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Chemistry and Structure Characterization of Bamboo Pulp with Formacell Pulping

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Abstract. Bamboo is one of the non-wood materials which can be utilized as raw materials of pulp. The purpose of this work was to study the effect of the ratio of acetic acid: formic acid on the chemical properties of pulp from bamboo. The results of the study showed that increases of the ratio of formic acid able to degraded of cellulose, hemicellulose, lignin content and decreases the pulp yield. The best condition of this research showed on the ratio of acetic acid: formic acid = 90:10. This condition produced the pulp with composition consist are cellulose 66,98%, hemicelluloses 16,83%, and lignin 3,59%, with the yield of pulp is 42,279%

Keywords : acetic acid, bamboo, formacell, formic acid, pulping.

1. Introduction

Recently, there are growing interest in the utilization of alternative fibrous material derived from lignocellulosic materials such as agricultural waste, and bamboo to pulp production. The advantages of using non-timber raw materials are ease to pulping, excellent fiber for the special type of papers and high quality bleached pulp [2]. Non wood material can also utilized as an effective substitute for the over-exploited forest wood resources [3]–[6]. Bamboo is one of the non-wood materials which can be utilized as raw material for making pulp. There are several advantages of bamboo compared to other woody plants, such as grow rapidly (up to 120 cm per day), easily to spread, highly productivity and easily to harvest. [7]. The productivity of bamboo is reach into 2-6 times higher than pine plants [8].

Moreover, the characteristic of bamboo almost similar with woody plant. It has high cellulose content which about 40% -60.and fibre lenght is about 2-3 mm. The fibre lenght is equivalent to red spruce wood, but longer than pine, with average of fibre length is 1980 µm. Bamboo chip consist of 22,4% lignins, 19,5% xylans, 49,3% cellulose, 16,8% extractive and 1,5% - 3% ash [10], [11]. This properties suggests that bamboo is the best material for papermaking compared to other lignocellulosic materials such as bagasse and rice straw[9], [14].

The common process for pulp-making process in Indonesia using chemical pulping such as sulfate process or is known as Kraft pulping. This process is known as not an environmentally friendly cause its produce several waste problem [15], [16] mainly due to the presence of sulfur compounds [17]. In order to minimize the waste from the pulping process, it is necessary to find the alternative environmentally friendly pulping process. In all parts of the world many alternative pulping processes have been introduced. One of alternative enviromentally friendly paper making process is organosolv pulping method. Organosolv pulping is a process for separation of macromolecular components, comprises the delignification which is the solubilization of the lignin fragments resulted from the breakage of chemical bonds of protolignin [18]. An organic solvents which is usually associated with water in the 10% to 50% ratio (by volume), such as acetone, ethanol, metahol, formic acid, acetic acid etc [5]. Most of organosolv process by using volatile solvent carried out at high temperatures (185 – 210 ^oC). However, organosolv by using an organic acids such as acetic acid and formic acid require lower temperatures and pressure which is closer to atmospheric pressure [19 –21].

The formacell process is one of the pulping methods using acetic acid and formic acid as a cooking chemical [2]. The formacell process has many advantages, ie: produce high pulp yield, low lignin content, high brightness and good strength[22] – [29]. The pulping process use an organic solvent which is easy recycled. This process produces a low lignin content; thus, it can be bleached by using ozone or peroxy acetic acid. In addition, the lignin removed from the pulping liquor can be recovered in the recyling process of organic solvent and used for raw material for adhesives production or other products. Sundquist (2000) reported that the formacell pulping process for the herbaceous plant produces the pulp stronger than soda processes [19]. The formacell pulping process is applied to herbacious material such as bagasse [20], bamboo [32], and wheat straw [31].

There are several factors have to be considered on paper-making by using acetosolv pulping process, such as ratio of solvent to water, ratio of solvent to raw materials, concentration of catalyst, temperature and reaction time. [32]–[35]. The catalyst concentration is the important factor for degragading lignin. Mormanne (2009) reported that formacell pulping of *Cephalostachyum virgatum* kurz bamboo produced pulp product with the yield of pulp, kappa number, freeness, breaking lenght, bursting strength, tearing strength, and ISO brighteness are 42.88%, 22.6%, 40 ^oSR, 5,702.23 m 431.43 kpa, 88.8 cN and 20.7%, respectively[32]. However, this reseach was not reported the effect of acetic acid ratio: formic acid on the chemical properties and the morphology of pulp product. Thus, the purposes of the present work was to evaluate, the effect of acetic acid: formic acid ratio on chemical characteristic and pulp yield. The scanning electron microscopy (sem) was also conducted in order to study the physical features of fibers as well as structures and pulp bamboo morphology.

2. Materials and Methods

2.1 Materials

This experiment was used bamboo Betung sp as raw material which colected from Bandar lampung area. All of chemicals used in this study such as formic acid, glacial acetic acid, HCl, H_2SO_4 were received from Merck.

2.2 Pulping Method

The pulping processes were performed in 1.3 liter lab-scale autoclave with type of flat-bottom, and wide-mouth flask equipped with a condenser. About 20 g of bamboo fibrous were mixtured with the cooking liquor in the ratio of 15:1. in varied ratio of acetic acid : formic acid as cooking liquor, i.e: 100: 1 (K1); 90:10 (K2); 85:15 (K3); 80:20 (K4); and 75:25 (K5). About 0,5% of HCl was added as the catalyst into the cooking liquor.

The pulping processes were conducted in an hour cooking at temperature of 130^{o}C. When the pulping processes ended, the autoclave was cooled into room temperature. Furthermore, the cooking liquor was colected, separated by using filter paper. The filtered residue was then washed by using distilled water until neutrality, dried and yielded as the amount of pulp.

2.3 Pulp Characterizations

For all experiments the main parameters defining of pulping processes were measured as: pulp yield after oven drying of a pulp into constant weight, and composition (i.e cellulose, hemicellulose, and lignin) by using Chesson methods [37]. In addition, the raw material and product were analyzed by using scanning electron microscopy (SEM) JEOL JSM 6510 LA in order to determine the effect of ratio of acetic acid : formic acid on the pulp morphology and fibre structural details. The samples were pre-treated for SEM analysis by sputter-coating with a thin layer of gold.

3. Results and Discussions

3.1 Cellulose

The results showed that the cellulose content of pulp bamboo ranged from 57 to 66.98% (Figure 1). The highest content of cellulose appeared on the ratio of acetic acid: formic acid 90:10. The same result was reported by Hidayati *et al.* (2017), on the ratio of acetic acid: formic acid 90:10 also produced the highest cellulose content in the pulp of empty palm oil bunches [37]. Increases of formic acid ratio of were not decreases the cellulose content, significantly. The result shows that the Formic acid is able to selectively delignifying of biomass with minor effects on cellulose [37].

Kupiainen *et al.* (2012) reported that the formic acid act simultaneously as an organic solvent and as an acid. In pulping process a significant amount of materials able to dissolved into the cooking liquor at relatively low processing temperatures, even working without mineral acid added as catalyst. During the chemical reaction, depolymerisation of lignin and hemicelluloses occurs by partial, and producing oligomers that are soluble in the liquid mixture [38, 41]. The result showed that, the application of short-chain organic acids (mainly formic acid and acetic) has emerged as an attractive and feasible alternative for the delignification of lignocellulosic materials. Cellulose and liquor were then able to separated by filtration, and the dissolved lignin can be recovered easily by the modification of the liquor pH. Furthermore, the recovery of formic acid enables conducted by using distilation process.

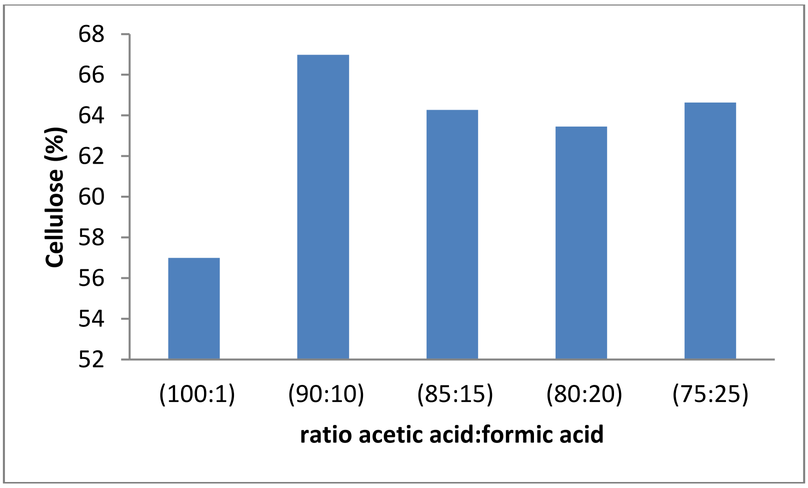

Figure 1. Effect of acetic acid: formic acid ratio on the cellulose contents of bamboo pulp.

3.2 Hemicellulose

The result shows that increase of formic acid ratios can reduce hemicellulose content (Figure 2). The hemicellulose content of bamboo pulp ranged from 7-18.52%. The degradation of hemicellulose occurs due to the acid condition. Sjostom (1981) reported that hemicelluloses are relatively easily hydrolyze into simple sugars by acids since their monomeric components consisting of D-glucose, D-mannose, D-xylose, L-arabinose, and small amounts of L-rhamnose. [41].

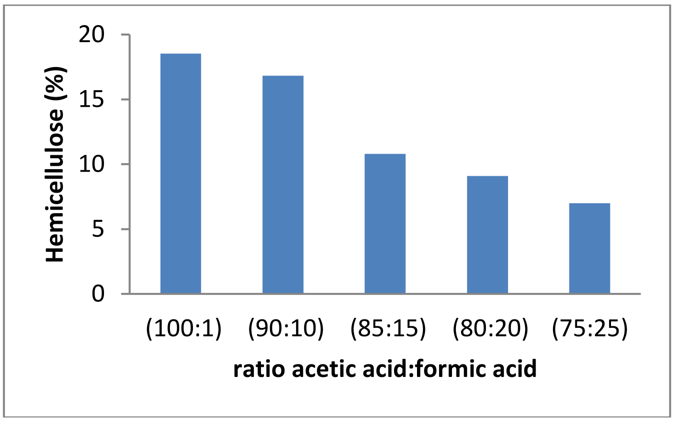

Figure 2. Effect of acetic acid: formic acid ratio on the contents of hemicellulose bamboo pulp.

This result in accordance with Jahan *et a.l* (2006) which was reported that the application formic acid as a cooking liquor in reaction time 2 h produced pulp with hemicellulose content of about 7.8% [43]. High concentrations of formic acid can lead to decrease hemicellulose content [36], [40],[41]; This occurs due to hemicellulose has similar properties with cellulose which that easily degraded in acid solution. Hemicellulose have bound consist of polysaccharides, pectin and lignin and is more soluble than cellulose [43].

The polysaccharide compounds such as cellulose and hemicellulose are glycoside bonds linking the chain of compounds [44]. Glycoside bonds are easy to hydrolyze by acid through a chemical reaction and this condition is accelerated by the heating. Hemicellulose will undergo oxidation and degradation reactions first than cellulose, because the hemicellulosic molecular chains are shorter and branched. Hemicellulose is insoluble in water but soluble in dilute alkaline solutions and more easily hydrolyzed by acids than cellulose [46].

3.3 Lignins

The results showed that the increase of formic acid ratio to a ratio above 10 able to increase the lignin content of bamboo pulp. In this study the resulting lignin content ranged from 3.59 to 6.375%. Lignin is smaller than lignin contained in the bamboo that has not been done pulping process is 22.4% [11]. Delignification process occured due to the acid hydrolysis of α-aryl ether bond [46]. The dissolution of lignin has been ascribed to the cleavage of α-aryl and aryl-glycerol-β-aryl-ether bonds in its molecule [47]. Hydrogen ion concentration plays a very important role in solvent pulping.

The lignin dissolution is expected to be influenced by the acid-catalyzed cleavage of α-aryl and ß-aryl ether linkages in the lignin macromolecule. However, when the formic acid ratio increases the lignin becomes re-condensate and resulting high yielding of lignin. This occurs due to the high concentration of organic acids encourage the reactivation of lignin polymerization that has dissolved in the cooking liquid, and it was making the lignin content of pulp increase [29], [48].

Hidayati *et al*.(2017) stated that the high lignin content of pulp cooking is higher than raw material due to the condensation process so that the lignin attached on the surface of the pulp so that the color becomes darker [35]. The condensation process is formed by combining carbon chains that form longer chains in which the formed compounds are the intermediates of carbonium ions formed on the pulp [46].

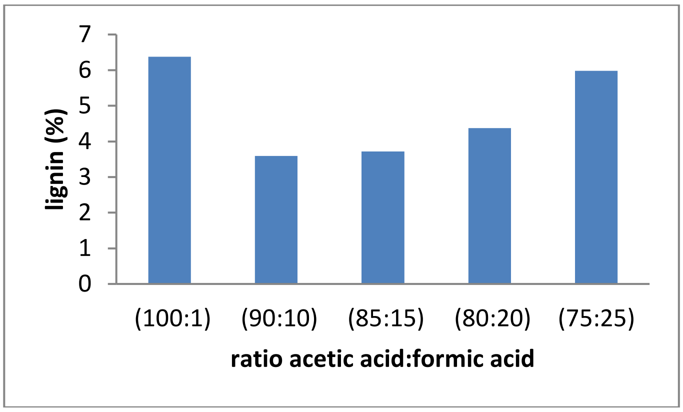

Figure 3. Effect of acetic acid: formic acid ratio on the lignins contents of bamboo pulp.

3.4 Yield

The results showed that increases of formic acid into20 able to decrease the yield of bamboo pulp (Figure 4). In this study the yield of pulp ranged from 36.75 to 44.5%. Yield of pulp decreases due to the degradation of cellulose and hemicelluloses.

Delignification process by formacell has been ascribed to the hydrolysis of α-aryl-ether and lignin-cellulose bonds, and conform to an *pseudo* first-order kinetics reaction. Pulping process by acid solution has properties reactive, so it can break the complex ties of lignin-polysaccharides that resulting the low yield of pulp. According to Fatriasari and Risanto (2011), increase concentrations of cooking liquor tend to decrease the total pulp yield [49].

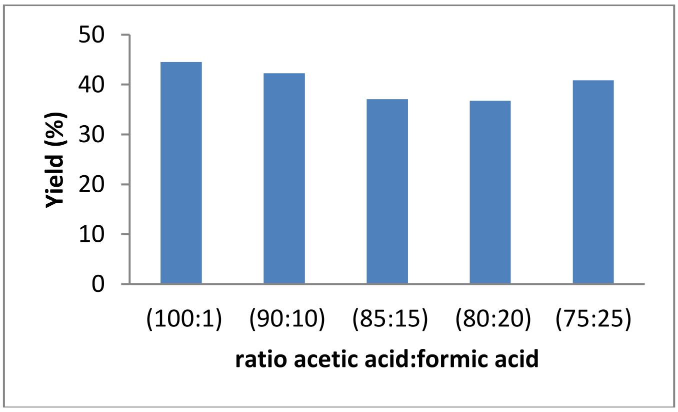

Figure 4. Effect of acetic acid: formic acid ratio on the contents of yields bamboo pulp.

3.5 Assessment the structure of bamboo pulp fibres

Scanning Electron Microscope (SEM) was conducted in order to understand the morphology change of the bamboo pulp fibers. This test was required to estimate the structure and mechanical properties produced by the fibers. The processes of formacell pulping in bamboo produce the morphological changes of bamboo fiber. The analysis was done using 500x magnification, shown on Fig. 5.

The analytical result shos that the fibers undergo randomization from a rigid or crystalline form to randomization. Formic acid as an active agent was able to effectively penetrate into the interior space of the cellulose molecules, thus collapsing the rigid crystalline structure and allowing hydrolysis to occur easily in the amorphous zone as well as in the crystalline zone. The application of formic acid as cooking liquor affected to breaking down the crystalline parts of cellulose [50]. Acid hydrolysis process of

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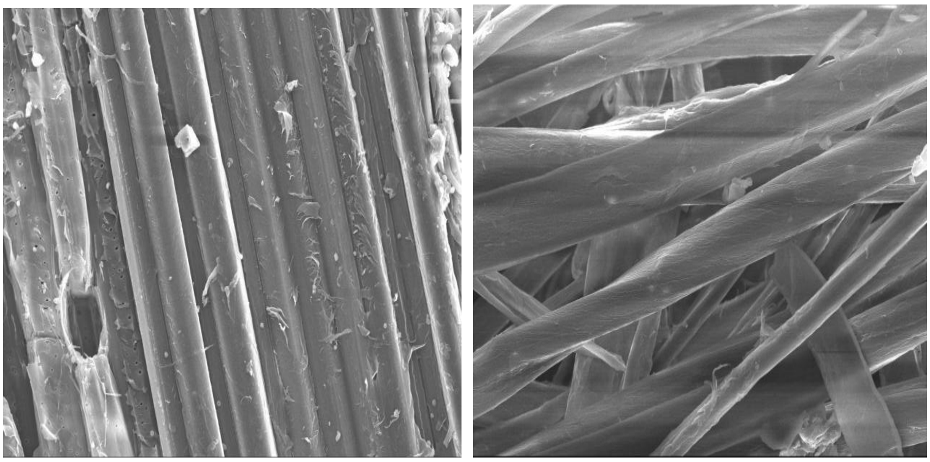
cellulose at bamboo pulp is heterogeneous and occurs on the structural surface of crystalline lattices of cellulose molecules [52].



a. Bamboo raw fiber b. Bamboo pulp by acetic acid:formic acid 75:25

Figure 5. Structure of bamboo pulp fibers

4. Conclusions

The results of the study showed that the increasing of the concentration of formic acid able to reduce cellulose, hemicellulose, lignin content and pulp yield of bamboo pulp. The best condition of this research showed on the ratio of acetic acid: formic acid = 90:10. This condition produced the pulp with composition consist are cellulose 66,98%, hemicelluloses 16,83%, and lignin 3,59%, with the yield of pulp is 42,279%.

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