Article

Synthesis of Carboxymethyl Cellulose (CMC) from Banana Tree Stem: Influence of Ratio of Cellulose with Sodium Chloroacetate To Properties of Carboxymethyl Cellulose

Hendrik Aditya Mulyatno, Odisaputra Ihsan Pratama, Inayati*

Chemical Engineering Department, Engineering Faculty, Sebelas Maret University
Jalan Ir. Sutami No. 36A, Surakarta, 57126, Indonesia
E-mail: inayati@staff. inayati@staff.uns.ac.id (Corresponding author)

Abstract. Banana tree stem contain of 63-64% cellulose that can be processed into more valuable product. In this research, carboxymethylcellulose (CMC) from banana tree stem was prepared through alkalization and carboxymethylation process. The aim of this research was to investigate the effect of cellulose to sodium chloroacetate 1:1 and 1:2 to the properties of CMC. Samples were analyzed their NaCl content, purity of CMC, and degree of substitution. The result showed that sample with ratio 1: 2 between cellulose with sodium chloroacetate resulted greater NaCl content, lower purity of CMC, and greater degree of substitution.

Keywords: cellulose, carboxymethyl cellulose (CMC), degree of substitution (DS)

EQUILIBRIUM Volume 16 No.2 Juli 2017
Online at http://equilibrium.ft.uns.ac.id

1. Introduction

Everyone needs food as a staple. The United Nations Economic and Social Affairs Department 2007 stated that the world's population is about 6.7 billion people and approximately 234 million people live in Indonesia (CIA World Factbook, 2008).

With the increase of the world population not only cause an increase in production but also demands on quality improvement. One way to improve the quality of food is to add some additives to the production process. One of the most commonly used additives in various industries is carboxymethyl cellulose (CMC).

Currently, CMC has been widely used and has important benefits in various applications. CMC is widely used in the sectors of food, chemical, textile, petroleum, and paper manufacturing. Especially in the sector of food, CMC is used as a thickener, stabilizer, emulsifier, and adhesive. The applications of it are in the processing of jams, sauces, ice cream, beverages, and syrups. Due to its extensive use, easy to use, and cheap price, CMC becomes one of the preferred additives.

The exploration for sources of raw materials to produce CMC other than wood cellulose is an alternative to utilizing non-wood cellulose. One source of cellulose in Indonesia is banana tree stem. Directorate General of Horticultural Production stated that the potential of bananas reached 31.87% of total fruit production in Indonesia. In 2003, Indonesian banana production reached 2,374,841 tons with plantation area around 56,728 ha. Furthermore, in 2004, the production and the area increased to 2,758,709 tons and 65,897 ha. From these data can be seen the potential of banana tree stems as a source of CMC in the year 2003-2004 amounted to 79,603,169 - 92,469,504 tons (Sumarjono, 2004).

The main factors that need to be considered in CMC synthesis are alkalization and carboxymethylation processes because it determines the characteristics of CMC produced. In the carboxymethylation process, sodium chloroacetate reagents are used. The amount of sodium chloroacetate used will have an effect on the substitution value of the anhydroglucose unit on cellulose. Considering the role of sodium chloroacetate as a reagent, so there is a need to investigate the effect of cellulose ratios from banana tree stems with sodium chloroacetate to characteristics of CMC properties which will facilitate industrial manufacturers using CMC such as cosmetics, food, pharmaceutical, paper, textile industries in using of CMC.

2. Methodology

1. Materials

   The materials were banana tree stem, isopropyl alcohol, NaOH, aquadest, sodium chloroacetate, sodium metabisulfite, NaOCl, NaCl, acetic acid, $AgNO_3$, K_2CrO_4 indicator, and PP indicator.

2. Equipments

   Equipment used in this research are three neck flask, electric scales, blender, oven, furnace, pH indicator, magnetic stirrer, water bath, thermometer, beaker glass, cooler ball, clamps and stative.

3. Procedure

   a. Raw material preparation

      Banana tree stem that has been cut into pieces then reduced to 60 mesh size by using a blender. Then the lignin content in the banana tree stem was removed by cooking 25 grams of banana tree powder and 500 ml of 8% NaOH solution for 3 hours at 100^{o}C, then filtered and added 10 ml of 10% glacial acetic acid solution and 10 gram of NaCl, then washed with water and filtered. The washing powder is bleached with 500 ml of 6% NaOCl solution for 3 hours at 60°C. Then the results obtained were cooked again with 250 ml of 3% sodium metabisulfite solution and 250 ml of aquadest for 3 hours at 60°C. Then the results obtained are dried by using the oven and blended.

   b. Alkalization process and carboxymethylation

      In the alkalization process, 5 grams of cellulose, 100 ml of isopropyl alcohol, and 25 ml of 15% NaOH are inserted into a three-neck flask placed into a water bath. This alkalization process takes place at a temperature of 30°C for 1 hour. After that proceed with carboxymethylation process by adding sodium chloroacetate to the three neck flasks in accordance with the predetermined ratio. This process lasts for 3 hours at 55^{o}C.

   c. Process of neutralization and smoothing

The resultant mixture of carboxymethylation process was neutralized with 3 ml of 98% acetic acid solution, then filtered and washed with 50% alcohol solution. The filtered residue was dried in the oven for 4 hours at 60°C. Then the dried CMC is mashed using a blender and stored in a closed place.

d. Test

- 0.5 grams of dried CMC was dissolved in 100 ml of aquadest and added K_2CrO_4 indicator. Then titrated using a 0.1 N $AgNO_3$ solution and recorded the amount of AgNO3 solution used.
- Determination of purity of CMC
- Determination FTIR
- CMC solution pH measurement
- 0.5 grams of dry CMC was dissolved in 50 mL of aquadest and was heated at 70°C while stirring. The solution was then cooled to ambient temperature and was measured its pH.
- Determination of degree of substitution
- 0.35 grams of CMC placed in a porcelain cup was fed to the furnace for 5 hours at 750°C. After that are dried in the oven for 12 hours at a temperature of 100°C. The sample was then fed into a beaker glass and added with 17.5 ml of 0.1 N H_2SO_4 solution and 125 ml of aquadest, then boiled for 30 minutes. After the cold, the sample was added PP indicator, then titrated with 0.1 N NaOH solution until color change occurred. Separately weighing 0.5 grams of CMC and putting it into a beaker glass, then added 2.5 ml of 0.1 N H_2SO_4 solution and 100 ml of aquadest, then heated for 10 minutes. After the cold, the mixture was added PP indicator and titrated with 0.1 N NaOH solution. Then recorded the amount of NaOH solution required. The blank test without CMC is done at the same time.

3. Result and Discussion

Table 1. Parameter Test and Results

No	Parameter Test	CMC (SNI) Quality I	Quality II	CMC Sample I	CMC Sample II
1.	NaCl Content	0.25 %	-	0.1559 %	0.1948 %
2.	Purity CMC	99.50 %	65.00 %	99.8441 %	99.8052 %
3.	Degree of Substitution	0.7-1.2	0.4-1.0	1.0382	1.1368
4.	pH solution 1%	6.0-8.0	6.0-8.5	7.6	7.2

Information :
CMC Sample I : Sample with ratio of cellulose: sodium chloroacetate = 1: 1
CMC Sample II: Sample with ratio of cellulose: sodium chloroacetate = 1: 2

1. NaCl content and purity of CMC

For the NaCl content, in terms of the ClCH2COONa change added, the NaCl contents increase with the increase of ClCH2COONa because NaCl is a side product of CMC synthesis due to excess of the added reagents.

For the sample I, the average test result of NaCl content in CMC product was 0.1559% with average product purity of 99.8441%. While for sample II, the average of the test result of NaCl content on CMC product was 0.1948% with average product purity of 99.8052%. The sample I and sample II have to qualify the criteria of CMC SNI 06-3736-1995 for quality I.

2. pH measurement

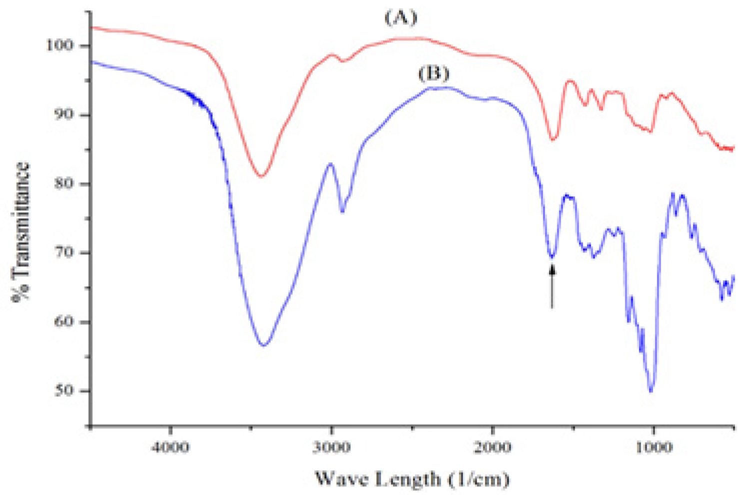
The second indicator that shows good CMC quality is pH. pH will determine how the viscosity of CMC. pH of 1% CMC solution ranged from 6-8 to quality I while for quality II ranged from 6-8.5 (SNI 06-3736-1995). For the sample I, the pH was 7.6. While for sample II, the pH was 7.2. This indicates that both samples are neutral and qualify the quality of I Indonesian National Standard. Too acidic pH will make the CMC precipitate when dissolved in water.

3. Renderman and CMC Colors

The average CMC weight is 8.102 grams with an average yield of 81.02%. CMC obtained is yellow. This may be due to a lack of maximal de-lignification process. But according to Inchem, CMC has a white color or slightly yellowish.

4. FTIR (Fourier Transform Infra Red spectroscopy)

Analysis of chemical bond structure using Fourier Transform Infra Red spectroscopy (FTIR) on banana tree stem cellulose can be seen in figure 1 (a). Peaks that appear indicate that the content of cellulose in the banana tree stem. Peaks with wavelengths between 3700 cm-1 - 3100 cm-1 indicate the -OH group. In the FTIR test of the banana tree stem, there is a wavelength with peak 3419.62 cm-1, the wavelength indicates the presence of -OH group on cellulose that has been isolated from banana tree stem.



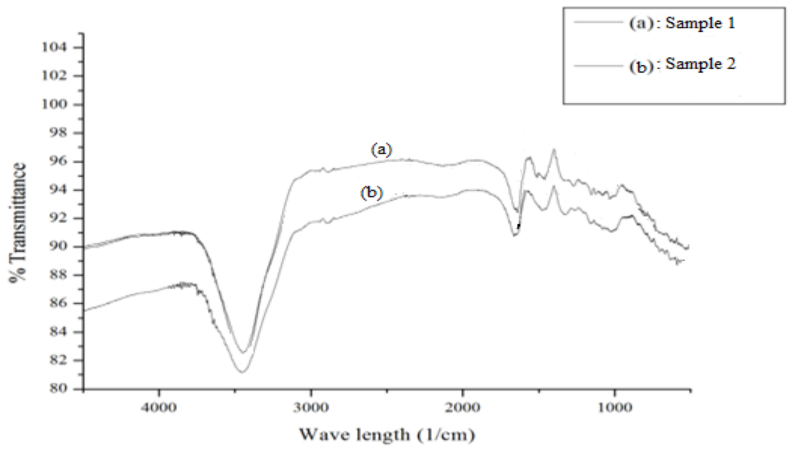


Figure 1. Graphic of FTIR Result of Banana Tree Stem and CMC Sample

Figure 2. Graphic of FTIR Result of Banana Tree Stem and CMC Sample

From figure 1, with the added ratio of sodium chloroacetate, the degree of substitution is also increasing, this result is similar to that of Nwokocha et. Al, (2008). The higher levels of sodium chloroacetate produce more and more carboxyl groups in the reactants. However, the higher the ratio of sodium chloroacetate will result in a higher amount of sodium glycolate. This occurs because, with the addition of an increasingly high ratio of sodium chloroacetate, it will produce high residues of chloroacetic sodium so it will react with NaOH to form sodium glycolate as proposed by Khalil et. Al., (1990).

In figure 2, there is the addition of carboxyl group (COOH) after variation of the cellulose ratio to sodium chloroacetate. The ratio of these variations is 1: 1 and 1: 2. Thus the carboxyl group attached to the CMC increases.

5. Degree of Substitution

The degree of substitution is the average number of clusters per anhydroglucose unit substituted by another group. Cellulose has 3 hydroxyl groups in each substituted anhydroglucose. The hydroxyl group of cellulose is substituted with carboxymethyl groups of sodium chloroacetate.

The value of degrees of substitution of CMC according to Indonesian national standard (SNI) there are two qualities. Quality one has degrees of substitution between 0.7-1.2 while the quality of two is 0.4-1.0. Quality one is a CMC product that can be used for food additives, while the quality of two is added to non-food products. For the sample I, the average degree of substitution generated is 1.0382. As for sample II, the average degree of substitution produced is 1.1368. The degree of substitution in sample I and sample II are both already meet the quality of Indonesian National Standard (SNI) which ranges from 0.7-1.2.

4. Consclusion

1. The test results showed that the CMC samples with the ratio of cellulose with sodium chloroacetate of 1: 1 and 1: 2 both meet the quality of SNI 06-3736-1995.
2. A CMC sample with a 1: 2 ratio between cellulose and sodium chloroacetate resulted in a greater NaCl content, lower purity of CMC, and a higher degree of substitution.
3. The addition of sodium chloroacetate to the preparation of CMC will increase the degree of substitution as more carboxymethyl groups attach to cellulose. However, the higher the added sodium chloroacetic level, the higher the NaCl content is formed as more and more of the unsubstituted amount of sodium chloroacetate reacts with NaOH.

References

Fennema, O.R., M. Karen, and D.B. Lund. 1996. "Principle of Food Science", The AVI Publishing, Connecticut

Khalil, M.I., A. Hashem, and A. Habeish, 1990. "Carboxymethylation of Maize Starch". Starch / Starke. 42 (2): 60-63

Nisa. 2014. "Making CMC from Cocoa Fruit Leather (Theobroma cacao L.) as Raw Material for Making CMC (Carboxymethyl Cellulose)". Universitas Brawijaya Malang. Journal of Food and Agro-industry, 2 (3): 34-42

Nwokocha, L.M., and Ogunmola, G.B., 2008. "Carboxymethylation of Cassava Starch in Different Solvents and Solvent-Water Mixtures: Optimization of Reaction Conditions", Cassava Starch. 8: 1581-1585

Sumarjono, Djoko. 2004. "Diktat Production Economics Lecture". Diponegoro University. Semarang