ISSN: 1410-8917
Jurnal Kimia Sains & Aplikasi
e-ISSN: 2597-9914

Jurnal Kimia Sains dan Aplikasi 23 (5) (2020): 147–151

Jurnal Kimia Sains dan Aplikasi
Journal of Scientific and Applied Chemistry

Journal homepage: http://ejournal.undip.ac.id/index.php/ksa

Production of Micro Crystalline Cellulose from Tapioca Solid Waste: Effect of Acid Concentration on its Physico-chemical Properties

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https://doi.org/10.14710/jksa.23.5.147-151

Article Info

Article history:

Received: 13th April 2020
Revised: 29th April 2020
Accepted: 1st May 2020
Online: 31st May 2020

Keywords:
microcrystalline cellulose; physicochemical properties; scanning electron micrograph; tapioca solid waste

Abstract

This study was aimed to examine the production of microcrystalline cellulose (MCC) from tapioca solid waste (TSW), using HCl hydrolysis with various concentrations, i.e., 2 N, 2.5 N, 3 N, and 3.5 N. MCC was produced by delignifying the TSW with NaOH 20%, and bleaching with NaOCl 3.5% to produce α-cellulose, and subsequently hydrolyzing α-cellulose with three different HCl concentrations to produce MCC. The physicochemical properties of MCC were then analyzed, including Scanning Electron Micrograph (SEM), X-ray diffraction (XRD), and FTIR spectra. The results showed that hydrolysis with 2.0 N HCl resulted in a higher yield of 61.28%, α-cellulose content of 56.33%, moisture 6.25%, pH of 6.54; ash 0.23%, and water solubility 0.34%. SEM analysis showed the morphology and size of the MCC produced were like those of a commercial MCC (Avicel PH101), while the XRD analysis showed the higher concentration of HCl gave rise to an increased crystalline index. FT-IR spectrum analysis indicated that TSW, MCC produced, and commercial MCC had similar functional groups.

1. Introduction

The tapioca industry is one of the industries in Indonesia that uses cassava as its raw material. In the process of making tapioca, by-products are produced in the form of solid waste and liquid waste; and solid waste accounts for around 75% of the raw material [1]. Solid waste contains high carbohydrates, so it is widely used as animal feed and raw material for bioethanol production.

Tapioca solid waste (TSW) can pollute the environment around the tapioca processing area if proper handling is not performed. TSW contains 14.51% water, 8.11% protein, 1.29% fat, 0.89% ash, 15.20% crude fiber, and 60% starch [1]. The largest types of carbohydrates in TSW are starch and lignocellulose, and the lignocellulose contains 59.9% cellulose, 20% hemicellulose, and 10.7% lignin [2]. α-Cellulose from TSW has the potential as a raw material to produce microcrystalline cellulose (MCC), which in turn can increase the added value and can reduce tapioca industry waste.

MCC can be employed as an additive in food, cosmetics, and pharmaceutical products [3, 4]. In the pharmaceutical industry, the use of MCC, as a filler, will produce tablets with high hardness, slight friability, rapid disintegration time, and a high percentage of drug release. Moreover, MCC is commonly used for the manufacture of direct compression tablets, in which the popularity of direct compression method is increasing because it has many advantages such as: providing a uniform particle size, does not require the granulation process, producing more stable tablet, and profitable in an economic perspective [5].

MCC can be made with controlled hydrolysis of α-cellulose, with a dilute mineral acid solution at high temperature. It is then washed with water until it is acid-free, dry and mechanically grounded [6]. Previous studies in the production of MCC with acid and base hydrolysis have been carried out with a variety of different cellulose sources, such as rice husk [7], oil palm empty fruit bunches [8], bamboo [9] and green algae [10]. The results of these studies indicated that differences in concentration in the hydrolysis process can affect the characteristics of the resulting MCC. Acid have advantages in the hydrolysis process in terms of economic and time point of view [11]. Making MCC using acid hydrolysis under controlled time and temperature can remove the amorphous portion of cellulose to form crystals [12]. This study examines the effect of HCl concentrations in the TSW hydrolysis process on the physicochemical characteristics of the resulting MCC.

2. Methodology

Materials and methods of analysis employed in this study are described in the following:

2.1. Material

Materials used in this study were TSW, a commercial MCC of Avicel PH101, HCl (2; 2.5; 3 and 3.5 N), NaOH 20%, NaOCl 3.5%, CH_3COOH 10%, indicator ferroin, iodized zinc chloride, filter paper, iodine 0.05M, and distilled water. TSW was obtained from a village small industry in South Konawe, Southeast Sulawesi, Indonesia. The sample was sun-dried for three days (8 hours per day) and continued by oven drying for 24 hours at 60°C.

2.2. α-Cellulose Isolation

α-Cellulose was isolated according to the method of TAPPI Test 203 os-74 [13]. A sample of 50 g was put into an Erlenmeyer flask containing 1 L of 20% NaOH, shaken for 24 hours at a speed of 150 rpm with a mechanical stirrer, filtered and washed to pH 7. The residue obtained was added with 1 L mixture of 3.5% NaOCl and water (1: 1), heated at 100°C for 15 minutes, filtered, and washed to pH 7. The residue obtained was α-cellulose.

2.3. MCC Production

The method of Dafit [14] was used in the production of MCC. A total of 50 g α-cellulose was placed in a beaker, hydrolyzed with various concentrations of 1 L HCl (2; 2.5; 3 and 3.5 N) by boiling for 30 minutes, cooled, filtered and washed to pH 7. The resulting MCC was oven-dried at 60°C for 12 hours.

2.4. Analysis of MCC Physicochemical Properties

The physicochemical characteristics of MCC analyzed were: α-cellulose content, yield, moisture content, ash content, acidity (pH), water-solubility, crystal morphology with SEM (TESCAN 20 kV), degree of crystallization with XRD (Shimadzu-7000L), and functional groups with FT-IR spectra (spectrophotometer Shimadzu Prestige 21).

3. Results and Discussion

Results obtained in this study are discussed in the following sections:

3.1. Content of α-Cellulose and Yield of MCC

This study indicates that the higher the α-cellulose obtained, the higher the purity of MCC. This is also related to the optimal delignification reaction that occurs. The content of α cellulose produced at various HCl concentrations ranged from 37.67 to 56.33% (Table 1). Optimal α-cellulose formation occurs at 2 N HCl concentrations of 56.33%. This is indicated by the formation of the most abundant α-cellulose content compared to other MCCs. The increase in HCl concentration is not proportional to the increase in the level of α-cellulose produced. This can be seen from the concentration of 2.5 N 47.33%, 3 N 42.33%, and 3.5 N 37.67%. At this concentration, a decrease in α-cellulose content occurs along with an increase in the concentration of HCl used in the delignification process.

The yield of MCC with the treatment of different HCl concentrations in the α-cellulose hydrolysis process showed that the higher concentration of HCl used produced a lower yield, as shown in Table 1. The yield of MCC produced ranged from 41.86 to 61.27%. The highest yield is in the hydrolysis process using 2N HCl, and the lowest yield is 3.5N HCl. Dafit [14] also found that the yield of MCC produced from sugar cane bagasse showed the greatest results in the treatment of a 1.5N HCl of 93.03%, while the lowest yield in the treatment of a 3.5N HCl was 77.60%. The use of higher HCl concentrations in the hydrolysis process will cause an increase in the hydrolysis process so that there will be more glucose monomers being washed, and it has been reducing the yield of MCC produced.

Table 1. α-Cellulose content, yield, water-solubility, moisture, ash, and pH of the MCC, TSW, and commercial MCC samples.

Samples	α-Cellulose Content (%)	MCC Yield (%)	Water Solubility (%)	Moisture (%)	Ash (%)	pH
MCC 2 N	56.33±1.16	61.27±1.39	0.34±0.02	6.25±0.15	0.23±0.01	6.54±0.04
MCC 2,5 N	47.33±1.76	51.85±1.10	0.36±0.01	5.70±0.12	0.35±0.10	6.21±0.01
MCC 3 N	42.33±1.26	49.13±1.00	0.41±0.01	5.42±0.13	0.47±0.08	6.00±0.01
MCC 3,5 N	37.67±2.84	41.86±2.14	0.50±0.02	5.41±0.11	0.59±0.05	5.85±0.02
Tapioca Solid Waste (TSW)	20.83±1.53	-	-	5.39±0.68	2.24±0.19	-
Avicel PH 101 [15]	-	-	0.10	-	-	6.64±0.20

3.2. Water Solubility, Moisture, Ash, and Acidity

The solubility of MCC in water is used to determine the purity of MCC based on the solubility of simple hemicelluloses, such as xylose and mannose in water. The water solubility of MCC ranged from 0.34 to 0.50% (Table 1). The high water solubility of MCC is thought to be influenced by the hemicellulose content of the sample, as also indicated by a study of Lanz [16]

The moisture content of the samples decreases as HCl concentrations increases. It will then upsurge the crystalline index of the samples and turn the structure from originally amorphous into crystals, as is also

supported by the crystalline index (Table 2). Dafit [14] states that the amorphous nature is easier to absorb and store water, compared to crystals. Hydrolysis using low concentrations of HCl causes the reaction process to be less than optimal, which makes some cellulose structures still amorphous in shape. This in turn will generate higher water absorption. Meanwhile, the ash content of MCC produced ranged from 0.22 to 0.58%; and its pH ranged from 5.85 to 6.54.

Table 2. Degree of crystalline of MCC compared to those of MCC made from other sources.

Sample	Degree of Crystallinity (%)
Tapioca Solid Waste (TSW)	38.71
α- Cellulose	81.58
MCC 2 N	62.51
MCC 2,5 N	67.17
MCC 3 N	83.51
MCC 3,5 N	94.16
MCC Agar Solid Waste (2,5 N) [a]	62.03
MCC Rice husk [b]	87.00
MCC Cotton [c]	83.00
MCC Oil palm bunches [d]	87.00

Sources: [a] [17]; [b] [18]; [c] [19]; [d] [20]

3.3. Scanning Electron Microscope (SEM) Analysis

Observation of the MCC characteristics is followed by morphological observations through the Scanning Electron Microscope (SEM) analysis. It aims to confirm the physical appearance of the MCC, which is then compared to commercial products.

Figure 1 shows that the results of the SEM MCC and Avicel PH 101 are similar in morphological features. The diameter is measured using a scale at each microgram with 500x magnification. The MCC diameter obtained in HCl 2N concentration was around 80.18 µm, HCl 2.5N of 68.04 µm, HCl 3N of 97.60 µm, and HCl 3.5N of 79.65 µm. Based on these results, the MCC produced has met the standard because generally, MCC has a diameter of 1-100 µm [21].

3.4. X-Ray Diffraction (XRD)

The degree of MCC crystallinity with different HCl concentration treatments showed different results, and ranged from 62.51 to 94.16%, as shown in Figure 2 and Table 2. The highest degree of crystallinity (94.16%) was found in the hydrolysis process using an HCl 3.5N, while the lowest (62.51%) was in the HCl 2N.

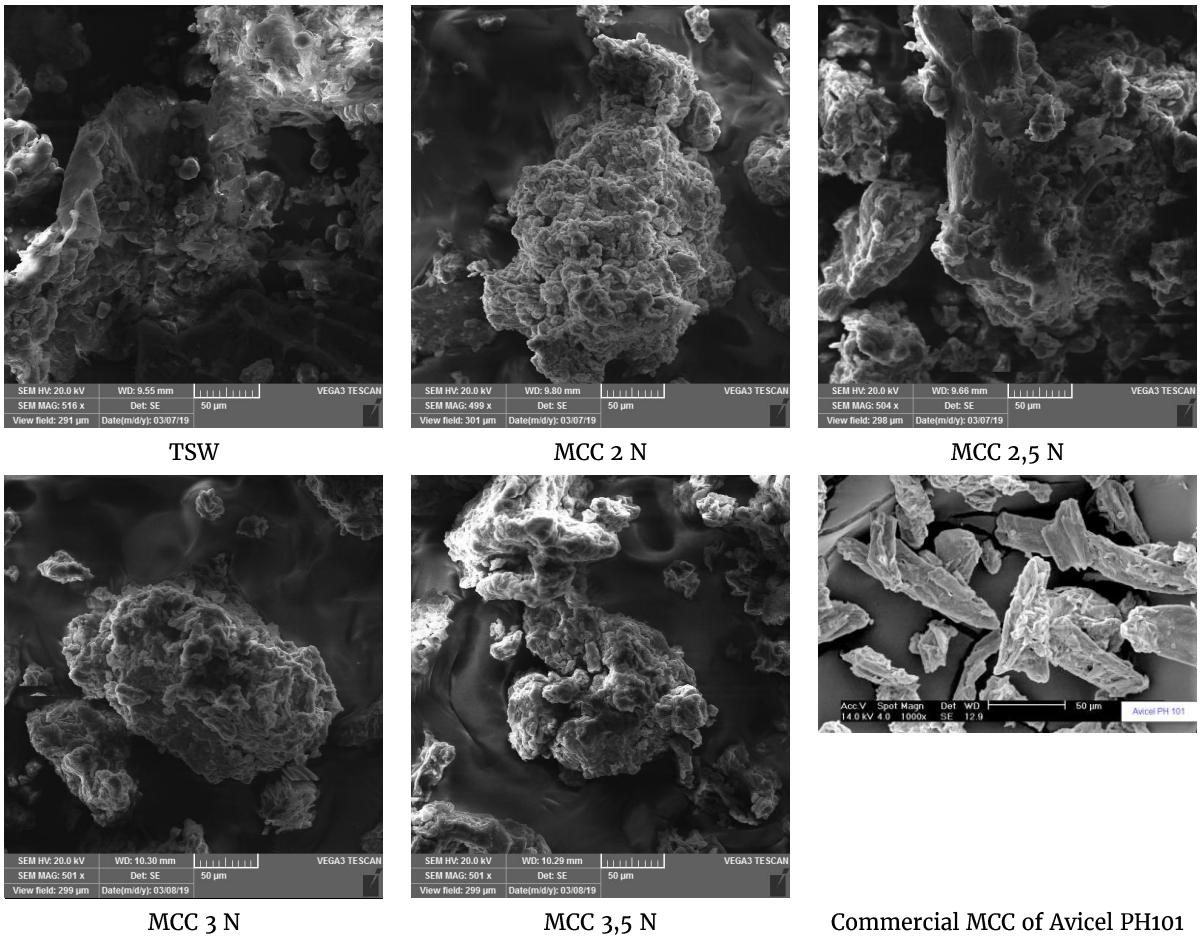

Figure 1. Scanning electron micrograph of TSW, commercial MCC, and MCC produced in various HCl concentrations, with a magnification of 500x.

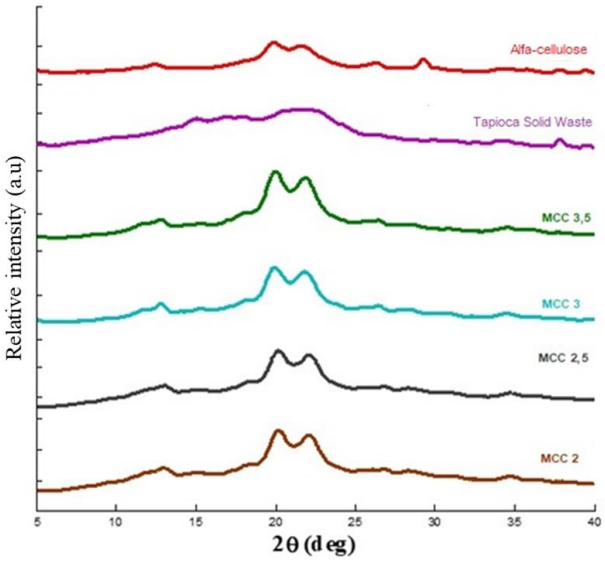

Figure 2. XRD diffractograms of MCC produced at different HCl concentrations, compared with those of tapioca solid waste and α-cellulose.

The results in this study were higher for the highest treatment of HCl 3.5N when compared to the studies of [18, 19, 20] each valued at 87%, 83%, and 87%, respectively. Higher acid concentrations are thought to cause an increase in crystalline due to the cutting speed of amorphous regions in cellulose [22]. Meanwhile, a low crystalline may be probably caused by higher hemicellulose content so that the structure is more amorphous [23].

3.5. FT-IR (Fourier Transform Infra-Red)

FTIR analysis was carried out to determine the existence of TSW and MCC functional group constituents produced. Their functional groups can be seen in the FTIR spectrum, as shown in Figure 3.

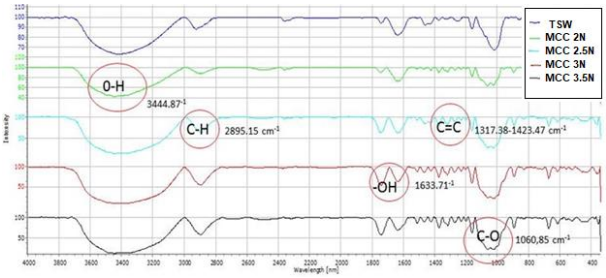

Figure 3. The functional groups of TSW and MCC in the FTIR spectrum.

In general, the spectrum of functional groups absorbed on MCC at each HCl concentration treatment is similar. The absorption peaks in the frequency region 3371-3413 cm^{-1} indicates the existence of stretch vibrations from the O-H group [24]. Haafiz *et al.* [20] obtained the peak absorption of O-H groups in the frequency region of 3471-3493 cm^{-1}. In the results of the analysis on MCC, the peak absorption of the O-H group was found at 3444.87 cm^{-1}, whereas the peak that occurred around 1633.71 cm^{-1} showed a fiber-OH group for cellulose water absorption. Rosa *et al.* [24] also explained that the absorption peak in the frequency region of 2897-2943 cm^{-1} showed the existence of stretch vibration from the C-H group. Based on the results of the analysis on MCC, the peak absorption of the C-H group is 2895.15 cm^{-1}. In addition, the absorption peak in the frequency region 1373-1430 cm^{-1} shows the C=C group as the identification of lignin [25], which is found at 1317.38-1423.47 cm^{-1}. The lignin transmittance values in MCC are higher than in TSW. This shows that the lignin component in MCC decreases. The absorption peak at the frequency area 1058 cm^{-1} indicates the existence of stretch vibrations from the C-O group [26]. In the results of the analysis on MCC, the peak absorption of the C-O group is found in the wavelength of 1060.85 cm^{-1}.

4. Conclusion

Different HCl concentrations in the TSW hydrolysis process produce MCC with different physicochemical characteristics. The results showed that hydrolysis with lower HCl concentrations (2.0N) resulted in a higher yield, α cellulose content, moisture, and pH, while the ash content and the water solubility were lower. SEM analysis shows the morphology and size of the resulting MCC are like that of a commercial MCC (Avicel PH101), while the XRD analysis shows the higher the concentration of HCl during the hydrolysis process, the crystalline index increases. FT-IR spectrum analysis shows that TSW, MCC, and commercial MCC have similar functional groups.

Acknowledgment

We acknowledge financial support to Universitas Halu Oleo in carrying out this study.

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