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Properties of microcrystalline cellulose prepared from oil palm empty fruit bunch at different sulfuric acid concentration and hydrolysis temperature

J Sukaimi, W N H Wan Abdullah, M A F Supian, S S Jamari, N A Mohd Azman, S Mohamad and M F Ali[*]

Faculty of Chemical and Process Engineering Technology, College of Engineering Technology, Universiti Malaysia Pahang, 26300 Gambang, Pahang, Malaysia

*Email: mohdfaizalali@ump.edu.my

Abstract. Microcrystalline cellulose (MCC) is a biodegradable crystalline powder that normally isolated through acid hydrolysis process of cellulose. However, the implication of high concentration of acid, such as more than 5M sulfuric acid (H_2SO_4) in MCC production is concerned. Therefore, this work studies the effect of low acid concentration (1.5, 2.5 and 3.5 M) and hydrolysis temperature (40, 60 and 80 °C) for the MCC isolation from oil palm empty fruit bunch (EFB) assisted with steam explosion process cellulose fibers. Yield, crystallinity and chemical properties of the isolated EFB-MCC were discussed and compared with the commercial MCC. The crystallinity result shows the range of 72 – 77% for the isolated EFB-MCC. The highest crystallinity (77%) achieved at 3.5M H_2SO_4 at 80°C, similar to the crystallinity of the commercial MCC. As for the yield, the trend is decreasing severely as the increment of temperature, however small reduction of yield detected at different H_2SO_4 concentration. While for the chemical properties, FTIR spectra illustrated consistent wavenumbers detection for the EFB-MCC, commercial MCC and exploded EFB-Cellulose. It can be concluded that the optimum condition for the acid hydrolysis process is 1.5M H_2SO_4 at 60 °C with the middle range of crystallinity (74.7 %) and yield (82.4 %).

1. Introduction

The palm oil industry is one of the key economic contributors in Malaysia, respectively [1]. In 2018, the Malaysian crude palm oil output leaped by 12.5% to 43 million tons compared to the previous year's [1, 2], and was estimated to increase by 4 -5% in 2019 [2]. A large amount of palm oil waste would be generated during palm oil extraction oil process [3]. Empty fruit bunches (EFB) is the main solid waste produced, estimated by 25 wt%, from the oil extraction in the palm oil mill [2-3]. Conventionally, this waste is directly disposed of either by mulching and composting in the plantation site or landfills [4]. This lead to the abundant of unused EFB, which not only consuming massive valuable area, triggering severe environmental pollutions but also a huge waste of natural resources [5]. Therefore, reuse and recycling of EFB for the conversion towards the value-added product is an effective opportunity for economic and environmental benefits [4-5].

Microcrystalline cellulose (MCC) is a fine, odorless, and whitish crystalline powder, normally utilized in many industry areas such as stabilizer, binder, and filler in food and medical tablets, emulsifier in certain dairy products, viscosity regulator, and as reinforcement agents in polymer composite development [6]. MCC produced as α-cellulose undergo partial hydrolyzation and

depolymerization and leaving mostly crystal regions in the final structure [7]. In term of properties, MCC is a non-toxic material, biodegradable, biocompatible, high mechanical strength, high surface area and crystallinity [6,7]. MCC is highly preferred as it has cheap resources due to its availability and abundance in nature [8]. Depending on the method, techniques, conditions and sources of the cellulose, the structures and features of the MCC could be displayed differently [9].

MCC has been successfully extracted from various sources like cassava bagasse [10], wood cotton waste [11], tea waste [12], bamboo [13], pomelo peel [14], and roselle fibers [15]. Different methods have been developed as to produce MCC such as physical treatment: microwave irradiation [16], high-pressure homogenization [17]; chemical treatment: alkaline and acid hydrolysis [18,19], carbonaceous catalyst [20] or biological treatment: enzymatic hydrolysis [21]. Several studies reported that hydrolysis condition such as temperature, acid concentration, type of acid, and duration give major effects on structures and properties of produced MCC [21-22]. However, by using a huge volume of concentrated acid and high temperature will lead to high installment cost and most crucially causing severe environmental issues [17,21]. Despite many research conducted to investigate the optimum condition to prepare MCC by means to avoid all the problems above, yet acid hydrolysis is the best way of producing MCC [22].

In this study, EFB-MCC was prepared from exploded EFB-Cellulose by the acid hydrolysis method at different sulfuric acid (H_2SO_4) concentration and temperature. The yield, crystallinity and chemical properties of the EFB-MCC have been discussed and compared with commercial MCC. Even though works on the hydrolysis process and characterization of MCC from EFB has been reported, however, no research reported on the isolation of MCC from EFB-Cellulose that has been pre-treated via steam explosion process.

2. Experimental

2.1 Materials
The EFB fibers were collected from the LCSB Lepar Oil Palm Mill (Pahang, Malaysia). The EFB fibers were firstly undergoing steam explosion pretreatment process before chemical treatments (alkaline and bleaching) to isolate the Exploded EFB-Cellulose. The pre-treatment and extraction procedures were described in details in the Supian et al. [23]. The chemical used for the EFB-MCC isolation was sulfuric acid (H_2SO_4) with purity 95% from Fisher Scientific, USA. The commercial MCC, Avicel® PH101, Fluka by Sigma Aldrich, USA, was used as the reference.

2.2 Methods

2.2.1 Preparation of EFB-MCC. The EFB-MCC was isolated from the Exploded EFB-Cellulose through acid (H_2SO_4) hydrolysis process for 30 minutes with constant agitation in the 10 wt% consistency (solid to liquid ratio). Different H_2SO_4 concentrations were used; which were 1.5 M, 2.5 M, and 3.5 M, during the hydrolysis process at different temperatures; 40, 60 and 80 °C. The mixture was then filtered at room temperature and washed repeatedly with water. The produced EFB-MCC was then dried in an oven at 60°C until constant weight.

2.2.2. Percentage Yield of MCC. The percentage yield of EFB-MCCs was calculated using equation (1), given; M_{MCC} = mass of isolated EFB-MCC (g), M_C = mass of exploded EFB-Cellulose (g).

$$Yield\ (\%) = \frac{M_{MCC}}{M_C} \times 100 \qquad (1)$$

2.2.3. Characterization. Selected sample of the produced EFB-MCCs were analyzed which are EFB-MCC hydrolyzed with constant concentration; 1.5 M at different temperature; 40, 60 and 80 °C and with constant temperature; 80°C at different concentration 1.5 M, 2.5 M and 3.5 M. The crystallinity of the EFB-MCCs was determined using Broker D8 Advance X-ray Diffractometer (XRD) with Ni-filtered CuK_α radiation. The scanning rate is 2°min^{-1} within a 2θ angle range from 5° to 40°. The crystalline

index (*CrI*) illustrated in Equation (2) by applying an established Segal method, where I_{002} is the intensity of both amorphous and crystalline regions; I_{am} is the intensity of amorphous regions.

$$CrI\ (\%) = \frac{I_{002} - I_{am}}{I_{002}} \times 100 \qquad\qquad (2)$$

Fourier Transform Infrared (FTIR) was conducted using Thermo Nicolet FTIR spectrometer to detect the presence functional groups in the samples. The spectrometer is equipped with a DTGS detector by direct scanning with fitted universal ATR accessory in the wavenumber range of 500 to 4000cm^{-1}.

3. Result and Discussion

3.1 Crystallinity analysis
MCC is typically characterized by the degree of crystallinity; based on grades with a typical value range from 55 – 80 %, as determined by XRD analysis [24]. The XRD patterns of EFB-MCC at different concentrations of acid sulfuric and temperatures are presented in figure 1. The x-ray diffraction pattern of all MCC-EFB shows similar trends with the 2θ values were found at 16, 18, 22.6 and 22.9°. It is reported by De Menezes et al. [25] that the typical XRD patterns for lignocellulosic are displayed at the crystal lattice of cellulose I at 2θ values of 15, 16, 22.6, and 34°.
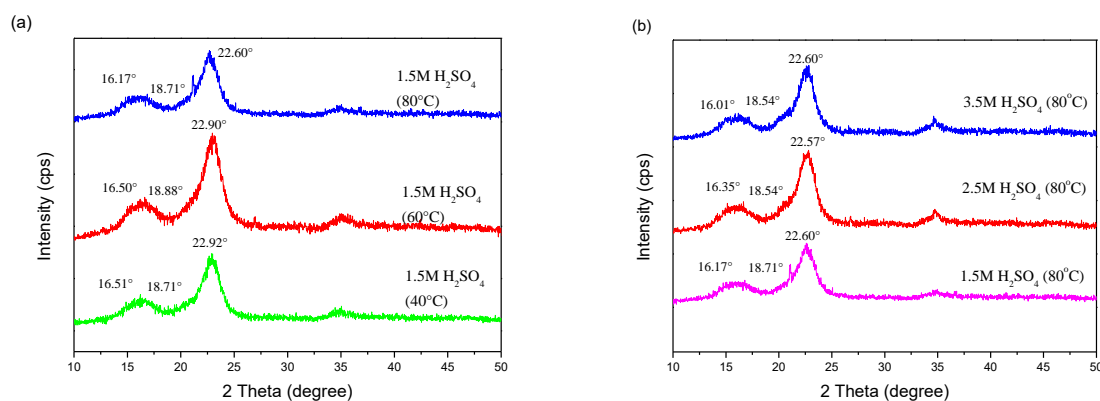

Figure 1. The XRD patterns of EFB-MCC (a) 1.5 H_2SO_4 at a different temperature, (b) different H_2SO_4 concentration at 80°C.

The crystallinity data for the isolated EFB-MCC and commercial MCC are tabulated in Table 1. Analyses showed that the crystallinity index of EFB-MCC isolated at a concentration of 3.5M and 80°C is the highest, which is at 77.03% and between the range of commercial MCC (76 -79%). The higher crystallinity of MCC related to the removal of amorphous regions of cellulose which stimulates the hydrolytic cleavage of glycosidic bonds that leads to rearrangement of cellulose molecules [26]. The percentage of crystallinity for other samples is slightly lower (~5%) than the EFB-MCC isolated at a concentration of 3.5M and 80°C, indicating no significant effect of the crystallinity of MCC from different acid concentration and hydrolysis temperature. Based on the data, the manipulation of concentration and hydrolysis temperature does not offer a significant effect on the crystallinity of the EFB-MCC.

Table 1. The crystallinity of EFB-MCC and commercial MCC.

Sample	Concentration (M)	Temperature (°C)	Crystallinity (%)	Reference
Commercial MCC	n/a	n/a	76 - 79	[24]
EFB-MCC	1.5	40	73.02	
		60	74.71	
		80	73.78	Experimental Data
	1.5		73.78	
	2.5	80	76.75	
	3.5		77.03	

* n/a is not available

3.2 Yield of EFB-MCC

Table 2 shows the percentage yield of the isolated EFB-MCC through different H_2SO_4 concentration and hydrolysis temperatures. Generally, the yield obtained is reducing as the concentration of H_2SO_4 increase along with the hydrolysis temperature. Compared to the 1.5M H_2SO_4, the greater influence of hydrolysis temperatures can be identified at a higher acid concentration as the yield reduction is around 35% difference from the temperature of 40 to 80 °C. The highest yield was recorded at 99.3% for the EFB-MCC hydrolyzed with 1.5M H_2SO_4 at 40°C.

This result is in agreement with the yield obtained by previous research [27] where the yield decreased when the temperature increased from 30°C to 40°C. The increment of hydrolysis temperature will promote the hydrolysis which will affect the crystalline region orientation [27] as a result, the cellulose tends to transform into glucose substances [28]. However, a minimal difference in yield is reported with the increment of acid concentration at a constant temperature. Besides, a similar trend is illustrated with the percentage of crystallinity recorded. Thus, it is important to obtain an optimum yield with good crystallinity of MCC.

Table 2. The yield of EFB-MCC at different acid concentrations and hydrolysis temperatures.

Concentration (M)	Temperature (°C)	Yield (%)
1.5	40	99.3
	60	82.4
	80	73.0
2.5	40	85.0
	60	79.7
	80	53.4
3.5	40	79.6
	60	86.6
	80	50.9

3.3 Functional groups analysis

The FTIR spectra of commercial MCC, EFB-MCC at different concentration and Exploded EFB-Cellulose are shown in Fig. 2. No major changes in the FTIR spectra can be detected following hydrolysis of cellulose with acids of different concentrations. The major detected regions are found at several wavenumbers such as 3500 – 3200 cm^{-1} for hydroxyl bonds, 2900 – 2800 cm^{-1} for C-H bonds, 1020 – 970 cm^{-1} for C-O-C bonds.
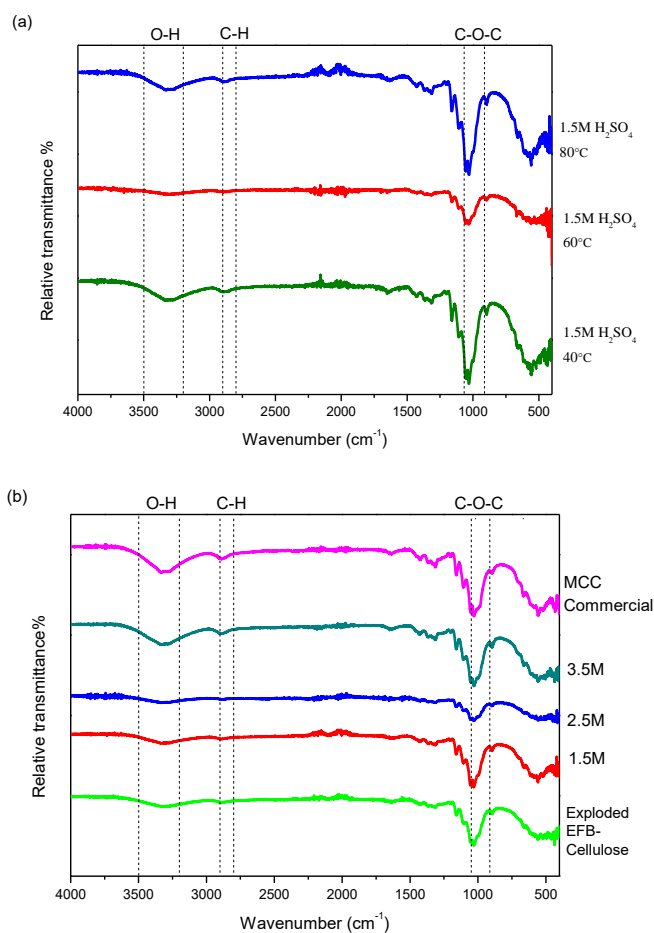
Figure 2. FTIR spectra of EFB-MCC (a) 1.5 H2SO4 at a different temperature, (b) different H2SO4 concentration at 80°C, Exploded EFB-Cellulose and MCC commercial.

The spectra obtained revealed that the similarities between all regions indicating that all isolated samples have similar chemical compositions. These results are also comparable with the spectra reported by Mohamad Haafiz et.al [24], which in their work compared the OPEFB-MCC, OPEFB-pulp and commercialize MCC (C-MCC). The effect of hydrolysis conditions is not affecting the chemical bonding on the prepared samples.

4. Conclusion

The MCC is successfully isolated from the exploded EFB-Cellulose, at different acid concentration and hydrolysis temperature. The XRD data shows that all the samples can be classified as crystalline cellulose material, with the range of crystallinity of 72 – 77%. The highest crystallinity (77 %) value is recorded at 3.5M H_2SO_4 at 80 °C; however, it recorded the lowest yield (50.9 %). Based on the yield obtained, different process temperature gives more influence to the hydrolysis process compare to the H_2SO_4 concentration. While the chemical bonds between the samples show that no changes on the EFB-MCC structure compared to the exploded EFB-Cellulose and commercial MCC. Based on these results, it can be concluded that the optimum condition for the acid hydrolysis process is 1.5M H_2SO_4 at 60 °C with the middle range of crystallinity (74.7 %) and yield (82.4 %).

5. Acknowledgments

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