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Synthesis and characterization of carboxymethyl cellulose from pineapple core

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Abstract - Pineapple core is one of waste left over after pineapple processing. It could be increased value by maximally utilizing certain composition. Cellulose, an abundant compound in pineapple core, could be extracted and purified by removing lignin and hemicellulose. Moreover, it could be converted into carboxymethyl cellulose (CMC) for wide application. The objective of this research was to synthesize the CMC extracted from pineapple core (P-CMC). This process provided P-CMC with the purity of 95.86% at the processing yield about 89.78%. The degree of substitution was 0.83, which is commercially acceptable. Fourier transform infrared spectroscopy revealed the chemical structure of the synthesized P-CMC. Observation of the IR spectra, peak at a wave number of 1588 cm^{-1}, exhibited the presence of a carboxyl group (COO-) in the P-CMC. The moisture content, water activity, viscosity, and solubility, which is similar to commercial CMC. The color of P-CMC was yellow but commercial CMC was white, which depended on the color of raw material. This suggested the similarity carboxymethyl substitution comparable to that of commercial CMC. The P-CMC expressed high potential for commercial production.

Keywords: Carboxymethyl cellulose, cellulose, degree of substitution, pineapple core, purity

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1. Introduction

The pineapple (*Ananas comosus* (L.) Merr.) is the one of economic crop in the world and Thailand is the 4th largest producer of pineapples, which has less productivity than the Costa Rica, Philippines and Brazil. However, the top supplier of processed pineapple products, particularly canned pineapple and pineapple juice has been documented currently to be Thailand (Hemung *et al.,* 2022). Pineapple plants can be grown throughout the country, including in the northern, northeastern, central, and southern regions. In order to process, only the flesh (30-60% of whole fruit) has been used for producing the canned pineapple. The other sections are considered by-products, which are crows, stems, peels, and cores, accounting for 2.7-5.9, 2.4-6.8, 29-42, and 9.4-20%, respectively. In 2020, the core has been estimated to produce approximately 247,089.9 tons from canned pineapple industries (Hemung *et al.*, 2022). Such huge by-products must be managed properly to prevent environmental pollution. Chemical compositions of core have been reported to contain 12.9% lignin, 11.5% cellulose and 14.1% hemicellulose (Srithiang *et al.,* 2019). Further utilization of this by-product for being higher value products would be the challenge to maximally utilize the pineapple resources. Extraction of cellulose from pineapple cores is an alternative valorization and has not been done (Prakongpan *et al.,* 2002).

Cellulose is an abundant component available in plant cell wall. It is normally conjugated either lignin or hemicellulose. It is accounted for approximately 40-55%, depending on plant species (Thomas *et al.,* 2002). The application of plant cellulose has been focused on textile and papers industries (Rachtanapun *et al.,* 2012). Since it is less soluble, its utilization in food system is limited. However, modification of cellulose to be carboxymethyl cellulose (CMC) improves solubility. This property of cellulose increases by substituting the present structure with carboxymethyl groups. CMC powder is a white solid and its solution shows the viscous, clear, odorless. This solution is safe for customers and the environment. The CMC has been used in the food industry and it is currently imported from other countries. For CMC preparation, cellulose must be activated by hot alkaline (NaOH) solution in an organic solvent prior to etherifying the active cellulose with the monochloroacetic acid. The carboxymethylation process allow the hydroxyl groups to substitute with carboxymethyl group. Production of CMC using cellulose extracted from agricultural waste have been reported in durian rind (Rachtanapun *et al.,* 2012), sago (Pushpamalar *et al.,* 2006), orange peel (Pormsila *et al.,* 2019), empty palm bunches (Rasid *et al.,* 2021), papaya peel (Rachtanapun, 2009), rice straw (Saengchu *et al.,* 2008), cocoa pod husks (Krisdayanti *et al.,* 2017) and young coconut husks (Kanokpanont *et al.,* 2017). However, CMC synthesis from cellulose extracted from pineapple core has not been reported. The objectives of this study were to produce the CMC from pineapple cores (P-CMC) and to determine the FT-IR, degree of substitution (DS), purity, yield, viscosity, solubility, moisture content, water activity and color of the obtained P-CMC. The outcome of this research might be strategy to increase the economic value of agricultural waste, particularly pineapple.

2. Materials and methods

2.1 Materials

Pineapple core (Smooth cayenne) was transferred from pineapple plantations in Sri Chiang Mai District, Nong Khai Province, Thailand. Actually, pineapple cores are by-products from pineapple processing factories. They contain both cellulose and hemicellulose which are not contact with the external environment, making them safe from chemical and physical contamination. They could be processed as safe ingredients in food. All chemicals used to prepare and analyze CMC were of analytical grade. Commercial CMC was purchased from Changzhou Guoyu Environmental S&T Co., Ltd. (Changzhou, China). Sodium hydroxide and glacial acetic acid were purchased from RCI Lab-scan Co., Ltd. (Bangkok, Thailand). Isopropanol, methanol and ethanol were purchased from Union Science Co., Ltd. (Khon Kaen, Thailand). Monochloroacetic acid was purchased from Laba Chemie Pvt., Ltd. (Maharashtra, India) The hydrogen peroxide was produced from QRëC®.

2.2 Methodology

2.2.1 CMC synthesis

Cellulose was extracted from pineapple core through alkalization according to Ratchtanapun *et al.* (2012). The cellulose was extracted using 10.0% NaOH at 100 ° C for 3 h under a pressure of 413 MPa. Moreover, the CMC synthesized method was adapted from the same reference. Cellulose from pineapple core (5.0 g) was mixed with 30.0% NaOH (50 ml) and isopropyl alcohol (150 ml). The mixture was stirred at 30 °C for 30 min before adding monochloroacetic acid (6 g). Thereafter, the mixture was continually stirred for 90 min prior incubating at 55 °C for 3 h. The incubated mixture was filtered through the filter paper (Whatman®) No. 1. The retentate was washed by mixing with 70.0% (v/v) ethanol (50 ml) and stirred for 5 min (adjusted pH to 7.00 with glacial acetic acid) before filtering through the filter paper. This washing step was repeated 4 more times. Then, the final retentate was dried overnight at 55 °C and used as P-CMC powders. The yield of CMC was calculated using equation (1). Mean values from the triplicated experiments was reported.

$$\%\text{Yield of CMC} = \frac{\text{Weight of CMC (g)}}{\text{Weight of cellulose (g)}} \times 100 \quad (1)$$

2.2.2 Determination of degree of substitution (DS)

The DS of CMC was determined according to previous research (Bono *et al.,* 2009), which based on potentiometric titration. The CMC (1.0 g) was mixed with 95% ethanol (50 ml) and stirred for 5 min before adding of 5 ml of 2 M nitric acid. The mixture was contiuous stirred for 10 min at room temperature before boiling for 30 min. The hot 95% ethanol (100 ml) and absolute methanol were used to remove the acid and salts. The washed material was dried at 70 °C for 3 h. The dried sample (0.5 g) was mixed with 100 ml of DI water. Then, 25 ml of 0.5 M NaOH was added into the mixture and boiled for 20 min. The solution was titrated with 0.3 M HCl using the phenolphthalein as indicator. The DS of CMC was calculated using equation (2) and (3).

$$A = \frac{BC - DE}{F} \quad (2)$$

$$\text{Degree of substitution, DS} = \frac{0.162A}{1 - (0.058A)} \quad (3)$$

where A is the milliequivalents of consumed HCl per gram of specimen; B is the volume of NaOH added; C is the molarity of NaOH; D is the volume of consumed HCl; E is the molarity of HCl used; F is the CMC in grams; 0.162 is the molecular weight of the anhydrous glucose unit divided by 1000 and 58 is the net increment in the anhydrous glucose unit for every substituted carboxymethyl group.

2.2.3 Purity of CMC

The purity of all CMC sample was evaluated according to the standard method ASTM (2016). Briefly, 3 ± 0.1 g of each sample to the nearest 0.001 g was placed in a beaker and stirred with two portions of 150 ml of ethanol at 60 °C (80% v/v) for 15 min. The supernatant was properly decanted at the end of each step. The undissolved matter was then dried and weighed to calculate the percentage of CMC, on a dry weight basis, according to the following equation (4)

$$\text{Purity (\%)} = \frac{\text{A} \times 10{,}000}{\text{B}\,(100 - \text{C})} \quad (4)$$

where: A = mass of dried residue (g)
B = mass of sample used (g)
C = moisture in the sample as received (%)

2.2.4 FT-IR spectroscopy of CMC

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

2.2.5 Color of CMC

The color properties of the powder samples were evaluated using a Color Quest XE Spectropolarimeter (Hunter Lab, USA). The L* value (lightness), a* value (redness), and b* value (yellowness) were determined. Prior to the measurement, the spectropolarimeter was calibrated using a white standard (tile: L* = 93.24, a* = -0.72, and b* = 1.53). The measurements were performed in triplicate, and the average values of L*, a*, and b* were calculated (Devani *et al.*, 2009).

2.2.6 Moisture content of CMC

Moisture content was measured using a Halogen Moisture Analyzer HE73. A reusable steel pan was first incubated in hot air at 105 °C for 1 h to ensure it was properly heated. Approximately 2 g of CMC was placed in the pan and covered with a lid. The moisture analyzer was then initiated, and the machine emitted a warning tone once the measurement was completed. The measured value was recorded for analysis.

2.2.7 Water activity of CMC

The water activity (aw) of the CMC samples was determined using the following method. First, CMC was crushed and packed into plastic cartridges, ensuring that the level did not exceed the specified

capacity of the cartridge. The water activity in the samples was measured using a water activity meter (Aqua Lab model series 3, USA). The cartridge containing the sample was placed in the chamber of the meter, and the internal conditions were allowed to reach equilibrium. The measured value was obtained once the alarm was triggered.

2.2.8 Viscosity of CMC

The viscosity of the samples was determined using a Brookfield viscometer (Model: NDJ-1, Henan, China). A sample solution with a concentration of 1 g per 100 ml was prepared, and the viscosity was measured at 6 min with a rotational speed of 160 rpm. All measurements were conducted in triplicate to ensure accuracy and reliability.

2.2.9 Water solubility of CMC

Solubility was determined using the A/S Niro Atomizer (1978). A 10% by weight concentration of CMC powder solution was prepared. The CMC powder solution was heated at 30 °C for 3 min, followed by a resting period of 15 min. Subsequently, the solution was centrifuged at 700 g for 5 min. To further process, 20 ml of water was added to the solution and centrifuged again. The quantity of sediment obtained was recorded for analysis.

3. Results & discussion

3.1 Properties of P-CMC

CMC was synthesized by alkalizing and carboxymethylating the pineapple cellulose. The yield (by weight compared to the cellulose used) of P-CMC synthesis was 89.78%, the purity was 95.86%, moisture content was 3.34%, water activity was 0.38 and solubility was 98.06%. The DS was found at 0.83, which was similar to commercial CMC (Table 1). The DS values accepted in commercial CMC was in the range of 0.4-1.5 (Hienze *et al.,* 2005). The high DS value of P-CMC indicated the high number of hydroxyl groups in the cellulose structure which have been substituted by carboxymethyl or sodium carboxymethyl groups. It has been reported that CMC is solubilized in water when the DS is greater than 0.6 (Borsa & Racz*.,* 1995). The DS is highly influenced by the viscosity of CMC. The higher the DS, the greater the viscosity and cation exchange capacity. According to the results in Table 1, P-CMC (1989 cPs) has a higher viscosity than commercial CMC (1940 cPs), which is similar to CMC from durian (Rachtanapun *et al.,* 2012).

The P-CMC purity was low but it can be improved by enhancing the separation of sodium chloride and sodium glycolate through the use of methanol or acetone. This results in higher purity of CMC for commercial production to achieve improved CMC quality. The water activity and moisture content of P-CMC were slightly higher than those of commercial CMC. Both P-CMC and commercial CMC exhibited low moisture content (water activity < 0.6 and moisture content < 12%). They could be stored for an extended period without microbial contamination and chemical reaction. It was advisable to store them in dry and airtight conditions to prevent moisture absorption from the environment. The lower moisture content led to increased solubility, which aligned with the experimental results indicating that P-CMC had slightly lower solubility than commercial CMC. P-CMC demonstrated high solubility (>98%)

and could be applied in various food applications, similar to commercial CMC.

Before extraction of the CMC from the pineapple cores, dried brown powder of pineapple cores cellulose was prepared, and its appearance is shown in Figure 1(a). The color of the CMC revealed substantial differences in color measures, as shown in Table 2, where P-CMC was yellow but commercial CMC was white, which depended on the color of raw material (Figure 1). The values were similar to CMC from orange peel (Pormsila *et al.* 2019). For commercial production, these can be improved by color bleaching using NaClO.

Table 1. Properties of P-CMC comparison to commercial CMC.

Properties	P-CMC	Commercial CMC
Yield (%)	89.78±0.06	95.56±0.03*
Degree of substitution (DS)	0.83±0.03	0.80±0.01
Purity (%)	95.86±0.15	99.57±0.25
Moisture content (%)	3.34±0.02	2.33±0.03
Water activity	0.38±0.01	0.34±0.01
Viscosity (cPs)	1989.00±0.02	1940.00±0.01
Solubility (%)	98.06±0.04	99.50±0.03

Values are means of three replicates ± standard deviation.
*Source: Saengchu *et al.* (2007).

(a) Pineapple core cellulose (b) P-CMC (c) Commercial CMC

Figure 1. The appearance of pineapple core cellulose, P-CMC and Commercial CMC

Table 2. Color of P-CMC comparison to commercial CMC.

Samples	L*	a*	b*
P-CMC	68.37±0.07	5.20±0.01	24.21±0.04
Commercial CMC	84.30±0.01	1.53±0.01	10.23±0.01

Values are means of three replicates ± standard deviation.

3.2 Fourier transform infrared spectroscopy (FTIR)

Infrared spectroscopy spectra of P-CMC were shown in Figure 2. The wave number at 1588 cm^{-1} exhibited the C=O stretching of acetyl or carboxymethyl groups and at 1411 cm^{-1} was that of CH_2 scissoring in plane banding. These indicated carboxymethyl constituent in P-CMC. The wavenumbers of carboxyl group were 1600 cm^{-1} and 1400 - 1450 cm^{-1} that was according to the previous research (Pescok *et al.,* 1976 & Biswal *et al.,* 2004). The obtained wave numbers in FT-IR spectra of P-CMC constituent, were shown in Table 3. The displacement was observed for the O-H stretching band of the carboxymethylated in C_6. The substitution of the hydroxyl group in C_6 affected to the increase of carbonyl group (-C=O) in wave number 1588 cm^{-1} and -CH_2 in wave number 1411 cm^{-1}. The wave number 889 cm^{-1} represented 1,4-β glycoside of cellulose (Viera *et al.,* 2007). Wave number 3587 cm^{-1} occured due to the stretching frequency of the -OH and the band 2909 to 2929 cm^{-1} due to C-H stretching vibration of anhydroglucose unit (AGU) (Pescok *et al.,* 1976; Biswal *et al.,* 2004; Meenakshi *et al.,* 2002). The patterns of spectra between P-CMC and commercial CMC were similar.

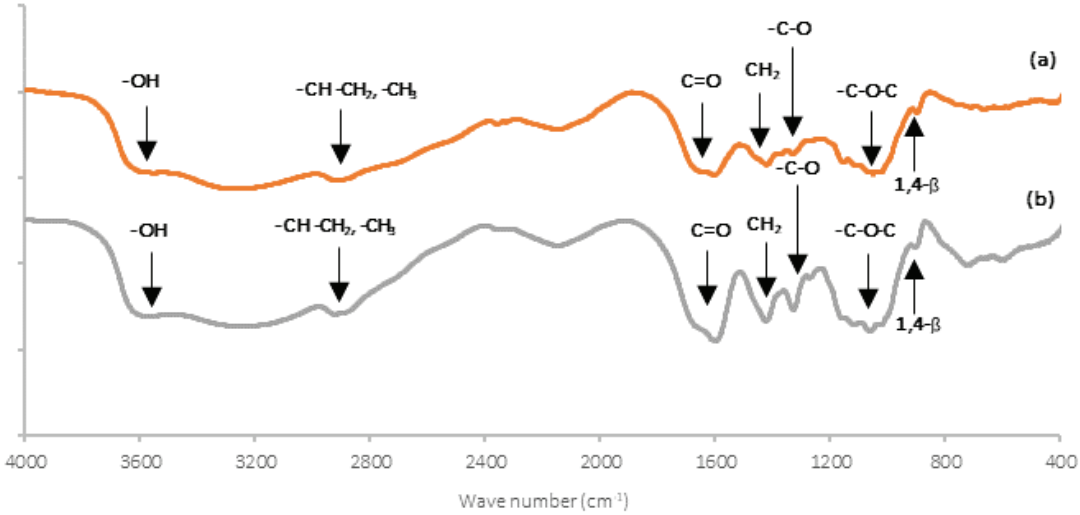

Figure 2. FTIR spectra of P-CMC (a) and commercial CMC (b).

Table 3. Assignment of main absorption band in P-CMC and commercial CMC.

Wave number (cm^{-1})		Assignment
Commercial CMC	P-CMC	
3611	3587	OH Stretching
2909	2929	CH Stretching CH_2 and CH_3 groups
1594	1588	C=O region (indicated CMC)
1434	1411	CH_2 bonding (indicated CMC)
1320	1318	OH in plane bonding
1053	1056	C-O-C asymmetry bridge stretching
1016	1010	C-O symmetry stretching alcohol
919	889	β glycoside linkage

4. Discussion and conclusion

Carboxymethyl cellulose could be synthesized successfully from pineapple core. FT-IR confirmed the presence of the carboxymethyl group in P-CMC. The DS, moisture content, water activity, viscosity, and solubility, which is similar to commercial CMC. The distinct differences observed in P-CMC compared to commercial CMC were its light yellow color, which depended on the original color of pineapple core, and lower purity. However, these can be improved by color bleaching using NaCl and enhancing the separation of sodium chloride and sodium glycolate through the use of methanol or acetone. This results in higher purity of CMC for commercial production to achieve improved CMC quality.

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