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The Effect of $FeCl_3$ On The Microwave-Assisted Hydrolysis Process Of Lignosellulose From Sugar Cane Bagasse (Saccharum Officinarum L)

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Abstract

Microcrystalline cellulose is a modification of cellulose that functions as an additive widely used in the food and pharmaceutical industries. The raw material for microcrystalline cellulose is a material that contains high cellulose content, one of which comes from sugarcane bagasse. This study aims to examine the effect of the $FeCl_3$ concentration variable on the hydrolysis process of sugarcane bagasse to produce microcrystalline cellulose. The research method is to isolate microcrystalline cellulose by hydrolysing α-cellulose from sugarcane bagasse using H_2SO_4 and $FeCl_3$ solutions with four different concentrations, namely 1%, 2%, 3% and 4%. The analysis parameters consist of lignin content, cellulose and characteristics of microcrystalline cellulose. The results of the analysis show that sugarcane bagasse contains cellulose content of 38%, lignin content of 20.6. The delignification, bleaching and hydrolysis processes using microwave heating for 30 minutes and the addition of $FeCl_3$ produce lignin content of 5.1% and microcrystalline cellulose content of 55%.

Keywords: Sugarcane Bagasse, Hydrolysis, Microcrystalline Cellulose $FeCl_3$,

INTRODUCTION

Industrial waste in the agricultural sector increases along with technological developments in agricultural processing, one of which is sugarcane bagasse waste. This waste is produced from the sugar industry and some sugarcane juice drinks. The sugar production process will produce 5% molasses, 5% water, and 90% pulp. Sugarcane bagasse is a lignocellulose-based material that has a fairly complex substrate. Husin (2007) reported that the composition of sugarcane bagasse consists of 3.28% ash, 22.09% lignin, 37.65% cellulose, 1.81% juice, 27.97% pentosan and 3.01% SiO2. This lignocellulose has a fibre length of between 1.7 and 2 mm with a diameter of around 20 microns. The high cellulose content makes sugarcane bagasse a fairly abundant source of cellulose in Indonesia.

The heating method used in the delignification, bleaching and hydrolysis processes in this study was through microwave irradiation. Heating by microwave irradiation is one of the techniques that has good potential because it provides a volumetric heating process on increasing heating efficiency, easy to operate electronically, fast reaction time and its highly reproducible nature (sen G, 2012).

The addition of Lewis Acid in the form of FeCl3 is carried out according to the theory of acids and bases. According to Lewis, where Acid is a Chemical Compound (Substance) that can accept Electron Pairs from other Compounds (Substances) or can be said to be an Electron Pair Acceptor. In this case, $FeCl_3$ can bind lignin because lignin is also known as a raw material that can bind metal ions and prevent metals from reacting with other components that will make them insoluble in water.

Microcrystalline cellulose is obtained from the breakdown of long alpha-cellulose chains by hydrolysis. Microcrystalline cellulose can be made through a chemical reaction, namely by strong acid hydrolysis at a controlled temperature. Controlled acid hydrolysis can damage the amorphous region in cellulose micro fibrils, which will leave intact crystalline segments leading to the formation of single crystals (Berglund et al., 2010).

Considering the potential of sugarcane bagasse to contain α-cellulose compounds that can be used as raw materials for microcrystalline cellulose. Therefore, it is necessary to conduct research on the manufacture of microcrystalline cellulose from sugarcane bagasse with delignification, bleaching, and acid hydrolysis treatments with variations in the addition of $FeCl_3$. This study aims to examine the effect of $FeCl_3$ concentration variables on the hydrolysis process of sugarcane bagasse pulp to produce microcrystalline cellulose.

METODHOLOGY

Materials

The tools that will be used in this study include MAE (Microwave Assisted Extraction), water bath, oven, sieve, beaker glass, flat bottom flask, Erlenmeyer, measuring cup, soxhlet, measuring pipette, watch glass, funnel, porcelain cup, stirrer, hose, sieve, filter paper, rope, clip, label, plastic, scissors, spoon, jar, and rubber.

The materials that will be used in this study are sugarcane bagasse, urea, aquadest, hydrogen peroxide (H_2O_2), ferric chloride ($FeCl_3$), sodium hydroxide (NaOH), wash benzene, 96% ethanol, sulfuric acid (H_2SO_4) 72%.

Research Procedure

The procedures carried out in this study include the preparation stage, delignification, bleaching, hydrolysis, soxhletation, and maceration. The preparation stage includes preparing the sugarcane bagasse that has been dried in the sun and then screened using a milled 80 mesh sieve.

Delignification process

Delignification was carried out with a solid: liquid ratio of 1:30. Weigh 5 grams of screened sugarcane bagasse powder and add 150 ml of hydrotrope solution (urea).

The reaction mixture was put into a round bottom flask and put into MAE (Microwave Assisted Extraction) processed for 30 minutes at a temperature of 800C. After completion, the extraction results were filtered using a cloth, then washed with 1000 ml of hot water and squeezed. The residue was dried in an oven at a temperature of 105˚C until constant and then weighed.

Bleaching Process

The delignification results that have been oven-dried are added with hydrogen peroxide and sodium hydroxide solutions with a solid: liquid ratio of 1:20, put into a round bottom flask and then put into MAE (Microwave Assisted Extraction) processed for 30 minutes at a temperature of 800C. After completion, it is filtered using a cloth and then washed with 1000 ml of plain water. The residue is dried in an oven at a temperature of 105˚C until constant and then weighed.

Hydrolysis Process

After the bleaching process, the next stage is the hydrolysis process to obtain microcrystalline cellulose. The bleached material is then weighed as much as 5 grams then added with H_2SO_4 and $FeCl_3$ according to the variables carried out. Then put into MAE. The hydrolysis results are then washed with hot water as much as 1000 ml of hot water. Then the residue is put in the oven at a temperature of 1050C for 24 hours and then weighed.

Analysis

The analysis process in this study uses the Klason method according to SNI 0492:2008. The Soxhlet and maceration processes are carried out to determine the lignin content that is still contained or lost in the hydrolysis process sequence.

The data obtained from the observation results will then be analysed which includes lignin and cellulose.

Lignin Content

The sample obtained from the hydrolysis of sugarcane bagasse was taken as much as ±1.5 grams then soxhlet for 3.5 hours with benzene and alcohol wash solvents. The soxhlet results were then macerated for 6 hours. After that the maceration results were filtered using filter paper and then washed with heated distilled water until the acid content was lost. After that the solid obtained was put in the oven until a constant weight was obtained.

Lignin (%) = $\frac{final\ weight}{initial\ sample\ weight}\ x\ 100\%$

Cellulose Content

The sample used was the remaining maceration put into Erlenmeyer, then added 10 ml of NaOH solution. After 5 minutes added 5 ml, after 10 minutes added 5 ml and after 15 minutes added 5 ml. Then the mixture was stirred and left for 45 minutes. After that 33 ml of distilled water was added and left for 1 hour. After completion, the mixture was filtered using filter paper then washed with 100 ml of NaOH and washed again with 250 ml of distilled water. After that the residue obtained was put in the oven until a constant weight was obtained.

$$\text{Cellulose (\%)} = \frac{final\ weight}{Initial\ Sample\ Weight}\ x\ 100\%$$

RESULT AND DICUSSION

Preliminary tests have been conducted on sugarcane bagasse used as raw material by analyzing its lignin and cellulose content. The aim is to determine the effect of delignification and bleaching processes on lignin and cellulose content in sugarcane bagasse.

Delignification and Bleaching Process

The process of destroying the structure of lignin bonds can result in an increase in the amount of free cellulose in the material. According to Hartati (2019), hydrotope compounds in the form of urea can reduce lignin levels. Therefore, in order to increase the degradation of lignin produced, heating treatment (microwave exposure) is added during the delignification process.

The bleaching process on the pulp aims to increase the degree of whiteness, namely by removing chromophore components that absorb light in the pulp that has not been bleached, especially the functional groups of degraded lignin and the remaining lignin that has been changed. In addition to lignin, other compounds such as extractives and ash components, polyose and particles that are not perfectly delignified can also be removed in the bleaching process (pamilia, 2015).

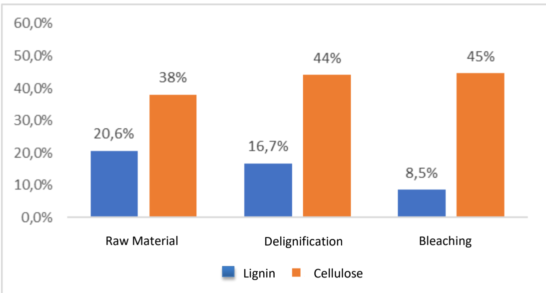

Figure 1. Comparison of lignin and cellulose content of sugarcane bagasse obtained through delignification and bleaching processes

Figure 1 shows the results of the delignification and bleaching process as an effort to reduce lignin levels and whiten sugarcane bagasse, quite significant results are seen in this process treatment, there is a decrease in lignin levels contained in the raw material which was initially 20.6% to 16.7% during the delignification process, and decreased drastically when the bleaching process was carried out, namely 8.5%.

The decrease in lignin during the delignification process reached 16.5% of the initial content.

The difference in the decrease in lignin levels in the bleaching process reached 49.10%, which was initially 16.5% to 8.5% with a yield of 58.74%. Meanwhile, research conducted by legiso (2018) provided yield results without mentioning lignin levels at a temperature of 110 minutes and a NaOH concentration of 3% of 66.1%. This shows that the concentration of NaOH is very influential in degrading lignin in the delignification and bleaching processes. Likewise, the cellulose content contained increased. The cellulose content in the raw material was 38%, during delignification it reached 44% and during bleaching it was 45%. The bleaching process was applied using microwaves at a constant temperature of 80 0C with medium power and a time of 30 minutes by adding 2% NaOH solution and 2% H_2O_2. Then separated by washing with hot water. Various impurities in the fiber are removed little by little and without causing serious damage to the fiber. The NaOH solution plays a role in breaking down lignin polymers into monomers that are dissolved in the liquid filtrate. The dissolution of lignin is caused by the transfer of hydrogen ions from the hydroxyl group in lignin to free hydroxyl ions to form water (Gilligan in Heradewi, 2007). The fiber bleaching process must use reactive chemicals to dissolve the lignin content in the fiber in order to obtain a high degree of brightness. However, it must be maintained that the use of these chemicals does not cause dangerous environmental pollution (Batubara, 2006). The resulting whiteness is also stable, not easy to turn yellow; the possibility of damage is small, because the oxidation power of hydrogen peroxide is smaller.

Effect of $FeCl_3$ Solution Concentration on Lignin

The results of this study analyzed the levels of lignin that can be removed using the Klason method. From Figure 2. Shows the results of successive lignin that can be dissolved in the FeCl3 concentration variable of 0%; 1%; 2%; 3%; and 4% are 9.5%; 6.3%; 6.0%; 5.6%; and 5.1%. The increase in FeCl3 concentration is directly proportional to the decrease in lignin, this can be seen from the graph above. During the hydrolysis process with variables without the addition of FeCl3, the lignin content was 9.5%, but when the FeCl3 concentration variable was 4%, the lignin content reached 5.1%. The lignin content value in the research process and raw materials decreased from 19.6% to 5.1%. The results are quite significant in reducing lignin levels. Lewis acid can bind lignin because lignin is also known as a raw material that can bind metal ions and prevent metals from reacting with other components that make them insoluble in water. FeCl3 as a popular Lewis acid, has been reviewed to be an efficient agent in hemicellulose degradation, increasing surface area, and enhancing hydrolysis of lignocellulosic biomass (Zhang et al., 2017). Therefore, the combination of Lewis acid (FeCl3) and acid hydrolysis can degrade hemicellulose into xylose and remove lignin fractions in lignocellulosic biomass.

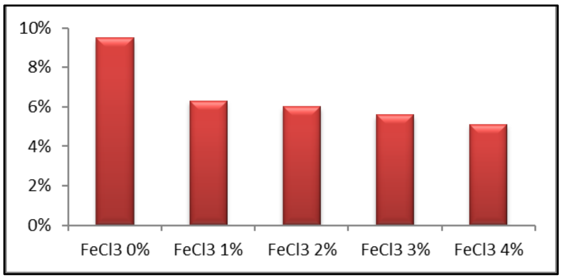

Figure 2. Lignin content of sugarcane bagasse obtained through the hydrolysis process

The method used in this study was assisted by microwave irradiation technology with an operating temperature of 80^{0}C for 30 minutes. This technology has also been tried in the preliminary treatment of lignocellulosic materials (Ooshima et al. 1984; Hu and Wen 2008; Keshwani 2009). Microwave irradiation technology has quite good prospects for development. Because microwaves have been able to break down complex lignin structures into simpler constituent structures (microwave digestion). Thus, lignin content can be reduced properly without damaging the cellulose structure.

Effect of $FeCl_3$ Solution Concentration on Cellulose Content

Figure 3. Shows that the cellulose content of sugarcane bagasse in the $FeCl_3$ addition variables of 0%; 1%; 2%; 3%, and 4% are respectively 47%; 50%; 49%; 52%; and 55%. The graph above shows that the effect of $FeCl_3$ concentration has an impact on increasing the cellulose yield obtained, this occurs because the lignin that is degraded is quite a lot so that the cellulose content is higher. The highest increase in cellulose at a $FeCl_3$ concentration of 4%, the higher the concentration, the pH in the acid solution will increase. These results are in accordance with research conducted by Nufus (2018) which states that the addition of $FeCl_3$ can affect the release of lignin so that it can increase the cellulose content. The cellulose content value in the process before and after pretreatment increased, from the control which was the cellulose content before the pretreatment process of 38% to 55%.

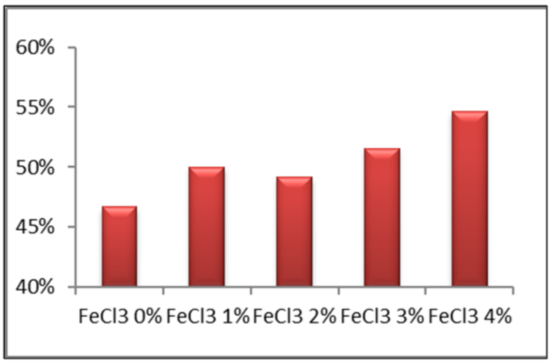

Figure 3. Cellulose content of sugarcane bagasse obtained through the hydrolysis process

Increasing the catalyst concentration will increase the rate of hydrolysis because the rate constant of the hydrolysis reaction will be directly proportional to the concentration of H+ in acidic conditions. The addition of low concentration strong acid can increase the quantity of cellulose in the lignocellulose hydrolysis process because the H+ ion in strong acid can break the glycosidic bonds that bind cellulose. With this hydrolysis, the cellulose contained in sugarcane bagasse will break down into microcrystalline cellulose.

Characteristics of Microcrystalline Cellulose

During the hydrolysis process, there is a partial separation of the cellulose micro fibril components where the amorphous form will break and leave a crystalline form, namely the area of cellulose molecules that are arranged regularly (Ma, Chang and Yu, 2008). The purpose of this process is so that α-cellulose which is a long-chain cellulose with a high degree of polymerization of 600-1500 is hydrolyzed so that the polymer is cut into smaller sizes (micro). According to Thoorens, et.al (2014) in the hydrolysis process using acid, there is a decrease in the molecular weight of microcrystalline cellulose between 30,000-50,000 g / mol because there is chain breaking in cellulose so that the DP of microcrystalline cellulose must be less than 400. The results of the polymerization degree test of hydrolyzed sugarcane bagasse can be seen in table 1.

Table 1. Data from polymerization degree testing results

Materials	DP test result	Source
sugarcane bagasse	925	Hallack and ragauskas (2011)
Microcrystalline Cellulose (MCC) Avicel PH	212	Zhang and lynd (2005)
Microcrystalline cellulose from hydrolysis process	373	This work

From table 1. shows that the results of the polymerization degree test of the hydrolysis results are 373, this proves that microcrystalline cellulose from sugarcane bagasse is suitable for use because it is still below the DP number set by Hallack and Ragauskas (2011) which is <400. However, this result is quite high when compared to Avicel PH as a microcrystalline cellulose product that has been circulating in the market. This is thought to be due to the process not running optimally, resulting in incomplete cleavage of the alpha cellulose chain.

Sensory analysis results Organoleptically including color, odor, taste and shape of microcrystalline cellulose with the use of 1N sulfuric acid and $FeCl_3$ have met the British Pharmacopeia (2002) standards, namely having a smooth texture, white, odorless, and tasteless. The results of microcrystalline cellulose can be seen in Figure 4.

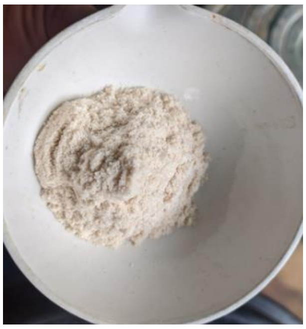

Figure 4: the result of Hydrolysis

Testing the degree of whiteness of isolated microcrystalline cellulose is needed to determine the quality of the powder color. The color of the powder that will be used as an excipient should be white so as not to interfere with the appearance of the resulting preparation, in addition to following the Handbook of Pharmaceutical Excipients (2009) standards which state that microcrystalline cellulose must be white.

CONCLUSION

Based on the research that has been done with various variables, it can be concluded that in the most optimum hydrolysis process based on the lignin: cellulose ratio, there is the addition of 4% $FeCl_3$ resulting in a lignin content of 5.1% and a microcrystalline cellulose content of 55%. The characteristics of the cellulose produced are also quite good, including a white color and a degree of polymerization of 373

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