Physical properties of furfurylated mangium (Acacia mangium Willd.) and pine (Pinus merkusii Jungh et de Vriese) woods

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Abstract. Wood from plantation forest contains a lot of sapwood and juvenile wood which has inferior in physical properties. Furfurylation could improve the properties through a reaction between Furfuryl Alcohol (FA) with a hydroxyl group of wood components. The purpose of the study was to improve the physical properties of mangium (Acacia mangium Willd.) and pine (Pinus merkusii Jungh et de Vriese) woods. The wood specimens for physical properties was prepared according to the ASTM D 143-94. They were vacuumed at 600 mmHg during 30 minutes, when the vacuum has been released, the FA reagent was inserted to the tank and followed with pressure at 10 kg/cm² during 30 minutes. The specimens were wrapped with aluminium foil and heated in the oven at 100°C for 24 hours. After conditioned for three weeks, the specimens were tested for physical properties including Weight Percent Gain (WPG), density, Moisture Content (MC), water absorption, swelling, shrinkage, and anti-swelling efficiency (ASwE) according to the ASTM D 143-94. Untreated specimens were also prepared for comparison purpose with five replications for each treatment. The results showed that furfurylated mangium and pine woods reached WPG 11.34% and 17.74%, densities were increased 8.95% and 3.75%, MC were decreased 88.41% and 84.74%, water absorption were decreased 41.76% and 46.84%, volume swelling were decreased 55.18% and 61.57%, volume shrinkage were decreased 55.18% and 64.75%, respectively. ASwE of mangium and pine woods was 55.1% and 61.6%. It could be mentioned that the furfurylated wood had better physical properties compared to untreated woods.

1. Introduction
Forest plantation was developed to substitute natural forest, especially for timber supply purposes. Mostly the planted trees were fast-growing species, because the demand for wood was increased year by year, and the stand could be exploited after 6-10 years old. Some favourite species for industrial plantation forest are mangium (Acacia mangium Willd.) and pine (Pinus merkusii Jungh et de Vriese). Total log production in Indonesia in 2017 reached 49.13 million m³, 63.36% of total production was mangium wood, and 0.39% of total production was pine wood [1]. The density of mangium wood was reported in the range of 0.59-0.61 [2]. The density of pine wood was 0.48-0.54 [3]. The wood from plantation forest was dominated with sapwood and containing juvenile wood which had lower physical-mechanical properties [4]. The low physical and mechanical properties of young mangium and pine
wood causes the limited utilization of the wood, hence special treatment is needed to improve the wood quality.

Wood modification was an effective way to increase wood stability, water resistance, and wood life [5]. Several technique in wood modification are chemical, thermal, and surface modification [5]. Chemical modification processes for wood modification are acetylation and furfurylation. Furfurylation was based upon the reaction of wood with the bio-chemical furfuryl alcohol at the cell wall level. Furfurylation significantly improved wood properties, protected against decay, decreased hygroscopicity and improved dimensional stability. Furfurylated wood has high dimensional stability and surface hardness [5-7]. Furfurylated wood had better dimensional stability and mechanical properties, and was more resistant to organism attack. Modification of wood with furfurylation shows better results and less impact on the environment, so this process was in high demand, especially in Europe [8].

The use of catalysts further develops the furfurylation process. Furfurylation study using boric acid catalyst on Cryptomeria japonica D. and Pinus sylvestris L. wood produced a higher weight percent gain (WPG) value than furfurylation without catalyst and produced wood with 70-86% ASwE value [9]. Tartaric acid was an organic compound derived from ascorbic acid, which is white, odourless, and stable in the air. Tartaric acid is very soluble in water and easily soluble in ethanol. The use of the tartaric acid catalyst in the furfurylation process of mangium and pine wood had not been studied. In this study, the furfurylation was conducted with the addition of tartaric acid as a catalyst. The purpose of this study was to improve the physical properties of mangium and pine woods through the furfurylation process.

2. Materials and Methods

2.1. Materials
The mangium and pine woods were obtained from Bogor, West Java, Indonesia. The wood samples taken from 6-10 years old trees. The materials for furfurylation process were Furfuryl Alcohol (FA) and tartaric acid.

2.2. Methods

2.2.1 Sample preparation
For physical properties test, the woods were cut into specimens with a size of 10 cm by 2.5 cm by 2.5 cm according to ASTM D 143-94 [10]. Impregnation process was carried out to fill the cell voids with FA solution. To accelerate the polymerization process, the FA solution was added with tartaric acid at the amount of 5/100 (w/w). The wood specimens were placed in the chamber and then vacuumed at 600 mmHg for 30 minutes. During the released period of vacuum process, the FA solution was allowed to flow into the chamber and subsequently pressurized at 10 kg/cm² for 30 minutes. After the vacuum-pressure process was finished, the wood specimens were wrapped with aluminium foil and then heated in an oven at 100°C for 24 hours. Afterwards, the aluminium sheet was removed, and the wood specimens were weighed for WPG calculation. For comparison purposes, untreated wood was included as the control, and five samples as replication were prepared for each treatment. The specimens were conditioned in a room condition for three weeks.

2.2.2 Physical properties test
The physical properties of wood were density, moisture content, water absorption, volume swelling, volume shrinkage, and anti-swelling efficiency (ASwE) were tested according to ASTM D 143-94 [10].

2.2.3 Functional groups test
Functional group testing was performed using Fourier Transform Infra-Red Spectroscopy (FTIR). This process was conducted to determine the functional groups in wood furfurylation. The process was carried out by mixing the powder from furfurylated wood with dry potassium bromide (KBr) (1: 100). The mixed powder was moulded and compacted to form a thin pellet, then the functional groups were
seen at wavelengths between 4000-500 cm\(^{-1}\). Untreated specimens were also prepared for comparison purpose.

2.2.4 Data analysis
To analyze the effect of treatments upon all responses, i.e. wood density, a 2 × 2 factorial in completely randomized design was used for data analysis. The first factor was wood species (mangium and pine), and the second factor was treatments (untreated and furfurylated woods). The data were analyzed with analysis of variance (ANOVA) by Microsoft Excel.

3. Results and Discussion

3.1. Effectiveness of the impregnation process
The effectiveness of the impregnation process could be observed from the amount of WPG. The WPG value for mangium and pine wood were 11.34%, 17.74%, respectively. The difference in WPG value was influenced by wood anatomical characteristics and also the chemical components of wood in the form of extractive substances whose proportions differ in the two types of wood. The higher WPG in furfurylated pine wood because pine belongs to conifer which had simpler anatomical characteristic, and mangium was hardwood which had more complex characteristics. The other factor that mangium wood contains more extractives which could inhibit chemical reactions between FA and wood [11,12].

3.2. Physical properties of furfurylated wood
Density was one of the important physical properties related to the use of wood [13]. The higher density of wood means that the content in the wood cell wall was higher which means the thicker the cell wall [14]. The results of physical properties testing can be seen in Table 1. The density of wood increased after the furfurylation process. Analysis of variance showed that the FA treatment had a significant effect on increasing the wood density (Table 2). According to Dong's research [15], the physical properties of furfurylated wood were higher than untreated wood because FA filled the cell walls.

| Wood Species | Treatments | Wood Density (g/cm\(^3\)) | MC (%) | Water Absorption (%) | Volume Swelling (%) | Volume Shrinking (%) |
|--------------|------------|---------------------------|--------|----------------------|---------------------|----------------------|
| Mangium      | Untreated  | 0.67                      | 15.53  | 33.71                | 8.10                | 7.63                 |
|              | Furfurylated | 0.73                     | 1.80   | 19.63                | 3.63                | 4.96                 |
| Pine         | Untreated  | 0.80                      | 2.15   | 14.09                | 9.37                | 10.13                |
|              | Furfurylated | 0.83                     | 13.81  | 25.98                | 3.60                | 3.57                 |

Furfurylated wood has a lower moisture content compared to untreated wood. Analysis of variance showed that the FA treatment had significantly affected the moisture content of the wood. The moisture content of wood was reduced after the furfurylation process [16]. Furfurylated wood was more hydrophobic or difficult to absorb water or water vapour from the environment due to chemical bonds between the FA and OH groups in the wood, so that furfurylated wood has a lower water content than untreated wood.

Furfurylated wood has lower water absorption compared to the untreated wood. Analysis of variance showed that the FA treatment had significantly reduced the ability of water absorption both in mangium and pine wood. The low absorption of wood to water showed that the furfural groups impregnated into the wood reacted with the chemical compounds in the wood. Penetration of chemical material into wood can produce cross bonds between hydroxyl groups in the cell walls of wood. Cross-linking could reduce the hygroscopicity of wood by reducing the bonding place for water inside the cell wall [14]. The lower water absorption of wood affects its dimensional stability [17]. Wood tissue will maintain water content in balance with its environment, through absorption and release of water [18]. Analysis of variance showed that the FA treatment had high significantly affected the volume swelling and volume shrinkage of the wood.
Dimensional stability was the ability of wood not to expand and shrink when it is in environmental conditions with fluctuating temperature and humidity changes. Criteria that could be used to determine the dimensional stability of wood was the value of the Anti-Swelling Efficiency (AswE) [19]. The AswE value for furfurylated mangium and pine woods in this study were 55.1% and 61.6% respectively. The AswE value in this study had a higher value than AswE from another study; those indicated that the furfurylated wood was more stable in dimensions. Furfurylation process could stabilize the dimensions of wood due to reduced empty volume in wood [20].

Table 2 Variance analysis of physical properties.

| Responses          | Wood species | Treatment |
|--------------------|--------------|-----------|
| Density            | **           | *         |
| Moisture Content   | ns           | **        |
| Water Absorption   | *            | **        |
| Volume Swelling    | *            | **        |
| Volume Shrinking   | *            | **        |

** Highly significantly different (P ≤ 0.01); * Significantly different (P ≤ 0.05)

3.3. Functional group of furfurylated wood

Analysis using FTIR was aimed to investigate changes in the chemical structure of wood after being treated. The results of FTIR analysis on FA treated wood and non-treated wood showed that the wave peak position and spectrum shape was relatively same in both wood species, although in mangium wood there was a difference in intensity. In general, O-H strain absorption bands (about 3400 cm⁻¹) and C-H absorption bands (around 2927 cm⁻¹) were derived from all wood components. Functional clusters located in the fingerprint area (1800-650 cm⁻¹) can be used as a differentiator between wood components [21], but it is difficult to identify. The hydroxyl group intensity of furfurylated wood was lower than untreated wood. The decrease in intensity was presumably due to some OH groups have been linked to FA. The decrease in the intensity of the hydroxyl group makes the wood more hydrophobic, so it was difficult to absorb water, and the dimensional stability is increased. The FTIR spectra of mangium wood for untreated and furfurylated wood (Figure 1) shows that there was an aromatic skeletal vibration of lignin at wave number 1590 cm⁻¹, indicated that furfural compounds impregnated was binded with lignin compounds in wood. These results are consistent with research conducted by Dong’s research [7].

![Figure 1. FTIR Spectra of mangium wood](image-url)
4. Conclusion
Modification of the furfurylation process with the tartaric acid catalyst can improve the physical properties of mangium and pine wood. Furfurylation increases the density and decreases the water content of mangium and pine wood. The dimensional stability of furfurylated wood increases compared to untreated wood. Improved physical properties of furfurylated wood are caused by chemical bonds between FA and wood components as evidenced by the changes in the intensity of functional groups in furfurylated wood.

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