

Chemical and Physical Process Combinations: Microwave in Lignin Degradation of Pecan Shells as Alternative Fuel Raw Materials

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Abstract—Pecan shell is an abundant amount of biomass waste and has the potential as one of the fuels, with a very hard texture and having holocellulose content of 49.22% and lignin 54.46%. Whereas the pecan shell composition after in the form of 100 mesh powder was 33% hemicellulose, 17% cellulose and 34% lignin. In order to be used as an alternative fuel, one of the initial stages that needs to be carried out is through the process of degradation of lignin or the delignification of components present in pecan shells.

The process of concentration and microwave process time at microwave power 440 Watts was successfully degraded through a combination of chemical and physical processes with variables of NaOH. The NaOH concentrations used were 1N, 2N, and 3N while the delignification times were 5, 10, 15, 20, and 25 minutes.

From the analysis with the Chesson method, the lowest lignin levels reached 6% at 2N NaOH concentration and 20 minutes process time. With the data generated, it can be concluded that the process of combination of chemistry and physics can reduce lignin levels in pecan shell powder by 82.35%

Keywords—*Delignification, NaOH-Microwave, Cellulose, Hemicellulose, lignin*

I. INTRODUCTION

The increasing need for renewable energy to meet the lifestyle of today's society makes the competition for food and energy from biomass a trending topic in all parts of the world today, as an alternative energy raw material given the declining fossil energy needs, this makes researchers continue to research and develop biomass materials that can be used to replace it. One of the biomass that can be used as alternative materials is candlenut shells, the quantity of which is very abundant in Indonesia. The composition of the candlenut shell consists of 49.22% holocellulose and 54.46% lignin [1]. From the content of the candlenut shell has the potential as a renewable fuel both used as liquid fuel (bioethanol) and solid fuel.

Pecan shell raw material when converted into fuel belongs to the second generation group, which to produce liquid fuels must pass through four important stages namely

pre-treatment, hydrolysis, fermentation, and ethanol purification. Pre-treatment is needed to break down the size and structure of material that are still macroscopic and microscopic from a biomass into microscopic compositions and chemical components simple one and get more yields [2]. The purpose of pre-treatment is to open the structure of lignocellulose so that cellulose becomes more accessible by enzymes that break down polysaccharide polymers into sugar monomers. Lignin can be an inhibitor of the hydrolysis process because it will inhibit the activity of enzymes in yeast in the conversion of simple sugars into ethanol [3]. Therefore the pre-treatment process plays an important role in bioethanol production. This pre-treatment is also called delignification. Delignification aims to reduce the levels of lignin in lignocellulosic material. This delignification process will dissolve the lignin content in the material so as to facilitate the process of separating lignin from fiber. The pretreatment process by using NaOH has been shown to eliminate the lignin component (delignification) and can increase the porosity of the cellulose component and is one of the effective and inexpensive methods [4]. In some studies, delignification generally uses NaOH. In his research on bagging delignification was using NaOH delignificator 2%, 4% and 6%. The results showed the most reductions in lignin were obtained through the use of 6% NaOH which was 32%, from 17.65% to 11.9%). [5]. Whereas previous studies using candlenut shells obtained 76% cellulose content at 15% NaOH concentration, KOH alkali type with a concentration of 15% with a value of 77.67%, and with a Ca (OH) 2 alkaline pretreatment type obtained at a concentration of 15% with a value of 65, 33%. [6]

Delignification research by physical-chemical method is still rarely done, Maharani did delignification with 0.5 M NaOH solution and 950 Watt microwave power on kepok banana stems yielding cellulose yield 27.265% and lignin 3.26% [7] While Sari did delignification on corncobs using corncobs NaOH 2N and a 40 minute microwave produce cellulose at 69.937% and lignin decreases to 9,006%. [8]

According to many researchers the combination of chemical and microwave pretreatments from various raw materials results in higher cellulose and alkaline solutions eliminating lignin. In addition, all previous research has done a lot of processing time for 1 hour, so we also use processing time as another research variable. The delignification of pecan shells is still rarely studied and researchers who have already been namely Dewi have not yet produced maximum cellulose levels or decreased levels of lignin so research needs to be done with the addition of appropriate variations to get optimal cellulose levels. [6]

From these problems the researchers tried to combine the decomposition of lignin through chemical and physical processes Microwave with 440 Watts power and the addition of NaOH to the candlenut shell.

II. MATERIALS AND METHODS

A. Material delignification process

Candlenut Shell powder obtained from the size reduction process of the Candlenut Shell with a size of 100 mesh, NaOH with concentrations of 1N, 2N and 3 N and acetic acid used for neutralization

B. Material preparation

In the early stages the candlenut shell is cleaned first from impurities which is followed then after cleansing the candlenut shell is dried in an oven at 105° C for 24 hours to remove the water content in the candlenut shell. After being dried the pecan shell is crushed with a disc mill until it becomes ± 100 mesh size powder.

C. Delignification process

Weighing as much as 3 grams of hazelnut powder is put into the beaker glass, adding a pre-treatment solution (NaOH) with a concentration according to a variable with a volume of 30 ml. Comparison of candlenut shell powder with a type of NaOH solution is 1: 10. Inserting into the microwave with a time variation (5, 10, 15, 20, and 25 minutes), the microwave power used is 440 Watts. After that the sample is neutralized with acetic acid to neutral pH. Lighten again using the oven with a temperature of 105° C for 12 hours. And finally the analysis of lignin, cellulose and hemicellulose was carried out by the Chesson Method.



Fig. 1. Lignin Delignification Process From Pecan Shells

III. RESULTS OF RESEARCH AND DISCUSSION

A. Delignification of physics (destruction)

Analyzing pecan shells powder with a size 100 mesh. From the analysis results obtained hemicellulose content of 33%, cellulose content of 17% and lignin content of 34%. While from the literature found in the early candlenut shells it has a lignin content of around 54% and 49.22% holoselulose. From the results of the initial treatment or physical pre treatment can reduce lignin levels as much as 38.18%. Because by changing the size can cause a lignin structure that is separated or detached.

However, the content of each lignocellulose compound depends on each raw material used.

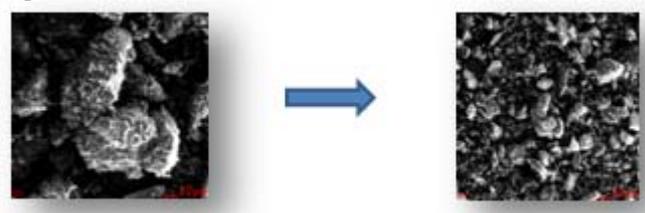


Fig. 2. Pecan Shell Structure with Sem-Edax

Scanning Electron Microscopy (SEM) With Energy Dispersive X-Ray Analysis (Edx or EDA) is also used provide elemental identification and quantitative compositional information. EDAX is a leading provider of innovative materials characterization systems encompassing Energy Dispersive Spectroscopy (EDS), Electron Backscatter Diffraction (EBSD), Wavelength Dispersive Spectrometry (WDS), Micro X-ray Fluorescence (Micro-XRF), and X-ray Metrology.

Based on Sun & Cheng's theory (2002) there are several factors that influence the physical delignification process, one of which is the sample size. The size of the sample can affect porosity which then affects the contact with the delignificator. [9] In addition, decreasing the sample size will break the long polymer chain into a shorter polymer chain making it easier to separate lignin from cellulose bonds [10].

According to Maharani (2015) in his research using kepek banana stems, the initial treatment (physical destruction) made the size of the material 100 mesh has a cellulose content of 31.89% hemicellulose 24.17% and lignin 6.845% [7]. Whereas in Permatasari research (2011), bamboo was crushed into 100 mesh powder and lignin was obtained at 9.13% [11]. In the study of pineapple leaves by Novia, making 100 mesh pineapple leaf powder contains 28% cellulose content and 3.392% lignin. [12]

B. Delignification Results Analysis (Lignin Degradation Process)

From the above explanation it can be said that the candlenut shell through the initial treatment process or the physical delignification process (destruction of the material)

can cause the breaking of the lignocellulose polymer chain which was originally long to be shorter. The next stage is candlenut shell powder, dissolved with NaOH will react chemically then put in a microwave to continue the chemical-physical delignification process.

The mechanism of lignin degradation is initiated by the attack of H atoms bound to the phenolic OH group by hydroxide (OH⁻) ions from NaOH [13]. The hydroxyl group in phenol is difficult to decide due to the shifting or movement of electrons due to the double binding bond next to it, so that phenol is only able to release hydrogen atoms in the hydroxyl group instead of OH⁻.

H atoms in that part are acidic because they are bound to atom O which has a large electronegativity. The more electronegative O atom will attract electrons on the H atom, so that the H atom will be positively partially charged and easily separated into H⁺ ions. Acidity is also affected by the resonance effect of the alkyl group in the para position, so that the H atom in the phenolic group will be more acidic. The hydroxide (OH⁻) ion from NaOH will also break bonds from the basic structure of lignin while the sodium ion (Na⁺) will bind to lignin to form sodium phenolate. This phenolic salt is easily soluble in distilled water [14]. The lignin phenolic hydroxyl group is ionized to form its salt and is polar so that the phenolic salt dissolves easily in water. The energy of electromagnetic waves and also the heat generated by microwaves, causes the ease of lignin as the outer layer to be degraded. In addition, the reaction with NaOH also accelerates this degradation process. Microwaves are expected to help accelerate the breakdown of H⁺ groups that bind to OH⁻ and then form phenolic salts so that from these two physics-chemical processes, the lignocellulose polymer chains will quickly decompose. Next, the lignin chain will separate.

Furthermore, the lignin chain will separate from the lignocellulose chain bonds by dissolving in water or distilled water. This is why in the analysis process reflux is done using distilled water. In addition, washing is also done for several times using warm water. In this process lignin which contains phenolic salts or other hydrophilic groups will dissolve with water and leave cellulose compounds and some hemicellulose.

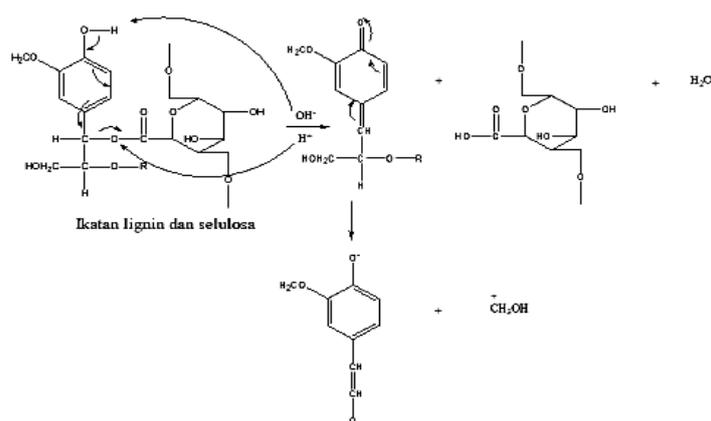
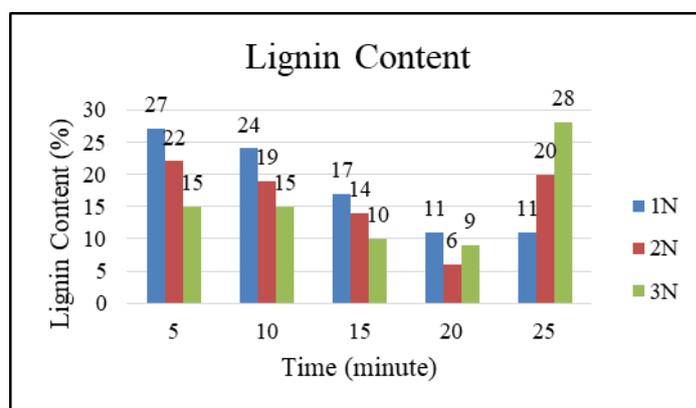


Fig. 3. Mechanism of Termination of Bonds between Lignin and Cellulose by Nucleophils OH

Chemical and physical pre-treatment can reduce levels of lignin and increase cellulose levels better than just physically or chemically. Candlenut shells as we know are very hard so that they will automatically contain more lignin, unlike other biomass wastes (such as rice straw, bagasse, banana fronds, etc). Delignification in microwaves using microwaves aims to break down the complex lignin structure into simpler constituent structures.

TABLE I. TABLE OF EFFECTS OF DELIGNIFICATION TIME AND NAOH CONCENTRATION ON LIGNIN CONTENT



As in Table 3.1 it was found that the longer the processing time the lower the lignin content. The lowest lignin content in 1N NaOH concentration is 11% at 20 minutes with a percent decrease reaching 67.65%, lignin at the 25 minute is also 11% which is the same as the 20 minute this shows that 20 minutes is the optimal time to degrade lignin so that in the 25 minute it cannot degrade lignin again. The lowest lignin content in 2N NaOH concentration is at the 20th minute which is 6% with a decrease in percentage reaching 82.35%. While the lowest lignin content was at the 3N NaOH concentration which was 9%, at 20 minutes with a percent reduction reaching 73.53%. This proves that the longer the lignin content also decreases and the most optimal time to reduce lignin is 20 minutes. Yang Haiping explained that hemicellulose degradation occurred at 220–315°C, cellulose occurred at 315–400°C and lignin occurred at 100–900°C [16]. So the

researcher's hypothesis states that at the 25 minute the temperature in the material reaches above 315°C which results in cellulose being degraded along with lignin. The incident was due to the longer exposure to microwaves to the ingredients in the alkaline solution resulted in more degraded lignin. This is related to the effect of heat caused during the time of microwave exposure. The longer the exposure time, the effect of heat generated by electromagnetic waves also increases so that it can degrade bonds in lignin more. This is in accordance with Sumada's opinion which states that temperature and pressure affect the delignification process, namely the greater the temperature and pressure, the faster the processing time [17]. Meanwhile, according to Maharani in his research, it shows that the longer the pretreatment time, the temperature that occurs also rises, this happens because of the heat transfer from the microwave to the material will continue to occur over time [7]

Based on the theory, there are several factors that influence the delignification process, namely the concentration of the cooking solution and the comparison of the cooking solution with the raw material. If the lignin content used is large, the concentration of the cooking solution must also be large. In addition, the smaller the comparison of the cooking solution with the raw material, the degraded lignin will also be smaller. The cooking solution in this process is an alkaline solution (NaOH), where the OH⁻ ion from NaOH will break the bonds of the basic structure of lignin while the Na⁺ ion will bind with lignin to form sodium phenolate. This phenolic salt is soluble. Dissolved lignin is marked in black in a solution called black liquor [14]. This is in accordance with this research that during the delignification process that is brown candlenut shell powder added with a solution of NaOH to become black.

The neutralizing filtrate at each residue becomes colorless and clear because the remaining NaOH solution, phenolic salt and hemicellulose which are still left in the residue are carried away during washing. The residual color from cellulose extraction from processing waste so that it is almost the same that is light brown and different from the initial sample color which is dark brown. According to Coniwanti, the destruction of lignin compounds by NaOH causes an increase in cellulose levels and can be seen through visual observation of softer color and structure changes [18]. This shows that the components of lignin and hemicellulose which are bound to cellulose in each residue are reduced. At 1N NaOH concentration, it can reduce lignin up to 67.64%. This also occurs at 2N concentrations which can reduce lignin reaching 82.35% and at 3N concentrations where the percent decrease in lignin reaches 73.53%. The decrease in lignin occurs along with the large concentration of the cooking solution in this case, namely NaOH. However, at 3N concentrations the decrease in lignin is still below 2N concentrations so that it is possible that at 3N concentrations the resulting temperature is greater and it is possible more than 315°C which causes cellulose to degrade with lignin.

So from the various factors that influence the delignification process, it is obtained the most optimal

results to reduce lignin in candlenut shell powder, namely the concentration of NaOH 2 N with 20 minutes with a percent decrease reaching 82.53% which produces 6% lignin content with 50% cellulose content. Microwave-NaOH delignification is a type of physics-chemical delignification. The main purpose of the microwave treatment process is to break the complex lignin structure into simpler constituent structures. So that the hydrolysis process and subsequent processes to get bioethanol will be easier to occur. Interaction of the microwave with the material during pre-treatment, will produce a thermal effect which is the response of polar molecules and ions to change the direction of the electric field produced by electromagnetic waves at microwave frequencies. Polar molecules are stretched outside the electromagnetic field, but oscillating (alternating movements) of the electric field from microwave radiation causes polar molecules to vibrate rapidly as a result of lignin which is straightened in the electric field [19].

According to Maharani in his research explained that the longer the pretreatment time, the temperature that occurs also rises, this can be expected that the transfer of heat from the microwave to the material will continue to occur over time. Then, if seen from the higher volume of the solvent, the lower the temperature that occurs, this is allegedly due to heat transfer that occurs when direct microwave irradiation heat of the material then heat spreads to all areas in the container through the solvent and the material itself so that heat transfer occurs convection. Heat transfer to all areas of this material will be faster to all areas if the volume used is the smallest volume. Because the fastest spreading of the temperature is the smallest volume, the high temperature is the smallest volume treatment. [7]

In the microwave there are also several variations in the strength of the power (P). It is estimated that the higher the power used, the greater the microwaves generated and the higher the temperature generated by the microwave so that degradation of lignin can occur more quickly in just a few time. However, the components of lignocellulosic compounds also have a limit or resistance to temperature until they degrade.

Microwave ovens convert electrical energy into heat energy so that this tool can work to heat the food in it. In accordance with the equation of the energy formula:

$$P = \frac{E}{t} \dots\dots\dots (1)$$

Power is directly proportional to the amount of energy produced per unit of time. The greater the power used, the higher the energy produced, so that the selection of microwave power in this study is 440 W which is the standard power of 950 W maximum power intended so that the heat generated is not too high during the delignification process so as not to damage the components of the compound that is not desirable like cellulose

IV. CONCLUSIONS

Based on the analysis results o NaOH solution, the more lignin is degraded and obtained the 2N NaOH concentration is the most optimal way to degrade lignin. And the longer the

delignification time, the more lignin is degraded and the most optimal time is 20 minutes to degrade lignin, which is produced by 6% or it can be said that these conditions can reduce lignin by 82.35%.

ACKNOWLEDGMENT

The researcher would like to thank the ITN Malang Research Institute and the Directorate of Higher Education for supporting our research and providing an opportunity to qualify for a 2019 external research grant.

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