

The Effect of Decomposition Time on Cellulose Degradation in Ionic Liquid/Acid with Pressurized CO₂

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Received: May 4, 2015

Accepted: June 5, 2015

Online Published: June 30, 2015

doi:10.5539/mas.v9n7p69

URL: <http://dx.doi.org/10.5539/mas.v9n7p69>

Abstract

Cellulose material is the most abundant carbohydrate that has a simple polymer structure, but it forms of crystalline micro-fibrils lead it insoluble in various solvent and highly resistant for hydrolysis process. The degradation of cellulose into glucose will increase the raw material for production of ethanol, isopropanol or butanol. The conversion into oligomer can be applied for pharmaceutical, food additives, etc. There are many technologies for conversion of cellulose such as degradation with ionic liquids, acid, enzymatic/fermentation, and hydrothermal. In this work, we studied cellulose decomposition by hydrothermal process, and a combination with ionic liquids. We used NaCl as a simple ionic liquid, oxalic acid as a catalyst, and CO₂ as pressurizing gas in order to enhance the degradability of cellulose in water. Cellulose and NaCl/oxalic acid solution (20 gr L⁻¹) was conducted under 70 bar of subcritical CO₂ in 125°C and various decomposition times (1 to 5 h). After decomposition time was achieved, the sample was separated between liquid and solid. For liquid product were analyzed by Dinitrosalicylic acid method (DNS method) using spectrophotometry UV-Vis and Liquid Chromatography – Mass Spectrometry (LC-MS). And solid products were analyzed by using X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). The result shows that the glucose concentrations was increase with an increasing decomposition time and reach a maximum at 4 hour. SEM and XRD showed the changes in the morphology and the structure of cellulose.

Keywords: cellulose, hydrothermal, hydrolysis, glucose

1. Introduction

Biomass is a valuable and available in abundance resource that can be obtained from various plants and can be converted into energy, chemicals, food, and other raw materials. The average biomass energy production in the world are 10 dry tons ha⁻¹ year⁻¹ (Cantero et al., 2012). In General, biomass contains some important substance; 35-50% of cellulose, 25-35% of hemicellulose, and lignin at 10-25% (Zhou et al., 2011). The main component of the biomass is cellulose. Cellulose is the most important component in plant or renewable materials sources since that are abundant in nature. The property of the cellulose which is insoluble in many solvent is a big challenge in the processing of cellulose for the effective utilization (Zhang et al., 2010). In fact, the degradation of cellulose without chemical modification is difficult to achieve because cellulose has a strong structure due to hydrogen bonding on the glucose chain.

There are several methods are commonly used in the degradation of cellulose; that is using ionic liquid, acid hydrolysis, enzymatic hydrolysis/fermentation, and hydrothermal processes (Zhang et al., 2010). The frequent method used for degradation of cellulose is fermentation and enzymatic. However, this method tends to take a long time and need a high level of sterilization equipment, so that high cost. Another promising method that can be used is processing with hydrothermal or; that use water at sub-/super- critical condition. At this condition water can dissolve almost all organic compound substances even with the gas phase. Another advantage of using water in this processing method is inexpensive, non-toxic, non-flammable and environmentally friendly.

Many studies about the hydrolysis of cellulose have been reported elsewhere. Sasaki et al propose a new method to hydrolyze cellulose rapidly in supercritical water (SCW) to recover glucose, fructose and oligomers (cellobiose, cellotriose, cellotetraose, etc) (Sasaki et al., 1998)). Stein et al conducted a study using NaCl and dicarboxylic acids (oxalic acid and maleic acid) in closed reactor system (T = 125°C and P = 30 bar) which produces oligomers and glucose products in the amount to 2.80-3.90 g/L (Stein et al., 2010). The use of NaCl

and oxalic acid under pressurization at low pressure gave a significant effect to glucose production. Therefore, it needs to improve the effectiveness and efficiency of the degradation process by investigation at higher pressure.

2. Method

Slurries of cellulose (20 g L⁻¹) were suspended in water, in which oxalic acid (0.1 M) and NaCl (20% w/w) were firstly dissolved. Cellulose degradation experiments were conducted at temperature of 125°C, pressures of 70 bar, and for various degradation times (1 to 5 hours). At the reactor, the slurry was rapidly heated up to its reaction temperature and the reaction was initiated. After the processing, the system was off and the reactor was taken out and immersed in an ice bath to stop the reaction. The sample was separated as liquid and solid to be analyzed. Solid component was washed with water and was analyzed with X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). Liquid component was measured by DNS method and Liquid Chromatography – Mass Spectrometry (LC-MS) analysis.

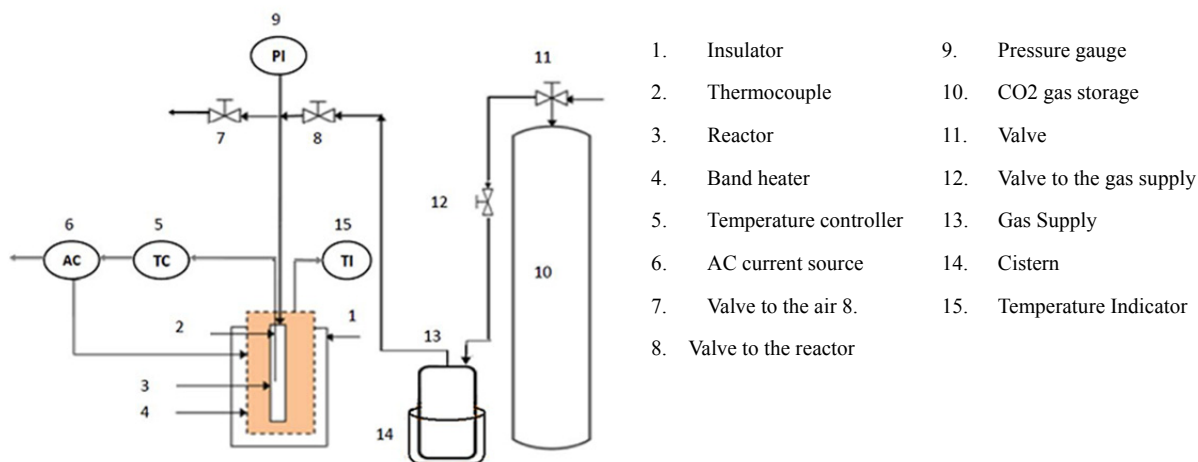


Figure 1. Experimental apparatus

3. Results

The process of cellulose degradation to produce glucose in the liquid NaCl and oxalic acid is addressed to improve ability to break cellulose chain. In this case, oxalic acid is as catalyst and has a role in the decomposition reaction. Products of hydrothermal process are liquid and solid. Liquid was analyzed by using 3,5-Dinitrosalicylic Acid (DNS) reagent and Liquid Chromatography – Mass Spectrometry (LC-MS), in order to estimate the concentration of glucose presence after decomposition reaction.

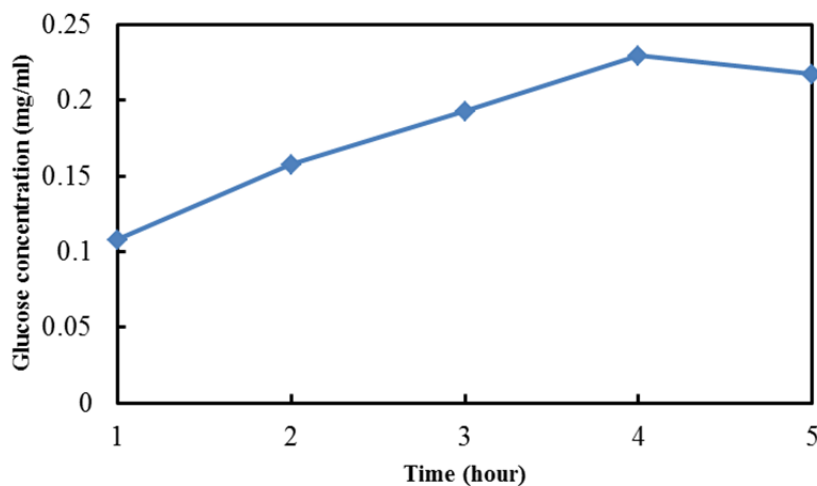


Figure 2. Effect of degradation time on the glucose concentration

Figure 2 shows the results of DNS analysis of sample processed for various degradation times (1 to 5 hours) and under 125 °C, and 70 bar. The glucose concentrations are increase with an increasing degradation time and reach a maximum value at 4 hour. The amount of glucose produced along the reaction of cellulose with ionic component of water, oxalic acid and sodium chloride. But, over then 4 hours further degradation reaction might be occurred, and lead to the decrease of glucose concentration. It can be understood that we found various glucose derivative compound in the product, such as 1,6-anhydroglucose, 5-HMF (hydroxymethylfuraldehyde), erythrose, from LC-MS analysis.

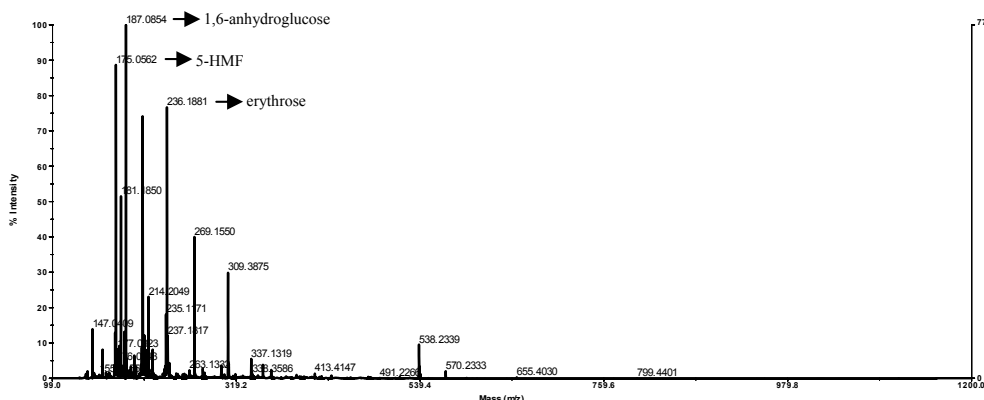


Figure 3. LC-MS of cellulose derivative products for 5 hours and at 125 °C

Figure 3 shows the results of LC-MS analysis of cellulose derivative products which indicates that the highest intensity with molecular weight of 187.0854 m/z is 1,6-anhydroglucose, followed by molecular weight of 175.0562 m/z is 5-HMF, molecular weight of 236.1881 m/z is erythrose, and as well as some of the same components with lower intensity.

Degradation process begins where the fluid system attack to damage intermolecular and intramolecular of hydrogen bonds, so as to break the chain of glycosidic bond between the glucose units. The presence of NaCl and ions can break the intermolecular and intramolecular bonds linking. Oxalic acid is dissociated to be dioxalic ions which were attach the glycosidic bond. Processing under subcritical pressure of CO₂ atmosphere lead to the existing of H⁺ and OH⁻ is higher than atmospheric. It causes the reaction to produce glucose monomer units were occurred fast. These are the catalytic condition triggered by multi ionic component amplified by subcritical pressurization by carbon dioxide under subcritical water, at which solubilisation of CO₂ in water occurred (Rogalinski et al., 2007).

Solid product was analyzed by using X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). SEM analysis obtained that change of cellulose structure and morphology in hydrothermal process, as seen in Figure 4.

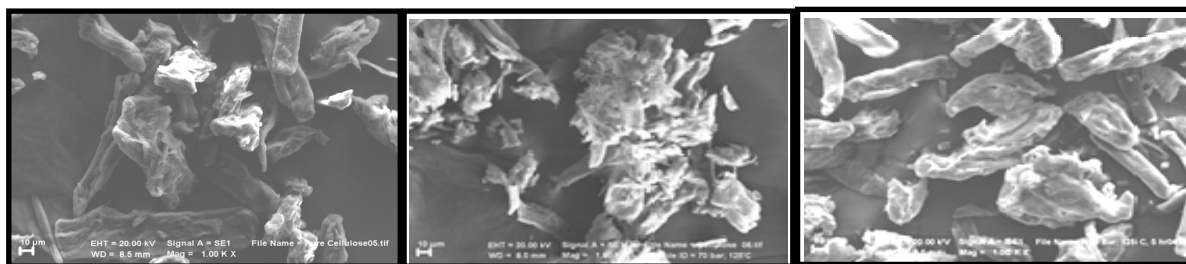


Figure 4. SEM analysis with 1000x magnification, (a) pure cellulose, and hydrothermal product at decomposition time: (b) 1 hour and (c) 5 hour

Figure 4 (a) is the result of SEM analysis of pure cellulose which indicates that the structure of main components is more tightly. While in Figure 4 (b) and 4 (c) are the result of SEM analysis with the longer hydrothermally decomposition time resulting in the surface structure of cellulose becomes more rugged and less dense. The changes in this structure are occurred because some surface of cellulose has degraded, so the degraded parts will

dissolve in water.

Furthermore, XRD analysis obtained that the cellulose crystallinity was changed after hydrothermal process. Pure cellulose has a crystallinity of 50.18%.

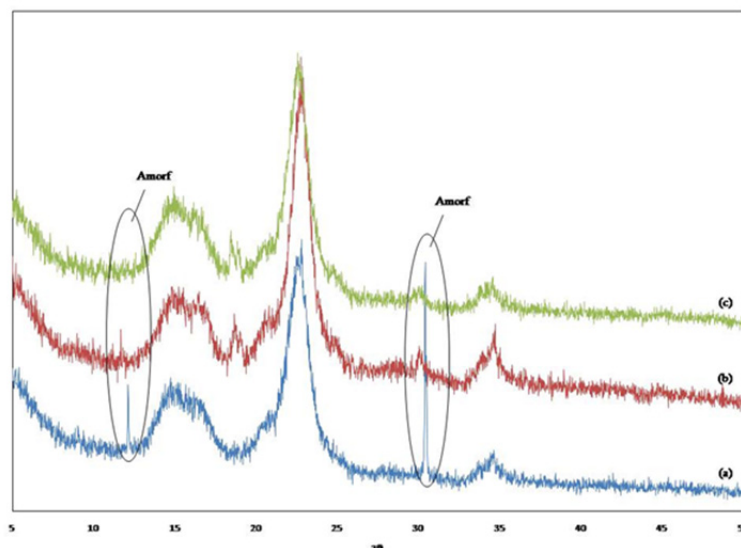


Figure 5. XRD chart of cellulose, (a) pure cellulosa, (b) hydrothermal at 1 hour, and (c) hydrothermal at 5 hour

Figure 5 show a XRD analysis graph of pure cellulose, and the cellulose after the hydrothermal processing. Cellulose after hydrothermal processing has a lower crystallinity compared to pure cellulose. Moreover, the crystallinity decreases with an increase in time. The crystallinity of cellulose after hydrothermal processing for a hour is 38.60% and for 5 hour is 29.79%. The decrease of crystallinity is caused by an increase of amorphous region in the bulk of cellulose. The addition of NaCl ions could disrupt hydrogen bonds in cellulose structure after after swelling and strongly water penetration of water under subcritical condition. Sasaki et al explains that the degradation of cellulose in hydrothermal conditions begins with the formation of swelling on the surface of cellulose. Water diffused on the surface of cellulose will stretch the constituent chains so will changes in the crystalline regions become amorphous (Sasaki et al., 2004).

4. Conclusions

Cellulose degradation process can be performed in subcritical water using NaCl and oxalic acid. The addition of NaCl is needed to break the intermolecular and intramolecular hydrogen bonds so that oxalic acid can easily enter and break the glycosidic bonds of cellulose. The result is the glucose concentration increase with time. For solid product, crystallinity of cellulose after hydrothermal processing for 1 hour is 38.60% and for 5 hour is 29.79%, as well as changes in the surface morphology of cellulose.

Acknowledgements

The authors are thankful for the financial support of the Directorate General of Higher Education of Indonesia through Penelitian Strategis Nasional 2014, grant No. DP DIPA-023.04.2.414964/2014.

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