Characterization a binderless particleboard of coffee husk using Hydrogen Peroxide (H$_2$O$_2$) and Ferrous Sulfate (FeSO$_4$)

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Abstract. Binderless particleboard is particleboard that can be made of a lignocellulose material which is formed into a board only by heat pressing without the addition of adhesive or resin. The particleboard in this study was made from coffee husk (endocarp) using H$_2$O$_2$ and FeSO$_4$ catalyst to activate lignin coffee husk component by oxidation method. Initial treatment of coffee husk is the variation of steam then Oxidation (S + O) and Oxidation without steaming (O). In this study H$_2$O$_2$ and FeSO$_4$ catalysts were varied, including H$_2$O$_2$ levels of 10, 20, 30 wt% based on particle dry weight and FeSO$_4$ is 5 and 7.5 wt% based on H$_2$O$_2$ weight. From the results of the study, it can be concluded that the coffee husk particleboard whose raw material is treated oxidation without steam can improve the physical properties of binderless particleboard. Increased wt% of H$_2$O$_2$ and FeSO$_4$ catalysts in the oxidation process of coffee husk particles produce binderless particleboard with good physical characteristics such as density, water content, water absorption and swelling thickness. Therefore, considering the efficient aspects of the use of chemicals, the combination of H$_2$O$_2$ and FeSO$_4$ catalysts that can be made according to JIS A 5908 2003 standard are 20% H$_2$O$_2$ and 7.5% FeSO$_4$. The ester linkages were detected by Fourier transform infrared spectroscopy, indicated that cross-link due to the incorporation of phenoxyl radicals.

1. Introduction

Particleboards are normally fabricated by using synthetic adhesives such as urea formaldehyde, melamine formaldehyde or phenol formaldehyde. Synthetic adhesives emit formaldehyde emissions, which may pollute the environment. Therefore, in this study, we utilize the extractive substances such as lignin, hemicellulose as a natural glue. These substances are contained in coffee husk waste from the skin of coffee beans known as endocarp.Particleboard from coffee husk waste is normally processed using polypropylene [1]. However, the quality of the product is still low due to its modulus of elasticity (MOE) value that has not met the standard.

The utilization of natural glue substance can reduce the dependence on synthetic adhesive obtained from the processed petroleum origin, which is a non-renewable resource [2]. Based on its polyphenol structure, lignin can also function as an adhesive since its structure is similar to phenol formaldehyde resins. Both materials have almost identical chemical components of the phenolic group. Thus lignin is able to substitute phenol formaldehyde. Some works by researchers that develop a method to produce lignin directly from wood have inspired the potential of lignin as an adhesive. It allows the fibers in the wood to bind themselves without additional adhesives [3]. One method that has been successfully developed is the oxidation method. This method uses hydrogen peroxide (H$_2$O$_2$) and ferrous sulfate.
(FeSO₄) catalyst to activate lignin component of wood particles [4]. Previously, particleboard was fabricated using a natural glue based on bamboo and wood, which was obtained by oxidation method in conjunction with boiling treatment [5]. The result showed that the particleboard obtained by this method has dimensional stability and high mechanical properties compared to particleboard obtained using formaldehyde adhesive. On the other hand, the development of particleboard by using steam heat injection has also attracted attention from researchers. It was shown that the particleboard manufactured from the kenaf core using a heat steam injection method has a high adherence strength at board density of 0.65 g cm⁻³ or more [6].

In this work, we fabricate and characterize binderless particle board using coffee husk with oxidation method. The optimal hydrogen peroxide (H₂O₂) and catalyst ferrous sulfate (FeSO₄) used for the oxidation process is also investigated.

2. Experimental Procedures
The experimental procedure is conducting in three stages; coffee husk treatment, preparation of percent weight of H₂O₂ and FeSO₄, preparation of molder and fabrication of particleboard. Coffee husk treatment; the materials are coffee husk, hydrogen peroxide (H₂O₂) and ferrous sulfate (FeSO₄). The raw material is coffee husk (Arabica coffee) which was obtained from the coffee-milling factory. The material is dried in the open air for one week until water sorption less than 8% before it is grinded into a particle. The grinding process uses coffee skin cutter, which then followed by filtering to obtain the same size of 20/24 mesh. Preparation of percent weight (wt%) of hydrogen peroxide (H₂O₂) and catalyst ferrous sulfate (FeSO₄) and type of treatment coffee husk can show from table 1.

| Type of treatment coffee husk | FeSO₄ (wt%) | H₂O₂ (wt%) |
|-------------------------------|------------|------------|
| Steaming with Oxidation (S+O) | 5          | 10,20,30  |
|                               | 7.5    | 10,20,30  |
| Oxidation only (O)            | 5          | 10,20,30  |
|                               | 7.5    | 10,20,30  |

Preparation of molder; particle molding tool was made from iron with the size of 100 x150 x 10 mm. The coffee husk particles are then molded to fabricate particleboard using the prepared iron molding tool.

Fabrication of particleboard; the amount of H₂O₂ used varies based on the dry weight of the particles, while the FeSO₄ content is also determined based on the weight of hydrogen peroxide (H₂O₂). The weighted particles are steamed for 15 minutes, before they are drained and cooled. The particles are treated with further oxidation with spraying hydrogen peroxide (H₂O₂) and ferrous sulfate (FeSO₄) onto the coffee husk particles to complete the oxidation treatment (S+O). The treatment of coffee husk without steam (O) can be done by directly spray with hydrogen peroxide (H₂O₂) and ferrous sulfate (FeSO₄) catalyst. The particles, which have been sprayed by H₂O₂ and FeSO₄ are then conditioned for 90 minutes before being heat-treated. Then the particles are inserted into the mold. The temperature of the fitting plate used is 200°C with duration of 15 minutes, and pressure 25 kgf cm⁻². Determination of the effectiveness of the treatment method is conducted based on physical properties test result of the particleboard without adhesive produced. In this research will be done physical properties tested include: density, water content, water sorption and swelling thickness. Tests are carried out refer to JIS A 5908 2003 [7].

3. Results and Discussions
The physical properties of the particleboard such as density, water content, water sorption and the swelling thickness are investigated and discussed with and without steaming during the oxidation process. We also perform Fourier Transform Infrared (FTIR) measurement for the fabricated particleboard. Figure 1 shows the density test result indicating the effect of the addition of H₂O₂ and
FeSO₄ on the treatment with steam and Oxidation (S + O) and Direct Oxidation (O). As shown in the figure, the density of the particleboards with steam and oxidation (S+O) are obtained in the range from 0.37 g/cm³ to 0.46 g/cm³. The treatment with direct oxidation is 0.47 g/cm³ to 0.53 g/cm³. It is observed that the treatment of oxidation without steam (O) can increase density. The highest density of 0.53 g/cm³ was obtained with the use of 20% H₂O₂ and 7.5% FeSO₄. This indicates that a heat oxidation process at this level capable to activate the lignocellulose material (cellulose, hemicellulose, and lignin). It is also revealed through this research that adhesive particleboard can be made of lignocellulosic material formed into a board only by hot presses without additional adhesives or resins [8]. However, at 30% H₂O₂ and 5% and 7.5% FeSO₄, degradation of density values were observed. This indicates the degradation of coffee husks chemical components which evaporates during the oxidation process or heat-forging process. This shows that extractive substances in the coffee husks play an important role in the bonding process and the oxidation process can strengthen the bonds between the fibers and provide the chance of fiber bonds, which is getting in contact with both and become compressed. All samples met density values, it means that they met the JIS standard (2003) ranging from 0.4-0.9 gr/cm³. However, the exception occurs only for steam with oxidation treatment (S + O) samples with 10% H₂O₂ and 5%FeSO₄ and 30% H₂O₂ and 5%FeSO₄.

The average water content value of the particleboards is shown in Figure 2. The average value of water content in the steam with dioxide (S + O) process ranges from 10.4-14.5% and in the direct oxidation process (O) ranges between 6.5-8.3%.

Figure 1. The density of particleboard with various wt % of H₂O₂ and FeSO₄  Figure 2. The water content of particleboard with various wt% of H₂O₂ and FeSO₄

Figure 2 shows that there is a decline of water content for both treatments (20% H₂O₂ and 7.5% FeSO₄), indicating the effect of H₂O₂ and addition of FeSO₄, where oxidation process at this level should activate the lignocellulose material (cellulose, hemicellulose, and lignin). Although lignin levels in the coffee husks are not too large since the lignin that lies on the surface of the fiber. Lignin is a component that tends to be hydrophobic so that it inhibits the absorption of H₂O₂ and air. This condition becomes the cause so that the H₂O₂ of the particleboard equilibrium with the oxidation treatment tends to be lower. In the treatment of coffee husks directly oxidation (O) can reduce the H₂O₂ level. This indicates that the oxidation treatment tends to decrease the hydrophilic nature of the particles so that the balance of H₂O₂ becomes low. In general, the higher density value, the lower water content will be [9]. The water content of the board is very important in maintaining its dimensional stability. Low water content can improve the dimensional stability of a board, which affects the board quality as well. All samples for the water content test in this study met JIS A (2003) standard (5-13%), except in 10-20% H₂O₂ and 5 wt % FeSO₄ in S + O coffee husk treatment.
Figure 3 shows the ability of particleboard in absorbing water as the ability of the particles to absorb water in its walls and cell cavities [10]. As shown in the figure, the water sorption of the particleboards with steam and oxidation (S+O) are obtained in the range from 58% to 75%. The treatment with direct oxidation is 48% to 61%. This phenomenon is usually followed by the return of the cell to its original form after previously collapsed due to high temperature and pressure. In addition, the inter-spaces between the particles can also be the entry of water that participates in improving the water sorption of the particleboard. However, the ability may decrease when the bonding capacity of the particles is sufficiently high. Thus, by preventing the cell from returning to its original shape and preventing water from entering empty spaces between particles, then the phenomenon of a reduced particle of water sorption along with increased H$_2$O$_2$ levels appears due to stronger bonds between particles as more oxidizing agents become available. In addition, the amount of lignin that is present on the surface of the particles due to the oxidation process and the heat crush seems to also be a barrier to the entry of water in the particle. The treatment of coffee husk without steam treatment (O) has water absorption properties that tend to decrease at 20% H$_2$O$_2$ and 7.5% FeSO$_4$. This indicates that in this level can decrease the hydrophilic nature of the particles so that it is more difficult to absorb the water caused by the bonding of the OH groups on the particles or substituting some of the OH groups into O radicals that form cross-links with other components.

Figure 4 also shows that H$_2$O$_2$ and FeSO$_4$ levels have an effect on the swelling thickness of particleboard. The addition of H$_2$O$_2$ decreases the swelling thickness property of particleboard. The value of swelling thickness decreases in the direct oxidation treatment, at 20% of H$_2$O$_2$ and 5% of FeSO$_4$ and also 30% H$_2$O$_2$7.5% FeSO$_4$ which are complied with JIS A 5908 (2003) standard is maximum 12%. Thus for application purposes, H$_2$O$_2$ and FeSO$_4$ catalyst levels in this range have cause no problems in particle quality regarding their dimensional stability. The smallest swelling thickness value is the best development since it can anticipate the absorption of water into the board through the pores of particles and empty space between the particles slowly [11]. The average value of swelling thickness in a combination of oxidation treatment tends to be lower. This phenomenon can cause by cross-linking between radical groups produced by oxidation processes and cross-linking.
between hydroxyl groups [12]. The radical groups generated during the oxidation process appear to form covalent bonds during the heat-pressing process so that the bonds are stronger and stable.

Figure 5 shows the infrared spectra of coffee husk binderless particleboard at different wt% H$_2$SO$_4$ and wt% FeSO$_4$ catalyst.

Figure 5 shows the particleboard has increased intensity on the board treatment by steaming and oxidizing (S+O). The peak change occurs in the area of 1050 wave number. This area is the area of the C-H or C-O deformation absorption band. Figure 6 shows the infrared spectra in the treatment of oxidation without steam, there is a change of indentation in the 1250 cm$^{-1}$ wave number which is the absorption area of ester. Based on this fact, one type of bond that plays an important role in the formation of bonds between particles on the particles without adhesive is a cross-link due to the incorporation of phenoxy radicals.

4. Conclusions
From the results of the study, it can be concluded that the coffee husk particleboard whose raw material is treated oxidation without steam (O) can improve the physical properties of binderless particleboard. Increasing levels of H$_2$O$_2$ and FeSO$_4$ catalysts in the oxidation process of coffee husk produces binderless particleboard with good physical characteristics such as density, water content, water sorption and swelling thickness. Therefore, considering the efficient aspects of the use of chemicals, the combination of H$_2$O$_2$ and FeSO$_4$ catalysts that can be made binderless particleboard according to JIS A 5908 2003 standard are 20 wt% H$_2$O$_2$ and FeSO$_4$ catalyst 7.5 wt% in direct oxidation treatment (O). The ester linkages were detected by Fourier transform infrared spectroscopy, indicated that cross-link due to the incorporation of phenoxy radicals.

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