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Lampiran 4. Conference international "The International Conference on Chemical Process and Product Engineering (ICCPPE) 2016 Kinetics study the decomposition of the cellulose into cellulose nanocrystals by hydrothermal with hydrochloric acid catalyst Zulnazri Department of Chemical Engineering, Malikussaleh University, North Aceh, Indonesia.

Name of main author: Zulnazri, Tel. +6285283059515, E-mail: zoelnazri@yahoo.co.id Abstract: Cellulose nanocrystals hydrolyzed cellulose-based biomass residues from oil palm by using hydrochloric acid under hydrothermal conditions. The characterization of cellulose nanocrystals was determain by Fourier transform infrared spectroscopy and X-ray diffraction.

The Infrared Spectroscopy showed there has been a removal of lignin and hemicellulose in the spectrum. Crystallinity which reaches 78.59% was obtained by hydrolysis using hydrochloric acid catalyst 3 mol/L with a reaction time of 1 hour. Based on the graph of -ln CA/CA0 vs time obtained that Cellulose nanocrystals forming reaction is of first order.

The reaction rate constants to the formation of glucose (k2) is greater than the reaction rate constant to the formation of Cellulose nanocrystals (k1), which indicates that the phase of slow reaction is the reaction of the most influential on the overall reaction rate, the reaction of the formation of Cellulose nanocrystals. Keywords: Cellulose, CNCs, hydrothermal, hydrochloric acid INTRODUCTION Biomass residue oil palm is abundant and renewable biomass in nature.

Biomass is also called lignocellulosic waste because the main content are cellulose, hemicellulose and lignin. Cellulose is the molecule soluble in acid but does not easily

dissolve in alkali, while the hemicellulose and lignin molecules soluble in alkali but not easily soluble in acid, so the hemicellulose and lignin easily removed from cellulose by using an alkali [1].

Cellulose nanocrystals (CNCs) can be synthesized from cellulose using acid catalyst, wherein the acid initially degrade amorphous regions of cellulose chain, further fragmentation by using sonication or hydrothermally to produce nanocrystals. Some common methods that have been used to synthesize CNCs are hydrolysis using sulfuric acid, unfortunately many crystalline cellulose is degraded, so that the yield obtained less than 35% [2] and the resulting product shows a low thermal stability [3-5].

Hydrolysis of cotton pulp fibers by optimizing the preparation conditions using sulfuric acid can only increase the yield becomes 63.8% [6]. Hydrolysis of cellulose-fiber sisal using 60% H2SO4 can improve the crystallinity index nanocellulose to 72% and a particle size of 9.1 nm [1]. Some low concentration of mineral acids such as hydrochloric acid and maleic acid can be used to prevent aggregation and degradation of CNCs [7-10].

Rosa and Correa reported that CNCs produced by hydrochloric acid hydrolysis showed high thermal stability, but that tends to provide liquid suspension flocculation and this can only be achieved with a low yield of 20% [11-12]. Filson and Andoh utilize high power ultrasonic irradiation with short periods of sonication have produced CNCs with a crystallinity of 78%, but the yield achieved only 5% [13]. Tang et al. reported the hydrolysis method of cation-exchange resin can be applied to produce CNCs with the yield obtained 50.04% and reached 84.26% crystallinity, but the removal of the cation-exchange resin with recurrent post-treatment can be time consuming chemical and many [14].

According to Yu et al., the high yield and crystallinity is evident from the use of hydrochloric acid because the acid penetrates quickly into the deep layers of the network of cellulose and hydrolyze the amorphous regions chains of cellulose, while the crystalline regions are more resistant to acid hydrolysis lighter because the strength of hydrogen bonds between cellulose molecules adjacent compared with amorphous regions [10].

Hydrolytic reaction was also limited by the relatively short reaction time so that the acid can only degrade amorphous regions in the cellulose [10]. In this study, cellulose fibers hydrolyzed using hydrochloric acid to produce CNCs by hydrothermal processes. This process is more depth than the influence of the reaction time to the CNCs.

Pursuant yield obtained CNCs do approach to the study of reaction kinetics in order to obtain the appropriate reaction order for this process. EKSPERIMENTAL Materials Biomass residue oil palm was taken from crude palm oil processing plant. Chemical substance that was used for residue oil palm extraction is 17,5% wt NaOH from Merck and 2% wt NaOCl were purchased from PT. Bratachem.

Acid solution that was used for cellulose hydrolysis is hydrochloric acid 3 mol/L from Merck. Aquadest that was used for washing the CNCs is taken from PT. Bratachem. Preparation of Cellulose 50 grams of dry weight residue oil palm was included in the 17.5% wt NaOH (1:10) w/v, and then it was extracted at 80 °C for 2 hours. Extract that obtained bleaching with 250 mL of 2% wt NaOCl at 70 °C for 1 hour was also performed. Then, producted obtained was filtered and washed until neutrals.

Preparation of Cellulose Nanocrystals Cellulose 6:360 3M HCl (g:mL) was inserted in the ultrasonics bath tipe SU-27 TH capacity 477(W) x 272(D) x 200(H) mm, frequencies 28 kHz, output 300 watts and heater 500 watts, during 30 minutes. After that, sample hydrolyzed in the hydrothermal Parr USA pressure batch reactor, then the reactor tube was closed tightly and N2 gas was flowed into the reactor.

The reaction was run at a temperature of 110 °C with a reaction time of 0; 1; 2; 3; 4 and 5 hours. After reaching the cellulosic suspension sampling time, the suspension obtained is added sufficient distilled water to stop the acid reaction, decanted in a bottle 1 to 2 days to precipitate particles of crystalline cellulose, and then washed with distilled water until neutral, centrifuged and dried.

Characterization Fourier Transform Infrared Spectroscopy The chemical structures of OPEFB and the resulting cellulose were characterized on a Nicolet 8700 FT-IR spectrophotometer. FT-IR spectra were recorded in the spectral range of 4000– 400 cm-1. X-Ray Difraction The crystal structures were characterized on a Philips PZ1200 X-ray difraction (X-RD) by using Cu Ka X-rays with a voltage of 40 kV and a current of 30 mA. X-ray diffraction data were collected over an angular range of 0–50 in steps of 0,02o at room temperature.

The crystallinity (CrI) of the samples was determined by Segal's method [15]. I(???????????????????) – I(?????????) ??c = _I(????????????????????) 100 % where I(crystalline) is the intensity of the crystalline peak at the maximum at 2? between 22 and 23 and I (am) is the intensity at the minimum at 2? between 18 and 19, whereqis the corresponding Bragg angle.

The crystallite sizes were estimated from the 110, 110, and 200 lattice planes of cellulose I by using the well-known Scherrer equation. ??. ?? Dh???? = Bh???? . cos ? where Dhkl is

the crystallite size in the direction normal to the hkl family of lattice planes, K is the Scherrer constant (1.00 for equatorial reflections of rod-like or needlelike crystallites), ? is the wavelength of the radiation (1.54 Ao), and Bhkl is the full width at half-maximum (FWHMLeft) in radians of the reflection of that family of lattice planes [10].

RESULT AND DISCUSSION Physic Analysis Physically the change of OPEFB may be seen in Fig 1, OPEFB colors that has been treated alkali (NaOH 17,5%) becomes clearer. It showed reduced levels of lignin and hemicellulose that contained in OPEFB. Then after the hydrolysis, celullosa nanocrystal showed whiter color. Figure 1. Physically of (a) OPEFB untreated (b) Cellulose (c) Cellulose nanocrystal Condition Preparation Cellulose Nanocrystals Table 1 shown the yield, crystallinity and crystallite size of CNCs hydrolyzed using hydrochloric acid catalyst by hydrothermal process.

All parametter using the ratio of cellulose-to- acid 6 g / 360 mL with reaction temperature of 110 °C. Figure 2 shows the longer the reaction time, the yield obtained tends to be down, this is due to long reaction times hydrochloric acid can attack the cellulose crystalline regions thus reducing the crystallinity of CNCs. According to Yu et al.,

hydrolytic reaction is limited by the relatively short reaction time so that the acid can only be lowered amorphous regions in the cellulose and leave the crystal region. So that the reaction time is believed to be one of the most important parameters to be considered to improve the quality of CNCs [10]. TABLE I. YIELD, CRYSTALLINITY AND CRYSTALLITE SIZE OBTAINED THROUGH HYDROLYSIS USING HCl Sample name _ Process _ Reaction time (hour) _ Yield _X-RD _ _ _ _ _ _Crystallinity (Crl) _Crystallite size (Dhkl) _ _Cellulose _extraction _- _- _61.37 _29.35 _ _CNCs-C0 _ _0 _0 _0 _0 _ _CNCs-C1 _ _1 _74.82 _78.59 _7.83 _ _ _hydrolysis _ _ _ _ _CNCs-C2 _ _2 _66.00 _77.07 _1.81 _ _ _using 3 mol/L _ _ _ _ _ _CNCs-C3 _ _3 _46.62 _76.85 _3.91 _ _ _HCl _ _ _ _ _ _CNCs-C4 _ _4_36.41 _76.62 _1.81 _ _CNCs-C5 _ _5 _28.33 _73.27 _4.70 _ _

Crystallinity _ Figure 2. Graph relationship yield of CNCs vs reaction time

Figure 3 shown the X-ray diffraction pattern of cellulose and CNCs prepared by hydrolysis of hydrochloric acid 3 mol/L. All the diffraction pattern for the cellulose crystals showed peaks around 2? = 16o, 220 and 35o, minimum diffraction pattern for amorphous plane showed around 2? = 18o and 19o. Compared to cellulose, CNCs have broader peaks.

It benefited as hydrochloric acid is more efficient in the removal of polysaccharides noncellulosic and dissolution of the amorphous zone, so CNCs have higher crystallinity [10]. Crystallinity CNCs-C1 which reaches 78.59% believed that the hydrolysis reaction using hydrochloric acid catalyst in a reaction time of 1 hour can help up to removal amorphous cellulose chains.

Furthermore, the crystallinity declined slowly with increasing reaction time, as seen in the CNCs-C2 fell to 77.07% and CNCs-C5 with a longer reaction time dropped further to 73.27% This is due to the long time of the hydrolysis reaction may decide fraction of crystalline regions of cellulose so degraded into simpler chain.

Hydrochloric acid hydrolysis with reaction time is too long can weaken the cellulose crystalline regions, even resulting in carbonization CNCs [10]. CNCs shown maximum crystal diffraction peaks located at the angle 2? = 22.6o ± 0.2 with 002 lattice planes, which shows crystalline cellulose I [16-17]. At an angle 2? = 35o all diffraction pattern still shows a peak crystalline cellulose are low, this indicates that hydrochloric acid catalyst capable of persevering region crystals that are at the peak of the weak areas [16]. Overall CNCs shows the crystallite size below 7.83 nm, this proves that the hydrolysis using acid catalysts are applied can reduce the size of crystalline cellulose. Figure 3. XRD of cellulose and CNCs are hydrolyzed with a reaction time of 1 to 5 hours Chemical Structure

The FT-IR spectrum in Figure 4 shown all the CNCs displaying a broad absorption peaks located at 3250-3500 cm-1 which is a stretch -OH group. The absorption peak at 2890-2920 cm-1 region associated with the group -CH2, while at the peak absorption 2890 and 2900 cm-1 is an overlapping of tape -CH2, this peak is only found in cellulosic feedstocks, while at the peak CNCs have been lost due to the amorphous cellulose chain termination. Figure 4.

The FT-IR spectrum cellulose and CNCs are hydrolyzed with a reaction time of 1 to 5 hours Absorption in the 1600-1650 cm-1 in the samples cellulose is an indication of the absorption of water or stretch O-H, in the spectrum absorption peaks are already getting smaller this is because the crystal structure is already happening removal of water. According to Johar et al., this peak indicates the bending form water molecules due to a strong interaction between cellulose and water [18].

Absorption peaks in the region 1300-1365 cm-1 in all samples a ribbon of vibration of C-H and C-O associated with aromatic rings polysaccharides [16], this absorption band according to data analyzed by the Nacos [19]. That looks sharp absorption peaks at 1000-1160 cm-1 caused by the deformation of vibration of C-H. According to Kagarzadeh et al., peak is a vibration deformations C-H and pyranose C-O-C is more prevalent [20].

Spectrum CNCs also shows the intensity has increased at the peak, it implies an increase in the value of crystalline cellulose [12]. Kinetics of reaction Reaction series of hydrolysis of cellulose to CNCs and glucose is shown in Figure 5. (C6H10O5)1500 3.512(C6H10O5) 426 1500C6H12O6

Reaction cellulose hydrolysis using hydrochloric acid catalyst The above reaction can be

as:

BM CNCs is 69,000 g/mol and BM glucose was 180.18 g/mol. As a reactant converted into product R is the yield CNCs and as product S is the concentration of glucose.

Based on cellulose hydrolysis reaction is obtained kinetic model of the reaction. The assumption of a homogeneous solution, the particles are small enough so that the resistance resulting from mass transfer can be ignored. Equation reaction speed of the reaction series, irreversible reaction is as follows:

where: $CA = CA0 - CA0X$ To determine the change in concentration on R, substitution of concentration A of equation (4.4) into the differential equation in the reaction speed changes for R from equation (4.2)

Multiplied by a factor of integration of ??? ?????? so be: ????? ?????? = ? ?? ??? ?????????? + ???????????????? (4.7) From equation (4.5) it can be seen that the integration factor ????2??, while the constant of integration, namely - ??1????0 , from the initial conditions $CR0 = 0$ to $t = 0$.

So we get the final equation (??2-??1) for the change in concentration of R is: equation (4.4) and equation (4.8) is obtained: (4.11) The maximum concentration of R can be calculated using the equation:

$CA/CA0$ as shown in Table 2.

VALUES CS, CR AND CA OBTAINED FROM THE CALCULATION

Time (h)	CA0	CS	CR	CR+CS	CA0X = (CR+CS)'	CA = CA0 – CA0X	-ln CA/CA0
0	0.0000247	0.0000000	0.0000000	0.0000000	0.0000000	0.0000247	0.0000000
1	0.0000247	0.0000012	0.0000049	0.0000061	0.0000017	0.0000230	0.0724715
2	0.0000247	0.0000024	0.0000040	0.0000064	0.0000018	0.0000229	0.0770538
3	0.0000247	0.0000044	0.0000028	0.0000072	0.0000021	0.0000226	0.0870748
4	0.0000247	0.0000073	0.0000022	0.0000095	0.0000027	0.0000220	0.1159935
5	0.0000247	0.0000105	0.0000015	0.0000119	0.0000034	0.0000213	0.1480321

From table 2 was obtained plot a graph of residual cellulose concentration (CA) vs time, the concentration of CNCs (CR) vs time and glucose concentration (CS) vs time. Figure 6.

Relationship between (a) the concentration of residual cellulose (CA) vs time, (b) the concentration of CNCs (CR) vs time and (c) the concentration of glucose (CS) vs time. Figure 6 shows the concentration of cellulose (CA) is reduced during the reaction, and the concentration of CNCs (CR) increases until it reaches a peak on reaction time 1 hour, then decreased in line with the length of time the reaction is followed by increased concentrations of glucose (CS) along the length of reaction time, so that the reaction is considered to be a series reaction.

Decreased in concentration CNCs (CR) due to excessive degradation of crystalline cellulose so that increased concentrations of glucose (CS), so that the reaction time becomes the main influential factor in the study of the kinetics of hydrolysis of cellulose into CNCs. The graph above may not be combined because of differences in scale.

From Figure 6 obtained kosntanta reaction (k1) forming CNCs, by plotting this graph shows that the CNCs forming reaction is first order one. Values k1 and k2 at a concentration of 3 mol/L and a temperature of 110 oC can be seen in Table 3 where the value k2 obtained from the substitution value CRmax into the equation (4.12). CRmax is a maximum point in Figure 6(b). Figure 7.

Relationship between –ln CA/CA0 vs time Figure 7 is a graph of -ln CA/CA0 vs time obtained from the calculation of the concentration of the remainder of the initial concentrations based on data from Table 2. This graph strengthen the evidence that the longer the reaction time, the remaining reactants concentration is getting smaller, where -ln CA/CA0 obtained increasing together with the increasing reaction time, so this graph reflects the equation of order 1. TABLE III.

CONSTANTS REACTION FOR 3 MOL/L HCL CATALYST Temperature (oC) _Catalyst HCl (mol/L) _k1 (Jam-1) _k2 (Jam-1) _ _110 _3 _0,0308 _3,545 _ _Can be seen in Table 3, the reaction rate constant in the formation of glucose (k2) is greater than the reaction rate constant to the formation of CNCs (k1). This is consistent with the study of Wang et al., who reported that the constant formation reaction of glucose faster than CNCs [22].

Value k2 > k1 indicates that the slowest reaction stage is the stage of reaction greatest influence on the overall rate of reaction is the reaction of the cellulose into CNCs. Figure 8. Relationship between glucose concentration (Cs) vs time Figure 8 can be seen experimental glucose concentration (CS experiment) higher than the concentration of glucose models (CS model), it indicates that the formation of glucose can occur directly from the decomposition of the cellulose without via formation of CNCs.

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