Cellulose Extraction from Pomelo Peel: Synthesis of Carboxymethyl Cellulose

J. Chumee, D. Seeburin

***Abstract*—**The cellulose was extracted from pomelo peel and an etherification reaction used for converting cellulose to carboxymethyl cellulose (CMC). The pomelo peel was refluxed with 0.5 M HCl and 1 M NaOH solution at 90°C for 1 h and 2 h, respectively. The cellulose was bleached with calcium hypochlorite and used as precursor. The precursor was soaked in mixed solution between isopropyl alcohol and 40%w/v NaOH for 12 h. After that, chloroacetic acid was added and reacted at 55°C for 6 h. The optimum condition was 5 g of cellulose: 0.25 mole of NaOH : 0.07 mole of $ClCH_2COOH$ with 78.00% of yield. Moreover, the product had 0.54 of degree of substitution (DS).

***Keywords*—**Pomelo peel, Carboxymethyl cellulose, Cellulose.

I. Introduction

POMELO is a tropical fruit, the largest of the citrus family. It is presently widely cultivated and consumed in Thailand, producing agricultural solid waste of pomelo peel from households and industry [1], [2]. This significant problem may be overcome by utilizing this waste to be useful. The pomelo peel has cellulose as major composition that can be extracted by refluxing with acidic or alkali solution [3]. Cellulose is a natural polymer, consisting of glucose units with a uniform chain structure. However, the application of cellulose is limited, caused by insolubility [4]. The purified cellulose can be converted to carboxymethyl cellulose (CMC) by etherification. There are two steps for synthesis of CMC. The first step is activation of cellulose with an aqueous NaOH in the slurry of an organic solvent as shown in (1). The last step is the activation of cellulose reacts with chloroacetic acid as shown in (2). By the way, the side reaction that occur are shown in (3) [5], [6].

$$\underset{\text{(Cellulose)}}{\text{CLL–OH}} + \text{NaOH} \rightarrow \text{CLL–ONa} + H_2O \quad (1)$$

$$\text{CLL–ONa} + \underset{\text{(Chloroacetic acid)}}{ClCH_2COOH} \rightarrow \underset{\text{(CMC)}}{\text{CLL–OCH}_2\text{COOH}} + \text{NaCl} \quad (2)$$

$$\text{NaOH} + \underset{\text{(Chloroacetic acid)}}{ClCH_2COOH} \rightarrow \underset{\text{(Glycolic acid)}}{HOCH_2COOH} + \text{NaCl} \quad (3)$$

The CMC is a soluble biopolymer; the degree of solubility depends on substitution of a carboxymethyl group instead of the hydroxyl groups in cellulose structure. There are many applications of CMC, for example, detergents, food exploration, paper, textiles, pharmaceutical and paint industries, because of CMC can be used as binder, gel former and stabilizer [6], [7]. Therefore, the aim of this work was synthesis of CMC from pomelo peel.

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II. Experiment

A. Materials

Pomelo peel and sticky rice flour were obtained from Talad Thai (Bangkok, Thailand). The chemicals for the extraction of cellulose were analytical grade sodium hydroxide (NaOH, Carlo Erba), 37% hydrochloric acid (HCl, Carlo Erba) and calcium hypochlorite ($CaCl_2O_2$, Chemipan). The chemicals for synthesis of CMC and determination of degree of substitution (DS) were isopropanol, ethanol and methanol in commercial grade and analytical grade chloroacetic acid ($ClCH_2COOH$, Acros Organic), acetic acid (CH_3COOH, J.T. Baker), 70% nitric acid (HNO_3, J.T. Baker), and carboxymethyl cellulose (CMC, Chemipan).

B. Extraction of Cellulose from Pomelo Peel

The dried pomelo peel powder was refluxed with 0.5 M HCl and 1 M NaOH solution at 90°C for 1 h and 2 h, respectively with ratio of weight of pomelo peel powder and volume of HCl or NaOH solution was 1:3. Then, the black cellulose was bleached with 1.5% calcium hypochlorite solution, filtered, washed several times with water until pH~7 and dried at 70°C for 12 h. The white cellulose was obtained and mashed into powder. The percent yield of cellulose was determined by following equation.

$$\%\ \text{Yield of cellulose} = \frac{\text{Weight of cellulose}}{\text{Weight of pomelo peel}} \times 100 \quad (4)$$

The pomelo peel cellulose was used as precursor for the synthesis of CMC by etherification reaction.

C. Etherification Reaction and Characterization

The pomelo peel cellulose was soaked in mixed solution between isopropyl alcohol and 40%w/v NaOH solution for 12 h. The chloroacetic acid was added and stirred at room temperature for 1 h. The solution was then transferred to an oven and kept at 55°C for 6 h. The obtained solid was adjusted to pH 7 with acetic acid, filtered and washed with ethanol and methanol for 6 times and 1 time, respectively. The purified solid was prepared by soaking in 80% methanol several times and the final product was called as CMC_p. The percent yield of CMC was determined by following equation.

$$\% \text{ Yield of CMC } = \frac{\text{Weight of } CMC_p}{\text{Weight of cellulose}} \times 100 \quad (5)$$

The DS of CMC was determined by the standard method modified from literature [6]. Soaking CMC_p 0.5 g in 20 mL of HNO_3–methanol mixture (108 mL of 65% HNO_3 was made to one liter with methanol) for 3 h. Then, filtered, washed with 70% methanol and dried at 55°C for 1 h. 0.2 g of dried CMC_p was dissolved in distilled water 20 mL and 1 M NaOH 3 mL. Finally, the mixture was titrated with 1 M HCl. The DS of CMC was calculated by following equations.

$$\text{DS of CMC } = \frac{0.162A}{(1-0.058A)} \quad (6)$$

$$A = \frac{(BC-DC)}{F} \quad (7)$$

where A is the equivalent weight of alkali required per gram of dried CMC_p (g), B is the amount of NaOH solution (mL), C is the concentration of NaOH solution (M), D is the amount of HCl solution (mL), E is the concentration of HCl solution (M) and F is the weight of dried CMC_p (g).

The CMC_p was characterized by Fourier transform infrared spectroscopy (FTIR; Thermo Scientific Nicolet 6700) and Color Quest XE Spectrocolorimeter (Hunter Lab, USA).

III. Results and Discussion

The cellulose was extracted from pomelo peel by refluxing with HCl for 1 h and NaOH for 2 h, respectively. The acidic method can damage the cellulose; however, it presents a higher purity of cellulose than the alkali method [3]. Hence, in this work, both the acidic and alkali methods were for purification of cellulose. The yield of cellulose was 41.71 percent. The pure cellulose was used for synthesis CMC in the etherification reaction with different conditions and showed percentage yield of CMC_p in Fig. 1.

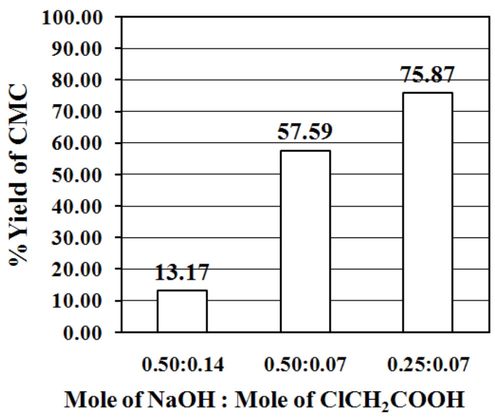

Fig. 1 % Yield of CMC_p with different moles of NaOH and $ClCH_2COOH$

The moles of NaOH and $ClCH_2COOH$ have effect to percent yield of CMC. The condition of mole NaOH and $ClCH_2COOH$ was 0.25:0.07 as $CMC_{p(0.25:0.07)}$ shows percentage of CMC yield higher than other conditions. It is possibly due to excess amounts of NaOH and $ClCH_2COOH$ that reacted as a side reaction therefore the percent yield is decreased. The average of DS is 0.54; this polymer can dissolve in water [5], [6]. Consequently, this condition was selected for repeating to confirm the result as shown in Table I.

TABLE I
% Yield and DS of CMC_p Repeated 3 Times

	% Yield *	DS*
1	75.87	0.56
2	87.37	0.53
3	70.76	0.54
Average	78.00	0.54
Standard deviation	8.51	0.02

(Condition*: 5 g of cellulose: 0.25 mole of NaOH : 0.07 mole of $ClCH_2COOH$)

TABLE II
Color Measurement

Sample	L* (Lightness)	a* (Redness/ Greenness)	b* (Yellowness/ Blueness)
CMC_p	70.73±0.01	5.41±0.01	17.78±0.03
CMC_{com}	92.16±0.16	0.80±0.80	6.58±0.01

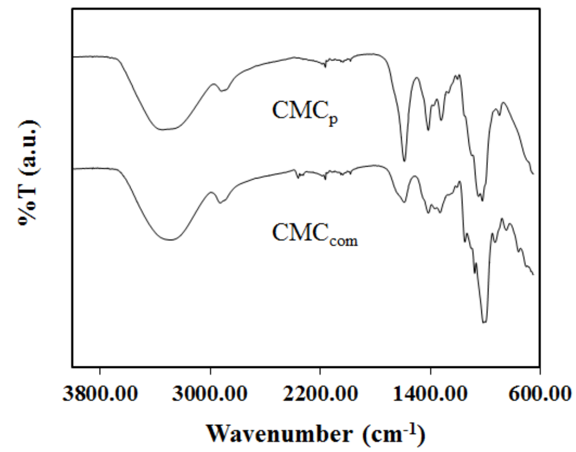

Fig. 2 FTIR spectra of $CMC_{p(0.25:0.07)}$ and CMC_{com}

$CMC_{p(0.25:0.07)}$ was furthermore characterized by FTIR and Color Quest XE Spectrocolorimeter. The FTIR spectra of $CMC_{p(0.25:0.07)}$ and CMC_{com} had a similar pattern. The –OH stretching broad band represents ~3319cm^{-1} and small band ~2871cm^{-1} attributable to C–H stretching. The COO^- group strong functional absorption band ~1581cm^{-1} and the bands ~ 1407 and 1311cm^{-1} corresponding with $–CH_2$ scissoring. The band ~1031cm^{-1} presented $OCH–O–CH_2$ stretching as displayed Fig. 2 [5]–[7]. The color of $CMC_{p(0.25:0.07)}$ was yellowish brown when compares with CMC_{com} as present in Table II. Noticeably, the optimum condition for synthesis CMC_p was 5g of cellulose: 0.25 mole of NaOH: 0.07 mole of $ClCH_2COOH$.

IV. Conclusion

Cellulose was extracted from pomelo peel and used for synthesis CMC_p by etherification. The 0.54 of DS presented the water soluble property of a polymer. Therefore, CMC_p can be used in many applications.

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REFERENCES

[1] B. H. Hameed, D. K. Mahmoud and A. L. Ahmad "Sorption of basic dye from aqueous solution by pomelo" *Colloids and Surfaces A: Physicochem. Eng. Aspects*, vol. 316, Mar. 2008, pp. 78–84.

[2] P. Methacanon, J. Krongsin and C. Gamonpilas "Pomelo (Citrus maxima) pectin: Effects of extraction parameters and its properties" *Food Hydrocolloids*, vol. 35, Mar. 2014, pp. 383–391.

[3] W. Xu, N. Reddy and Y. Yang, "Extraction, characterization and potential applications of cellulose in corn kernels and Distillers' dried grains with solubles (DDGS)", *Carbohydr. Polym.*, vol. 76, May 2009, pp. 521–527.

[4] X. Hu, K. Hu, L. Zeng, M. Zhao and H. Huang, "Hydrogels prepared from pineapple peel cellulose using ionic liquid and their characterization and primary sodium salicylate release study" *Carbohydr. Polym.*, vol. 82, August 2010, pp. 62–68.

[5] P. Rachtanapun, S. Luangkamin, K. Tanprasert and R. Suriyatem "Carboxymethyl cellulose film from durian rind" *LWT - Food Sci. Technol.*, vol. 48, Sep. 2012, pp. 52–58.

[6] H. Toğrul and N. Arslan "Production of carboxymethyl cellulose from sugar beet pulp cellulose and rheological behaviour of carboxymethyl cellulose" *Carbohydr. Polym.*, vol. 54, Oct. 2003, pp. 73–82.

[7] V. Pushpamalar, S. J. Langford, M. Ahmad and Y.Y. Lim, "Optimization of reaction conditions for preparing carboxymethyl cellulose from sago waste" *Carbohydr. Polym.*, vol. 64, May. 2006, pp. 312–318.

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