, NaOCH<sub>3</sub>, or KOCH<sub>3</sub>. This process runs quickly and efficiently at a relatively low temperature. Even so, the cost of biodiesel production is still expensive and becomes an important issue. The production costs can be reduced by means of cheap raw material selection, production proper place, and the efficiency of the process. For example, the current began to use used cooking oil and non-edible oils such as castor oil (*Jatropha curcas*) as the base material.

Homogeneous process actually has some advantages, but there are a number of missing values efficiency. In addition to biodiesel, a transesterification process in conditions produce byproducts such homogeneous catalysts, glycerol, and excess alcohol all of which require additional washing and drying step to obtain pure biodiesel product. In the homogeneous process, the base catalyst will be lost by leaching. This leads to reduced efficiency and increased production costs. One way to improve efficiency is using heterogeneous catalysts. In principle, the heterogeneous catalyst, the catalyst material can be taken back (not lost) and can be reused as a catalyst so that the process of making biodiesel becomes more simple. A number of studies

have been done to take advantage of heterogeneous catalysts for transesterification process. One polymer that has potential as a heterogeneous base catalyst is chitosan (Gotch, 2008).

Chitosan is a polysaccharide made up of units of *N*-acetyl-D-glucosamine and D- glucosamine produced from the *N*-deacetylation of chitin natural polymers derived from the shells of marine animals, or fungi (Dunn, 1997). High reactivity of free amino groups makes chitosan has potential as a Lewis base. The longer the chain of chitosan, the more the content of free amino groups, the higher the alkalinity properties. Alkalinity is expected to replace the homogeneous alkaline catalysts used in transesterification processes such as NaOH and KOH. Additionally alkalinity chitosan amine group can be improved by incorporating the driving force electrons to the cluster amine group. One of the driving force of the electron is an alkyl group. Forces driving the electrons will increase the stability of the amine cation independent so alkalinity increased (Fessenden, 1994).

The Indonesian people are consuming particular foods using cooking oil as the processing of eating. The rest of the frying pan can no longer be used as food or as ingredients other. Usually the rest of the discarded frying pan without any benefits. This wasted material adverse impact on the environment if the capacity is large enough. Seeing a considerable amount of this kind of oil it would be worth if it be processed and used as fuel for diesel engines (Sandford, 1989; Shahidi, 1999; Sudhir, 2007).

## RESEARCH METHODS

### Chemicals and Analysis Instruments

All chemicals were obtained by Merck, Germany. Chitosan was kindly donated by LIPI Yogyakarta. Used cooking oil was collected from “pecel lele” food stalls around campus of Islamic University of Indonesia.

Gas Chromatography-Mass and functional group analysis was performed using *Gas Chromatography* merk Agilent Technologies 6890 N, *Mass Spectrometer* merk Agilent Technologies 5975 B, and Spectrophotometer FTIR Thermo Nicolet Avatar 360.

### Synthesis of N-methyl chitosan

Synthesized chitosan derivative refers to the study of Kim and Choi (2001) is 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<sub>4</sub> 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 by conditioning the pH 10. 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 in order to obtain dry *N*-methyl chitosan. Products were then characterized using FTIR spectrophotometer.

### Synthesis of N-isopropyl chitosan

Synthesized chitosan derivative refers to the study of Kim and Choi (1997) is 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<sub>4</sub> 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. 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 in order to obtain dry *N*-isopropyl chitosan. Products were then characterized using FTIR spectrophotometer.

### Determination of Alkalinity of chitosan and *N*-alkyl chitosan

A total of 0.5 grams of chitosan dissolved in 60 mL of HCl 0.0782 N. Few drops of phenol pthalein indicators incorporated into the solution. The solution was titrated using 0.108 N NaOH and recorded volumes titrannya to know the volume of HCl remaining. Total volume of HCl that interact with chitosan and *N*-alkyl chitosan from the reduction of the initial volume of HCl with HCl remaining. Moles of HCl determine the level of alkalinity chitosan.

### Treatment of used cooking oil

Used cooking oil was filtered with filter paper to remove solid particles ballpark. Then the second stage of cleaning is done by using adsorbents such as activated charcoal. As much as 100 grams of cooking oil put into different glass beaker is then heated to a temperature of 100°C. After the temperature reached 100°C adsorbents 5 grams put in a glass beaker containing used cooking oil. Further stirring for 80 minutes at 100°C with a speed of 500 rpm. The mixture was then filtered.

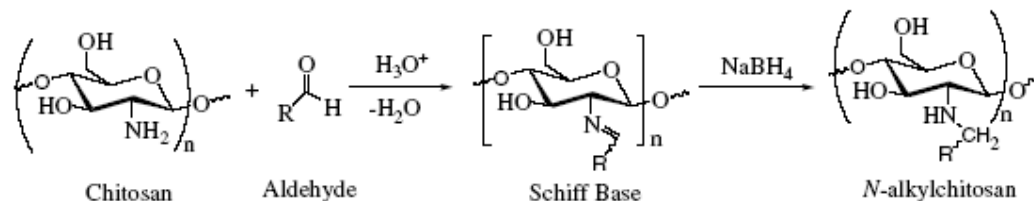
### Transesterification reaction of used cooking oil

Transesterification reaction was carried out in a two-neck round bottom flask of 250 mL capacity that has been equipped with a hot plate, thermometer, magnetic stirrer, and cooling systems. One gram of chitosan incorporated into a two-neck round bottom flask and then coupled with the cooling system, a certain amount of oil and methanol added to the flask with a mole ratio of used cooking oil : methanol is 1:12 and refluxed for 2 hours at a temperature of 60°C. In the solution of the many used cooking oil is 10 grams and as much as 5.67848 mL methanol. After 2 hours, the reflux was stopped and the mixture formed was poured into a test tube, the mixture was allowed some time at room temperature resulting in the separation solution. In order for the separation process completely formed then the mixture was centrifuged, and then will get 3 layers of the mixture is a row from top to bottom is the methyl ester, glycerol, and catalyst. Then methyl esters were taken, weighed and calculated yield of methyl ester produced. Transesterification process above is repeated for the other catalysts, *N*-methyl chitosan and *N*-isopropyl chitosan

## RESULT AND DISCUSSION

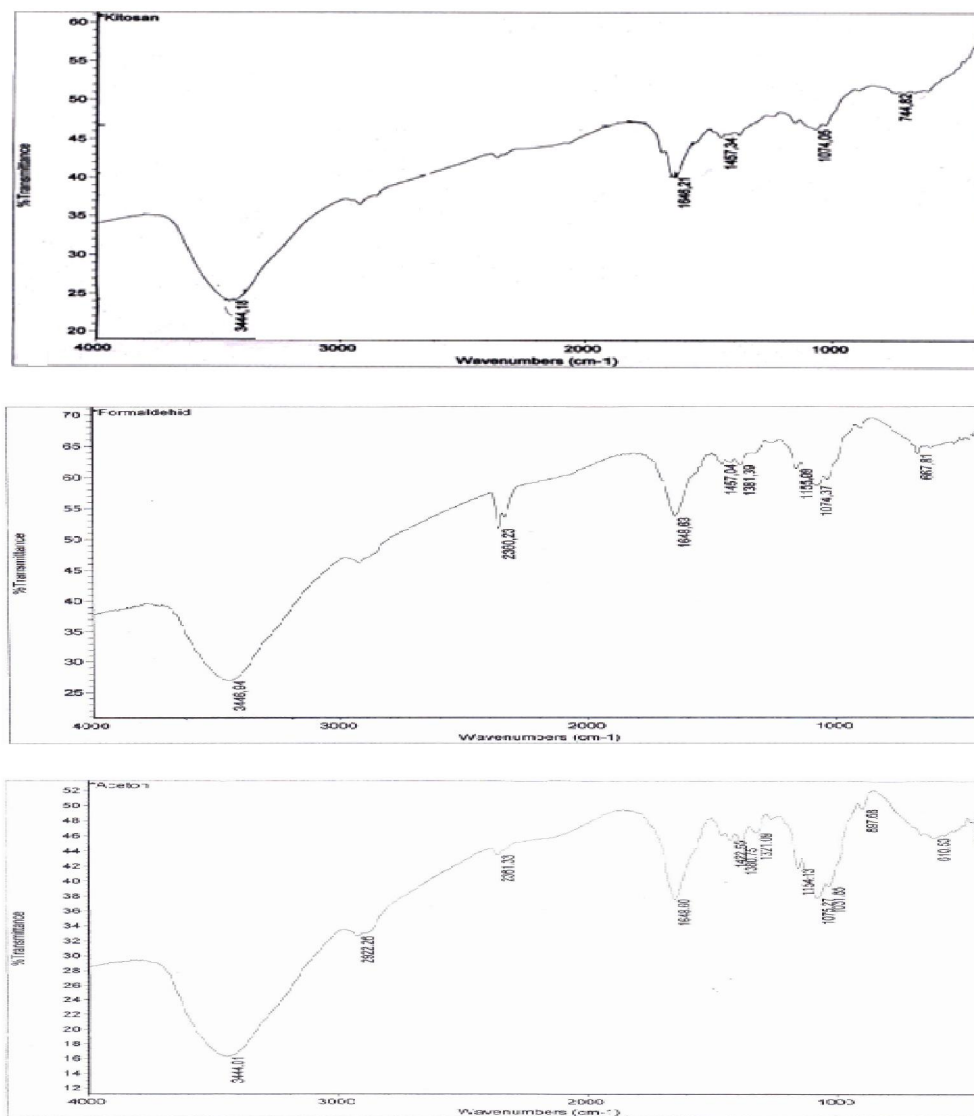
### Synthesis and characterization of chitosan and *N*-alkyl chitosan

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<sub>4</sub>.



*N*-methyl chitosan 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.



**Figure 1.** FTIR Spectra of (A) chitosan, (B) *N*-methyl chitosan, (C) *N*-isopropyl chitosan

FTIR spectra of chitosan in Figure 4(A) shows that  $3444\text{cm}^{-1}$  is the absorption of hydrogen bonded OH groups. Absorption band at  $1020 - 1155\text{cm}^{-1}$  shows the C-O vibration of chitosan in the ring and has several peaks due hydroxide on chitosan. Absorption band at  $2919\text{cm}^{-1}$  is the uptake of alkanes and enhanced absorption at  $1457\text{cm}^{-1}$  which indicates the type  $\text{CH}_2$ - alkanes. Uptake in the region  $1580 - 1650\text{ cm}^{-1}$  ( 2 peak ) showed uptake of primary amine  $\text{NH}_2$ . The difference between the uptake of chitosan and chitosan *N*-methyl group is located on NH absorption.  $\text{NH}_2$  on chitosan uptake occurred in the  $1580 - 1650\text{cm}^{-1}$  with 2 peaks , while the *N*-methyl chitosan uptake is only formed one peak which means the  $\text{NH}_2$  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 among NH with  $-\text{CH}_3$  CN formed at  $1250\text{cm}^{-1}$ . FTIR spectra of *N*-isopropyl chitosan in Figure 1(C) has an absorption at  $\sim 1380 - 1400\text{cm}^{-1}$  ( 2 peak ) with a high intensity . This suggests that there has

been isopropyl group in the *N*-isopropyl chitosan catalysts such.

FTIR spectra generated from it can be seen that there are some differences between the spectra of chitosan catchment area with *N*-methyl chitosan and *N*-isopropyl chitosan due to the modification of chitosan with increasing alkyl chain length. In the *N*-methyl chitosan chain is donated by methyl aldehyde group on formaldehyde interacts with the amine group on the chitosan. While the *N*-isopropyl chitosan, isopropyl group donated by a group of ketone from acetone.

#### Alkalinity of chitosan and *N*-alkyl chitosan

Determination of alkalinity of chitosan and *N*-alkyl chitosan showed that inclusion of alkyl groups to the chitosan structure leads to increase in the level of alkalinity in which chitosan, *N*-methyl chitosan, and *N*-isopropyl chitosan respectively are 0.066 mol/g, 0.0068 mol/g, 0.0070 mol/g.

#### 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) laboratory scale is influenced by the type of catalyst (acid/alkaline), the mole ratio of methanol to oil, the content of impurities (usually free fatty acids and water) and the reaction temperature. The most important issues in the process of catalysis using heterogeneous catalysts is a slow reaction speed compared with the homogeneous catalyst.

These problems can be solved one by raising the reaction temperature (100-250°C). According to Sakurai et al. (2000) chitosan has a thermal stability up to 203°C so it is still possible if done further research on the effect of temperature on the reaction rate.

Methyl palmitate and methyl oleate are the main compounds of methyl esters. Area of chromatogram showed that methyl esters yield increased with the use of catalysts.

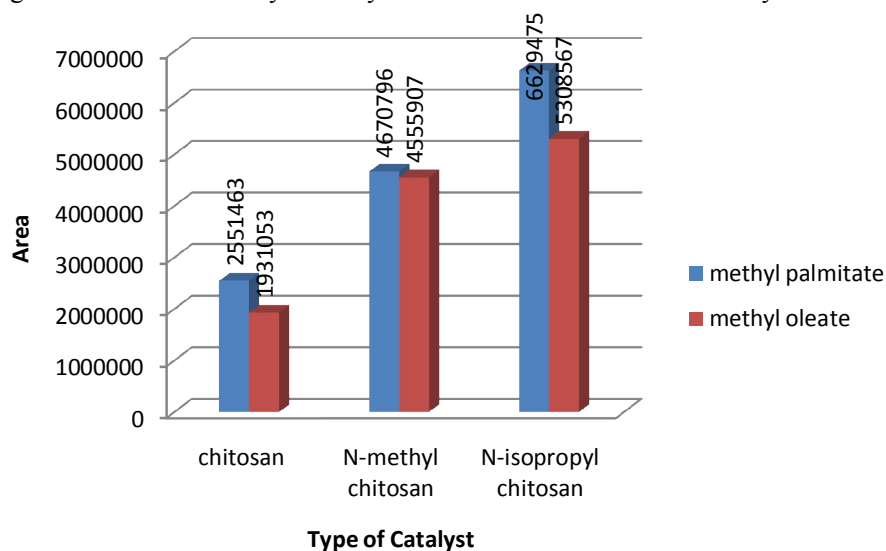


Figure 2. The methyl esters yield of methyl palmitate and methyl oleate with variation of chitosan and *N*-alkyl chitosan as catalyst of transesterification reaction

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

### CONCLUSION AND SUGESTION

Inclusion of alkyl groups to the chitosan structure leads to increase in the level of alkalinity in which chitosan, *N*-methyl chitosan, and *N*-isopropyl chitosan. The increasing of alkalinity enhanced the methyl ester yield of methyl palmitate and methyl oleate. The problem of the very low methyl ester yield can be solved by raising the reaction temperatur up to 203°C base on the thermal stability of chitosan.

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