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Original Article

Carboxymethyl cellulose from rice stubble waste

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Abstract

Rice stubble is an agricultural waste with 30.67% yield of cellulose (90.05% α-cellulose content) to be synthesized as carboxymethyl cellulose (CMC). Hemicellulose and lignin were first removed and later rice stubble cellulose was swollen in 30% NaOH and isopropanol as a solvent. Synthesis conditions such as chloroacetic acid content (5–7 g in 5 g of alkali cellulose), reaction temperature (50 and 70 °C) and time (180, 270 and 360 min) were investigated to obtain CMC from rice stubble (CMCr). The 7 g of chloroacetic acid at 50°C for 180 min provided the best quality of CMCr based on 5 g of rice stubble cellulose with degree of substitution, viscosity and purity of 0.64, 36.03 cP and 90.18%, respectively. The presence of carboxymethyl substituents was verified by Fourier transform infrared spectroscopy. CMCr showed commercially low viscosity material and possibly used as a film forming packaging material for food and pharmaceutical products.

Keywords: rice stubble, waste, carboxymethyl cellulose, degree of substitution, purity

1. Introduction

The 10.4 million hectares of rice area production in Thailand during 2017–2018 generated rice straw (stalk portion after harvesting rice grains) and rice stubble (root mass and remaining shoot portion after harvesting and leaving in the field) at 25.5 and 16.9 million tons, respectively (www.aecth.org/upload/13823/Yg2qaxoQyg.pdf). Therefore, rice stubble is a substantial content of agricultural waste from rice production in Thailand. Rice stubble is generally burnt resulting in undesirable effects on environmental pollution and its effect on human health. Rice straw contains approximately 60% leaves and 40% stem (Vadiveloo, 2000). Previous studies showed that rice straw consists of approximately 30-45% yield of cellulose (Fan *et al*., 2013; Jiang *et al*., 2011; Sarnklong, Cone, Pellikaan, & Hendriks, 2010) similar to the amount as found in rice stubble. Rodsamran and Sothornvit (2015) reported that rice stubble possessed 30.67% yield of cellulose with 90.05% α-cellulose content. Its large amount of cellulose in rice stubble is drawn an attraction to investigate its potential as a cellulose derivative. Generally, cellulose derivatives were done by etherification. For example, carboxymethyl cellulose (CMC) is one of the most versatile cellulose derivatives. CMC is a water-soluble hydrocolloid and widely used as a viscosity modifier and stabilized emulsions in food and pharmaceutical products including forming an edible film.

Production of CMC is simply and it can perform at atmospheric pressure by using commercially available chemical reagents and easy to handle with high yield (Pushpamalar, Langford, Ahmad, & Lim, 2006). The carboxymethylation is a reaction between chloroacetic acid, or its sodium salts, and alkali cellulose swollen in aqueous sodium hydroxide solution and a surplus of organic solvent (Adinugraha, Marseno, &

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Haryadi, 2005; Pushpamalar *et al*., 2006; Yaşar, Toğrul, & Arslan, 2007). Hydroxyl groups in the anhydroglucose units of cellulose usually react with sodium hydroxide and replaced by carboxymethyl groups of chloroacetic acid (Bono *et al*., 2009; Pushpamalar *et al*., 2006). The main factors in CMC synthesis condition, such as solvent, NaOH concentration, acid content, temperature and time, have been investigated in various agricultural wastes. Mostly, the important factors to synthesize CMC are NaOH concentration and acid content as shown in studies of sugar beet pulp (Toğrul & Arslan, 2003), sago waste (Pushpamalar *et al*., 2006), banana pseudo stem (Adinugraha *et al*., 2005), durian rind (Rachtanapun, Luangkamin, Tanprasert, & Suriyatem, 2012) and rice straw (Panchan *et al*., 2017; Ragheb *et al*., 2012). The optimum synthesis condition found in the previous work was shown in Table 1. Therefore, the objective of this study was to determine the effects of acid content, temperature, and time of reaction on CMC production from rice stubble cellulose (CMCr) and to characterize the quality of CMCr.

2. Materials and Methods

2.1 Materials

Rice stubble (*Oryza sativa* cv. KhaoDawk Mali 105) was obtained from local rice field (Rachaburi, Thailand). Rice stubble was washed and cut into small pieces (0.1 – 0.5 cm long) and dried in a hot air oven at 60 °C for 10 h. Dried rice stubble was kept and sealed in polyethylene bag at room temperature (28 ± 2 °C) prior to further use.

All chemicals used in the synthesis and analysis of CMC were laboratory grade, food grade or 99% minimum purity. Chloroacetic acid ($ClCH_2COOH$), nitric acid (HNO_3), ethanol (C_2H_5OH) and methanol (CH_3OH) were purchased from Merck KGaA (Darmstadt, Germany). Isopropanol (C_3H_8O), glacial acetic acid (CH_3COOH) and hydrochloric acid (HCl) were purchased from QRëc™ (Auckland, New Zealand). Diethyl ether ($C_2H_5OC_2H_5$) and sodium hydroxide (NaOH) were purchased from PanreacQuímica S.L.U. (Barcelona, Spain) and Ajax Finechem Pty Ltd (New South Wales, Australia), respectively. Sodium hypochlorite (NaOCl, Food grade, 10%) was obtained from U&V Holding (Thailand) Co., Ltd (Nonthaburi, Thailand). Commercial CMC (CEKOL® 700 Cellulose gum, purity 99.5%, DS 0.75 – 0.85) was supplied by Winner group Enterprise Plc. (Bangkok, Thailand).

2.2 Isolation of rice stubble cellulose

Rice stubble cellulose was prepared with the method described by Rodsamran and Sothornvit (2015). The dried rice stubble was boiled in distilled water for 30 min and filtered. Then, hemicellulose and lignin were removed by using 10% NaOH at 55 °C for 3 h and 5% NaOCl at 75 °C for 15 min, respectively. The rice stubble cellulose was filtered and washed with distilled water until odorless and final washed with 95% ethanol until the pH of the filtrate was neutral. Rice stubble cellulose was dried in a hot air oven at 60 °C for 8 h. According to the Technical Association of Pulp and Paper Industry (TAPPI) standard T 203 cm–99 (TAPPI, 1999), rice stubble cellulose contains 90.05% α-cellulose content.

Table 1. Degree of substitution (DS) of carboxymethyl cellulose from various agricultural wastes at each optimum synthesis condition.

Raw material	Synthesis condition	Degree of substitution (DS)	Reference
Sugar beet pulp	30% sodium hydroxide 1.5 g (w/w) sodium monochloroacetate 70 °C for 360 min.	0.66	Toğrul & Arslan (2003)
Banana pseudo stem	15% sodium hydroxide 1.2 g (w/w) sodium monochloroacetate 55 °C for 180 min.	0.75	Adinugraha *et al*. (2005)
Sago waste	25% sodium hydroxide 1.2 g (w/w) sodium monochloroacetate 45 °C for 180 min.	0.82	Pushpamalar *et al.* (2006)
Orange peel	30% sodium hydroxide 1.5 g (w/w) sodium chloroacetate 70 °C for 360 min.	0.67	Yaşar *et al*. (2007)
Palm kernel cake	17.5% sodium hydroxide 1.2 g (w/w) sodium monochloroacetate 50 °C for 120 min	0.67	Bono *et al.* (2009)
Durian rid	30% sodium hydroxide 1.2 g (w/w) monochloroacetic acid 55 °C for 180 min.	0.87	Rachtanapun *et al*. (2012)
Rice straw	30% sodium hydroxide 0.75–1.25 g (w/w) monochloroacetic acid Overnight at room temperature	0.66-1.03	Ragheb *et al*. (2012)
Rice straw	5.5% sodium hydroxide 3.2 g (w/w) sodium chloroacetate 7.97 min under microwave of 320W	0.697	Panchan *et al*. (2017)
Rice stubble	30% sodium hydroxide 1.4 g (w/w) chloroacetic acid 50°C for 180 min.	0.64	This study

2.3 Factors affecting CMCs synthesis from rice stubble

The carboxymethylation was done in two steps as alkalization and etherification. In the first step, 5 g of rice stubble cellulose was alkalized in 100 mL of isopropanol as a solvent and 25 mL of 30% (w/w) of NaOH and stirring at room temperature (28 ± 2 °C) for 90 min. After alkalization, full factorials of three levels of acid content (X_1), 2 levels of temperature (X_2) and 3 levels of time (X_3) with three replicates in completely randomized design were performed in the etherification step. Chloroacetic acid (5, 6, and 7 g) was added in the alkali cellulose mixture. The acid was completely dissolved by stirring for 30 min at room temperature. After that, the reaction mixture was shaken for 180, 270, and 360 min in a shaking water bath with controlled temperature at 50 and 70 °C as a reaction temperature. At the end of reaction time, the mixture was filtered and soaked for 10 min in 70% ethanol (100 mL). The mixture was neutral with 90% acetic acid. The rice stubble CMC (CMCr) was washed with 70% methanol for three times and final washed with absolute ethanol (99.8% v/v). CMCr was left at RT to remove ethanol and then dried in a hot air oven at 60 °C for 8 h. CMCr was ground and sieved through 0.18 mm sieve. The yield of CMC was calculated as a percentage using Equation 1 (Rachtanapun *et al*., 2012):

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

2.4 Characterization of CMCr

The pH of CMCr solution, prepared by slowly adding 1 g of CMCr in 100 mL of distilled water (25 °C) and stirring for 1 h until completely dissolved, was determined using a pH meter (PB–10, Sartorius AG, Goettingen, Germany) at 25±2 °C. The moisture content, degree of substitution (DS), viscosity and purity of CMCr was determined by the ASTM D1439–03 standard methods (American Society for Testing and Materials [ASTM], 2008). The infrared spectra of rice stubble cellulose, commercial CMC and CMCr, which were ground and compressed into a disc prior to analysis, were recorded by using an attenuated total reflectance–Fourier transform infrared (ATR–FT–IR) spectrometer (Perkin Elmer, Spectrum two, Illinois, USA) within the wave number range of 4,000–600 cm^{-1}.

2.5 Statistical analyses

Full factorials of 3 levels of acid content (X_1), 2 levels of temperature (X_2) and 3 levels of time (X_3) with 3 replicates in completely randomized design were performed with the analysis of variance (ANOVA) procedure in SPSS software (Version 11.5, SPSS Inc., Chicago, IL). Duncan's multiple range test ($p<0.05$) was used to detect differences among mean values of CMC properties. Multiple regression analysis was used to evaluate the statistical significance of the main factors on CMC properties.

3. Results and Discussion

3.1 Factors affecting CMCs synthesis from rice stubble

From the statistical analyses, no interaction between 3 independent variables (acid content, X_1, temperature, X_2 and time, X_3) was found on characterizations of CMCr properties except viscosity and purity. Moreover, acid content, temperature and time of synthesis of CMC did not affect moisture and pH of CMCr. The multiple regression models were fitted to determine the effect of independent variables on degree of substitution (DS), viscosity and purity which were the most important qualities of CMC. Stepwise method was used to obtain the regression coefficients of fitted second order polynomial with a probability value less than 0.005. The regression equations for DS (Equation 2), viscosity (Equation 3) and purity (Equation 4) represented the true relationship among the variables chosen.

$$DS = -2.473 + 0.734X_1 + 0.003X_3 - 0.039X_1^2 - 0.0007X_1X_3 + 0.00001X_2X_3 \quad (2)$$

$$Viscosity = -108.683 + 41.833X_1 + 0.099X_3 - 2.889X_1^2 - 0.019X_1X_3 \quad (3)$$

$$Purity = -66.008 + 46.370X_1 + 0.089X_3 - 3.329X_1^2 - 0.017X_1X_3 \quad (4)$$

The coefficient of determination (R^2) values of regression equations for DS, viscosity and purity were 0.812, 0.896 and 0.783, respectively. Based on regression equations, the most significant terms were the acid content (X_1), time (X_3), X_1^2 and X_1X_3. Meanwhile, temperature (X_2) did not show significant effect on qualities of CMCr. Thus, data of characterization of CMCr which produced at 50 and 70 °C were pooled to determine the effects of synthesis condition.

3.2 Characterization of CMCr

The visual appearances of cellulose and CMCr were shown in Figure 1. Rice stubble cellulose represented short and whiteness fibers, while CMCr possessed a fine powder with a slight yellowness in color. Similarly, Chumee and Seeburin (2014) found that the color of CMC from pomelo peel was yellowish brown, compares with a commercial CMC.

Figure 1. Appearance of cellulose and carboxymethyl cellulose (CMCr) from rice stubble.

The acid content was more influenced on the yield rather than the reaction time. As the acid content increased, yield also increased at the same level of reaction time (Table 2). Increase in yield might be indicating of a large amount of carboxymethyl group substituted in each anhydrous glucose unit of cellulose chain. The yield of CMCr in this work was in a range of 139.12–153.26%. The CMCr were similar to the yield of CMC from durian rind (120–160%) (Rachtanapun *et al*., 2012). Moisture (6.92–7.07%) and pH (8.09–8.23) of all CMCr were no significant differences (Table 2). This might have been due to all CMCr similarly neutralized with 90% acetic acid and dried at 60°C for 8 h in a hot air oven after etherification.

The degree of substitution (DS) is the replacement of hydroxyl group of cellulose with carboxymethyl group during the carboxymethylation. DS indicates the solubility of CMC. CMC is generally swellable but insoluble at DS < 0.4 while CMC is fully soluble with its hydro–affinity increasing at a higher DS value (DS > 0.4) (Bono *et al*., 2009). The highest DS (0.64) of CMCr was obtained at using 7 g of acid with reaction of 180 min (Figure 2). The DS of CMCr (Table 1) was similar to those of CMCs from sugar beet pulp (Toğrul & Arslan, 2003) and palm kernel cake (Bono *et al*., 2009). Likewise, the DS of CMC from agricultural wastes such as banana pseudo stem (Adinugraha *et al*., 2005), sago waste (Pushpamalar *et al*., 2006), durian rid (Rachtanapun *et al*., 20 12) and rice straw (Panchan *et al*., 2018; Ragheb *et al*., 2012) were in the range of 0.75–1.03. The difference of DS in each material might be due to the differences in experimental conditions and chemical used.

The high acid content also increased DS at the same reaction time. It was possibly due to the higher content of carboxymethyl group at the higher acid content, thus more substitutions of carboxymethyl groups with higher DS values. The data was corresponding to the previous works of CMC from sugar beet pulp (Toğrul & Arslan, 2003), banana pseudo stem (Adinugraha *et al*., 2005), sago waste (Pushpamalar *et al*., 2006) and pure cellulose (Ismail, Bono, Valintinus, Nilus, & Chng, 2010). At 5 g of acid, the DS of CMCr was the lowest and the reaction times did not show any significant differences on DS of CMCr. We hypothesized that the limited content of acid available for substituting cellulose resulting in a lower DS.

However, the increase in reaction time showed the increase in DS of CMCr at 6 g of acid used. This meant that it was sufficient acid content available to react with. Moreover, a longer reaction time in carboxymethylation process resulting in a better interaction between the etherifying agent and cellulose biopolymer molecules (Bhattacharyya, Singhal, & Kulkarni, 1995; Pushpamalar *et al*., 2006). Nonetheless, the higher acid content (7 g of acid) showed a decrease in DS with longer time of the reaction. It was possibly due to an excessive acid content and a longer reaction time resulting in sodium glycolate which is the by–product of CMC production. Generally, choloacetic acid not only can substitute with hydroxyl group of cellulose polymer, but can also react with NaOH to give sodium glycolate which is an undesirable reaction. As the reaction time is longer, sodium glycolate can react with itself or excessive acid to form sodium diglycolate (Tijsen, Kolk, Stamhuis, & Beenackers, 2001). Moreover, an increased atmospheric oxidative degradation of CMC at the longer time of reaction was explained by a lower of DS value (Varshney *et al*., 2006).

The viscosity of CMCr was in a range of 28.75–36.03 cP at 25°C (Figure 3). Commercially, if the viscosity of CMC is in the range of 20–50 cP at 2% of CMC concentration, it is classified as a low viscosity category (Bono *et al*.,

Table 2. Yield, moisture content and pH of carboxymethyl cellulose from rice stubble.

Acid content (g/ 5 g cellulose)	Time (min)	Yield (%)	Moisture content (% d.b.)	pH
5	180	$139.12^{a} \pm 8.34$	$6.95^{a} \pm 0.05$	$8.16^{a} \pm 0.08$
5	270	$140.58^{a} \pm 11.09$	$6.98^{a} \pm 0.17$	$8.14^{a} \pm 0.06$
5	360	$140.43^{a} \pm 4.46$	$6.92^{a} \pm 0.15$	$8.23^{a} \pm 0.09$
6	180	$144.23^{ab} \pm 2.74$	$7.03^{a} \pm 0.12$	$8.09^{a} \pm 0.04$
6	270	$146.16^{ab} \pm 8.09$	$6.97^{a} \pm 0.08$	$8.15^{a} \pm 0.10$
6	360	$145.90^{ab} \pm 8.19$	$7.07^{a} \pm 0.04$	$8.14^{a} \pm 0.06$
7	180	$150.80^{b} \pm 4.92$	$6.99^{a} \pm 0.11$	$8.21^{a} \pm 0.11$
7	270	$153.26^{b} \pm 3.97$	$7.01^{a} \pm 0.05$	$8.17^{a} \pm 0.11$
7	360	$150.63^{b} \pm 10.04$	$7.01^{a} \pm 0.07$	$8.15^{a} \pm 0.10$

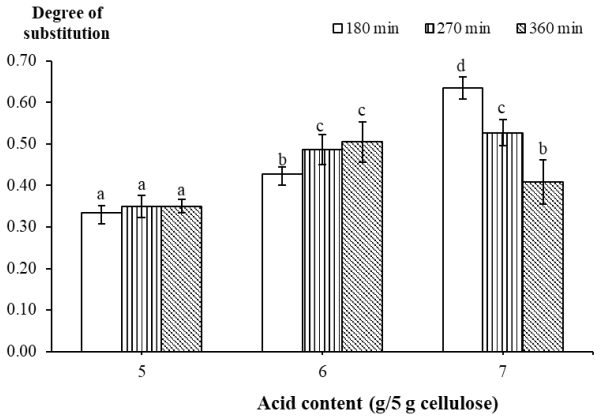

Figure 2. Effect of synthesis conditions (acid content and time) on degree of substitution (DS) of carboxymethyl cellulose from rice stubble. The same letters (a, b, c, d) were not statistically different ($p < 0.05$).

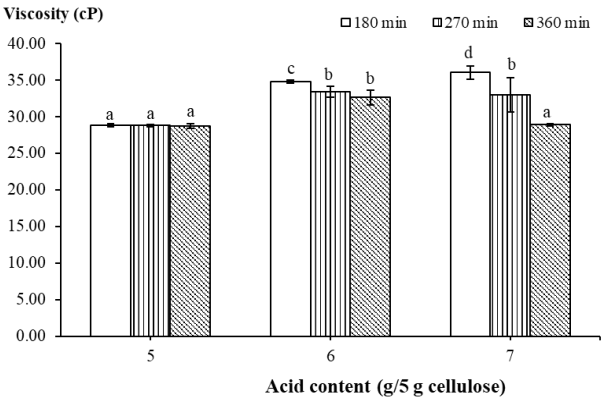

Figure 3. Effect of synthesis conditions (acid content and time) on viscosity of carboxymethyl cellulose from rice stubble. The same letters (a, b, c, d) were not statistically different ($p < 0.05$).

2009). Thus, CMCr was classified as a low viscosity biopolymer. This might be due to the remaining of NaOH which could not be removed during the washing process by alcohol. The higher amount of NaOH left in CMC biopolymer chain caused a lower viscosity (Bono *et al*., 2009). Low viscosity CMC is usually used in film applications over viscous grades, because higher CMC concentration or higher solid content can be achieved in casting film solution (Nieto, 2009).

At the same reaction time, increase in acid content significantly increased viscosity except at the longest time (360 min). The carboxymethylation process probably occurred better at a high acid content with a short reaction time. The result was in agreement with the viscosity of CMC from banana pseudo stem which increased from 2,500 cP to 3,600 cP when increased in acid content from 5 g to 7 g (Adinugraha *et al*., 2005). However, the higher acid content (7 g) lowered the viscosity of CMCr at longer reaction time (Figure 3) since the longer reaction time might cause the degradation of cellulose chain and CMC structure (Ismail *et al*., 2010). The shorten CMC polymer chains resulted in an easier dissolution of CMC in water (Adinugraha *et al*., 2005). Furthermore, the low viscosity of CMCr was due to the low value of DS. As known, sodium glycolate formation also occurs at higher acid content and longer reaction time resulting in a decreased DS value (Ismail *et al*., 2010). Moreover, the higher substitutions of carboxymethyl groups acting as hydrophilic groups increase DS value and the ability of CMC to immobilize water in the system. Adinugraha *et al.* (2005) showed a positive linear relationship between DS and viscosity of CMC solution from banana pseudo stem as the increase in DS provided a higher viscosity.

The purity of CMCr at 5 and 6 g of acid content was similar independent on the reaction time (Figure 4). However, the purity of CMCr at 7 g of acid content decreased with increase in reaction time. It was possibly due to the higher acid content interacted with NaOH producing a higher content of sodium glycolate at a longer reaction time (Adinugraha *et al*., 2005). This is a side reaction caused a decrease in DS resulting in a decrease in purity (Toğrul & Aslan, 2003). The purity values of CMCr at DS of 0.64 and 0.35 were 90.18 and 83.69 %, respectively. This result showed the same trend with the previous work of Adinugraha *et al.* (2005). They found that CMC from banana pseudo stem possessed 87.72% and 98.63% purity at DS of 0.4 and 0.75, respectively. The purity can be used to categorize grade of CMC. Technical grade has less than 98% purity, while purified grade often has at least 98% purity for industrial applications and at least 99.5% for food and pharmaceuticals applications (Stigsson, Kloow, & Germgrad, 2001). Lower purity of CMCr in this work (82.76–90.18%) corresponded to the α-cellulose content of rice stubble (90.15%). Higher than 90% of α-cellulose content implies the presence of high molecular oligosaccharides, which may affect the purity and quality of CMC (Mark, Bikales, Overberger, & Menges, 1985). The report of Latif, Anwar, and Noor (2007) confirmed that 89.83% of α-cellulose content from *Eucalyptus globules* pulp provided CMC with 95.8% purity, while 93.70% of α-cellulose content from *Eucalyptus globules* pulp provided CMC with 98.0% purity.

The FT–IR spectra indicate the structure and chemical compositions of CMCr. The CMCr using 7 g of chloroacetic acid per 5 g of rice stubble cellulose for 180 min at 50 °C represented the same spectra at 70 °C (data not shown). The CMCr spectra were similar to the commercial CMC (Figure 5). The broad bands at a wavenumber around 1,600 cm^{-1} and 1,400 cm^{-1} are assigned to carboxyl group (COO–) and theirs salt, respectively (Adinugraha *et al*., 2005; Rachtanapun *et al*., 2012). A new and strong absorbance band of CMCr at 1,587 cm^{-1} confirmed the presence of carboxymethyl substituent, while this absorbance band was not observed on rice stubble cellulose spectra. The band at 1,409 cm^{-1} and 1,322 cm^{-1} presented $–CH_2$ scissoring and –OH bending vibration, respectively.

The FT–IR spectra of CMCr was similar to the spectra of CMC from other cellulose resources such as pod husk Cacao (Hutomo, Marseno, Anggrahini, & Supriyanto, 20 12), pomelo peel (Chumee & Seeburin, 2014) and water hyacinth (Saputra, Qadhayna, & Pitaloka, 2014). The similarity of absorbance band of CMCr and commercial CMC concluded that rice stubble cellulose could be used as a CMC synthesis material.

4. Conclusions

Carboxymethyl cellulose was successfully synthesized from rice stubble cellulose. CMCr was done by using 7 g of chloroacetic acid per 5 g of rice stubble cellulose at 50°C for 180 min. The appearance of CMCr was a fine powder with slight yellowness in color and easily dissolvable in water. The obtained CMCr was 150.08% of yield with 6.99% moisture, 8.21pH, 0.64 DS, 33.03 cP of viscosity and 90.18% purity. CMCr can be categorized as a technical grade with low viscosity commercial CMC. However, the synthesis condition of CMC from rice stubble cellulose should be developed to provide the higher qualities. A higher DS and purity of CMC can be widely used in food and pharmaceutical applications. However, CMCr in this study has a potential as a new biopolymer to possibly utilize as a film–forming material and it can be a value–added of agricultural waste such as rice stubble.

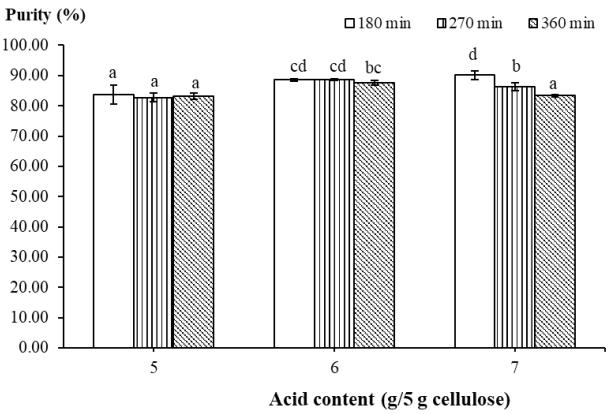

Figure 4. Effect of synthesis conditions (acid content and time) on purity of carboxymethyl cellulose from rice stubble. The same letters (a, b, c, d) were not statistically different ($p< 0.05$).

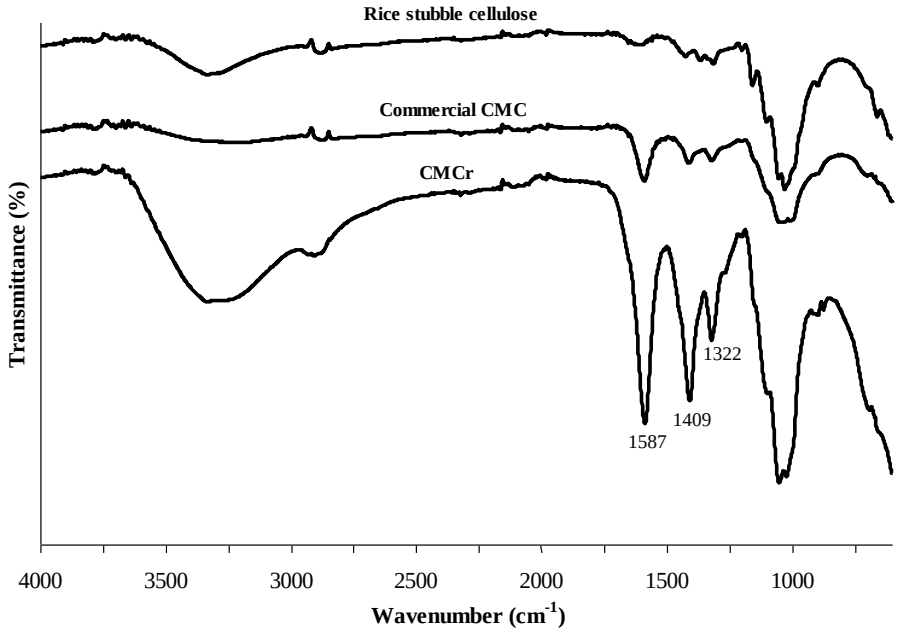

Figure 5. FTIR spectra of rice stubble cellulose, commercial carboxymethyl cellulose (CMC) and CMC from rice stubble cellulose using 7 g of chloroacetic acid per 5 g of rice stubble cellulose for 180 min at 50°C (CMCr).

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