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Carboxymethyl Celulose (CMC) From Snake Fruit (*Salaca edulis* Reinw) Kernel of "Pondoh Super": Synthesis and Characterization

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Abstract

Snake fruits kernel has high cellulose content thus potential to be an alternative source of carboxylmethylcellulose (CMC) production. However there are several condition that have to be optimized to increase the CMC synthesis which are concentration of NaOH solution, NaMCA addition, and the reaction temperature based on the degree of substitution (DS). The aim of this study was to determine the optimum conditions of synthesis CMC from "Salak Pondoh Super" kernel. Some factors that likely influence the synthesis were concentration of NaOH solution , NaMCA addition, and the reaction temperature based on the degree of substitution (DS) as the responses. Synthesis of CMC was optimized using completely randomized design. The result then was characterized by several parameters including water content, viscosity, purity, Water Holding Capacity (WHC), Oil Holding Capacity (OHC), lightness, crystallinity, and FT-IR spectra. Optimization was achieved by the use of 15% NaOH solution, 5 gram NaMCA per 5 gram cellulose and reaction temperature of 55ºC. The characteristics of the optimized CMC were DS 0.825, purity 90.86%, water content of 7.16 (% wb), viscosity 3.86 cps, 142.72 yield (% db), WHC 2.37 (g/g), OHC 2.31 (g/g), lightness 78.48, and crystanillity 32.69%. The FT-IR spectra of snake fruit kernel CMC was similar with the CMC Standard.

Keywords: cellulose, CMC, "Salak Pondoh Super", kernel

Introduction

Salacca edulis or snake fruit is one of the tropical fruit commodity in Indonesia. Production of snake fruit in Indonesia has been increasing for each year. Data from the Ministry of Agriculture of the Republic Indonesia, the production of snake fruit in Indonesia for the year of 2010, 2011 and 2012 were 749.876 tons, 1.082.115 tons and 1.035.406 tons, respectively. "Salak Pondoh" is one of the snake fruit variety from Sleman region, Yogyakarta. It has a sweet taste even though the fruit is still young and flowering throughout the year (Santoso, 1999). Salak is a table fruit that only its flesh is consumable. Edible part of the fruit is about 57-69%, while 31-43% is the waste. The waste source are from its skin and kernel. Snake fruit kernel can be used as alternative source of monosakarida (Nugroho, 2014). Snake fruit kernel was used as coffee like (Anggrahini, et al., 2014; Astuti, 2013) and additionally, snake fruit kernel as a powder was used to absorb Cr (VI) (Aji and Kurniawan, 2012). Snake skin fruitis believed by many people to have some remarkable properties such as improving intelegence, maintaining eye health, treating prostate cancer, repairing pancreas in diabetic patients, preventing high blood pressure and arthritis. But all that still require further research (Kurniawan et al., 2015). According to Supriyadi et al. (2002) the portion of kernel reaches 25-30% of the total weight of the fruit. If the calculated production of snake fruit in 2012 was 1.035.406 tons, it means the waste of kernel around 260-310 tons, which is a large amount of waste.

From the latest update, it has been found that, snake fruit's kernel has not been utilized into a more useful products with a higher economic value. Snake fruit kernel has high cellulose content-- about 31.10 % (db) (Fathoni, 2014). The snake fruit kernel is a potential source for synthesis of Carboxymethyl Cellulose (CMC) that can be used as food additives because it has functional and good physico-chemical properties, such as high solubility in water, high binding capacity to water, metal ions, oil, as well as its role in decreasing the surface tension of the emulsion system.

Cellulose that has been isolated from snake fruit kernel was then synthesized into CMC with some different methods. Research was carried out by two steps, i.e. cellulose isolation, followed by synthesis and characterization of CMC. The CMC synthesis includes alkalization and carboxymethylation process. Alkalization was conducted using NaOH to activate the OH groups from cellulose, break the hydrogen bonds and develop cellulose molecule thus extend the distance of the cellulose molecule. This process, further on, will facilitate the deployment of cellulosic diffusion of carboxymethylation's reagent, using sodium monocloroacetat. Carboxymethylation and alkalization reaction determine the characteristic of CMC which was obtained with this research. The concentration variations of NaOH solution, the amount of sodium monocloroacetate, and temperature were studied for the optimization to acquire CMC with a degree of substitution (DS) that is suitable to be used in food industry.

The DS determination was calculated by using completely randomized design. From the obtained optimized CMC, purity and viscosity were characterized afterward. DS determines the solubility of CMC and DS is also a major parameter in food industry. Commercial CMC has a DS of 0,7-0,9. The purity of CMC determines the quality of the produced CMC. Hence, this research can provide solutions in utilization snake fruit kernel variety "Pondoh" into food additives product which has many uses in the food industry. This research has never been done before, therefore producing biopolymer technology innovation is an expected result so that it can contribute to the advancement of knowledge in terms of the waste utilization into products with

The aim of this study was to determine the optimum conditions of the synthesis of CMC (carboxymethylcellulose) from salak pondoh kernel with synthesis factors i.e. concentration of NaOH solution, the reaction temperature and NaMCA weight based on DS responses. The studied CMC quality parameters include water content, viscosity, purity, WHC, OHC, lightness, crystallinity, and FT–IR spectra.

Materials and Methods

Materials

Raw materials used in this research was "Salak Pondoh Super" harvested from Donoasih, Donokerto Village, Turi district, Sleman Regency, Yogyakarta Province, Indonesia. Commercial cellulose, NaOH, NaOCl, $NaHSO_3$, NaMCA, Isopropanol and Ethanol Grade Analysis were obtained from Sigma Chemical Co., USA.

Synthesis of Carboxymethyl Cellulose

Carboxymethyl Cellulose synthesis was done through the following procedure: 5 grams of cellulose powder of pondoh snake fruit kernel was alkalized 25 ºC for 60 min in waterbath shaking with 20 ml NaOH in various concentrations (5; 10; 15; 20 and 25%) in 100 ml isopropanol as a solvent. After the alkalization process over, it was followed by carboxymethylation with the addition of sodium monochloroasetate (NAMCA) in various amount (3; 4; 5; 6 and 7 g) at various temperature (45, 50, 55, 60 and 65 ^{o}C) for 180 min. The slurry was neutralized with 90% acetic acid and then poured. Sodium carboxy methyl cellulose as residue was washed with ethanol 96%. The obtained sodium carboxymethyl cellulose was dried at 60 °C for 30 minutes, grounded and filtered into 60 mesh in size to get CMC.

Characterization of sodium carboxymethyl cellulose

The moisture content, degree of substitution (DS), and purity of CMC were determined by the ASTM D1439-94 standard method (Anonim, 1994). The water holding capacity (WHC) and oil holding capacity (OHC) were detected by the method of Larrauri et al. (1996).

Water holding capacity (WHC) and oil-holding capacity (OHC)

Twenty-five milliliters of distilled water or commercial olive oil were added to 1 g of dry sample, stirred and incubated at 40 °C for 1 h. After centrifugation, the residue was weighed and WHC and OHC calculated as g water or oil per g of dry sample respectively.

FT-IR spectroscopy of sodium carboxymethylcellulose

Infrared spectra of the CMC samples were recorded with Shimadzu FTIR-8201. Pellets were made by using CMC samples (~3 mg) ground with potassium bromide (~800 mg) and transmission was measured at the wavelength number range of 4000 - 400 cm^{-1}.

Results and Discussion

The data in **Fig. 1** showed that the increase of DS depend significantly on the increase of NaOH. This data suggested that NaOH had penetrated the cellulose, changed the cellulose crystalline to be amorphous so that the reaction of carboxymethylation could be carried out.

There are three hydroxyl groups available in anhydroglucose for chemical modification. Sodium hydroxide changes the form of cellulose type I to be cellulose type II. The change of cristalinity and poly-morphism maybe due to the partition of sodium hydroxide between the reaction medium and the cellulose chain. This partition occurs when mixture of an organic solvent, water and sodium hydroxide are suspended. However, DS decreases if NaOH concentration is more than 15%. In higher concentration of sodium hydroxide in the vacinity of the cellulose, will give impact to the substantial change of polymorphism from cellulose type I to cellulose type II during alkalization (Pushpamalar et al., 2006).

Fig. 1. Surface plot of DS versus NaOH

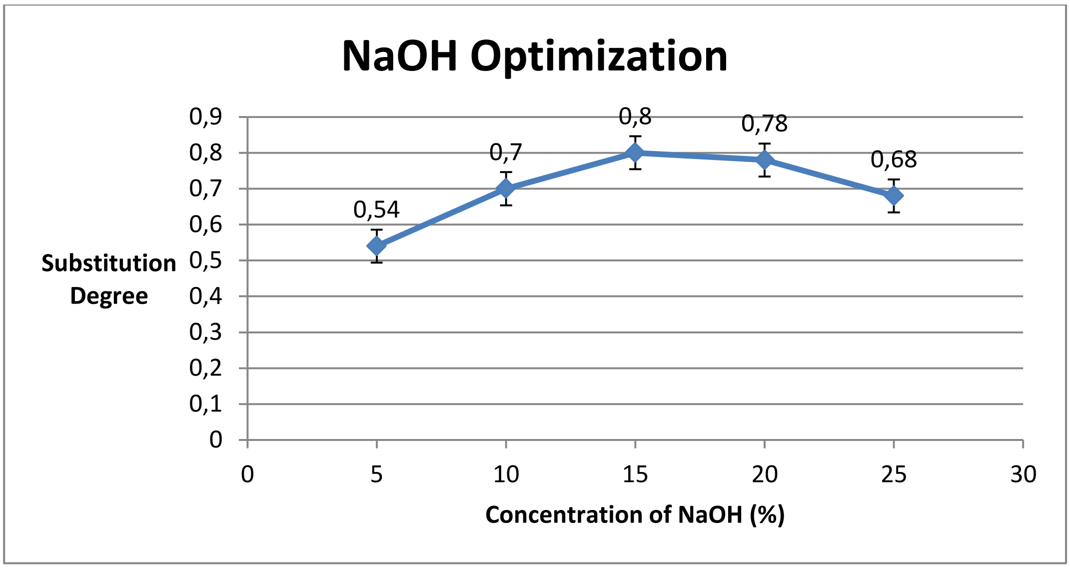

Fig. 2 indicated that NaMCA affecting significantly on the increase of DS. However, data in Fig. 1 and Fig.2 showed that the increase of DS was influenced by the increase of NaOH than the increase of NaMCA. This data suggested that CMC synthesis was affected by NaOH where crystalline region in cellulose wouldchange into amorphous region and then atom of C6, C2 and C3 could be accessed easily by NaMCA in Anhydrous Glucose Unit (AGU) (Olaru et al., 1997). If using NaMCA very high DS to be decrease, it may be due to the production of sodium glycolate.

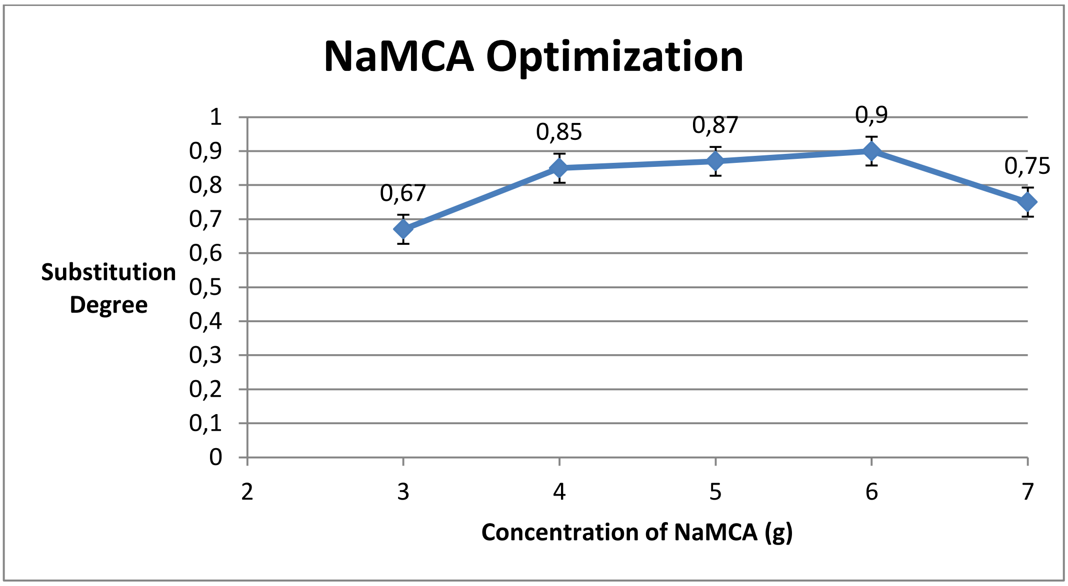

Fig. 2. Surface plot of DS versus NaMCA

In **Fig.3**, it demonstrated that temperature significantly affected on the increase of DS. Temperature would affect the affinity of the Na^+ in AGU in the formation of amorphous region and then NaMCA would replace Na^+ into CMC in atom C6, C2 and C3. This data was similar to Heinza and Pfeffer (1999). The data concluded that NaOH concentration, NaMCA weight and temperature were the main factors that affected the synthesis of CMC similar with previous reports of Heinze and Pfeiffer (1999), Togul et al. (2003) and Pushpamalar et al. (2006).

Optimum condition of CMC synthesis could be simulated by RMS with sodium hydroxyde 15%, NaMCA 55 g and at temperature 55ºC. The results of CMC characteristics were as follows, D S : 0.83, WHC: 2.37 g/g, OHC: 2.31 g/g, lightness: 78.48, crystallinity: 32.6%, moisture content: 7.16%, viscosity: 3.86 cpsand purity: 90.86% (see **Table 1**).

Table 1. Comparison of the characteristics of seed pondoh CMC and CMC Commercial

Characteristics	CMC Pondoh Snake Fruit Kernel	CMC Standard
DS	0.83	0.85
WHC (g/g)	2.37	0.86
OHC (g/g)	2.31	2.55
Lightness	78.48	8.51
Crystallinity (%)	32.69	18.92
Moisture content (%)	7.16	9.18
Viscosity (cps)	3.86	1464
Purity (%)	90.86	99.48

In Table 1 indicated that WHC of CMC Pondoh snake fruit kernel was lower than the CMC standard. The ability of NaOH solution which aimed to activate the -OH group of cellulose molecules had not been effective, thus affecting in diffusion process of NaMCA reagent for carboxymethylation process was inhibited. The process of destruction of crystalline cellulose structure was lower, indicated by the higher crystallinity value of CMC Pondoh snake fruit kernel than CMC standart. It is due to the small amount of amorphous structure of CMC Pondoh snake fruit kernel, resulting in low water holding capacity. The lightness of CMC pondoh snake fruit kernel was lower than the CMC standard since the purity was also lower. In term of crystallinity, CMC Pondoh snake fruit kernel was more higher than CMC standard.

Infrared spectroscopy spectra of CMC with DS 0.83 was showed in **Fig. 4**. The displacement could be observed from the stretching band of O-H which was methylated in C6. Hydroxyl group substitution in C6 significantly changed by rising carbonyl group (-C=O) in wavelength 1604 cm^{-1} and $-CH_2$ in wavelength 1419 cm^{-1}. In wavelength 894 cm^{-1},1,4-β glycoside of cellulose was detected (Viera et al., 2007). Wavelength 3433 cm^{-1} was detected due to the stretching frequency of–OH and band 2916 to 2924 cm^{-1} due to C-H streching vibration from AGU (Pescok et al., 1976; Meenakshi et al., 2002).

The peak in wave number 1327 cm^{-1} was the –OH peak of AGU stretching vibration. Salt of carboxyl group had wave number about 1600 cm^{-1} and 1400 cm^{-1} according to Pescok et al. (1976). Spectra patterns between snake fruit kernel CMC CMC standard were similar. Data of the obtained peaks in FT-IR spectra from CMC constituent was shown in **Table 2**.

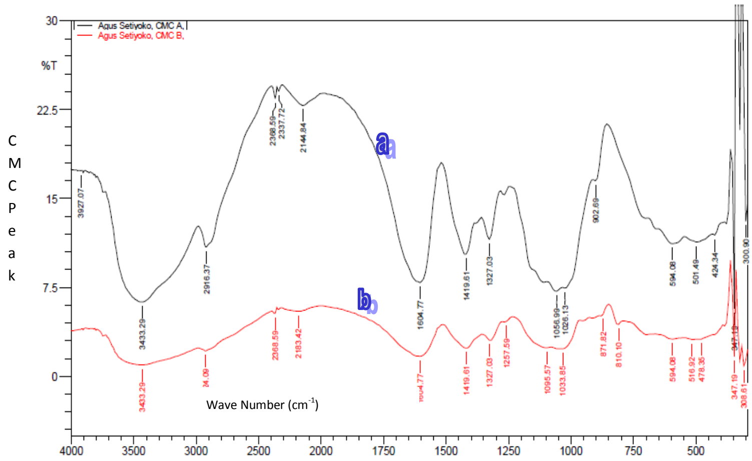

Fig. 4. (a) FT_IR spectra of the CMC standard and (b) CMC of Pondoh snake fruit kernel

Table 2. Assignment of main absorption bonds in CMC of Pondoh snake fruit kernel

Wave number (cm^{-1})		
CMC Standard	CMC of Pondoh Snake fruit kernel	Assignment
- 3433	- 3433	-OH streching
- 2916	- 2924	-CH streching CH2 and CH3 group
- 1604	- 1604	-C=O region (Constituent CMC
-1419	- 1419	-CH2 bonding (Constituent CMC)
- 1327	- 1327	-OH Plane Bonding
- 1095	- 1056	-C-O-C asymetry bridge streching
- 1056	- 1056	-C-O asymetry streching Alcohol
- 902	- 871	-1-4-βglycoside

Conclusion

Isolated cellulose could be modified in 15% NaOH, 5 g NMCA and temperature 55°C, in 3 h for carboxy methyl cellulose which had DS 0.83. The obtained carboxy methyl cellulose had 2.37 g/g of WHC, 2.31 g/g of OHC, 78.48 of lightness, 3.86 cps of viscosity, 32.69 % crystallinity, 9.18 % of moisture content, 90.86% of purity, and yield of 142.72 (%db). The spectra patternsbetween CMC of Pondoh snake fruit kernel was similar with CMC standard.

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