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Effect OF $FeCl_3$ and Al_2O_3 Addition Toward Lignin Content on Corn Cob Delignification with NaOH as the Solvent by using Ultra Sonic Assisted

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ABSTRACT

Corn cobs are one of the many lignocellulose wastes highly available in all over Indonesia, one of them is in Banten. Lignocellulose waste is agricultural waste containing cellulose, hemicellulose, and lignin. Corn cobs contain cellulose (40-60%), hemicellulose (20-30%) and lignin (15-30%). To be able to utilize the cellulose content contained in corn cobs optimally, it is necessary to separate the lignin content in corn cobs. This study aims to examine the effect of the addition of FeCl3 and AL_2O_3 on the delignification process of corn cob with NaOH solvent using ultrasonic waves. In the previous study, 40% lignin in cellulose was obtained by using NaOH solvents with the help of ultrasonic waves at a temperature of 60 ^{0}C and an ultrasonic frequency of 40 KHz. Therefore, in this study a delignification process was carried out at a temperature of 60 ^{0}C with the ultrasonic frequency of 40 kHz with the addition of $FeCl_3$: NaOH, AL_2O_3: NaOH, AL_2O_3: $FeCl_3$ and $FeCl_3$: AL_2O_3 0:1; 1:1 and 2:1 respectively. The test results using the Chesson method showed that the lowest lignin content in cellulose was 12% at the ratio of NaOH: AL_2O_3 as 1:2.

Keywords: *delignification, corn cob, ultrasonic, cellulose*

1. INTRODUCTION

Corn is one of many agricultural products produced in Indonesia. Corn production in 2015 reached 11.87 thousand tons of dry shelled rice it was increased by 12.90% compared to 2014 which was 10.51 thousand tons. This increase was greatly affected by the increase in harvested area by 11.61 percent and an increase in the province by 1.15 percent (BPS 2018). With the increase in corn production, there will be an increase in unutilized biomass. One part that is not utilized from corn is corn cobs which contain 30% of whole corn (Fachry, 2013). Therefore from the data of corn production and the content of corn cobs in whole corn, in Indonesia, the potential of corn cobs waste is up to 356,100 tons per year.

Corn cobs are one of the many lignocellulose wastes available in Indonesia. Lignocellulose waste is agricultural waste containing cellulose, hemicellulose, and lignin. Each compound is potential to be biologically converted into other compounds. Cellulose is a carbon source that can be used by microorganisms as a substrate in the fermentation process to produce products which have high economic value (Shofiyanto, 2008). Agricultural wastes (including corn cobs), contain cellulose (40-60%), hemicellulose (20-30%) and lignin (15-30%). So far, corn cobs have not been utilized optimally.

The delignification process to obtain cellulose from corn cobs waste using chemical pretreatment has been carried out by Kanani (2017). From the cellulose content of corn cobs waste of 40-60%, only about 23% can be taken using this chemical pretreatment. Generally, these chemical pretreatments require a long time and usually use large amounts of solvents. According Hayati et al. (2012) extraction process with high temperature is known to be able to degrade components that are sensitive to heat, therefore it is necessary to look for non-thermal processes that can increase the effectiveness of extraction so that the time needed in the extraction process is not too long. One method to increase extraction capacity and effectiveness is by using non-thermal extraction methods, namely by sonication (Santos et al., 2009). In this study, the use of corn cobs waste will be produced to produce cellulose from corn cobs waste using ultrasonic radiation waves.

Corn contains approximately 30% corn cobs while the rest is skin and seeds. The composition of fibers in corn cobs can be seen in the following table:

Table 1. Corn Cob Composition

Composition	%
Water content	13.9
Ash	1.17
Chemical content analysis	
C	43.42
H	6.32
O	46.69
N	0.67
S	0.07
Abu	2.30
HHV (MJ/Kg)	14.7–18.9
cellulose	41
Hemicellulose	36
Lignin	16
Water and other	7

Source: Lachke, 2002; Saha, 2002

Lignocellulose is the main component of plants that describes the number of renewable sources of organic matter. The main elements of lignocellulose are cellulose, hemicellulose, and lignin (Perez et al., 2002). Lignocellulose is composed of microfibrils of cellulose which form clusters, with spaces between microfibrils filled with hemicellulose, and these clusters are strongly bound into one unit by lignin (Soerawidjaja and Amiruddin, 2007). Thus chemically, lignocellulose consists of three main components, those are lignin, hemicellulose, cellulose, and a little extractive content.

Lignin is a complex molecule composed of phenylpropane units that are bound in a three-dimensional structure. Lignin is thermoplastic, can soften at high temperatures (120^{o}C). Lignin is an adhesive material that is very effective and economical, which acts as a binder and can prevent metals from reacting with other components and makes them insoluble in water, Lignin is the most powerful material in biomass, but is very difficult to degrade, both biologically, enzymatically , and chemistry (Indraini, 2005 and Girisuta, 2007).

According to Anindyawati, Trisanti (2010), lignin is a compound which consists of phenylpropane units and derivatives that are bound in three dimensions as shown in figure 2.3. This complex three-dimensional structure causes lignin to be difficult to decipher by microorganisms. The lignin component in plant cells (guasil and syringe monomers) has an effect on the release and polysaccharides hydrolysis.

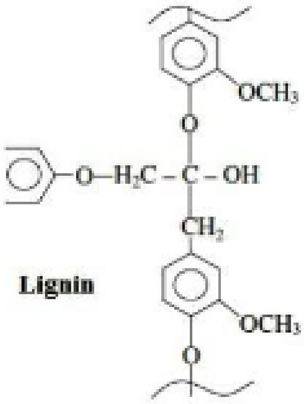

Fig. 1. Lignin Structure

From the cellulose content of corn cobs waste of 40-60%, only about 23% can be taken using chemical pretreatment (Kanani, 2017). Generally, this chemical pretreatment takes a long time and uses a large amount of solvent. High-temperature extraction processes are known to degrade heat-sensitive components (Fachry, 2013). Therefore, it is necessary to look for non-thermal processes that can increase the effectiveness of extraction so that in the extraction process less time is needed and less solvent is used. One method for increasing extraction capacity and effectiveness is by using non-thermal extraction methods, namely sonication. Sonication is a technology that utilizes ultrasonic waves (Sholihah, 2017).

Extraction assisted by the ultrasonic wave is an alternative extraction method that can overcome the limitations of conventional extraction processes (thermal processes). One of them is sonication extraction, which is extraction using ultrasonic wave.

Sonication extraction can increase the effectiveness of extracting alkaloid compounds, flavonoids, and polysaccharides from various parts of the plant. The sonication process starts from the formation of ultrasonic waves by a vibration source that propagates in the form of longitudinal mechanical waves in a solvent medium. These mechanical waves cause the phenomenon of acoustic streaming, which is a mechanical wave that can attenuate the corn cobs cell wall layer (Yuliandari, 2017).

In addition, the water medium which is traversed by ultrasonic waves will experience sealing when the wave pressure is high and will stretch when low wave pressure is followed by the formation of cavitation bubbles which increasingly enlarge until they finally break. The ruptured bubble releases a large amount of energy which masks the corn cobs cell wall to increase the pore diameter of the material that causes diffusion, thus bringing the material to be extracted into the water solvent used.

The sonication extraction process is affected by several factors, including temperature and time (sholihah, 2017).

The workings of the ultrasonic method in extracting are by means of ultrasonic waves which are formed from the generation of ultrasonic locally from the micro-cavitation around the material to be extracted so that heating occurs on the material, thus releasing the extracted compound. There is a dual effect produced, namely the cell wall disruption, thus freeing the content of the compounds in it and local heating in the liquid and increasing the diffusion of extracts. Kinetic energy is passed through all parts of the liquid followed by the appearance of cavitation bubbles on the wall or surface so as to increase mass transfer between solid-liquid surfaces (Fanggidae, 2013).

The addition of Lewis Acid in the form of $FeCl_3$ / AL_2O_3 / $FeCl_3$ + AL_2O_3 is carried out in accordance with the theory of acid-base according to Lewis, where acid is a chemical compound that can accept electrons from other compounds or as electron pair acceptors, while bases compound According to the Lewis Base Acid Theory is a Chemical Compound that can give an Electron pair to another Compound or as a Donor for Electron pairs (lathifa, 2015).

The mechanism for giving electron pairs based on Lewis acid theory can be seen in the following figure: Lewis Acid Theory

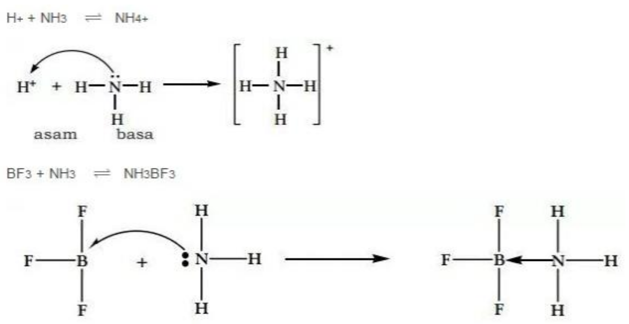

Fig. 2. Lewis acid

Lewis is a basic acid theory that developed the theory of acid and bases according to Bronsted Lowry because this theory has limitations and weaknesses such as when describing reactions involving compounds without proton (H^+). Gilbert Newton Lewis argues that the problem of the acid-base theory must be solved with the basis of Atomic Structure Theory, not just based on the results of experiments (research) only (Lathifa, 2015).

The advantage of Lewis's acid-base definition is that it can explain other acid-base reactions in solid, gas, and solvent media other than water that does not involve the transfer of protons. For example, reactions between acid oxides (eg CO_2 and SO_2) with basic oxides (eg MgO and CaO), complex ion formation reactions such as [Fe (CN) 6] $^{3-}$, [Al $(H_2O)_6$] $^{3+}$ and $[Cu(NH_3)_4]^{2+}$, and some reactions in organic chemistry (Lathifa, 2015).

In this case, Lewis acid binds to lignin and hemicellulose. Lewis acid can bind lignin because lignin is also known as a raw material capable of binding metal ions and preventing metals from reacting with other components and making them insoluble in water (Perdana, 2013), while hemicellulose is more soluble in alkaline solvents and easier to hydrolyze with acid (Pradana, 2017).

2. METHODS

2.1. Format

The stages of this research include preparation of raw materials in the form of sweet corn cobs and preparation of solvents in the form of $FeCl_3$/AL_2O_3/$FeCl_3$ + AL_2O_3 and distillate water, the extraction process uses the help of ultrasonic radiation waves and analysis of lignocellulose content on corn cobs.

2.2. Process for preparing raw materials.

This stage is carried out as follows: corn cobs are chopped into small sizes and then dried under the sun, the corn cobs are milled and sieved with a 60 mesh sieve until corn cobs powder was obtained.

2.3. The stages of cob powder delignification with the help of ultrasonic waves.

At this stage, corn cob powder is added to the sonicator. With a ratio of $FeCl_3$ + NaOH and Al_2O_3+ NaOH as1:1; 2:1 and 1:2 respectively. It was heated at a temperature of 60 ^{0}C for 2 hours. Then filtered and washed with water until PH neutral, then dried using an oven at a temperature of 105 ^{o}C until the weight is constant.

2.4. Methods of data collection and analysis

The analysis used in this research was Chesson-Datta method (Datta, 1981). The following are the steps:

a) Water content analysis procedure
b) Hemicellulose content
c) Cellulose content
d) Lignin content

3. RESULT AND DISCUSSION

This experiment was carried out by adding solvents varied between $FeCl_3$+NaOH; Al_2O_3+NaOH and $FeCl_3$+Al_2O_3 with their respective ratios of (0:1; 1:1; 1:2). The mashed corn cobs are added with various variations of the solvent and delignified using ultrasonic waves.

From the experiments that have been done the results of the smallest lignin content in cellulose are 11% at the ratio of NaOH: AL_2O_3 as 2:1. The results of the experimental analysis can be seen in Table 2 and the profile of lignin levels obtained is shown in the following figure 3.

Table 2. Analysis result

No	Concentration			Lignin	Cellulose
	$FeCl_3$ (%)	NaOH (%)	Al_2O_3 (%)	(%)	(%)
1	0	1		14	47.5
2	1	1		17	45.7
3	2	1		19.5	24
4		1	0	14	47.5
5		1	1	14	42.5
6		1	2	12	52.5
7	1		0	23	29
8	1		1	32	13.5
9	1		2	27.5	30.5
10	0		1	28.8	41
11	1		1	32	13.5
12	2		1	18.5	11

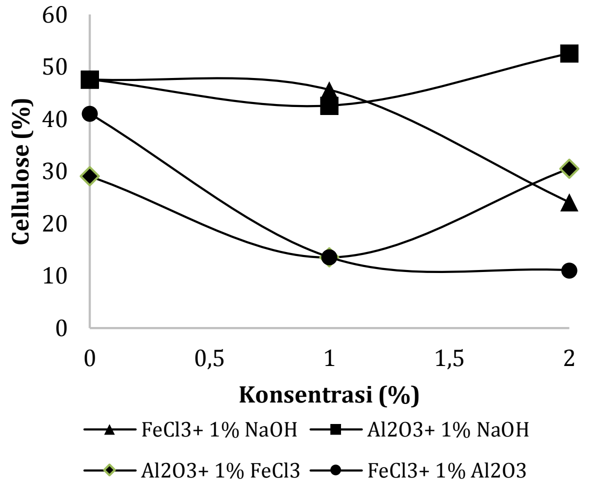

Fig. 3. Effect of solvent concentration toward cellulose content

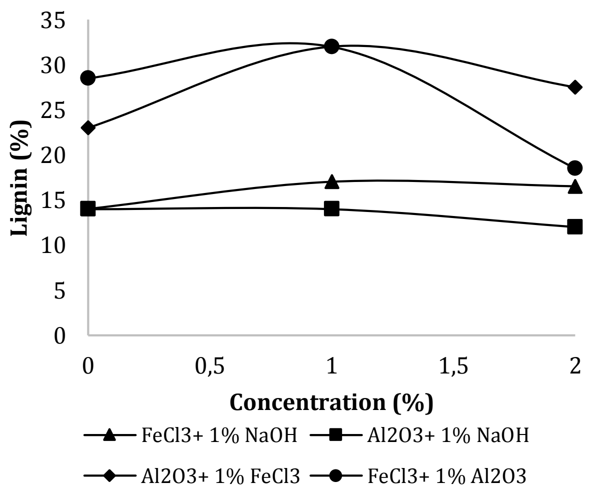

Fig. 4. Effect of solvent concentration toward lignin content

The profile of the influence of lignin levels measured in various variations of solvent concentration has increased first and then decreased. This phenomenon is suspected because there is the addition of Lewis Acid compounds in the form of $FeCl_2$ and Al_2O_3 in NaOH solvents. When using Lewis Acid as a solvent, the lignin content contained in cellulose is still very high. However, when a mixture of Lewis acid and NaOH was used, a decrease in lignin levels was contained in cellulose. The addition of Lewis acid to the NaOH solvent will make the phenol hydroxyl group protonate, condense and settle in polar solvents so that the cellulose will be degraded and the lignin content decomposes into monomers and the monomer reacts with lignin which is still present in the corn cobs to produce new lignin. (Pratiwi et al., 2016). The lowest lignin content in cellulose was 12% was obtained at the ratio of NaOH: Al_2O_3 as 1:2.

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