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Synthesis and characterization of sodium carboxymethylcellulose from cavendish banana pseudo stem (*Musa cavendishii* LAMBERT)

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Abstract

Banana pseudo stem has been known as a potential cellulose source, though usually discarded as agricultural waste in Indonesia. This work reports concisely on a method to utilize cavendish banana pseudo stem for preparing sodium carboxymethylcellulose (CMC) and its characteristics. The banana pseudo stem was obtained shortly after the mature fruit had been harvested. The pseudo stem was dried, ground to pass 20 mesh screen. The powder was extracted using 8% NaOH at 100 °C for 3.5 h, and then bleached using 5% NaOCl at 30 °C for 3 h. The cellulose was alkalized using NaOH at 5–30% at 25 °C for 1 h. Sodium Monochloracetate ($ClCH_2COONa$, NaMCA) at 3–7 g per 5 g cellulose was added to the slurry and the temperature was adjusted to 55 °C for 3 h.

Alkalization using 15% NaOH and etherification using 1.2 g (w/w) NaMCA gave CMC the highest degree of substitution (DS), viscosity, purity and crystallinity, i.e. 0.75; 4033 cps; 98.23 and 38.33% respectively.

Keywords: Cellulose; Sodium carboxymethylcellulose; Cavendish banana pseudo stem

1. Introduction

Banana pseudo stem is usually discarded as an agricultural waste from banana plantation in Indonesia. Banana pseudo stem has been known to be a potential cellulose source (Chandra & Adinugraha, 2002; Meenakshi et al., 2002). Cellulose is a linear and high molecular weight polymer as well as natural, renewable, and biodegradable material. However, due to its inter- and intra-molecular hydrogen bonds, cellulose neither melts nor dissolves readily in common solvents (Hattori, Abe, Yoshida, & Cuculo, 2004). In order to utilize cellulose in food industry, cellulose must be converted to its derivatives. Conversion from cellulose to sodium carboxymethylcellulose (CMC) is an example. Sodium carboxymethylcellulose is a linear, long-chain, water-soluble, anionic, man-modified polysaccharide. Purified CMC is a white- to cream-colored, tasteless, odorless, free-flowing powder (Keller, 1986).

Some papers have reported the synthesis of CMC from various sources (Baar, Kulicke, Szablikowski, & Kiesewetter, 1994; Barai, Singhal, & Kulkarni, 1997; Heinze, Heinze, & Klemm, 1994; Heinze, Erler, Nehls, & Klemm, 1994; Heinze & Pfeiffer, 1999; Käuper et al., 1998; Lin, Qu, & Qi, 1990; Mann, Kunze, Loth, & Fink, 1998; Olaru, Olaru, Stoleriu, & Timpu, 1998; Sri Hidayati, Kapti, & Haryadi, 2000; Toğrul & Arslan, 2003; Yokota, 1985) and none of them utilize banana pseudo stem as cellulose source.

Sodium carboxymethylcellulose was produced by conversion of alkali cellulose swollen in aqueous NaOH and a surplus of organic solvent (e.g. isopropanol, or ethanol) with monochloracetic acid or its sodium salt (Heinze & Pfeiffer, 1999). Hydroxyl groups in cellulose usually replaced by carboxymethyl groups in the order of C2 > C6 > C3 (Ho & Klosiewicz, 1980; Reuben & Conner, 1983; Tezuka, Tsuchiya, & Shiomi, 1996). The objectives of this work were to develop a method of utilizing cavendish banana pseudo stem for preparing and characterizing the resulted CMC product.

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2. Materials and methods

2.1. Extraction of cellulose

Cavendish banana pseudo stem was obtained shortly after the fruit has been harvested from a plantation in Central Java Province in Indonesia. The obtained pseudo stem was cut into small pieces (1 cm) then dried at 70 °C in a cabinet dryer (Heraeus Instruments). The dried product was ground into powder to pass through a 20 mesh sieve. Then the cellulose powder was cooked in 8% NaOH at ratio of cellulose to solvent 1:20 (w/v) for 3.5 h at 100 °C, the obtained black slurry was filtrated and washed using distilled water and bleached with 5% NaOCl for 3 h at 30 °C. The bleached cellulose was washed again using distilled water until the odor of hypochlorite could no longer be detected, then dried at 60 °C in a cabinet dryer.

2.2. Synthesis of sodium carboxymethylcellulose

Five grams of the cellulose powder was alkalized at 25 °C for 1 h in a shaking waterbath (Haake SWB) with 20 mL of various (5, 10, 15, 20, and 25%) concentration of NaOH in 100 mL of isopropanol as a solvent. After the alkalization process is over, various amount of sodium monochloracetate (NaMCA) 3, 4, 5, 6, and 7 g per 5 g cellulose was added and the temperature raised to 55 °C and the reaction continued for 3 h. The slurry was neutralized with 90% of acetic acid and then filtrated. The solid obtained as CMC was washed by 70% ethanol for four times to remove undesirable byproducts. The obtained cellulose derivative (CMC) was dried at 60 °C in an oven.

2.3. Characterization of sodium carboxymethylcellulose

The moisture content, degree of substitution (DS), viscosity and purity of CMC were determined by the ASTM D1439-94 standard method (ASTM, 1994).

2.4. X-Ray diffraction and FT-IR spectroscopy of sodium carboxymethylcellulose

A Shimadzu XRD-6000 X-Ray diffractometer was operated at Cu Kα wavelength of 1.54 Å, 30 mA and 40 keV. The spectra were recorded at a scan rate of 0.02° 2θ/s. The crystallinity of cellulose was calculated using the method from Sakaguchi, Tsutsumi, Kaji, and Abe (2002).

Infrared spectra of the CMC samples were recorded with Shimadzu FTIR-8201 PC. Pellets were made from CMC samples (~3 mg) ground with KBr (~800 mg). Transmission was measured at the wave number range of 4000–400 cm^{-1}.

3. Results and discussion

The obtained DS from this work was in the range of 0.26–0.75, while according to Reuben and Conner (1983) CMC which obtained with alkalization of cellulose then followed by carboxymethylation process using NaMCA was in the range of 0.4–1.3. When the DS is below 0.4 CMC is swellable but insoluble, above this value, CMC is fully soluble with its hydroaffinity increasing with increasing DS (Waring & Parsons, 2001). The effect of NaOH and NaMCA levels to the DS of CMC are shown in Fig. 1. As shown on Fig. 1, the DS of CMC increased with increase in NaMCA level. This is due to the greater availability of the NaMCA molecules at higher level of NaMCA in the proximity of cellulose molecules as earlier reported by Barai et al. (1997); Mann et al. (1998); Toğrul and Arslan (2003).

At the same level of NaMCA with increasing concentration of NaOH the declining of DS was observed. This was likely due to the sodium gycolate formation as byproduct in the synthesis of CMC and polymer degradation was occurred due to high concentration of NaOH. Barai et al. (1997) reported that at high concentration of NaOH, formation of sodium glycolate was increased, thus lowering the DS and CMC content (purity) because partly the NaMCA molecules tends to react with NaOH. At the low level of NaMCA (3 and 4 g) per 5 g cellulose and NaOH concentration below 15%, low DS were obtained, this phenomena might be occurred due to limited amount of NaMCA available for substituting cellulose and the NaOH concentration was not adequate to complete the conversion of cellulose to alkali cellulose. The declining of DS at higher concentration of NaOH (>15%) could also be due to degradation of CMC polymers. The best DS of CMC from this work was 0.75, and synthesized using 15% of NaOH and 6 g NaMCA per 5 g cellulose. The effect of NaOH concentration and NaMCA amount to the purity of CMC are shown in Fig. 2.

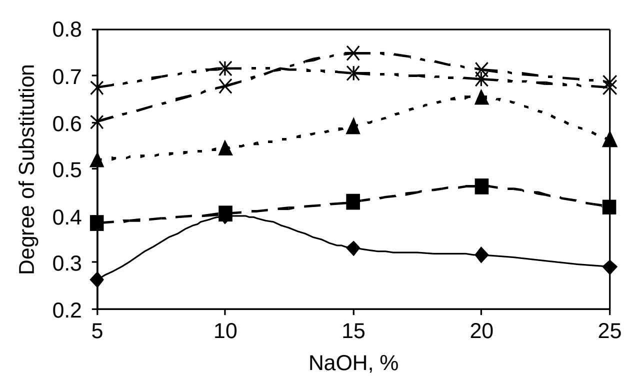

Fig. 1. Effect of various concentration of aqueous solutions of NaOH and amount of NaMCA to the DS of CMC made from cavendish banana pseudo stem cellulose (◆ NaMCA 3 g, ■ NaMCA 4 g, ▲ NaMCA 5 g, × NaMCA 6 g, ✳ NaMCA 7 g).

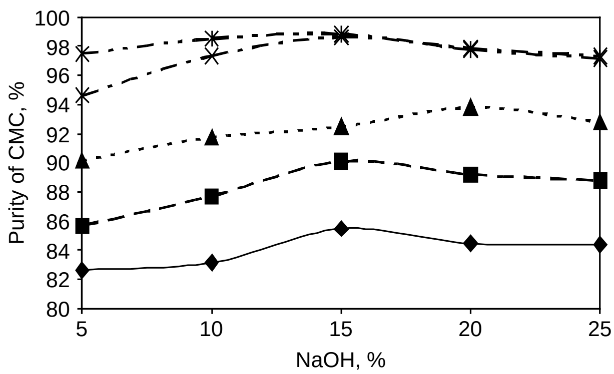

Fig. 2. Effect of various concentration of aqueous solutions of NaOH and amount of NaMCA to the purity of CMC made from cavendish banana pseudo stem cellulose (♦ NaMCA 3 g, ■ NaMCA 4 g, ▲ NaMCA 5 g, × NaMCA 6 g, ✳ NaMCA 7 g).

It could be seen that at the same level of NaMCA with increasing NaOH concentration (above 15%), the purity of obtained CMC decreased (Fig. 2). At the low level of NaMCA (3 and 4 g) per 5 g cellulose and NaOH concentration below 15%, the purity of CMC was low. This phenomenon might because at that condition, side reaction was more dominant than the main reaction. At NaMCA level of 6 and 7 g per 5 g cellulose, the CMC purity curve was adjacent, especially at NaOH concentration above 15%. This phenomenon could be occurred because at high concentration of NaOH (above 15%) and high amount of NaMCA (7 g per 5 g cellulose), the reaction tended to shift to byproducts formation as also reported by Barai et al. (1997).

From Fig. 3, it is obvious that etherification at the same level of NaMCA with increasing NaOH concentration lowered the viscosity of resulted CMC, while at the same level of NaOH concentration, with increasing level of NaMCA increased viscosity of the CMC, which was in accordance with the work of Heinze and Pfeiffer (1999). In this work, viscosity was measured in 2% (w/v) CMC in water at 28 °C. The decrease of viscosity might be because of the degradation of CMC polymer. If the polymer chain of CMC is shortened, the CMC is easier to dissolve in the water. At low level of NaMCA (3 and 4 g) per 5 g of cellulose with NaOH concentration below 15%, low viscosity of CMC solution was obtained. This probably, the DS of CMC was low, that the ability of CMC to immobilize water was reduced owing to the lack of hydrophilic groups.

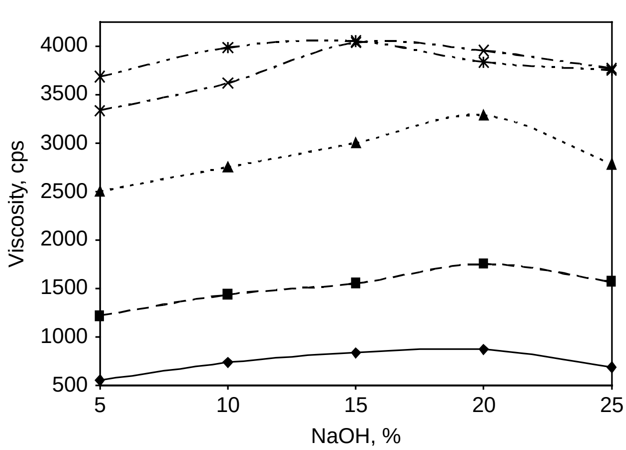

Fig. 3. Effect of various concentration of aqueous solutions of NaOH and amount of NaMCA to the viscosity of CMC made from cavendish banana pseudo stem cellulose (♦ NaMCA 3 g, ■ NaMCA 4 g, ▲ NaMCA 5 g, × NaMCA 6 g, ✳ NaMCA 7 g).

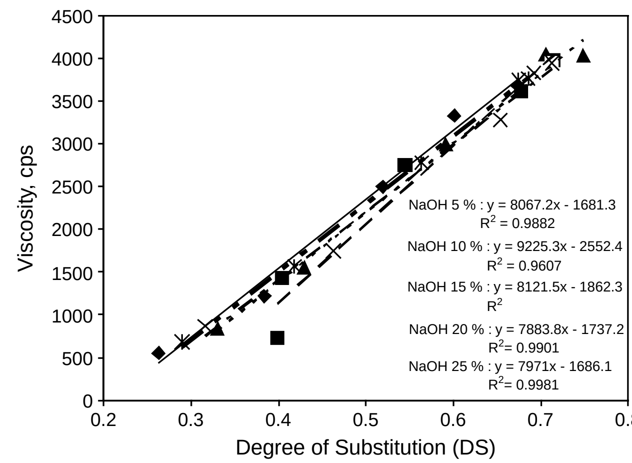

Fig. 4. Relationship between DS and viscosity of CMC made from cavendish banana pseudo stem cellulose (♦ NaOH 5%, ■ NaOH 10%, ▲ NaOH 15%, × NaOH 20%, ✳ NaOH 25%).

The relationship between DS and viscosity could be plotted as a linear curve, to show the effect of increase of DS to higher the viscosity of CMC solution (Fig. 4). Surely this was due to more carboxymethyl groups substituted the hydroxyl groups of cellulose polymers. These carboxymethyl groups act as hydrophilic groups, therefore with the increase of DS thus improved the ability of CMC to immobilize water in a system.

From Fig. 5, it could be seen that the relationship between DS and purity of CMC could be plotted in linear

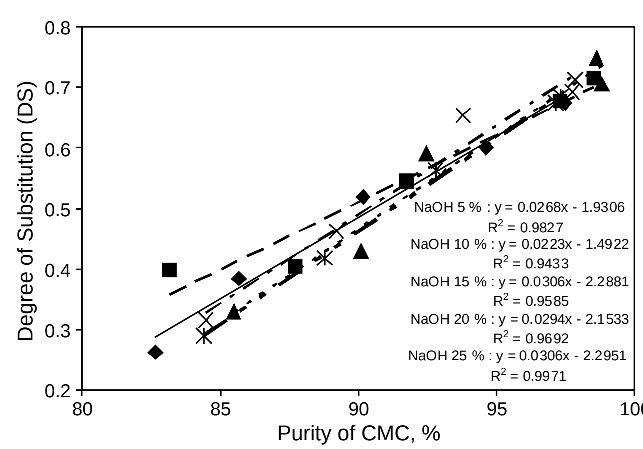

Fig. 5. Relationship between DS and purity of CMC made from cavendish banana pseudo stem cellulose (♦ NaOH 5%, ■ NaOH 10%, ▲ NaOH 15%, × NaOH 20%, ✳ NaOH 25%).

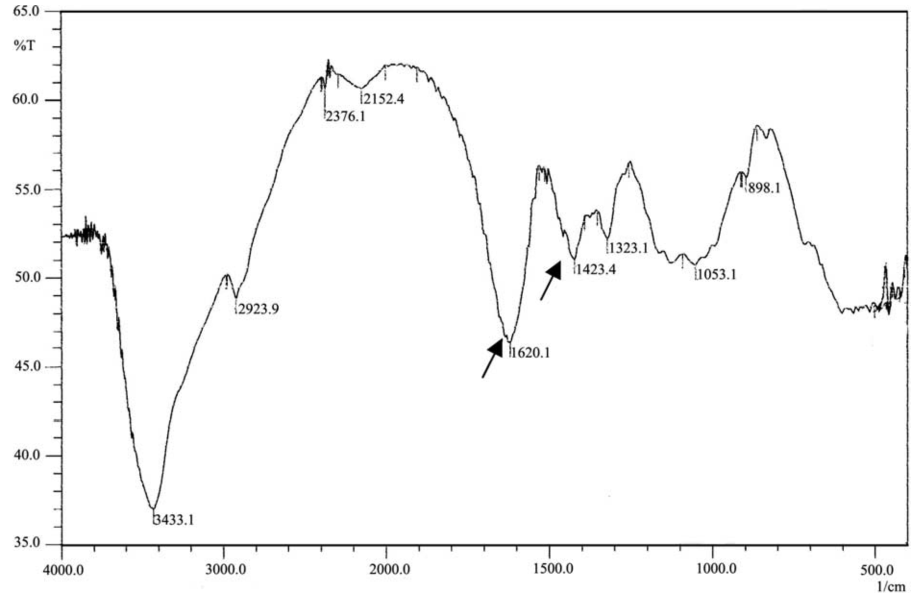

Fig. 6. FTIR spectra of CMC made from cavendish banana pseudo stem cellulose with DS of 0.75 which was synthesized using 15% NaOH and 6 g of NaMCA (carboxyl groups substituent are indicates by arrows).

curve; hence the CMC purity increased with increasing DS. This phenomenon might be because at the higher DS, more NaMCA molecules is substituted to the cellulose polymer, thus the possibility of NaMCA to reacts with NaOH to form byproducts decreased. In this work, at the DS of 0.75 the CMC purity was 98.63% while at the DS of 0.4 the CMC purity was 87.72%.

Infrared spectroscopy spectra of CMC with DS of 0.75 was shown in Fig. 6. The peaks at wave number of 1620.1 and 1423.4 cm^{-1} indicated of the presence of carboxymethyl substituent. According to Pecsok, Shields, Cairns, and McWilliam (1976), carboxyl groups as its salts have wave number about 1600–1640 cm^{-1} and 1400–1450 cm^{-1}. The spectra in Fig. 7 was similar to that shown in Fig. 6, but no peaks at wave number 2152.4 and 2376.1 cm^{-1} in Fig. 7. These peaks were supposed to be contamination from impurities or combination band from water. The similarity of Figs. 6 and 7 showed that CMC could be synthesized from cavendish banana pseudo stem cellulose.

It is obvious that after alkalization process with 15% NaOH, the crystallinity of cavendish banana cellulose was reduced (Fig. 8). The crystallinity of native cavendish banana cellulose and cavendish banana cellulose after

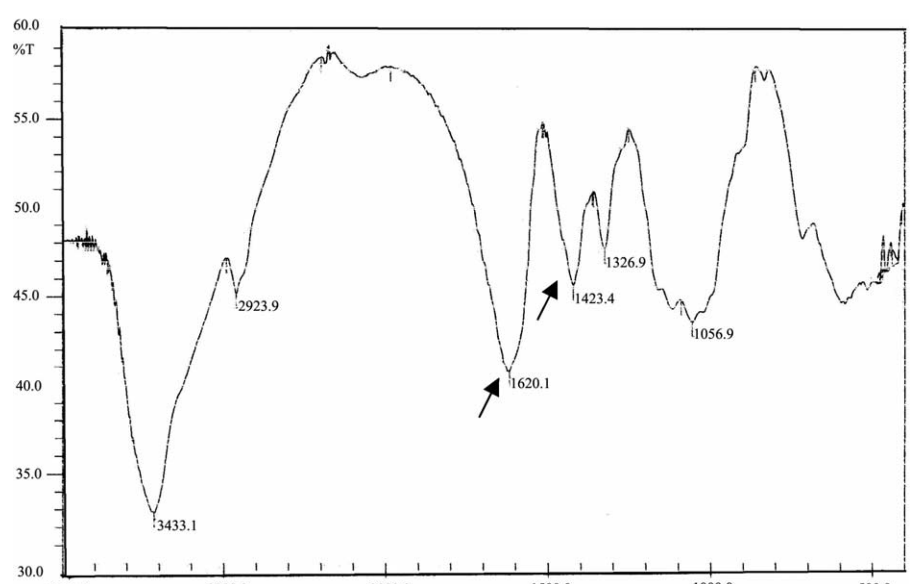

Fig. 7. FTIR spectra of commercial CMC (HP-8A) with DS of 0.77 (carboxymethyl groups substituent are indicates by arrows).

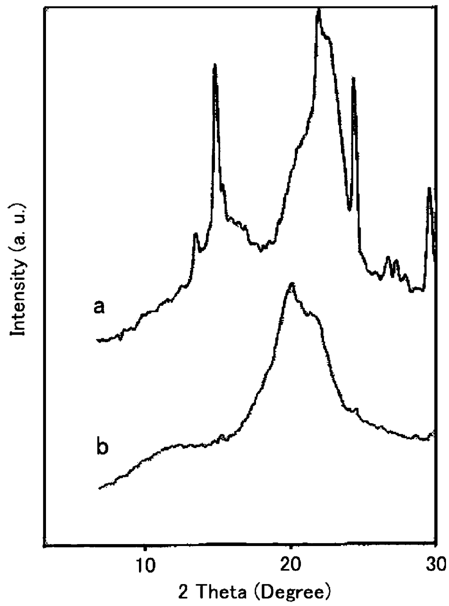

Fig. 8. X-Ray diffractogram of cavendish banana pseudo stem cellulose. (a) Native cavendish banana pseudo stem cellulose, (b) Cavendish banana pseudo stem cellulose after treatment with 15% NaOH.

alkalization treatment were 49.27 and 43.75%, respectively. The crystallinity of cellulose was associated with inter- and intra-molecular hydrogen bond of cellulose.

The decrease of crystallinity when the cellulose was treated with 15% NaOH was due to the cleavage of hydrogen bonds because of NaOH. From Fig. 8, it is also shown that cellulose I was converted to cellulose II. This conversion was marked with the shifting of peaks of 002, 101 and $10\bar{1}$ in 2θ degree. According to Fengel and Wegener (1989) this conversion was also result in the broadening the distance between cellulose polymer molecules, thus the substitution of NaMCA molecules to the

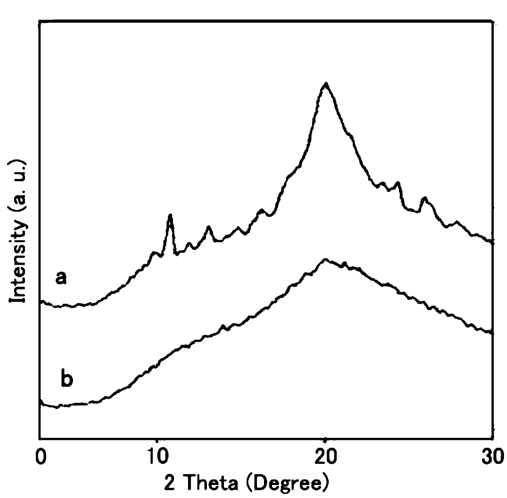

Fig. 9. X-Ray diffractogram of CMC. (a) CMC from cavendish banana pseudo stem cellulose with DS 0.75, (b) commercial CMC from unknown source with DS 0.77.

Table 1
Characteristics of the CMC resulted from this work, commercial CMC and those specified the regulation

Parameter	CMC resulted	Commercial	Regulation[a]
DS	0.75	0.77	≤0.95
Viscosity of 2% (w/v) solution	4033	10,333	≥25
Cps	98.63	99.13	≥99.5
Purity (%)	38.33	16.33	–
Crystallinity (%)	7.37	7.54	≤10
Moisture (%)			

[a] Source: Food Chemicals Codex, 1996

cellulose polymers will be relatively easier than cellulose without alkalization treatment with NaOH.

The CMC (DS 0.75) resulted from this work had higher crystallinity (38.33%) than the commercial sample (DS 0.77) did (16.33%), this was shown in Fig. 9. The crystallinity of CMC with DS 0.75 was lower than that of cellulose heated with 15% NaOH. This phenomenon was supposed to be the cleavage of the broadening hydrogen bonds due to carboxymethyl substitution at the hydroxyl groups of cellulose. According to Lin et al. (1990), the higher the DS of CMC thus resulted in the decrease of the crystallinity, whereas in CMC with DS higher than 1, the crystallinity peak was almost disappeared.

Neither CMC obtained from this work nor the commercial sample did not meet the specification regulation according to Food Chemicals Codex as shown in Table 1. Therefore, further work is needed to gave higher the purity of CMC. This CMC was categorized as technical grade CMC because the purity is below 99.5%. The CMC resulted from this work could be categorized as medium viscosity CMC, while the commercial CMC was as high viscosity grade CMC, based on Keller Classification (Keller, 1986).

4. Conclusion

Sodium carboxymethylcellulose could be synthesized from carboxymethylation of cavendish banana pseudo stem cellulose. The leading characteristics of CMC obtained from this work was CMC with DS of 0.75, which had viscosity 4033 cps, purity 98.63%, and crystallinity 38.33%. This CMC was synthesized using 15% NaOH and 6 g NaMCA per 5 g cellulose. Sodium carboxymetylcellulose resulted from this work could be categorized as technical grade CMC and medium viscosity CMC, while appearance of the CMC was fair.

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