Carboxymethyl cellulose synthesis from durian seed flour:
The effect of sodium chloroacetate variation

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Abstract. Carboxymethyl Cellulose (CMC) is cellulose derivative that is soluble in water, CMC is synthesized by reacting cellulose with sodium hydroxide and chloroacetate acid or its salt. This study purpose is to see the effect of sodium chloroacetate salt in carboxymethylation reaction to the CMC degree of substitution. To test the quality of the CMC product, the analysis that is conducted in this study are: degree of substitution analysis as written in ASTM D 1439, FTIR, and SEM-EDX. The best result that is got from this study is producing the CMC with degree of substitutions of 0.42 with addition of 3 gr sodium chloroacetate salt.

1. Introduction

Carboxymethyl Cellulose (CMC) is cellulose polysaccharides derivative that is produced by substitute the 2nd, 3rd and 6th hydroxyl groups of cellulose with carboxymethyl group [1]. CMC is synthesized by reacting cellulose with chloroacetate acid or its salt [2]. CMC is usually made with cellulose from wood or pulp [2,3]. The study of CMC synthesis by using seed cellulose has never been done before, durian seed contain cellulose so it is a potential cellulose source to produce CMC. CMC synthesis from durian seed doesn’t need to be delignificated so the yield of product that is produced can be maximum. Durian seed contain lignin about 10% but only in its shell [4], so the shell will be peeled first from the seed flesh.

The CMC character is depend on the way it is produced. CMC synthesis involve the cellulose carboxymethylation reaction. In the carboxymethylation process, cellulose become more rough so it will increase the surface area of reaction. With the increase of the surface area, the chloroacetate group will have more chance to reacted with the cellulose so the degree of substitution of CMC will be higher [5].

Degree of substitution is a value that shows how much the carboxymethyl group that contained by the CMC. Degree of substitution is one of the main parameters that show the success of CMC synthesis process. Theoretically, the maximum value of degree of substitution in CMC synthesis process is 3, but the CMC that is sold commercially has the value of the degree of substitution in 0.4-1.5 range. For the food product, the degree of substitution of CMC that is used as the range of 0.2-1.5 [6]. CMC with the degree of substitution that is higher than 0.7 will dissolve perfectly in water [5].

In the synthesis process, the degree of substitution can be affected by the carboxymethylation reactant [7]. The Chloroacetate group acted as the reactant in the carboxymethylation process. The ratio of sodium chloroacetate, sodium hydroxide, and cellulose must be in the right amount to produce the optimum degree of substitution. This is because excess sodium chloroacetate can be reacted with...
sodium hydroxide which this reaction can produce sodium glycolate so the purity of CMC will decrease [7].

2. Materials and methods

Durian seed is collected from various durian sellers in Jln. Pelajar, Medan. Chemical materials that are used in this study are: Acetic acid, Calcium hydroxide, Sodium hydroxide, Isopropanol, Methanol, and ethanol are bought from CV Rudang Jaya Medan, Sodium metabisulfite is bought from T&T Chemical Bandung, and Sodium chloroacetate is bought from CV Aneka Chemical Medan.

2.1 Raw material treatment
Durian seed in which the shell has been peeled is soaked in 5% calcium hydroxide solution and 5% sodium metabisulfite solution for 24 hours. Then, durian seed flesh is mashed and dried by then, then sifted using 70 mesh sieve [8].

2.2 Carboxymethyl cellulose synthesis
CMC is synthesized by reacting cellulose with sodium hydroxide and sodium chloroacetate in isopropanol solution. The ratio of cellulose and sodium hydroxide is 1:3 (w/v), the reaction with sodium hydroxide takes 1 hour to be completed [9, 10]. Carboxymethylation reaction between Na-Cellulose with sodium chloroacetate takes 1.5 hours to be completed with the amount of sodium chloroacetate variation 1.5; 2; 2.5; 3; 3.5 gr. The solution is left to form two phases, then the solid phase is dissolved in methanol solution and left for 12 hours, then neutralized by using acetic acid. Then, The solid is filtered and washed by using 96% ethanol and methanol [11, 12] the solid then dried in the oven at 50°C for 5 hours and left in desiccator for 24 hours.

2.3 Degree of substitution analysis
CMC degree of substitution analysis is referring to ASTM D 1439, done in 2 times repetition and was conducted in Process of Chemical Industry Laboratorium, Universitas Sumatera Utara. The degree of substitution is defined using

\[
A = \frac{BC - DE}{F} \tag{1}
\]

\[
\text{Degree of substitution} = \frac{0.162 \times A}{1 - (0.058 \times A)} \tag{2}
\]

Where:
- A = mili-equivalent of acid consumption (mL.M.gram⁻¹)
- B = Sodium hydroxide volume (mL)
- C = Sodium hydroxide concentration (M)
- D = Hydrochloric acid volume (mL)
- E = Hydrochloric acid concentration (M)

2.4 Fourier transform infra-red (FTIR)
FTIR analysis was conducted at the Belawan Customs Laboratory, Medan using the 10th Thermo Scientific Nicolet ™ iS ™ Spectrometer with a strong current of 3.2 A, a voltage of 100-240 VAC, and a frequency of 47-63 Hz produced by Thermo Fisher Scientific.

2.5 Scanning electron microscopy – energy diffraction X-Ray (SEM-EDX)
SEM-EDX analysis was carried out at the Integrated Laboratory, Diponegoro University using JSM 6510LA and JED 2300 devices with a voltage of 20 kV and magnification of 3000 times.
3 Result

3.1 Degree of substitution (DS)

![Graph showing the effect of sodium chloroacetate weight variation to Durian Seed CMC Degree of Substitution at 55°C.](image)

**Figure 1.** Effect of sodium chloroacetate weight variation to Durian Seed CMC Degree of Substitution at 55°C

Figure 1 showed durian seed CMC degree substitution has increased with the addition of chloroacetate natriums of 1.5 to 3 gr. The highest CMC substitution degree is 0.42. The increase in the degree of substitution occurs due to the exchange of carboxymethyl groups between Na-cellulose with sodium chloroacetate. The more hydroxyl groups in cellulose substituted by carboxymethyl groups from sodium chloroacetate will increase the degree of substitution value. The degree of substitution dropped in the addition of 3.5 gr sodium chloroacetate is caused by the reaction between sodium hydroxide and sodium chloroacetate to form sodium glycolate, this is supported by Rachanapun et al (2012). Besides, the CMC formation reaction also occurs the formation of sodium glycolate and NaCl salt. In the process of alkalinization using sodium hydroxide, Sodium Chloroacetate reacted with sodium hydroxide formed sodium glycolate [13].

3.2 Fourier transform infra-red (FTIR)

![FTIR analysis of commercial CMC (A), Durian seed CMC (B).](image)

**Figure 2.** FTIR analysis of commercial CMC (A), Durian seed CMC (B)
Groups Information [14]

| Wavenumber | Chemical Group          |
|-------------|-------------------------|
| 3650-3600   | O-H (Free)              |
| 3450-2400   | O-H (Carboxylate)       |
| 1680-1600   | C=C (Aromatic)          |
| 1450-1400   | -CH2-                   |
| 1350-1000   | C-N (Amine)             |
| 1300-1000   | C-O (Ether)             |

Based on the data presented in Figure 2, in commercial CMC there is an O-H group (free) which is an O-H group that is not attached to any chain with a wavenumber of 3600.90; O-H group (carboxylate) with wavenumber 2921.59; C=C (aromatic) group with wavenumber 1604.27; -CH2- group with wavenumber 1423.09; C-N group (amine) with wavenumber 1327.71 and C-O group (ether) with wavenumber 1063.84. Aromatic groups and identified ether groups show cellulose compounds. Carboxylic groups and -CH2- groups show carboxymethyl groups.

Figure 2, we can see that the CMC from durian seeds also has an O-H group (free) with a wavenumber of 3615.25; O-H group (carboxylate) with wavenumber 2928.90; C=C (aromatic) group with wavenumber 1649.96; -CH2- group with wavenumber 1430.78; C-N group (amine) with wavenumber 1328.41 and C-O group (ether) with wavenumber 1160.25. Carboxylic groups, aromatic groups, -CH2 groups, and ether groups are the same group in commercial CMC. These groups indicate durian seed has been synthesized into CMC. O-H group (free) found in commercial CMC and CMC from durian seeds showed that in both analysis samples there was still water content. The presence of C-N (amine) groups in commercial CMC and CMC from durian seeds is caused by the source of cellulose. Commercial CMC uses pulp as a source of cellulose, pulp made from Acacia mangium wood where the wood contains 4-6% protein [15, 16]. While durian seeds used as manufacturing of CMC contain protein at 2.6% [17, 18].

3.3 SEM-EDX analysis

![Figure 3. Durian seed CMC morphology and chemical compounds with degree of substitution of 0.42](image)
Figure 3 showed the durian seed CMC has large molecules with mostly irregular shapes, but there are also spherical shapes. The main constituents of CMC are Carbon (C) at 82.01%, Oxygen (O) at 6.33%, and Sodium (Na) at 7.66%. The presence of carbon (C) and oxygen (O) groups in the test sample is because CMC is a cellulose-derived compound in which cellulose is composed of carbon (C), oxygen (O), and hydrogen (H) elements. While the presence of the element sodium (Na) because in the CMC synthesis process sodium hydroxide (NaOH) is used.

In CMC from durian, seeds found the element Phosphorus (P) of 0.23% and Calcium (Ca) of 0.29%, this is because the flour used in this study was sourced from durian seeds. The presence of Phosphorus (P) and Calcium (Ca) elements is due to durian seeds containing phosphorus (P) and calcium. In addition to the source of flour, the element calcium (Ca) contained in CMC from durian seeds is also influenced by the use of Calcium hydroxide/Ca(OH)₂ as a solvent in the pre-treatment stage of durian seeds. Figure 3 also shows the presence of Sodium oxide (Na₂O) thought to originate from NaOH used in the CMC synthesis process.

4. Conclusion
The conclusion obtained from this study is the maximum degree of substitution value is 0.42 with the addition of 3 gr sodium chloroacetate

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ZAF Method Standardless Quantitative Analysis (Oxide)
Fitting Coefficient : 0.0479
Total Oxide : 24.0

| Element | (keV) | Mass% | Sigma | Mol% | Compound | Mass% | Cation | K |
|---------|-------|-------|-------|------|----------|-------|--------|---|
| C K     | 0.277 | 82.01 | 0.39  | 96.31| C        | 82.01 | 0.00   | 79.6720 |
| O       |       | 6.33  |       |      |          |       |        |   |
| Na K    | 1.041 | 7.66  | 0.16  | 2.35 | Na₂O    | 10.32 | 20.21  | 12.7977 |
| P K     | 2.013 | 0.23  | 0.05  | 0.05 | P₂O₅    | 0.53  | 0.45   | 0.4293 |
| S K     | 2.307 | 1.91  | 0.11  | 0.84 | SO₃      | 4.77  | 3.61   | 3.8213 |
| Ca K    | 3.690 | 0.29  | 0.04  | 0.10 | CaO      | 0.40  | 0.43   | 0.5887 |
| Cu K    | 8.040 | 0.82  | 0.10  | 0.18 | CuO      | 1.03  | 0.79   | 1.4075 |
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