Utilization of sugarcane bagasse and banana midrib mixture as raw materials for paper making using acetosolve method

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Abstract. Paper making requires raw materials with high cellulose and hemicellulose content. The alternative materials that can be used in the paper making are sugarcane bagasse and banana midrib. The paper production method used in this study is acetosolve which involves acetic acid as an organic solvent. The objectives of this research are to figure out the acetic acid concentration in delignification process and the ratio between sugarcane bagasse and banana midrib that produce pulp with the highest yield, cellulose and kappa number. In this research, there are some variables, the first is the levels of acetic acid concentration in delignification process, which are 70%, 75%, 80%, 85%, 90%, the second is the ratio between sugarcane bagasse and banana midrib, which are 20:0, 18:2, 16:4, 14:6, 12:8, 10:10. The results show that the best pulping conditions are found to be 80% acetic acid concentration with 12:8 (w/w) ratio between sugarcane bagasse and banana midrib, and also 1:20 (w/v) ratio between raw material and solution of acetic acid at two hours cooking duration. The highest yield of pulp in acetosolve process was 63.1%, and its characteristics are 84.67% of cellulose and 10.44 kappa number.

1. Introduction
The use of paper in the world recently continues to increase and begins to reach a very high number, so it can be predicted that the need for wood as paper’s raw material will increase sharply, this will lead to massive forest exploitation that can affect the environment, thus this needs special attention. In Indonesia, the level of paper consumption is very high. According to the Pulp and Paper Association Directory of Indonesia, paper’s consumption makes trees become less and less. 65 - 97 million trees per year were logged to meet pulp and paper’s production needs [1].

In paper’s production, the main ingredient used is known as pulp. There are several agro-industrial wastes that can be used as raw materials for pulp making, one of those is bagasse and banana midrib. There is a large quantity of waste from sugarcane agro-industry. Therefore, we may obtain around 140 kg dry weight bagasse. In this way, around 80 million tons of bagasse is produced annually in 8.4 million hectares of land. Bagasse consists about 40 - 50% cellulose and 20 - 30% hemicellulose and lignin of 18 - 25% [2].

Xylose is the main carbohydrate found in the hemicellulose fraction, which represents about 80% of the total sugar from hemicellulose [3], [4]. Because the ash content is low (1 - 3%), bagasse has many advantages compared to the rest of other plants such as rice straw and wheat straw, which each contains 17 and 11.0% of ash [5]. Therefore, bagasse is a potential lignocellulose material for pulp production [6]. Bananas are one of the most traded fruits in the world, especially by developing
countries and industrialized countries. In addition to sufficient nutrition, banana plants also contain various kinds of polymers such as cellulose, hemicellulose, pectin and lignin which have fiber with strong mechanical properties.

One of pulping process that is often used is organosolve. The organosolve’s delignification takes advantage of the higher affinity of lignin oligomers to dissolve in organic solvents [7]. Organosolve process has several advantages, including high yield of pulp and black liquor extraction which can be done easily, also obtained byproducts in the form of lignin and hemicellulose with relatively high purity [6], [8]. Organosolve pulping is also known as acetosolve process. The acetosolve process is a process based on the solubility or oligomeric lignin in certain organic solvents such as ethanol, organic acids and ketones. In addition, the catalysts (sulfuric acid, hydrochloric acid or phosphoric acid) are used to initiate the breakdown process of the ether’s configuration and to increase the lignin extraction [9].

Main factors that influence the success of acetosolve pulp cooking are the ratio between the amount of solvent and water, the ratio between the amount of solvent and the raw material, cooking temperature, cooking time, the type and concentration of the catalyst used [7], [10]. The addition of HCl is to accelerate the reaction and reduce the temperature of the pulping process, so that the energy needed for the pulping process will be less [10]. Therefore, it is necessary to study the concentration of cooking solution, the ratio between the amount of cooking solution and raw material, also the ratio between bagasse and banana midrib as well as the cooking time in order to produce pulp with a good quality.

2. Material and Method

The raw materials used in this study were sugarcane bagasse and banana midribs obtained from Lawang District of West Sumatra and the banana-type is Musa acuminate. The chemicals used include: glacial acetic acid, HCl, H$_2$O$_2$, CMC (Carboxyl Methyl Celulose), and aquades. The equipments used were pulp delignification using pyrex 1000 ml erlenmeyer, hotplate (polyscience), thermometer, 4-digit analytic balance (Ohaus), desiccator, oven, acid chamber, and chemical test analytical tools.

Sugarcane bagasse and banana midribs are firstly dried in the sun and then cut into 4-6 cm. After that, smooth them in a blender and dry the mixture using an oven at 110°C. The ratios of sugarcane bagasse and banana midribs used in this study are 20:0 ; 18:2 ; 16:4 ; 14:6 ; 12:8 and 10:10 (w/w). The cooking process of sugarcane bagasse and banana midrib was carried out using 70%, 75%, 80%, 85% and 90% of acetic acid solvent with the addition of 1% HCl as the catalyst. The weight of each of raw material with cooking solution used in every time cooking in this study is 20 gr. The raw material is put into 1,000 ml of erlenmeyer along with glacial acetic acid and HCl on each treatment. The cooking temperature used is 110°C. The duration of cooking is 120 min after the process temperature is reached. Afterwards, the mixture is filtered and washed with running tap water at a room temperature until it neutral or the washed water becomes clear. The mixture is now can be called the wet pulp is proceeded to the bleaching process using hydrogen peroxide. The bleached pulp is then washed again and placed evenly on flat surface and then dried using an oven at 80°C. Finally, the dried pulp is now can be analyzed for the yield, cellulose and kappa levels to determine the best pulp from the treatment given.

3. Results and Discussions

Choosing sugarcane bagasse and banana midrib as biomass to substitute wood in pulp making in this study is very beneficial, they are economical and easy to obtain, they have relatively high cellulose content (65% and 40%) and also quite low lignin content (5% and 20%) [11]. In pulping, we choose the organosolve process which is the acetosolve method. Acetosolve is a process of fiber separation using acetic acid solution as an organic solvent with a high temperature and pressure which has some advantages: are low cost, environmental friendly, and can be carried out with or without the help of catalysts But in this study, we used the help of 0.1% HCl catalyst to accelerate the delignification reaction, because in the previous studies [12], it was concluded that the catalyst was able to produce the lowest lignin of 26% with the yield of 84.2%.
In the process, the pulp goes through two stages, namely cooking (delignification) and bleaching. Delignification is the process of lignin removal from cellulose which occurs due to the breaking of the ether and macro bonds of lignin molecules with the aid of organic solvents [13]. The removal of lignin from cellulose in this process is marked by the discoloration of the cooking solution that turns black which is called black liquor or black liquor. The black liquor is formed due to the degradation of the lignin content into smaller molecules that can be dissolved in organic solvents. Bleaching is the process of purifying cellulose from the remaining lignin by using peroxide (H₂O₂) as the solution and CMC (carboxyl methyl celulose) as the adhesive. Hidrogen peroxide (H₂O₂) is chosen in this study because it does not give any damaging effect to the cellulose and it is free of chlorine so it is not harmful to the environment, but not only that, H₂O₂ is also able to increase the brightness of white colour from delignified pulp [14]. While the use of CMC as an adhesive aims to strengthen the bonds between fibers and can preserve paper so that paper can be obtained with high tensile quality, then ready to be printed into sheets called paper [13]. In the pulp making, the effects of the variation in the ratio of pulp raw materials are tested, sugarcane bagasse and banana midrib with various concentrations of cooking solution namely green acetic acid (CH₃COOH) through several pulp quality tests such as yield, cellulose content and kappa number. All of these characteristics are related to each other in supporting the quality of the pulp produced. Pulp can be categorized as high quality with high rendering, high cellulose content and small kappa numbers. The purpose of this study was to obtain pulp yields with quality resembling the quality of wood-based pulp.

3.1. The Effect of Sugarcane and Banana Midrib Mixture Ratios with Acetate Acid Concentration on Pulp Yield (Rendemen)

Sugarcane bagasse and banana midribs are a type of biomass from wastes that can replace wood as raw material for pulp. This is because sugarcane bagasse is the solid waste from sugar indutry with cellulose content of 32% - 48%, pentose 27% - 32% and lignin 19% - 24% [5]. Whereas both banana midribs are used as raw material for pulping due to low lignin content of 5%, cellulose 63% - 64% and hemicellulose of 20% with relatively long fiber which is about 4.29 mm [11]. In paper making, it is desirable for raw materials with high cellulose content. This is due to the high levels of cellulose can produce high yields and have the function of forming inter-fiber links with H bonds between hydroxyl groups in cellulose [4].

Based on the explanation above, it is known that the composition of the raw material for making pulp and the concentration of acetic acid as the cooking solution has an important role to produce high pulp yield. This is shown from the results of the research that has been carried out as illustrated in figure 1.

![Figure 1](image-url)

**Figure 1.** The effect of raw materials ratio and acetic acid concentration on pulp yield
Based on figure 1 above, it is known that the greater the composition of sugarcane bagasse added, the greater the yield produced, this is because the cellulose content of the sugarcane is greater than the banana midrib. The variation of acetic acid concentrations in the graph shows a significant difference on each yield produced. The greater concentration of acetic acid causes the mole of acetic acid to react with lignin to become larger so that when the cooking solution has almost completely hydrolyzed lignin, the solution also reacts by destroying cellulose polymerization bonds and decreases the levels of cellulose which results in lower yield of pulp [15]. Therefore, at the concentration of acetic acid 90%, the pulp yield decreases.

3.2. The Effect of Sugarcane Bagasse and Banana Midrib Ratio with Acetate Acid Concentration on Cellulose Percentage

Cellulose (C_{6}H_{10}O_{5}) is a major component in paper making. Cellulose is the main organic compound that forms the cell wall of plants. From the results of the study, it has been known that the ratio of sugarcane bagasse and banana midrib with variations in the concentration of cooking solution has an important role for cellulose content in pulp to achieve the best pulp quality. It is known that the more cellulose contained in the pulp, the better the quality of the pulp [16]. The following is the effect of the ratio of raw materials and acetic acid concentration on cellulose levels as shown in figure 2.

Based on the previous research, it was found that the concentration of acetic acid during the cooking process and the ratio of the raw material affected the pulp cellulose content produced. The cellulose content of sugarcane bagasse is lower than banana midrib, this causes the more mass of banana midribs used as raw materials, the greater the cellulose produced. Based on the graph above, it can be seen that the ratio of sugarcane bagasse : banana midrib (12: 8) produces the highest cellulose content of 84.67%. The decrease in cellulose pulp content is because of the release reaction and hydrolysis of the polysaccharide chain in the pulp. Polysaccharide compounds such as cellulose and hemicellulose have glycoside bonds that connect the chains of these compounds. Glycoside bonds are easily hydrolyzed by acids through chemical reactions and this condition is accelerated by heating (delignification process) [17].

3.3. The Effect of Sugarcane Bagasse and Banana Midrib Ratio with Acetate Acid Concentration on Kappa Number

Kappa number is a number that indicates the lignin content in a pulp which is indicated in the standard conditions. The determination of the kappa number aims to determine the quality of the pulp
produced, the smaller the kappa number, the smaller the lignin content of the pulp will be. If the kappa number is high, then the lignin content of the pulp is also high, and vice versa. This is due to the use of acetic acid solution in the cooking process. The kappa number decreases with increasing acetic acid concentration, because the acid concentration is proportional to the mole of acetic acid which reacts in the following reactions:

$$[\text{C}_{10}\text{H}_{10}\text{O}_2]_n + n.\text{CH}_3\text{COOH} + n.\text{H}_2\text{O} \rightarrow n.\text{C}_6\text{COOH} + n.\text{CH}_3\text{COOH}$$

(Lignin) (Acetic acid) (Water) (Black liquor)

The higher the concentration, the higher the mole and the lignin obtained also increases so that the lignin remaining in the pulp gets smaller making the kappa number smaller. The following figure 3 shows the effect of acetic acid concentration and raw material ratio on kappa numbers:

**Figure 3.** The effect of raw materials ratio and acetic acid concentration on kappa number

Based on figure 3 above, the kappa number tends to decrease along with the increase on the ratio of raw materials and the concentration of acetic acid. It is known that the ratio 12:8 of sugarcane bagasse and banana midrib has the smallest kappa number compared to the other ratios on each concentration of acetic acid, at 80% of acetic acid concentration has the kappa number of 8.57.

4. **Conclusions**

- The best ratio of sugarcane bagasse and banana midrib in this study is 12:8 (w/w) which can produce the best yield pulp, cellulose content and kappa number.
- The best cooking solution concentration in this study is 80% with the ratio of solution and raw material is 1:20 (w/v) and 2 (two) hours cooking time can produce the best cellulose content of pulp and kappa number.
- The best quality of pulp produced in this study has the yield of 63.1% with cellulose content of 84.67% and the kappa number of 10.44. This is not much different from pulp produced from wood which has the yield of 50-80%, cellulose content of 45-60% and kappa numbers of 14-20.
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