

The Effect of Alkalization on Carboxymethyl Cellulose Synthesis from Stem and Peel Cellulose of Banana

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Abstract

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BACKGROUND: North Sumatra is one of the regions in Indonesia that produce bananas. Banana stems and peels contain cellulose and it can be isolated in nanofiber form. Carboxymethylcellulose is a cellulose derivative that undergoes an alkalization and etherification process

AIM: This research was conducted to evaluate the alkalization effect on synthesis of carboxymethyl cellulose from stem and peel cellulose of banana.

METHODS: Stem and peel of banana was extracted with NaOH 17.5% and the extract was synthesized to carboxymethyl cellulose (CMC). The synthesis of CMC was beginning with alkalization process in variation of NaOH concentration and the reaction was then etherificated with sodium monochloroacetate. CMC was characterized by FTIR and DS values were determined.

RESULTS: FTIR spectra of synthesized CMC had different pattern compared to cellulose. It showed that an etherification reaction had been occurred in the cellulose compound. Spectra of CMC with variation in alkali concentration was not much different from one another. The synthesized CMC from stem and peel cellulose of banana had different degree of substitution (DS) values due to variate concentration of NaOH in alkalization.

CONCLUSION: Alkalization on CMC synthesis affects the DS value of synthesized CMC. The increase DS value is proportional to the rise in NaOH concentration even though there is a boundary concentration to obtain the optimum DS value.

Introduction

Bananas are widely grown in tropical regions such as Indonesia. North Sumatra is one of the regions in Indonesia that produce bananas. The stem and peel are part of a banana plant that is removed and not used but contains a lot of cellulose. Banana stems contain cellulose and lignin up to 83% [1]. Pelissari et al., (2014) [2] and Khawas and Deka (2016) [3], have isolated cellulose from banana peels in nanofiber form.

Carboxymethylcellulose is a cellulose derivative that undergoes an alkalization and etherification process. First, cellulose is alkalinized with NaOH to facilitate the etherification process involves sodium monochloroacetate [4]. The concentration of sodium hydroxide increases the degree of substitution and viscosity to the optimum condition and then

decrease again [5]. Carboxymethylcellulose has been synthesized from cellulose of abaca, sisal, linen, jute, *Miscanthus sinensis* [6], Cavendish banana pseudo stem [7], sago waste [8], palm kernel cake [9], papaya peel [10], Water Hyacinth [11], oil palm fronds [4], and sugarcane bagasse [12].

However, no one has synthesized carboxymethylcellulose from the stem (CMCs) and peel of banana (CMCp) by looking at the effect of NaOH concentration on the alkalization process until now. The effect of NaOH concentration in the acclimatization process on the synthesis of carboxymethylcellulose from a stem and peel cellulose of banana is related to the degree of substitution. The degree of substitution is one of the factors that influence the character of carboxymethylcellulose. CMC usually has a degree of substitution with a range of 0.4-1.8. The degree of substitution states the number of units of

carboxymethyl groups. CMC which is soluble in water has a degree of substitution > 0.5 [13]. The degree of substitution can be determined by titrimetry and infrared spectroscopy. The degree of substitution is calculated from the differences of degree in the cellulose substitution with the absorbance ratio of methyl and carboxyl group of carboxymethylcellulose [14].

Material and Methods

The materials that used in this study were stem and peels of bananas were collected from farms in Medan, Indonesia. Sodium hydroxide, sodium hypochlorite, ether, acetic acid, isopropyl alcohol was prepared from Smart Lab Indonesia, sodium monochloroacetate, carboxymethylcellulose were purchase from the Merck Chemical Co. Aquadest was provided from the local market.

An amount of 50 g of the dried banana stem was mashed and heated with 1L NaOH 1% for 6 hours at 100°C with occasional stirring to remove the lignin and then washed with distilled water to neutral pH. The residue was soaked for 24 hours at room temperature with 3.5% sodium hypochlorite for bleaching and washed with distilled water. The residue was heated with 17.5% NaOH at 80°C for 1 hour to get alpha cellulose and washed with distilled water to neutral pH. If the level of bleaching was not good, then the residue was bleached again with 3.5% sodium hypochlorite for 5 minutes at 100°C. Then the residue was washed again with distilled water to a neutral pH. The same thing was done to extract cellulose from banana peels [15].

Synthesis of CMC was carried out by following the Tasaso procedure (2015), with a few modifications. 3 g of dried cellulose was dissolved with 30 ml of isopropanol and 10 ml of NaOH with varying concentrations of 10%, 15%, 20%, 25%, 30% in the Erlenmeyer. The alkalization process was conducted at 30°C for 60 minutes with the hotplate stirrer. Each of alkalization product was added 3 grams of sodium monochloroacetate and stirred for 3 hours at 50°C until carboxymethylation process was complete. This mixture was filtered and the residue suspended in methanol and neutralized with glacial acetic acid. The residue was washed with ethanol, filtered and dried at an oven temperature for 6 hours. The yield of synthesized CMC was calculated based on the dry weight of CMC and cellulose, following the formula below [10]:

$$\text{CMC yield (\%)} = \frac{\text{weight of prepared CMC (g)}}{\text{weight of dried cellulose (g)}} \times 100$$

Determination of the degree of substitution (DS) based on the absorbance of the infrared

spectrum. All samples were analyzed using the KBR method. Dry samples were mixed with KBR powder and analyzed by the Fourier-Transform Infrared Spectrophotometer (FTIR) in the wave number area between 400-4000 cm^{-1} . The Value of the degree of substitution was calculated based on the absorbance of carboxyl groups and methyl groups from cellulose and carboxymethylcellulose [14].

Results

CMC was synthesized from the stem and peel cellulose of the banana with a variety of NaOH concentrations. The yield of synthesized CMC (%) was different depending on the variation of NaOH concentration in the alkalization process. The yields of CMC from stems and peels cellulose of banana were shown in Table 1.

Table 1: Yield of the CMC from stem and peel cellulose of banana

Concentration of NaOH	CMC _s		CMC _p	
	pH	Yield (%)	pH	Yield (%)
10%	7.6	124.67	7.6	98.33
15%	7.6	132.67	7.0	104.66
20%	6.6	191.33	7.3	113.33
25%	7.8	160.00	7.5	133.66
30%	7.3	141.67	7.5	112.33

Table 1 shows that the concentration of NaOH in the alkalization process affects the percentage of the CMC obtained.

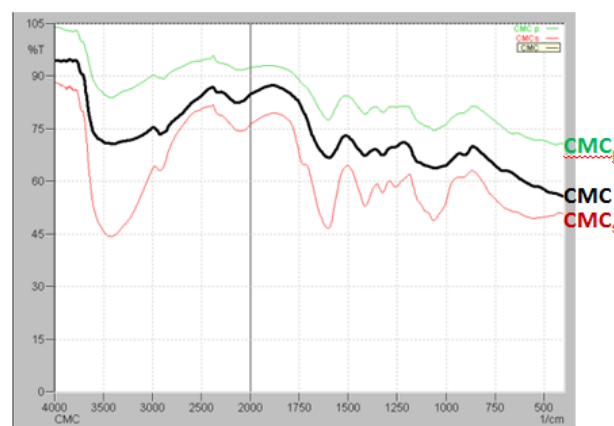


Figure 1: Infrared Spectrum of CMC_s and commercial CMC

The infrared spectrum of CMCs, CMC_p and commercial CMC were compared to Figure 1. It purposed to prove that the carboxyl and methyl groups had been substituted into the structure of the stem and peel cellulose of bananas to be carboxymethylcellulose.

Figure 2 demonstrates that the NaOH concentration in the alkalization process affects the DS from CMCs and CMC_p.

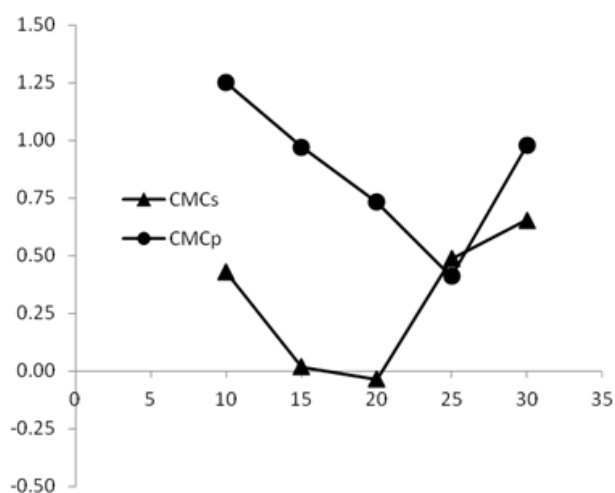


Figure 2: The Effect of NaOH concentration on the degree of substitution (DS)

Discussion

Percentage of CMC yield inclined with increasing NaOH concentration until the optimum value and then it decreased. NaOH concentration 20% gave the optimum value for the yield of CMCs, while the optimum yield of CMCP obtained in NaOH concentration 25%. The Alkali functioned open cellulose bonds by damaging crystalline clusters to form alkaline-cellulose complex and allowing water to enter. Making it easier for an alkali-cellulose complex to react with sodium monochloroacetate to produce sodium CMC [11].

The infrared spectrum patterns of CMCs and CMCP are similar to the commercial CMC. It indicated that the carboxyl and methyl groups have substituted into the cellulose structure of the stem and peel of a banana.

The highest DS was produced by NaOH concentration 25% for CMCs and NaOH concentration 30% for CMCP. It was suitable with the resultant study of Alizadeh et al., (2017) [12], which states that using of NaOH concentration over about 30% will decrease the DS values. High NaOH concentration would degrade the CMC polymer chain. In addition, there were two competing reactions in the carboxymethylcellulose synthesis in the use of monochloroacetic acid and sodium hydroxide, namely the reaction between cellulose and monochloroacetic acid in alkaline conditions and the reaction between sodium hydroxide and monochloroacetic acid in the formation of sodium glycolate [5]. DS of CMCs was higher than DS of CMCP. This proved that the source of cellulose also influenced the DS values as stated

by Alizadeh et al., (2017) [12]. DS values were obtained are less than 0.5. It indicated that CMCs and CMCP had low solubility in water. This could be influenced by the size of the cellulose particle from the stem and peel of a banana. The smaller particle sizes the higher surface area and the number of OH-free groups for substitution reactions. It would be easier for reagents to penetrate into cellulose and increase the affinity between cellulose particles and reactants. In addition, it can increase the rate of impregnation and carboxymethyl substitution [16], [17]. So that, it was necessary to reduce the particle size of the stem and peel cellulose of the banana.

The study found the NaOH concentrations 20% and 25% gave the optimum yield of CMCs and CMCP sequentially. While the optimum DS value was achieved at 25% and 30% of NaOH concentrations for CMCs and CMCP, respectively. The DS value produced was less than 0.4 which indicated that CMC insoluble in water. It is concluded that the NaOH concentration in the alkalinization process affects the yields and DS values of synthesized CMC. The more NaOH concentration the higher yield is acquired until the optimum point reached and then decreased again.

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