Oligosaccharides can be formed at a temperature of 300 °C and a pressure of 3 MPa with and without ultrasound pretreatment was hydrothermally hydrolysed at the temperatures of 300, 320, 340, 360, 380 °C and at the pressure of 250 bars for 15 seconds. The ultrasonic pretreatment was conducted during an hour at 40 °C. We proved that ultrasonication made the cellulose more susceptible to be hydrolysed. The yield of glucose and oligosaccharide as a hydrolysis product with ultrasound pretreatment was higher than that of without ultrasound pretreatment. The highest yield of oligosaccharides was 8.59% obtained when the hydrolysis was carried out at the temperature of 380 °C. Whereas the highest yield of glucose was 33.6 % obtained when it was performed at a temperature of 300 °C. These hydrolysis products, glucose and/or oligosaccharides, were expected to be more easily converted into bio-ethanol.

Keywords: glucose, microcrystalline cellulose, oligosaccharide, renewable energy, sonication.

Introduction

Cellulose can be degraded by hydrolysis into glucose and/or oligosaccharides. Glucose, one of a hydrolysis product, can be used as a sweetener in foods and beverages as well as raw material for synthesis of ethanol, vitamin C (through Reichstein process), citric acid, gluconic acid, polylactate acid, and sorbitol (Schenck, 2006). Meanwhile, oligosaccharides can be used as a prebiotic substance that plays a role in the production of SCFAs (short-chain fatty acids). SCFAs compounds can prevent cancer, colitis and lowering cholesterol. (Niness, 1999; Mussato and Mancilha, 2007; Rivero and Santamaria, 2001; Qiang et al, 2009).

Some of hydrolysis methods has being developed such as enzymatic, acid catalytic, and hydrothermal hydrolysis. Mok and Antal (1992) conducted a study of the cellulose hydrolysis by combining hydrothermal high pressure with sulphuric acid as a catalyst. The temperature used in this study is 215 °C and a pressure of 34.5 MPa. by using a 0.05 wt% sulphuric acid and reaction time of 120 minutes obtained yield of glucose 71%.

Yu and Wu (1993) investigated a cellulose hydrolysis using supercritical water with and without a catalyst of nickel. Hydrolysis carried out at a temperature of 300 to 350 °C, in both processes was hydrogen gas produced either with or without a catalyst.

Sakaki et al (1996) conducted a cellulose hydrolysis and obtained 80% by weight of water soluble cellulose decomposition. They used a pipe shape of batch reactor and bath salt as a heater. The operating conditions used were 355 °C and 22 MPa. Reaction was carried out during 15 seconds. Definition of the reaction time in this study is the time needed to heat up until the variable temperature is reached. in this study was glucose obtained with the yield of 40 wt%.

Minowa et al (1998) conducted an experiment of cellulose hydrolysis in an autoclave at the temperature of 200, 300, 350 °C and the pressure of 3 MPa with nitrogen as pressurizer gas. The reaction was conducted for an hour counted after the reaction temperature is reached. Three variations of the process undertaken were namely cellulose hydrolysis without catalyst, with Na2CO3(s) or Nickel catalyst. The experiment showed that the hydrolysis of cellulose with the third variation has the resemble reaction pathway. The Cellulose is hydrolysed to glucose and then quickly the reaction continues to produce gas of H2, CO2, CH4 and char. The decomposition proceeded quickly at a reaction temperature between 260 to 300 °C. in this experiment was a little yield glucose...
obtained. The highest yield of glucose achieved at the temperature of 300 °C.

Sasaki et al (1998) propose a method for rapidly hydrolyse cellulose in supercritical water (SCW) to obtain glucose, fructose, and oligomers as Cellobiose, cellotriose, and others. Experiments were carried out in a flow reactor made of 1/8 in stainless steel pipes (SUS 316) with a temperature range of 290 to 400 °C and a pressure of 25 MPa. Hydrolysis products were oligosaccharides, fructose, glucose, and further decomposition such as erythrose, glyceraldehyde, 5-HMF, dihydroxy-acetone, piruvaldehid, 1,6-anhydrogluksa, and acid with a total yield of 75%. The results also showed that the temperature and reaction time could affect the hydrolysis products with high selectivity.

Ehara and Saka (2005) studied the decomposition of cellulose by using supercritical water (400 °C, 40 MPa) and subcritical water (280 °C, 40 MPa) as well as a combination both of them. The reactor used was two pieces of pipe flow reactor made of Hastelloxy C-276. The first pipe has a measurement of 19 mm length and 4 mm ID used for the process of supercritical water and a second pipe has length size of 7000 mm and 5 mm ID was used to process subcritical water. The experimental results obtained degradation products in the form of mono- and oligosaccharides and obtained the highest product yield of 66.8 wt% when it was used in combination of supercritical water and subcritical water.

Kamio et al (2008) studied the effect of the heating rate in the liquefaction of cellulose using hot compressed water. Reactor used in the study was a batch reactor with the temperature range of 443 to 553 K. The heating rate used in this case was between 0.0167 to 0.167 K/min. Based on the investigation results were known that cellulose was degraded at temperatures around 480 K and also known that the heating rate affected product yield.

Zhao et al (2009) used supercritical technology for hydrolysis of cellulose to obtain oligosaccharides. The reactor used in the study was a pipe reactor batch of stainless steel SS-316 with a capacity of 5 mL. Microcrystalline cellulose was used as a sample and a salt-bath was used as heating equipment. Hydrolysis products obtained in the study were oligosaccharides 34.9 wt% and glucose 7.2% that were achieved at the temperature of 380 °C and the pressure of 25 MPa during 15 seconds reaction time.

In the other hand, there are some researches of ultrasonic treatment on polymer that ultrasound be able to decrease intrinsic viscosity or molecular weight of the polymer (Zhou et al, 1997; Ostlund and Striegel, 2008, Mohod and Gogate, 2010; Goodwin, 2010). Thereby, the ultrasonic pretreatment on cellulose is expected to increase the effectiveness of the process of cellulose hydrolysis.

**Methodology**

**Materials**

Avicel microcrystalline cellulose (MCC) that has fiber length in the range of 60-80 µm, average particle diameter of 19.88 µm, and 77.70 % crystalline was used. This sample was produced by Asahi Kasei Chemicals Corp. Deionized water was used as a solvent as well as a hydrolysis reagent. Most samples were given cellulose pretreatment sonication while others without pretreatment. Sonication was carried out for an hour at 40 °C. Based on the study about effect ultrasound on the cellulose (Sumari et al, 2013) revealed that sonication on this polymer resulting optimal product.

**Methods**

Slurry of 1 % (w/w) cellulose in water was ultrasonicated at 40 °C within 1hour period. Ultrasonic bath SU-27TH which has an output power of 300 watts, frequency of 28 kHz, and 500 watts heater was used in this study. After ultrasonication, the colloid suspension was hydrolysed in a batch reactor during 15 seconds at various times. The resulting solution was stored at 5 °C for further testing. Each sample with and without sonication was hydrolysed using hydrothermal method. Stainless steel pipe SS-316 has a measurement of 3 in OD, 0.18 in ID, and length of 34 cm was used as a batch reactor with a capacity of 5.6 mL. Heater for hydrolysis process used in this study was band heater in the form of solid brass. Reactor temperature was set by using the heater control. Ultra High Purity (UHP) of Nitrogen gas is passed to raise the pressure in the reactor in accordance with a given pressure. The reactor was heated by means of inclusion in the band heater in various temperatures. Hydrolysis products were analysed using HPLC Knauer 2300 with RI detector (RID). Column Waters with the size of 3.9 x 300 mm used in this study. A flow rate of 0.9 ml/min of eluent acetonitrile 65 wt% at 30 °C was applied.

**Results and Discussion**

Slurry of 1wt% cellulose in water, with and without ultrasound pretreatment, was hydrolysed during 15 seconds in various temperatures of 300, 320, 340, 360, 380 °C. The results of cellulose hydrolysis were shown on Figure 1 and Figure 2. Hydrolysis product of sample with ultrasonic pretreatment produced yields of glucose and/or oligosaccharides was larger than that of non-ultrasonic pretreatment. The total yield of glucose product of sample was 33.6% much higher that of non-pretreatment ultrasonic. These results showed that there was a significant effect of ultrasound pretreatment on the yield of hydrolysis product. This phenomena indicated that ultrasonic make the
decomposition of easier to hydrolyse become monomer and/or oligomer of cellulose. The explanation for this phenomenon is that ultrasound presented in cellulose can reduce its crystallinity and particle as well as crystallite size (Sumari et al., 2013). Cellulose with more amorphous, lower particle and crystallite size cause water, a hydrolysis reagent, easily to penetrate into the cellulose structure so that cellulose more susceptible to hydrolysis than that of crystalline structure. Thereby, more cellulose reacts with water to produce glucose and/or oligosaccharides. It can be stated polymer of cellulose having smaller particle size and smaller crystallites size, and more amorphous structures was more reactive and more easily decomposed into glucose and/or oligosaccharides. Like the data shown in Figure 2, it can also be seen that cellulose sample with ultrasonic pretreatment when it was hydrolysed tended to produce glucose trend when the experiment was conducted at relatively low temperature 300 °C. But the highest product of cellulose hydrolysis preferred oligosaccharides, when it was done at relatively high temperature 380 °C. Cellulose hydrolysis with ultrasonic pretreatment performed at 300 °C was obtained yield glucose 33.6 wt%. While the highest yield of 8.59% oligosaccharides were obtained at the operating temperature of 380 °C. Glucose and oligosaccharides product occur from depolymerisation of cellulose through hydrolysis reaction. At a high temperature and pressure was concentration of H⁺ ion increased up to 100 times. 

The H⁺ ions play a role in breaking the glycosidic bonds in cellulose chain. Cellulose was decomposed to become smaller molecules namely glucose and oligosaccharides. The mechanism of glycosidic bond breaking can be described on Figure 3. Each sample was hydrolysed within 15 seconds counted since the desired temperature had been achieved, while the transient time between preheating temperature up to the desired temperature was not counted. The data showed that the highest total yield of hydrolysis product obtained at the lowest temperature 300 °C. It can be stated that at higher temperature glucose and/or oligosaccharides as a hydrolysis product were
degraded further and faster that formation of glucose and/or oligosaccharides. Therefore in order to obtain the optimum condition, hydrolysis reaction should be conducted at the lower temperature than 300 °C.

The highest yield of glucose obtained in this investigation was 33.6 wt%. It is high enough for the hydrolysis process without any catalyst Zhao et al (2009) in their study got the highest glucose yield of 27.2% when the hydrolysis product was done at the temperature of 378 °C, and a reaction time of 17 seconds. The results of this research also revealed that at low temperature was the hydrolysis product preferred to form glucose, but at high temperature was the hydrolysis product preferred to form oligosaccharides.

Conclusion

Ultrasonication made the cellulose more susceptible to be hydrolysed. The yield of glucose and oligosaccharide as a hydrolysis product with ultrasound pretreatment was higher than that of without ultrasound pretreatment. The temperature process of hydrolysis influenced selectivity of product. The highest yield of oligosaccharides was 8.59% obtained when the hydrolysis was carried out at the temperature of 380°C. Whereas the highest yield of glucose was 33.6 % obtained when it was performed at a temperature of 300°C.

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