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Enhancement Mechanical Properties of Simalambuo Wood *(Loppophetalum spp)* Delignified using NaOH in the Thermomechanical Densification Method

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Abstract

One of the problems with fast-growing wood is the low density, which causes poor mechanical properties, so a densification process is carried out to increase the wood's density, surface hardness, and strength. In this study, the delignification process using NaOH was carried out at variations of 12.24, and 48 hours and then continued with the thermomechanical densification process. This study decreased lignin content in delignification simalambuo wood from 30% to 4%. The value of the Modulus of Rupture, Modulus of elasticity, and surface hardness increases with increasing immersion time during the delignification process. The highest values of Modulus of Rupture, Modulus of elasticity, and surface hardness were obtained by simalambuo wood soaked for 48 hours, namely, 2828.23 kg/cm^2, 97.47 kg/cm^2, and 256.73 kg/cm^2.

Keywords: Delignification, densified, modulus of rupture (moe), modulus of elasticity (mor), surface hardness

Introduction

Simalambuo wood (*Lophopetalum spp.)* is a soft wood whose population is spread in Indonesia (Juliaty & Ernayati, 2003), but this wood has not been widely studied to improve its character. Efforts to enhance the character of wood with various methods have been carried out, chemically and physically, or a combination of both (Reinprecht, 2016). One of the problems with fast-growing wood is the low density, which causes poor mechanical properties, so a densification process is carried out to increase the wood's density, surface hardness, and strength (Budakçi et al., 2016; Gong et al., 2010; Yu et al., 2017).

One of the environmentally friendly physical densification methods is the thermomechanical method. This method is done by applying heat to the surface of the wood to compress the wood (Budakçi et al., 2016; Laine et al., 2016; Yu et al., 2017; Yunianti et al., 2019). An essential factor in the thermomechanical densification process is the elasticity of the wood. The more elastic the wood, the higher the compression ratio of the wood. In previous studies, many methods were involved in increasing the compression ratio of wood, one of which was by adding water or giving a specific temperature for a particular duration so that the stiffness of the wood drops drastically (Esteves et al., 2017). Increasing the compact and even compression ratio is one goal that needs to be considered in densification. One of the drawbacks of the thermomechanical densification method is cracking the wood cell walls (Budakçi et al., 2016). Previous studies provided a relatively high temperature for the densification process to avoid this. However, this progressively deteriorates mechanical properties (Kiaei et al., 2018). So there needs to be another effort to reduce the use of high temperatures in the wood densification process.

One way to increase the elasticity of wood is by delignification. The lignin content in wood with an irregular structure can make the wood difficult to press, so the compressed surface is uneven and cracked. Several previous studies have succeeded in eliminating lignin levels in wood by using H_2O_2 mixed with acetic acid (Frey et al., 2018), NaOH (Raman & Liew, 2020), or NaOH mixed with Na_2SO_4 (Shi et al., 2020). Previous research has determined the right concentration to increase the elasticity of wood. So, in this study, researchers will see how the effect of delignification duration on the

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thermomechanical densification process of simalambuo wood. In this study, the delignification process was carried out with NaOH at variations of 12, 24, and 48 hours before the wood was compressed at a temperature of 100 °C with a compression ratio of 30% for 1 hour. The wood was characterized by its mechanical properties.

Method

Materials

The equipment used in this research includes glassware, analytical balance, hot plate, hot press set, Agilent/Cary 630 FT-IR spectrophotometer, SEM JSM-35C Shimadzu, 1 set of bending test tensilon RTF 1350.

The materials used in this research is Simalambuo wood (*Lophopetalum spp.)* was obtained from Nias Island, North Sumatra. *Merck* supplied sodium hydroxide (NaOH) and sulfuric acid (H_2SO_4).

Sample preparation

Simalambuo wood is obtained from the island of Nias, North Sumatra. The wood is cut to a size of 15 × 2 × 1cm^3, and then the dimensions and weight of the wood are measured.

Simalambuo wood delignification

Wood is soaked with NaOH 2,5 M at a liquid level of 5 mm (Raman & Liew, 2020). The wood was soaked for 12, 24, and 48 hours, and then each was washed with distilled water at 100 °C for 5 hours (modified from (Frey et al., 2018).

Simalambuo wood densification

The delignification wood surface was compressed at 100 °C for 1 hour with a compress ratio of 30%. Then the sample was dried at room temperature. Then the wood is measured for its weight and dimensions (Raman & Liew, 2020).

Simalambuo wood characterization after modification

Determination of lignin levels

After the modification, the lignin content was calculated using the Chesson method, where 1 g of simalambuo sawdust sample was added to as much as 150 ml of distilled water, then filtered and washed until the pH was neutral, put in an oven at 105 °C to dry, then weighed. The residue was added with 150 ml of 0.5 M H_2SO_4 and refluxed for 2 hours. The sample was then filtered and washed until the pH was neutral and put in an oven at 105 °C to dry. This procedure was carried out until three times the residue was obtained to determine the lignin content. The residue obtained is then weighed and calculated using the following equation (1):

$$Lignin\ Percentage = \left(\frac{m_2 - m_1}{m_1}\right) x\ 100 \quad (1)$$

Functional group analysis using FT-IR

Characterization of functional groups using Agilent Cary 630 FTIR Spectrometer with a wave number range of 650-4000 cm^{-1}.

Measurement of modulus of rupture (MoE), surface hardness, and modulus of elasticity (MoR)

Modulus of elasticity (MoE) is a value that indicates the nature of stiffness which is a measure of the ability of beams and piles to withstand changes in shape or bending that occur due to pressure. Modulus of rupture (MoR), also known as modulus of rupture, buckling strength, or transverse rupture strength, is a material property defined as the stress in a material just before yielding in a flexural test. MoE and MoR were calculated based on ISO 13061-3 (2014) on the following equation (2) and (3):

$$MoE = \frac{3PL^3}{4ybh^3} \quad (2)$$

$$MoR = \frac{3PL^3}{2bh^2} \quad (3)$$

Where P is the maximum load given to the sample (kg), y is the limit of bending deflection (cm), b is the sample width (cm), and h is the sample height (cm).

The surface hardness value is represented by the average value of the radial and tangential hardness. This value is calculated using the following equation (4):

$$H = \frac{Pmaks}{A} \quad (4)$$

Pmax is the maximum load given to the sample (kg), while A is the surface area of the sample under pressure (cm^2).

Characterization of morphology using a scanning electron microscope (SEM)

Morphological changes in each modified sample were observed using TM3000 (*Hitachi*) at 15 kV.

Result and Discussion

Lignin content

The densified wood after the delignification process is shown in **Figure 1**.

In **Figure 1**, it can be seen that the dimensions of the delignification wood are different from those of the undelignification wood. Changes in the volume of wood are getting smaller, allowing the loss of the lignin component in the wood to have occurred. Thus, the determination of lignin content was carried out on control wood and post-delignified wood after being treated by the thermomechanical densification method, which can be seen in **Table 1**.

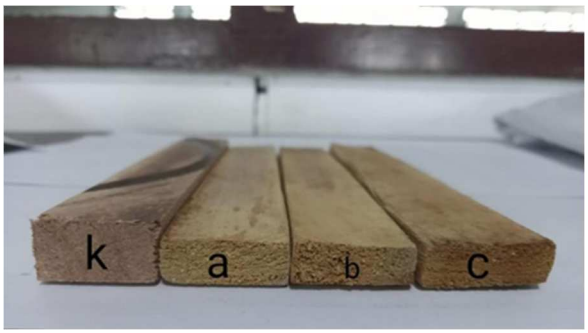

Figure 1. Dimensional changes are seen in the control sample (k) and the delignified sample at variations of immersion (a) 12 hours, (b) 24 hours, and (c) 48 hours.

Table 1. Changes in lignin content in smalambuo wood (loppophetalum spp.)

Sample	Lignin Content (%)
Control	30
12 hours delignification	18
24 hours delignification	10
48 hours delignification	4

Based on the table above, the lowest lignin content was at the delignification soaking time of 48 hours, and the most remaining content was at the 12-hour immersion time. This matter happens because the NaOH solution is not maximal enough to seep into the wood, so there is still a lot of lignin in the simalambuo wood. Soaking with NaOH for a longer time has been shown to reduce lignin levels. Reducing the lignin content will facilitate the densification process that is carried out afterward. This also happened in previous studies which showed the effect of the smaller the lignin content would have an impact on the mechanical properties of wood (Frey et al., 2018). It used a temperature of 100 °C in the delignification procedure by considering previous studies, which showed a decrease in MoE/MoR results when the temperature was increased (Kiaei et al., 2018). So, in this study, this temperature was used to minimize damage to the wood cell walls. Based on the results of the study, it is known that the extended duration will help the NaOH to be absorbed into the wood cells optimally so that it can provide better densification results.

Functional group analysis using FT-IR

Based on **Figure 2**, it was seen that the stretching absorption bands of 3332.2 cm^{-1} and 3324.8 cm^{-1} in all samples, both control samples and samples that had been given delignification treatment indicated the presence of hydroxyl groups (OH) from cellulose as reported by various researchers (He et al., 2019; Li et al., 2020; Okon et al., 2018; Zhang et al., 2019). The absorption of the C = C functional group from the hydroxyl compound will appear at wave number 2140 - 2260 cm^{-1}. The absorption of the C = O carbonyl group, indicating the presence of hemicellulose, was found at wave numbers 1700 cm^{-1}, 1724, and 1730 cm^{-1} for acetyl ester bonds contained in lignin, hemicellulose (Jiang et al., 2021).

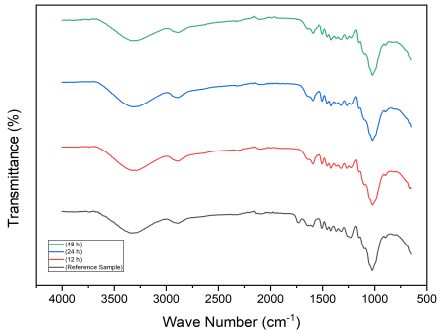

Figure 2. The results of the FTIR spectrum analysis on the reference sample and after densification in the delignification pre-treatment with 12 hours, 24 hours, and 48 hours of immersion variations

Analysis of modulus of rupture (MoR), modulus of elasticity (MoE), and surface hardness

Values of the Modulus of rupture (MoR), Modulus of elasticity (MoE), and surface hardness are shown in **Figures 3, 4, and 5**.

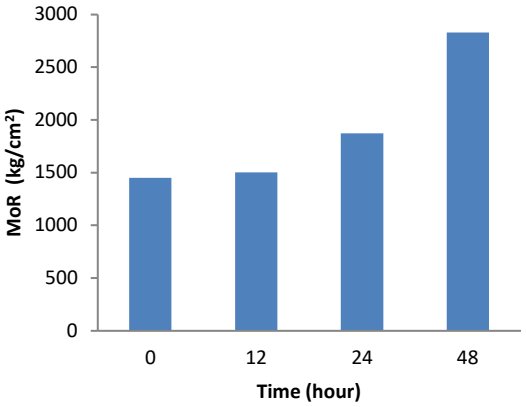

Figure 3. MoR analysis results on samples after densification in the delignification pre-treatment with 12 hours, 24 hours, and 48 hours of immersion variations

The Modulus of Rupture (MoR) value for simalambuo wood fractures was in the pre-treatment of immersion in NaOH solution for 48 hours, and the lowest flexural strength value for simalambuo wood fractures was in the 12-hour pre-soaking treatment. This matter shows that the pre-treatment with NaOH immersion increases the flexural strength of the simalambuo wood fracture, which has been densified (compacted) due to changes in the cell structure in the wood. Soaking with NaOH which can remove lignin, will facilitate the densification process (Frey et al., 2018). The density of wood increases along with the increase in the mechanical properties of wood, which also occurs in poplar, spruce, pine, walnut, and other

woods (Laine et al., 2016; Kiaei et al., 2018; Mania et al., 2020; Budakçi et al., 2016).

The MoE value of simalambuo wood densified without delignification was 15.38 kg/cm^2. Still, after the delignification process before densification (compacting), the average MoE value of simalambuo wood increased to 34.92-97.47 kg/cm^2. The highest MoE value of simalambuo wood was pre-treatment with NaOH solution immersion for 48 hours, and the lowest static flexural toughness was pre-treatment with 12

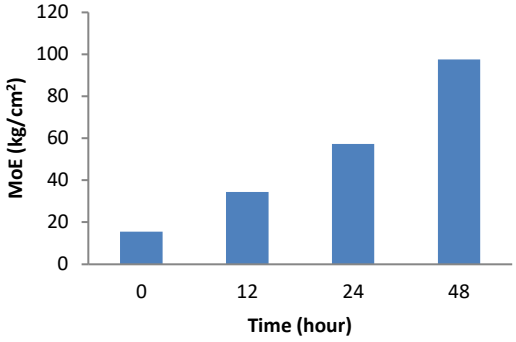

Figure 4. MoE analysis results on samples after densification in the delignification pre-treatment with 12 hours, 24 hours, and 48 hours of immersion variations.

Based on the MoE value, it can be seen that there has been a softening of simalambuo wood so that it can increase the static flexibility value of the wood. This matter is due to NaOH's ability to penetrate the wood to degrade lignin, the longer the soaking process with NaOH, the more lignin can be degraded, so the flexibility of the wood will increase (Raman & Liew, 2020).

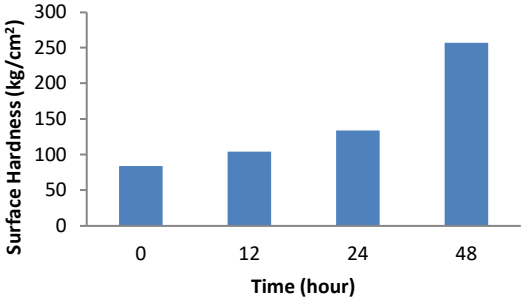

Figure 5. Graph of surface hardness analysis on samples after densification in the delignification pre-treatment with 12 hours, 24 hours, and 48 hours of immersion variations.

Figure 5 shows that the surface hardness value of simalambuo wood has a controlled average of 83.7 kg/cm^2, while after densification, the average surface hardness value in simalambuo wood is 103.92-256.73 kg/cm^2. The highest value of simalambuo wood surface hardness was in the preliminary immersion treatment in NaOH solution for 48 hours, and the lowest value of simalambuo wood surface hardness was in the 12-hour pre-soaking treatment. In the pre-treatment of immersion in NaOH solution for 12 hours, 24 hours, and 48 hours, the surface hardness on the control simalambuo wood was due to the shrinking of the wood pores in the wood due to the densification method. This matter happens because the density of the wood increases due to the compression applied during the densification process.

Analysis morphology with scanning electron microscope (SEM)

The results of Morphological Analysis using Scanning Electron Microscopy (SEM) on simalambuo wood can be seen in **Figure 6**.

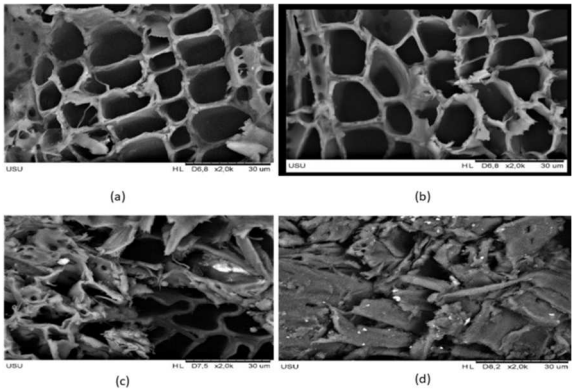

Figure 6. SEM micrograph of simalambuo wood (*Loppophetalum spp*.) (a) control wood, (b) delignified wood, (c) non-delignified densified wood, (d) delignified and densified wood with a magnification of 2000x

Figure 6 shows the results of morphological changes in each treatment. Each shows the surface of the wood as seen from the pores in the cell wall, whereas, in **Figure 6** (a), the control wood shows large wood pores so that the wood's ability to absorb water is considerable due to the pores or cavities in the wood. In **Figure 6** (b), it can be seen that the pores of the wood are getting bigger. There is damage to some parts of the wood cells due to the delignification treatment using 2.5 M NaOH solution, which is less than perfect and cracks in some parts because there is still a lot of lignin content as wood reinforcement, so when pressed, cracks occur. While in **Figure 6** (d), the densified wood that carried out the delignification pre-treatment, it can be seen that the wood's pores look narrower, which causes the wood to lack hygroscopic properties, namely the nature of quickly absorbing water and the wood becomes denser. This appearance does not look much different in thermomechanically densified pine wood (Laine et al., 2016) and Norway spruce treated with densification at room temperature (Frey et al., 2018).

Conclusions

The study's results on simalambuo wood, delignified with NaOH, reduced the lignin content from 30% to 4%. The thermomechanical densification process at 100°C after delignification increases elasticity, flexural fracture resistance, and surface hardness. This result is supported by the morphological analysis of wood which shows better pore density by delignification before the thermomechanical densification process.

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