

# CARBOXYMETHYL CELLULOSE SYNTHESIS FROM TREATED OIL PALM EMPTY FRUIT BUNCH USING IONIC LIQUID AND HYDROGEN PEROXIDE

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Received Date: May 7, 2020; Revised Date: April 14, 2021; Acceptance Date: June 2, 2021

## Abstract

The synthesis of carboxymethyl cellulose (CMC) generally uses isolated crude cellulose with alkaline or acid pretreatment followed by bleaching with sodium chlorite. In this study, the simple [BMIM][Cl] ionic liquid was used as a solvent in the pretreatment process before conduct the bleaching process with hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) to isolate cellulose from empty fruit bunch (EFB) for further synthesis of CMC. The isolated crude EFB cellulose obtained was converted to CMC by adding 30 wt.% NaOH and various concentrations of sodium monochloroacetic acid (SMCA) at 55 °C for 3 h. The effects of SMCA concentration on the degree of substitution (DS) and CMC yield were investigated. The physicochemical properties of the CMC products were characterized using proton nuclear magnetic resonance, scanning electron microscope-energy dispersive spectrometry, X-ray diffraction, and thermogravimetric analysis. Based on the results, CMC was demonstrated to be synthesized using ionic liquid pretreatment with H<sub>2</sub>O<sub>2</sub> bleaching. Carboxymethyl cellulose synthesized in this study showed a high DS of 0.82. The CMC synthesized from EFB cellulose through ionic liquid pretreatment presented good chemical and physical properties as that reported in other studies.

**Keywords:** Biomass, Carboxymethyl cellulose, Empty fruit bunch, Ionic liquid, Oxidizing, Pretreatment

## Introduction

The growing demands and interest in the production of green chemicals from lignocellulosic biomass to develop environmentally friendly and affordable chemicals has increased in recent years. As one of the leading producers and exporters of oil palm worldwide, Malaysia produces a large amount of empty fruit bunch (EFB) which is one of the major oil palm wastes generated at oil palm mills. Due to the plentiful nature of this waste, most palm oil production companies have to face problems regarding the disposal of this EFB. Hence, to avoid the continuation of the problems, alternatives to make use of EFB have been widely studied. EFB contains a high percentage of cellulose, followed by hemicellulose, lignin, and extractive components. Therefore, it is sensible to convert EFB into useful products, such as carboxymethyl cellulose.

Carboxymethyl cellulose (CMC) is a non-toxic, biodegradable, highly viscous, and non-allergenic anionic linear polysaccharide [1] which has the ability to bind and absorb water due to the existence of numerous hydroxyl and carboxylic functional groups in its

structure. The synthesis of CMC involves a two-step chemical process of alkalization of cellulose followed by etherification with sodium monoacetate (SMCA) to form carboxymethyl (CM) groups [2, 3]. The CMC has been used by various industries such as pharmaceutical, paint, food, textile, and cosmetic industries, as it can function as a binding, thickening, emulsifying, lubricating, stabilizing, film-forming, and gelling agent [1, 4].

Nowadays, research conducted on CMC synthesis uses cellulose from agricultural waste cellulose sources such as papaya peel waste [5], sugar beet pulp [6], corn husk [7], durian rind [2], and other leftovers, including pseudo stem from cavendish banana [8], sago waste [3], and waste from mulberry paper [9] and mimosa pigra peel [10]. The biomass conversion to CMC is related to the isolation of cellulose from biomass precursor for synthesis of CMC. The cellulose extraction using NaOH [5] and cellulose isolation by sodium chlorite as bleaching agent [3] are among the methods applied to obtain cellulose for CMC synthesis. A combination of sodium chlorite bleaching and NaOH treatment is commonly used for cellulose isolation, has been implemented on corn husk to obtain  $\alpha$ -cellulose for CMC synthesized [7]. Generally, the combination of pretreatment and bleaching can be conducted to improve the cellulose isolation from biomass. Various pretreatment processes such as alkali/acid, ionic liquid, ball mill, and steam explosion can be applied as an alternative in combination with bleaching process for cellulose isolation. An approach of using hydrogen peroxide as potential bleaching agent with the combination of NaOH treatment was conducted on durian rind to extract cellulose for CMC synthesis [2].

There are very limited information found on the synthesis of CMC using EFB and also the implementation of other pretreatment processes such as using an ionic liquid solvent. Thus, this study investigated the fractionation of EFB using ionic liquid (IL), namely [BMIM][Cl], and followed by bleaching with hydrogen peroxide as oxidizing agent to isolate cellulose for subsequent used in the synthesis of CMC. [BMIM][Cl] is one of the ionic liquids that commonly used for biomass pretreatment since it can mainly dissolve lignin. The existence of imidazolium cations [BMIM] can has good interacts with lignin, while anion chloride [Cl] has strong effect in breaking the hydrogen bonding and good disruption affinity to lignin [11–13]. Characterization was conducted to study the properties of CMC synthesized by this approach since it is an alternative method of synthesis of CMC from EFB compared to NaOH treatment with sodium chlorite bleaching.

## Experimental

### Chemicals and materials

1-Butyl-3-methylimidazolium chloride ([BMIM][Cl], 98%) IL, sodium hydroxide (NaOH), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 30%), *iso*-propanol (C<sub>3</sub>H<sub>8</sub>O, 99%), absolute methanol (CH<sub>4</sub>O, 99%) acetone (C<sub>3</sub>H<sub>6</sub>O, 99%), and glacial acetic acid (CH<sub>3</sub>COOH, 99%) were purchased from Merck, Germany. Ethanol (C<sub>2</sub>H<sub>6</sub>O, 95%) was purchased from Qrec, New Zealand and chloroacetic acid sodium salt (SMCA)(C<sub>2</sub>H<sub>2</sub>ClNaO<sub>2</sub>, 90%) from Nacalai Tesque, Japan. All chemicals in this work were used directly as received.

Empty fruit bunch in its original form was supplied from a local palm oil mill located at Kluang, Johor, Malaysia. The EFB was cut into small pieces before being dried in an oven at 105 °C/24 h followed by grinding and sieving into powder form of 300–500  $\mu$ m particle size.

## Pretreatment and bleaching of EFB

The pretreatment of EFB using [BMIM][Cl] ionic liquid was according to previous studies [11–13] where the EFB powder was mixed with [BMIM][Cl] in the ratio of 1:5 and heated for 3 h at 130 °C. After the reaction, the [BMIM][Cl] IL was regenerated with water and the supernatant containing the IL was filtered by vacuum filtration. The precipitate was washed repeatedly with distilled water to ensure the removal of excess IL. Then, a 1:1 volume ratio acetone/water mixture was added and stirred vigorously to dissolve the lignin. The suspension was filtered and the solid residue collected. The residue was oven-dried to constant weight at 105 °C to obtain cellulose-rich EFB, which was then bleached with H<sub>2</sub>O<sub>2</sub>. The bleaching process was conducted by mixing the cellulose-rich EFB with H<sub>2</sub>O<sub>2</sub> (30%) (at 0.1 g/L) in the beaker and heated at 80 °C for 3 h. The pure EFB cellulose was obtained by separation of the solid part and H<sub>2</sub>O<sub>2</sub> solution by using vacuum filtration before continuing the washing step of the bleached sample with distilled water for few times to remove the excess H<sub>2</sub>O<sub>2</sub> on the sample. The sample was dried and pure EFB cellulose obtained was then ground and sieved to a size  $\leq 300 \mu\text{m}$  for use in CMC synthesis.

## Synthesis of CMC

The synthesis of CMC from EFB cellulose (CMC-EFB) followed the method described by Rachtanapun et al. [2], which involves alkalization followed by etherification. EFB cellulose (15 g) was stirred in 30% (w/v) aq. NaOH (50 mL) and *iso*-propanol (450 mL) for 1.5 h at ambient temperature. Then, to the solution was added pre-dissolved SMCA (1–1.47 w/w) in 10 mL of *iso*-propanol for etherification to take place when the solution was heated at 55 °C for 3 h. The mixture was cooled after the reaction and the solid product separated by filtration. The solid was purified in methanol (100 mL) and neutralized with glacial acetic acid (10 mL). The solid residue was then washed with 100 mL of ethanol several times to remove undesired by-products followed by final washing with 50 mL absolute methanol. The white CMC-EFB product was obtained after drying in an oven at 60 °C for 3 h.

The CMC-EFB yield was calculated using Equation 1, while its degree of substitution (DS) was estimated using Equation 2 and 3. The DS refers to the average number of hydroxyl group in a glucose monomer unit that have been substituted by CM groups. The DS values were determined by acid titration. The sample preparation for titration was conducted by dissolving CMC-EFB (1 g) in ethanol (50 mL) and stirring for 5 min. Nitric acid (2 M, 5 mL) was poured into the mixture under continuous stirring for 10 min followed by boiling for 30 min. The acid and salts inside the CMC were then removed by washing the mixture with hot ethanol and absolute methanol using vacuum filtration, followed by drying in an oven at 70 °C for 3 h. For the titration, 0.5 g of CMC was added to distilled water (100 mL) and 0.5 M NaOH (25 mL) added to the mixture followed by 20 min boiling. The solution was titrated with 0.3 M HCl until the phenolphthalein indicator changed color from purple to colorless.

$$\text{CMC yield (wt. \%)} = \text{CMC weight (g)} / \text{cellulose weight (g)} \times 100\% \quad (1)$$

$$\text{Degree of substitution, DS} = 0.162A / (1 - 0.058A) \quad (2)$$

$$A = (BC - DE) / F \quad (3)$$

where A is milliequivalents of HCl consumed per gram of specimen, B is NaOH volume (mL), C is NaOH molarity (M), D is HCl volume (mL), E is HCl molarity (M), and F is CMC weight (g).

## Characterization of carboxymethyl cellulose

A Bruker Advance 400 MHz (Bruker UltraShield) spectrometer was used to determine the chemical structure of CMC-EFB via proton nuclear magnetic resonance ( $^1\text{H-NMR}$ ) in  $\text{D}_2\text{O}$  at  $25\text{ }^\circ\text{C}$ . The morphology and elemental composition of CMC-EFB was detected using scanning electron microscopy with energy dispersive X-ray spectrometry (SEM-EDX). The XRD pattern of the CMC-EFB was evaluated using a Rigaku SmartLab X-ray diffractometer (XRD) and the  $2\theta$  angle between  $10^\circ$  and  $60^\circ$ . Thermal decomposition of CMC-EFB was determined using a Perkin Elmer TGA 7 under  $\text{N}_2$  flow ( $10\text{ }^\circ\text{C}/\text{min}$ ) and heated from  $30\text{--}900\text{ }^\circ\text{C}$ . The EFB was also characterized using XRD and TGA for evaluation of physical properties and comparison with CMC-EFB.

## Results and Discussion

The SMCA concentration is one of significant parameters that affect the CMC synthesis. Sodium hydroxide concentration of 30% is used as constant parameter based on previous studies [7, 14–16]. The effect of SMCA concentration on the DS and yield of CMC-EFB is shown in Figure 1. Different SMCA concentrations of 1 and 1.2 w/w resulted in small changes in the DS of CMC-EFB (Figure 1(a)). CMC-EFB with 0.82 of DS and 113 wt.% yield were obtained at 1.2 w/w SMCA concentration. The DS value was observed to be reduced as the SMCA concentration increased. As stated by Barai et al. [17], the increase in SMCA concentration promotes greater accessibility of the acid molecules to facilitate the carboxymethylation of the cellulose hydroxyls. Further increases in SMCA concentration resulted in decreasing DS due to a side reaction of SMCA to produce sodium glycolate. Huang et al. [1] stated that the increase in SMCA concentration may cause the formation of sodium glycolate. At high SMCA concentration, the cellulose-alkoxide, having been fully reacted with SMCA, thus contributes to the formation of sodium glycolate [18]. The yield of CMC-EFB was increased when the SMCA concentration was increased, even as the DS was reduced. This was possibly caused by high formation of sodium glycolate that was not completely removed during the washing and filtration step. Thus, CMC synthesis at high SMCA concentration required more solvent for washing during the purification step, which is not efficient for the production of CMC.

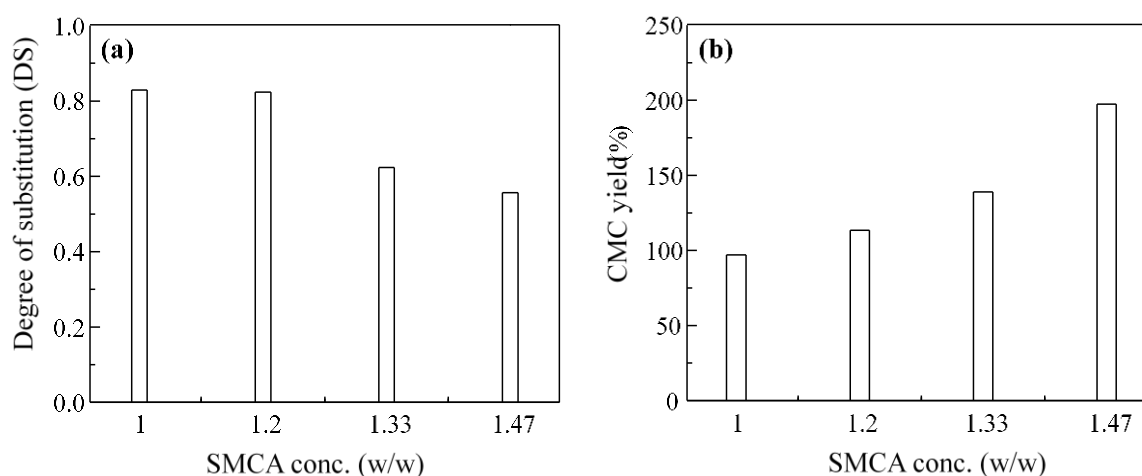


Figure 1. Effect of SMCA loading on (a) DS and (b) CMC yield (30% NaOH,  $55\text{ }^\circ\text{C}$ , 3 h).

The effect of reaction parameters was used to enhance the reaction in order to obtain high DS levels. The DS of CMC-EFB obtained from this study is comparable with those from other CMC synthesis studies as shown in Table 1. Carboxymethyl cellulose has

been synthesized from sago waste cellulose with a DS of 0.33–0.82 [3], from sugar beet pulp cellulose with a DS of 0.11–0.67 [6], and cotton ginning cellulose with a DS of 0.87 [19]. As to oil palm waste, CMC has been synthesized from palm kernel cake [20] and EFB [14], with DS values of 0.67 and 0.6, respectively. For CMC synthesis from EFB, sodium hydroxide treatment followed by bleaching with acetate buffer and sodium chlorite mixture has been used [14]. However, the present study used [BMIM][Cl] IL fractionation of EFB followed by H<sub>2</sub>O<sub>2</sub> bleaching to obtain EFB cellulose for CMC synthesis with a comparable DS of 0.82.

**Table 1. CMC form Various Feedstock with Different Isolation and Synthesis Condition**

Feedstock	Pretreatment and Isolation Method	Synthesis Condition				DS	Ref.
		SMCA Conc. (%)	NaOH Conc. (%)	Temp. (°C)	Time (h)		
Sago Waste	Sodium Chlorite	1.2	30.0	45.0	3.0	0.82	[3]
Sugar Beet Pulp	Chemical Extraction	1.5	30.0	70.0	3.0	0.67	[6]
Cotton Gin Waste	H <sub>2</sub> SO <sub>4</sub> + NaOH + H <sub>2</sub> O <sub>2</sub>	1.0	20.0	60.0	3.0	0.87	[19]
EFB	NaOH + Sodium Chlorite	1.2	30.0	55.0	3.0	0.60	[14]
EFB	[BMIM][Cl] + H <sub>2</sub> O <sub>2</sub>	1.2	30.0	55.0	3.0	0.82	This work

The selected CMC-EFB was further characterized to study its chemical and physical properties. Figure 2(a) shows the <sup>1</sup>H-NMR spectrum of the synthesized CMC-EFB in D<sub>2</sub>O. The main signals are seen at  $\delta$  3.254,  $\delta$  3.355,  $\delta$  3.545,  $\delta$  3.678,  $\delta$  3.854,  $\delta$  3.997, and  $\delta$  4.147 ppm. These signals are similar to those reported in previous works on CMC [21–24]. As described by Yang et al. [25], the characteristic peaks of proton substitution at the C6, C2, and C3 positions are in the signal range of  $\delta$  3.7–4.3 ppm. The signal ranges of  $\delta$  3.7–3.9 ppm,  $\delta$  4.0–4.2 ppm, and  $\delta$  4.2–4.3 ppm are assigned to proton substitution at C2, C3, and C6, respectively [26]. Therefore, the characteristic <sup>1</sup>H-NMR peaks showed that CMC-EFB had been successfully synthesized.

The SEM image with the EDX spectrum is presented in Figure 2(b). Based on the morphology of CMC-EFB, the exterior surface appears as a rough and ruptured structure, which is related to the EFB cellulose structure caused by IL treatment and the bleaching process. The elements present in the synthesized CMC-EFB product were determined from the EDX spectrum. The result shows that the elements found in CMC-EFB are carbon, oxygen, and sodium, the elements that exist in the structure of CMC. A similar result has been reported regarding the presence of sodium in the CMC structure [27]. Based on EDX, the elemental composition of C, O, and Na are 55.8 wt.%, 40.4 wt.%, and 3.8 wt.%, respectively. Thus, this result has supported the synthesis of CMC from EFB cellulose through the alkalization and etherification process.

The XRD patterns of the synthesized CMC-EFB and raw EFB are presented in Figure 2(c). Based on the XRD spectra of EFB, the crystallinity of cellulose was high, with an intense peak at 23°. The XRD peak of EFB between 10° and 25° decreased and the maximum peak in EFB was shifted from 23° to a lower 2 $\theta$  region (20°) showing that the crystalline structure of cellulose was reduced. The pretreatment and bleaching processes cause the crystalline structure of cellulose to change to a more amorphous structure as both

processes involve the breaking of bonding and also remove other constituent polymers such as lignin and hemicellulose from EFB cellulose. The etherification in CMC synthesis may affect the cellulose structure due to reaction with SMCA. The phase change occurs due to the increasing cleavage of hydrogen bonds of the cellulose hydroxyl group with SMCA [21].

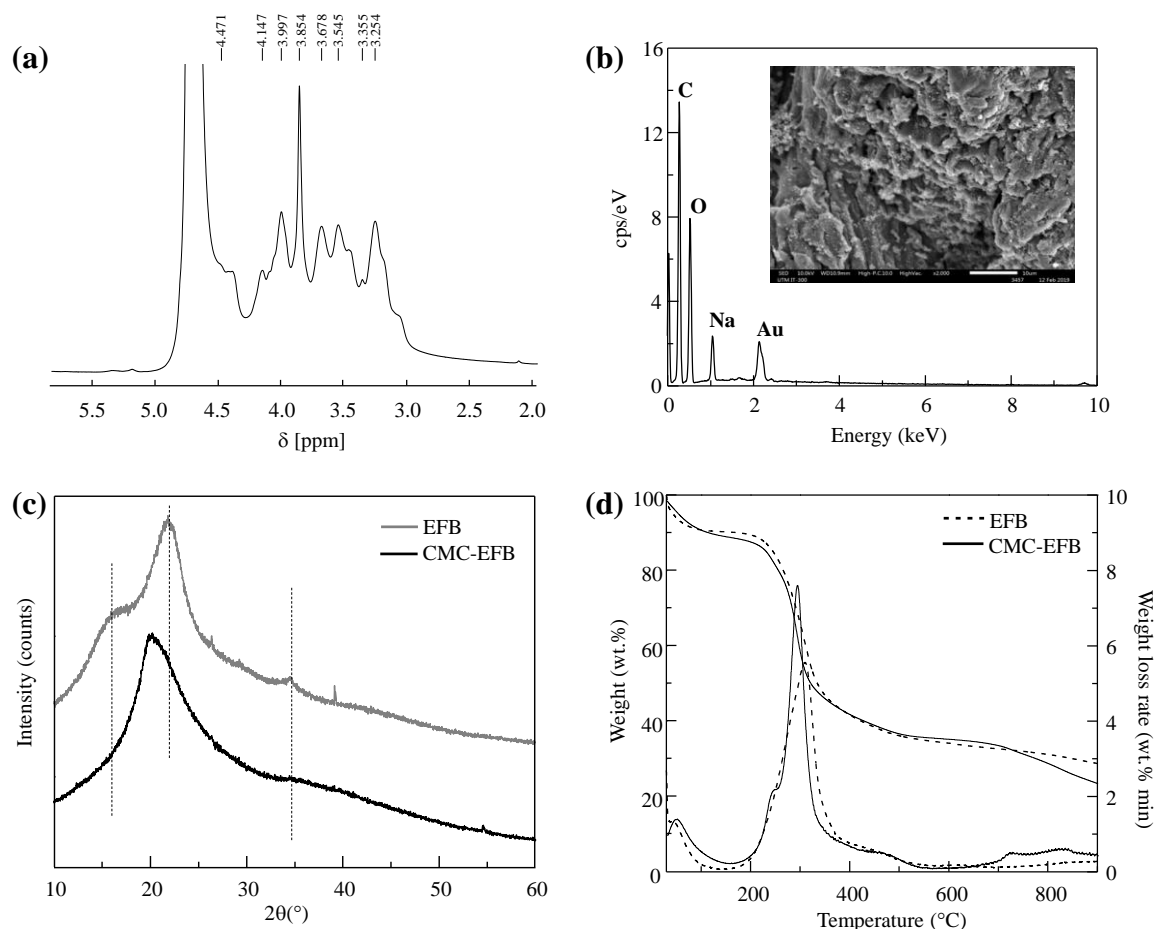


Figure 2. (a)  $^1\text{H}$ -NMR spectra and (b) SEM image with EDX spectrum ( $\times 2000$ , 10 kV) of CMC-EFB, and (c) XRD pattern and (d) TG-DTG curves of EFB and CMC-EFB.

As for the TG-DTG result in Figure 2(d), the thermal behavior of EFB shows a major decomposition in the range 200–400 °C. The first decomposition occurring at up to 150 °C is generally due to evaporation of moisture. The second decomposition occurring at 200–400 °C is due to decomposition of hemicellulose and cellulose (maximum degradation temperature 320 °C). The decomposition of lignin is considered begin lower, at a temperature almost similar to that of hemicellulose; the degradation temperature range of lignin is broad, between 200 and 900 °C. Hence, the third degradation peak observed at >600 °C is due to the continuous degradation of lignin micropolymers and carbonaceous residues of EFB components. The degradation of the phenylpropane building block of lignin has been reported from a previous study [28]. Based on the DTG peaks, the high rate of weight losses of CMC-EFB observed compared to those of EFB is due to the high composition of cellulose after pretreatment and bleaching, and also to the substitution of carboxymethyl at the cellulose hydroxyl groups. As stated by Haleem et al. [21], the phase change occurred due to the cleavage of hydrogen bonds at the cellulose hydroxyl group caused by SMCA; thus possibly reducing the thermal stability of the cellulose structure of CMC-EFB. The DTG shoulder peak at 260 °C clearly observed for CMC-EFB may be due

to the removal of lignin during pretreatment, which increased the visibility of hemicellulose peak. Furthermore, small peaks above 600 °C observed for CMC-EFB are suggested to be due to decomposition of small number of lignin components present as impurities in CMC-EFB; subsequently, lower amounts of residue were produced compared to EFB. Thus, it could be suggested that an improvement in the EFB pretreatment and bleaching processes are required to improve the purity of CMC-EFB.

Based on the overall results in this work, the synthesis of CMC-EFB using different fractionation method and bleaching process has obtained DS values similar to other CMC syntheses. This shows the potential of the combination of [BMIM][Cl] IL fractionation with H<sub>2</sub>O<sub>2</sub> bleaching. Based on the characterization results, CMC-EFB had been synthesized from EFB cellulose through the alkalization and etherification reaction.

## Conclusions

Carboxymethyl cellulose-EFB was successfully synthesized by the reaction with SMCA and NaOH with maximum DS of 0.82 at 1.2 w/w SMCA concentration, 30% NaOH concentration, and a reaction temperature of 55 °C for 3 h. The <sup>1</sup>H-NMR spectrum showed that the signal peak of CMC obtained was similar to those of other CMC reports. The EDX analysis of CMC-EFB also shows that elements present were indicative of the synthesis of CMC. The [BMIM][Cl] IL fractionation and H<sub>2</sub>O<sub>2</sub> bleaching have shown to be a potential approach for future work on the synthesis of CMC. This includes the pretreatment study using other suitable IL with H<sub>2</sub>O<sub>2</sub> bleaching for CMC synthesis from various potential biomass feedstock. Thus, this approach can be an alternative for biomass conversion to CMC which can be used for various industrial applications.

## Acknowledgments

This project was financially assisted by the Universiti Teknologi Malaysia (UTM) through PRGS-ICC (Vote 4J325) and Professional Development Research University Post-Doctoral Fellowship (Vote 04E18 and 04E51) Grants.

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