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Full Length Research Paper

Synthesis and characterization of sodium carboxymethylcellulose from pod husk of Cacao (*Theobroma cacao* L.)

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Cacao pod husk (*Theobroma cacao* L.) is a by product of the cacao industry, rich in cellulose. The methodology to synthesize and uniqueness of the sodium carboxymethylcellulose (Na-CMC) is suggested by cellulose extraction from pod husk of cacao. Na-CMC was synthesized by using 20 ml NaOH at five various concentrations (11.59, 15, 20, 25, and 28.41% w/v) at 25°C for 1 h; followed with 5 sodium monochloracetate (NMCA) samples 3.18, 4, 5, 6 and 6.68 g, respectively with 5 g of cellulose was added to slurry at various temperature (46.59, 50, 55, 60 and 63.41°C) for 3 h. The response surface methodology used to determine the optimum condition for synthesis of NaCMC. The data showed that the optimum condition is 15% NaOH with 4 g NMCA, at 55.93°C for 3 h. Extracted Na-CMC has 0.75° of substitution (DS), 3.73 g/g water holding capacity (WHC), 2.12 g/g oil holding capacity (OHC), 56.61 lightness, 206.10 cps viscosity, and 141.60% yield.

Key words: Cellulose, carboxymethylcellulose, cacao pod husk.

INTRODUCTION

Indonesia is the third largest cacao (*Theobroma cacao* L.) producer in the world that accounted for about 800,000 tons nib in year 2011. This amount is equal to 8,000,000 ton pod husk cacao (75% water content) as by product in which containing 35% (db) cellulose. Previous data has shown that the isolated cellulose from pod husk cacao has characteristics of lightness, ash content, yield and crystallinity were 42.64, 2.74, 26.09 and 27.14%, respectively. When compare with those of commercially available cellulose which has 56.99% lightness and 20.13% crystallinity. Also its shows; the degree of polymerization and molecular weight of the isolated cellulose are 390.40 and 63,342 respectively (Hutomo et al., in press).

The product could be classified as α-Cellulose having at least 200 anhydrous glucose units and not soluble in 17.50% of sodium hydroxide solution (Browning, 1967; Othmer, 1982). Normally commercially available cellulose has degree of polymerization about 983.40 units of anhydrous glucose and molecular weight about 159,408 (Hutomo et al., in press). Sobamiwa and Longe (1994) have been reported cellulose from African pod husk cacao containing 11% hemicellulose, 35% cellulose, 15% lignin, 6% pectin, and mineral element likes K (3.18%), Ca (0.32%) and P (0.15%). Properties of cellulose base on fruits are difference than those of cellulose from cotton or wood. Cellulose usually occurs in the cell wall and is generally associated with many kinds of substance such as lignin, pectin and hemi cellulose, which make it difficult to find in a pure form. However, cellulose is non soluble material need to be modified before utilized in food industries as thickening, gelling or stabilizing agents. One of derivative product of cellulose is carboxymethylcellulose. The chemical characteristic of carboxymethylcellulose relies almost exclusively on the

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average degree of substitution, which is attains value of 3 in complete substitution reaction by carboxymetylations of the 3 hydroxyl groups in anhydrous glucose unit (AGU). Carboxymethylcellulose with degree of substitu-tion of 0.70 to 0.85 was used as food additive to obtained better functional properties of food products.

Production of carboxymethylcellulose (CMC) is simpler than others cellulose ethers such as methyl cellulose (MC), hydroxypropyl cellulose (HPC) and hydroxypropyl methyl cellulose (HPMC). Cellulose was etherified using reagent sodium monochloracetate, sodium hydroxide and isopropanol which are easier to handle and control efficiently. Most of the sources of cellulose that modified to carboxymethylcellulose are wood and cotton, but many others resources could also be used such as paddy straw (Mohdy et al., 2008), sugar cane bagasse (Viera et al., 2007), kenaf (Miyata, 2003), pulp beet (Sun and Hughes, 1998; Togrul and Arslan, 2003), bagasse of sago (Pushpamalar et al., 2006), orange peel (Yasar et al., 2007), cavendish banana pseudo stem (Adinugraha et al., 2005), and none of them utilized the pod husk cacao as a cellulose source. Previous research on synthesis of CMC from pseudo banana stem need 6 g NMCA that obtained yield 142.91% and DS 0.75 (Adinugraha et al., 2005). According to Suzana (2009) synthesis of carboxy-methylcellulose from 5 g cellulose of pineapple crown in 15% NaOH, temperature 55°C, and 4 g NMCA during 3 h reaction time was obtained yield 115% and DS 0.98.

The data shows the potentials of utilization of pod husk of cacao as a substrate for cellulose extraction would be beneficial; and can be used as source of other cellulose derivatives such as CMC, HPC, MC, and HPMC although its degree of polymerization is more than 200 anhydrous glucose unit.

MATERIALS AND METHODS

Pod husk cacao (*Theobroma cacao* L.) was obtained from Samigaluh Districs of Kulon Progo, Yogyakarta Province, Indonesia. Commercially available cellulose, NaOH, NaOCl, $NaHSO_3$, NMCA, Isopropanol and Ethanol are grade for analysis.

Synthesis of sodium carboxymethylcellulose

In my previous research cellulose of pod husk of cacao was extracted by using various concentrations of NaOH (12% w/v) at 100°C for 3 h. Then bleached using 6% NaOCl at 60°C for 60 min and followed by 3% sodium bisulfite at 60°C for 60 min. Cellulose was obtained from pod husk cacao according to our previous method (Hutomo et al., in press). Synthesis of carboxy-methylcellulose was carried out as follows. Five grams of cellulose powder was alkalized 30°C for 60 min in waterbath shaking with 20 ml NaOH of various concentrations (11.59, 15, 20, 25, and 28.41%) in 100 ml isopropanol as a solvent (Adinugraha et al., 2005). After the alkalization process is over, followed bycarboxymethylation by the addition of various amount of sodium monochloracetate (NMCA) (3.18, 4, 5, 6, and 6.68 g) at various temperature (46.59, 50, 55, 60 and 63, 41°C) for 180 min. The slurry was neutralized with 90% acetic acid and then decanted. The residue as sodium carboxymethylcellulose was washed by 96% ethanol. The obtained sodium carboxymethylcellulose was dried at 50°C in cabinet drier (Togrul and Arslan, 2003; Pushpamalar, et al., 2006; Adinugraha et al., 2005). Verification process was carried out based on simulation process using response surface methodology output.

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 (ASTM, 1994). The water holding capacity and oil holding capacity 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 (Larrauri et al., 1996).

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}.

Statistical analysis

Response surface methodology (RSM) was used to analyze the optimum condition for CMC synthesis. The design experimental consists of 3 factors (NaOH, NMCA, and temperature) in which 5 levels of each with alpha ±1.682 for total sample 20. Data was processed by software Minitab 14.0. Center point as best condition was adopted from previous report (Togrul and Arslan, 2003; Adinugraha et al., 2005; Pushpamalar et al., 2006; Olaru et al., 1997; Susana, 2009).

RESULTS AND DISCUSSION

The data in Figure 1 showed that the increase of DS depended significantly on the increase of NaOH than that of increase in temperature until 3 h of reaction. This data suggested that NaOH had penetrated the cellulose, changing the cellulose crystalline to be amorf 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 may be due to the partition of sodium hydroxide between the reaction medium and the cellulose chain. This partition occurs when suspending in mixtures of an organic solvent, water and sodium hydroxide. In higher concentration of sodium hydroxide in the vacinity of the cellulose, giving rise to substantial change of polymorphism from cellulose type I to cellulose type II

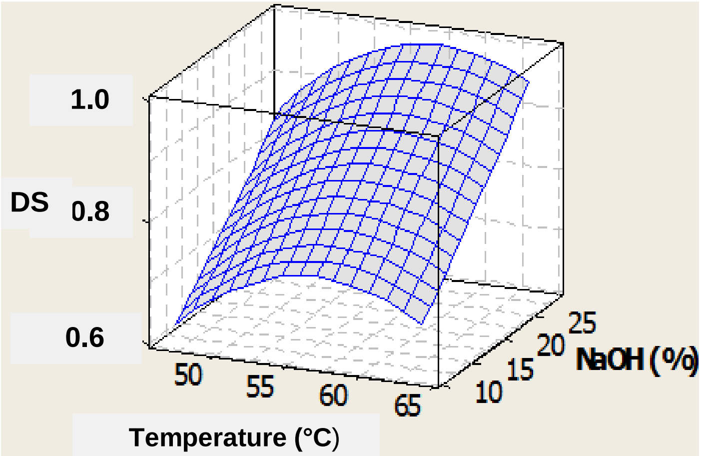

Figure 1. Surface plot of DS versus sodium hydroxide and temperature.

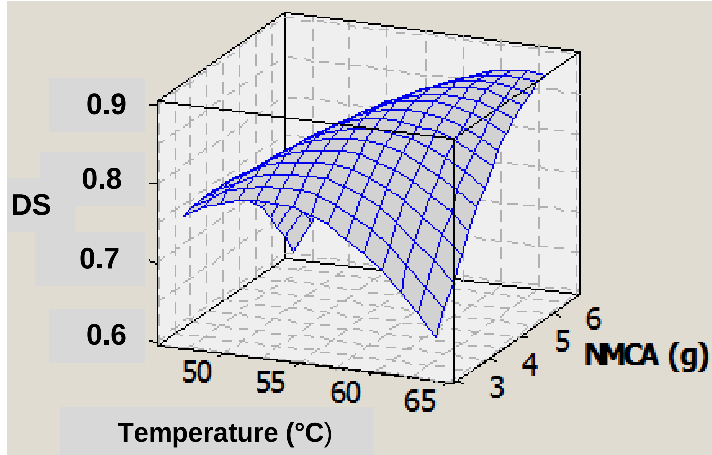

Figure 3. Surface plot of DS versus NMCA and temperature.

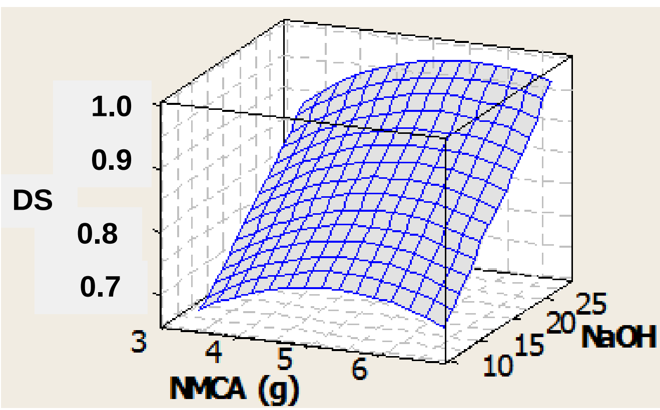

Figure 2. Surface plot of DS versus sodium hydroxide, and NMCA.

during alkalization (Pushpamalar et al., 2006). In this case, H^+ at C2, C3 and C6 of AGU will be substituted by Na^+. In the previous study reported by Bai et al. (2011); Heinze and Pfeiffer (1999) mentioned that the probability of carboxymethylation in alkaline condition will occur at C6, C2 and C3 positions, respectively. The data also suggested that the temperature will support increase of DS when the concentration of sodium hydroxide increased.

The data in Figure 2 showed that increased of DS was depended significantly by increased of NaOH than that of increased of NMCA until 3 h of reaction. This data suggested that synthesis of carboxymethylcellulose affected by NaOH in which crystalline region in cellulose will change to be amorf region and then atom C6, C2 and C3 could be accessed easily by NMCA in AGU (Olaru et al., 1997). This data is similar to Heinze and Pfeiffer (1999) findings that carboxymethyl reaction sometime to become tri-carboxymethyl or di-carboxymethyl or mono-carboxymethyl.

Surface plot of DS versus temperature and NMCA in Figure 3 showed that good interaction between temperature and NMCA. Both temperature and NMCA will affects significantly on increased of DS. Temperature will affects on the affinity of the Na^+ in AGU in the formation of amorf region and then Na+ will be replaced by NMCA to be carboxymethylcellulose in atom C6, C2 and C3. This data was similar to Heinze and Pfeiffer (1999). The data concluded that sodium hydroxide concentration, temperature, and NMCA were the main factors that affected the synthesis of carboxymethylcellulose similar with previous reports of Heinze and Pfeiffer (1999), Togrul et al. (2003) and Pushpamalar et al. (2006).

Optimum condition of synthesis carboxymethylcellulose can be simulated by response surface methodology with sodium hydroxide 15%, temperature 55.93°C and NMCA 4 g. It was given characteristics yield of 146.11%, 0.78 DS, 3.78 g/g WHC, 2.16g/g OHC, and lightness of 57.73. The results of the simulation process were verified and data was showed in Table 1. The data between simulation and verification were almost similar when results of the verification have yield of 141.60%, 0.75 DS, 3.73 g/g WHC, 2.12 g/g OHC, and lightness of 56.62. Correlation between the yield and degree of substitution is shown in Figure 4. The data showed that the higher DS the higher yield of carboxymethylcellulose. Increasing of DS means that each AGU constituent will react with carboxymethyl, the weight of the product of sodium carboxymethylcellulose also increased. Increasing each 0.1 of DS will cause an increase in the yield of carboxymethylcellulose about 8% based on linier regression analysis: $Y = 79.922\ X + 84.441$ and $R^2 = 0.65$.

Infrared spectroscopy spectra of CMC with DS 0.75, was shown in Figure 5. The peak in wave number 1604 and 1419 cm^{-1} indicated of the presence of carboxymethyl constituent. The wave number 1604 cm^{-1} plot of C=O group stretching of acetyl or carboxymethyl

Table 1. Verification on synthesis of carboxymethylcellulose in best condition (NaOH 15%, temperature 55.93°C, and NMCA 4 g for 180 min).

S/N	Characteristic	Replications			Average
		1	2	3	
1.	Degree of substitution	0.74	0.76	0.75	0.75±0.01
2.	WHC (g/g)	3.76	3.70	3.73	3.73±0.03
3.	OHC (g/g)	2.12	2.10	2.14	2.12 ± 0.02
4.	Lightness	56.23	56.88	56.75	56.62±0.39
5.	Yield (%)	142.20	140.94	141.65	141.60 ± 0.40

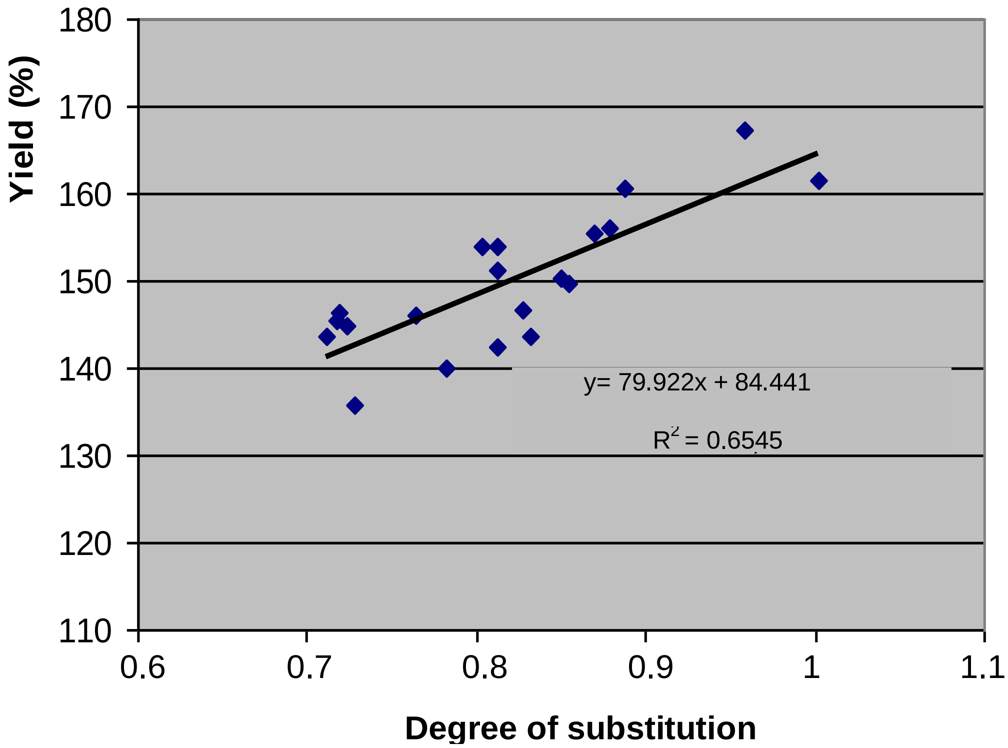

Figure 4. Relationship between DS and yield of Na-CMC (%).

and 1419 cm^{-1} plot of CH_2 scissoring in plane banding there were indicated about carboxymethyl constituent.

Salt of carboxyl group had wave number about 1600 cm^{-1} and 1400 cm^{-1} -1450 cm^{-1} that was according to Pescok et al. (1976) and Biswal and Sing (2004).

Detail data of some peaks that obtained in FT-IR spectra of carboxymethylcellulose constituent, was shown in Table 2. The displacement may be observed for the O-H stretching band of the carboxymethylated in C6. The substitution of the hydroxyl group in C6 significantly changes that it raised carbonyl group (-C=O) in wavelength 1604 cm^{-1} and $–CH_2$ in wavelength 1419 cm^{-1}. Wavelength 894 cm^{-1} was detected 1,4-β glycoside of cellulose (Viera et al., 2007). Wavelength 3417 cm^{-1} was showed due to the stretching frequency of the –OH and the band 2924 to 2931 cm^{-1} due to C-H stretching vibration of AGU (Pescok et al., 1976; Biswal and Sing, 2004; Meenakshi et al., 2002). The patterns of spectra between CMC of pod husk cacao and CMC standard are similar.

Conclusion

Cellulose from pod husk cacao has degree of polymerization with anhydrous glucose unit about 390.40 and its molecular weight about 63,342 and classified as α-cellulose. Furthermore, isolated cellulose could be modified in 15% NaOH, temperature 55.93°C, and 4 g NMCA in 3 h to carboxymethylcellulose having DS 0.75

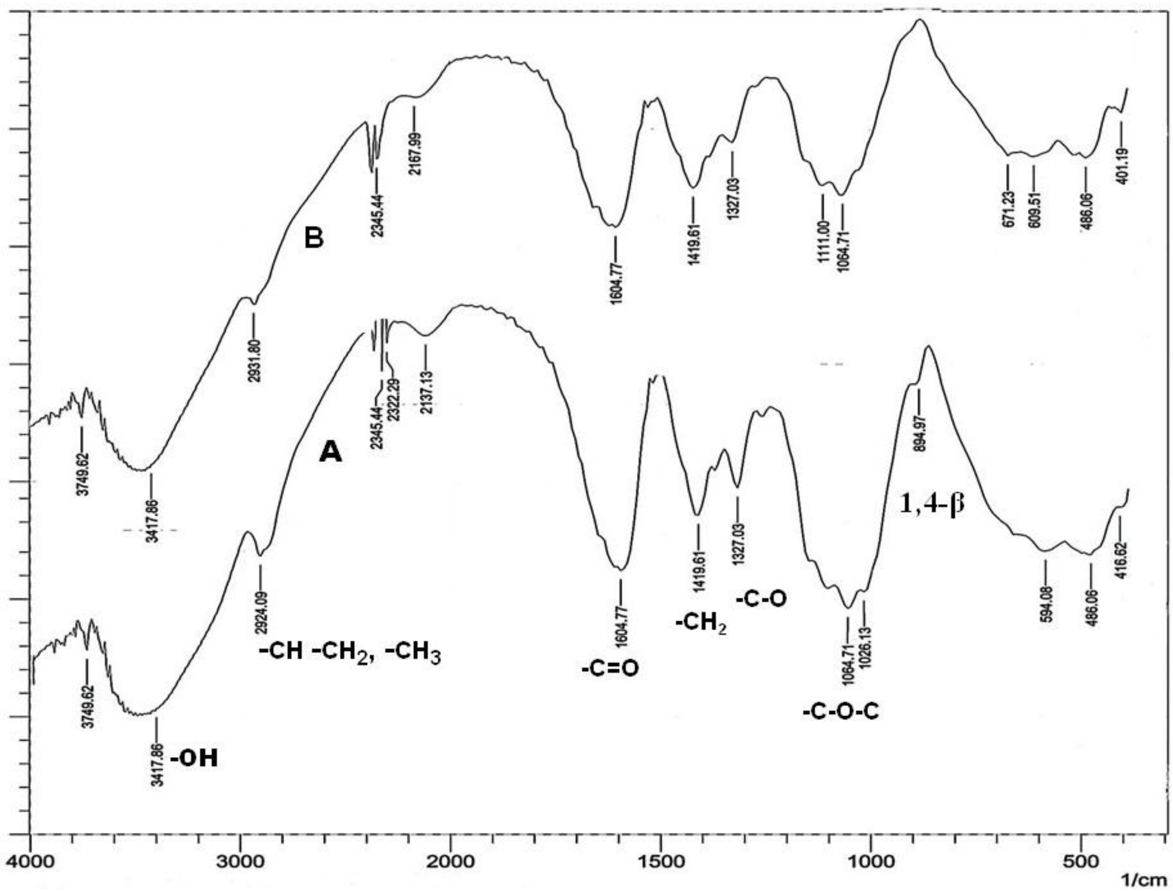

Figure 5. (A) FT-IR spectra of the sodium carboxymethylcellulose commercial and (B) sodium carboxymethylcellulose of pod husk cacao.

Table 2. Assignment of main absorption bonds in carboxymethylcellulose of pod husk cacao.

Wave number (cm^{-1})		Assignment
CMC Standard	**CMC of pod husk cacao**	
- 3417	- 3417	- OH Stretching
- 2924	- 2931	- CH stretching CH_2 and CH_3 groups
- 1604	- 1604	- C=O region (indicated CMC)
- 1419	- 1419	- CH_2 bonding (indicated CMC)
- 1327	- 1327	- OH in plane bonding
- 1111	- 1084	- C-O-C asymmetry bridge stretching
- 1084	- 1026	- C-O symmetry stretching alcohol
- 894	Not detected	- β glycoside linkage

The obtained carboxymethylcellulose has 3.73 g/g of WHC, 2.12 g/g of OHC, 56.62 of lightness, 206.10 cps of viscosity, and yield of 141.60%.

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