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Hydrolysis of Cellulose from Oil Palm Empty Fruit Bunches to Produce Cellulose Nanocrystals Zulnazri*, Achmad Roesyadi, Sumarno, Department of Chemical Engineering, Sepuluh Nopember Institute of Technology, Surabaya, Indonesia.

Abstract- This study examines the process of hydrolysis of cellulose from oil palm empty fruit bunches (OPEFB) in order to produce cellulose nanocrystals (CNCs) using hydrochloric acid as catalyst under hydrothermal and reflux condition.

Yields of CNCs obtained by refluxing hidrolysis using 3 M and 6 M HCl are 73,30 % and 35,82 %wt respectively, and CNCs showed high crystallinity until 76,63 %wt and 86,93 %wt respectively. This results, then compared with the results under hydrothermal conditions, showed lower crystallinity that are 62,41%wt and 56,86%wt respectively.

FT- IR analysis showed a peak difference between the spectrum of OPEFB, cellulose and CNCs, such as the wave number of 123 cm-1 is an absorption peak of COC aryl-alkyl contained in lignin, this peak is not shown in the spectrum of cellulose and CNCs.
Keywords: hydrolysis reflux, hydrothermal, cellulose nanocrystal. INTRODUCTION CNCs are generally produced from biomass is the most abundant and renewable in nature including from oil palm empty fruit bunches (OPEFB).

The main content of OPEFB is 43-44 % cellulose, 34 % hemicellulose, and lignin reach 17-20 % [1]. CNCs that produced by a two-step process: (1) initial hydrolysis to remove the amorphous regions of the cellulose polymer, and (2) fragmentation of the crystalline segments to produce nanocrystals.

So far, the main production method has been hydrolysis of a partially crystalline cellulose material with about 60 % by weight of sulfuric acid followed by fragmentation of the resulting crystalline cellulose [2] - [5]. However, this method has the disadvantage, because not only the amorphous chain broke yet crystalline cellulose chain region also fragmented and degraded into shorter chain. In addition, for the most common acid hydrolysis, the yield is less than 30 % [6].

Therefore, please note that good hydrolysis material is required to provide higher thermal stability and yields of CNCs. As alternatives to strong sulfuric acid, some mild mineral acids (hydrochloric acid) and organic acids (maleic acid) were utilized under ultrasonic or microwave irradiation [7] - [9].

It has been reported that the CNCs produced through hydrochloric acid hydrolysis exhibited high thermal stability, but their aqueous suspensions tended to flocculation, and only a low yield of 20 % can be achieved [10] - [11]. Filson and Dawson-Andoh shortened the preparation period of CNCs by utilizing high-power ultrasonic irradiation, but only 2–5 % yield was obtained.

They also obtained a yield of 38.2 % by introducing endoglucanase enzyme and

microwave heating [12]. Tang et al. reported a yield of 50.04% by applying a cation exchange resin hydrolysis method; however, the removal of cation exchange resin by post treatment and repetitive centrifugations is very time-consuming [9].

The hydrolytic reaction was restricted to the relatively short reaction time so that the acid could degrade only the amorphous regions in cellulose, leaving behind the crystalline ones. Thus, the reaction time and acid concentration is believed to be of the most important parameters to consider in _the acid hydrolysis of the cellulose.

In this study, CNCs was produced from cellulose based on OPEFB through hydrolysis process using hydrochloric acid under hydrothermal and reflux conditions. RESULTS AND DISCUSSION Hydrolisis Effects Table 1 shown yield of cellulose and CNCs under prosses extraction, hydrolysis reflux and hydrothermal. TABLE-1 YIELD, CRYSTALLINITY AND CRYSTAL SIZE COMPARISON Sample _Process Hydrolysis _Reaction time (jam) Y _Analysis _ _ _ _ _ield (%) _Xc (%) _Dhkl(nm) _ _Cellulose _Exstraction _2 _50,04 _63.02 _0.29 _ _CNCs-a _Reflux using 3M HCl _2 _73,30 _76.63 _0.59 _ _CNCs-b _Reflux using 6M HCl _2 _35,82 _86.93 _0.29 _ _CNCs-c _Hydrothermal using 3M HCl _2 _32,20 _62.41 _0.24 _ _CNCs-d _Hydrothermal using 6M HCl _2 _23,10 _56.86 _0.78 _ _ Chemical Structure From spectrum, it is shown that broad absorption peaks located at 3250-3500 cm-1 which is stretching of –OH group.

Absorption peaks at 2897-2917 cm-1 relevant with -CH2 group, whereas the absorption peaks at 2847 dan 2844 cm-1 is an overlapping of the tape -CH2. This peak only show of OPEFB raw material and cellulose whereas at CNCs, this peak not shown due to amorphous chain of cellulose was cracked. Absorption in 1600-1650 cm-1 region for samples of OPEFB and cellulose is indication for water or O-H stretching absorption. According to Johar et.al.

[13], this peak is related to the curve form of molecular water because strong interaction between cellulose and water. Absorption peak at 1454 dan 1419 cm-1 is suspeted to vibration bent of O-C-H from lignin component, both of them appear only in OPEFB spectrum while they not visible in cellulose and CNCs spectrum. Dissapearance its absorption peak in cellulose and CNCs spectrum showed that lignin removal has taken place perfectly.

CNCs exhibited increases in the intensities for the band at 1053 cm-1 assigned to the C-O-C stretching of pyranose and glucose ring skeletal vibration, respectively implying the increase in the crystalline cellulose content. This is consistent with the result from the XR-D. (a) (b) (c) Fig. 1. FTIR Spectrum of (a) OPEFB (b) Cellulose (c) CNCs

Crystal Structure Figure 2 shows diffractogram of cellulose and CNCs that was prepared through different preparation routes. The crystallite sizes and crystallinities are listed in Table 3.

All of diffraction pattern for crystalline cellulose showed peaks around 2? = 16o, 22o-23o and 35o, and minimum diffraction for amorphous showed around 2? = 18o and 19o, indicating the typical cellulose structure, these results fit with previous research conducted by Rosli et al. [14] and Yu et al. [15]. CNCs-a crystallinity that was produced by hydrolysis process under reflux condition using 3 M HCl is 76, 63 % with 0, 59 nm of crystal size.

When acid concentration was increased to 6 M HCl, its crystallinity is rise to 86,95% with a crystal size of 0,29 nm. CNCs-b shows that diffraction peaks where located at 22,7? becomes sharper than compared with the diffraction peak of CNCs-a wherein located at 22,6o, which showed an increase in crystallinity. Increased crystallinity is associated with increased structural rigidity cellulose, which can lead to a higher tensile strength.

Weaker peak that appear at 35o is shown in figure CNCs-a and CNCs-b, indicates that hydrochloric acid can provide a relatively stable condition to maintain the crystalline domains of CNCs during the hydrolysis reaction. When compared with CNCs-c-d, CNCs-a-b has a higher crystallinity. It is believed that hydrothermal conditions can help remove amorphous regions of cellulose, however, the reaction conditions of high-pressure may also attack the cellulose crystal region. (002) (110) (am) (b) (c) (d) (e) Fig. 2.

Diffractogram of (a) cellulose, (b) CNCs-a, (c) CNCs-b, (d) CNCs-c, (e) CNCs-d Morphology Analysis Micrographs of cellulose and CNCs are shown in Fig. 3. From the fig, cellulose and CNCs show much difference, where CNCs has a more regular and organized arrangement. This result explains the fact that in the crystalline regions of cellulose, raw material can withstand the attack of HCl and can remove amorphous component of cellulose, resulting in small dimensions of CNCs. Overall, structure of the cellulose surface looks regular with a width of 1 to 15 mm.

Micrographs show the morphological changes because it is influenced by the size and degree of fineness of fiber. So that, the fiber fineness must be considered to provide a better surface structure, as seen in fig. 3b-c, CNCs with enlargement 2 μm provide a better structure and regularly compared with cellulose fig. 3a showed surface structures tend to be less uniform.

_(b) (c) Fig. 3. SEM Structure of (a) cellulose, (b) CNCs hydrolyzed by 3M HCl, (c) CNCs hydrolyzed by 6M HCl CONCLUSIONS An approach for producing CNCs have been

presented through the hydrolysis process of cellulose from OPEFB under reflux extraction and hydrothermal conditions using hydrochloric acid. The analysis result shows 73.30 % of yield can be achieved with hydrolysis under-reflux extraction conditions using 3 M of HCl. While the high crystallinity up to 86.93 % can be achieved with hydrolysis under extraction- reflux conditions using 6 M of HCl.

The chemical structure of CNCs shows lignin and hemicellulose removal that shown in FT-IR spectrum. CNCs shows more compact morphology and has regularly structure compared to cellulose which is less compact. REFERENCES [1] D. Anggraini and H. Roliadi, "Preparation Pulp from from Oil Palm Empty Fruit Bunch for cardboard on the scale for small businesses," Forest products Risearch 29 (2011), pp. 211-225.

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