High quality sugarcane bagasse-citric acid particleboards

F A Syamani*, Sudarmanto, Subyakto and B Subiyanto

Research Center for Biomaterials, Indonesia Institute of Sciences (LIPI), Cibinong, 16911, Indonesia

*E-mail: firda.syamani@biomaterial.lipi.go.id

Abstract. The productivity of Indonesian sugarcane plantation, especially in East Java province reached 1,186,515 tonnes in 2017. Sugarcane liquid is extracted as sugar raw material and set aside sugarcane bagasse as waste of about 30% from total sugarcane weight. Usually sugarcane bagasse is burned to operate boiler in sugarcane mill. Meanwhile, the utilization of sugarcane bagasse, combine with citric acid for high quality particleboards production would be highly recommended. In this study, effect of citric acid content and pressing temperature on sugarcane particleboards properties were analysed. The size and target density of particleboards were 300 x 300 x 9 mm and 0.8 g/cm³, respectively. Citric acid liquid (59%) were sprayed onto sugarcane particles, with varied citric acid content (10, 15, 20 % of sugarcane particle weight). To evaporate water, sugarcane particles which already contain citric acid were pre-dried in oven of 80°C for 6h until the moisture content in sugarcane particles-citric acid was less than 3%. Subsequently, the boards were produced under pressing temperature of 180°C and 200°C, for 10 min. The physical properties of boards produced using 25% citric acid and pressed at 200°C (thickness swelling 4.43%; water absorption 29.48%) were superior than the others boards. The infrared (IR) spectra analysis showed the presence of ester linkage, representing that the carboxyl groups of citric acid had reacted with the hydroxyl groups of the sugarcane particles, providing the boards good physical properties. The boards mechanical properties were fulfilled the requirement of the JIS A 5908:2003 for particleboards type 18 (modulus of rupture 21.88 N/mm², modulus of elasticity 3944 N/mm², internal bond 1.03 N/mm², screw withdrawal 393 N).

1. Introduction
Sugarcane (Saccharum officinarum) produces sugarcane juice which is the raw material for sugar. The area of sugarcane plantation throughout Indonesia is estimated at 453,456 hectares [1]. The largest sugarcane plantation area in Indonesia is in the East Java region with an area of 203,566 hectares and productivity of 1,186,515 tons in 2017. Sugarcane stalks are harvested and squeezed to extract sugarcane juice and leave sugarcane pulp which is called sugarcane bagasse with yield of about 28% [2]. The sugarcane mill only operates during the milling season, which is around May to October (5 months or 150 days) each year. During milling season, one sugarcane milling factory with a production capacity of 4000 tons sugarcane per day, can produce sugarcane bagasse of 180,000 tons (30% x 600,000 tons of sugarcane stems). The amount of sugarcane bagasse is so large, it has not been managed properly and can cause environmental pollution, because the sugar content which is left in sugarcane bagasse creates an unpleasant odour due to the fermentation process of sugar by decomposing microorganisms. Meanwhile, the chemical composition of sugarcane bagasse consists of cellulose (38.4 - 45.5%), hemicellulose (22.7 - 27.0%), lignin (19.1 - 32.4 %), ash (1.0 – 2.8%) and
extractive substance (4.6 - 9.1%) [3]. Based on its availability and chemical composition, sugarcane bagasse can be used for particleboard raw materials. So far, raw materials for particleboard industry have become a problem in Indonesia because wood from natural forests is decreasing and expensive. Alternative raw materials such as sugarcane bagasse can be an option.

Generally, the process of making particleboards requires adhesives. Adhesives that are often used for making particleboards commercially are urea formaldehyde (UF), phenol formaldehyde (PF), melamine formaldehyde (MF), and isocyanate. All these adhesives are synthetic chemical adhesives and are made from non-renewable materials. In addition, adhesives such as UF, PF and MF emit formaldehyde emissions that are harmful to human health. At present, natural-based particleboard adhesives are developed that are renewable and do not contain harmful ingredients for human health. In addition to natural adhesives, adhesive agents have been developed for the manufacture of particleboards, namely citric acid [4-8]. Citric acid is an ingredient found in citrus fruits such as lemons, but for commercial purposes it is usually made by fermentation of ingredients containing glucose or sucrose. Citric acid is widely used in the food and pharmaceutical industries.

So far, the raw material for particleboards with citric acid adhesives that have been researched and developed includes wood, bamboo, sorghum bagasse, and alang-alang (Imperata cylindrica) [4, 6, 7, 10]. There was study of particleboard made from sugarcane bagasse and citric acid, to produce low density particleboards: 0.3 g/cm³ to 0.5 g/cm³ [9]. But research on high density particleboard (above 0.7 g/cm³) from sugarcane bagasse and citric acid has not been reported. The use of high-density particleboard products are usually for indoor or outdoor furniture, or for functional and structural building materials.

Regarding the use of citric acid for molded products and so on, the invention regarding the use of sugarcane bagasse as molded product raw material, including particleboard can be found in patents registered in Japan in 2009 under the title "Compositions that cure by heating and pressing" (JP5472639B2). The patent states that a composition is cured due to heat treatment and pressure, at a temperature of 180°C to 250°C, pressure of 5 kgf/cm² or more, with the main component being powder or a small part of the plant (a), carboxylic acid (b); where the weight ratio of small parts of plants (a) and carboxylic acids (b) is 1:1 to 1:8; carboxylic acid used in the form of powder; another component that can be added is saccharide (c); composition of small parts of plants (a) and carboxylic acids (b) with saccharides (c) of 1:0.1 to 1:5.0; the resulting product is molded. Patent JP5472639B2 also states that a small part of the plant (a) can be added to carboxylic acid (b) in the form of a solution, and by heat treatment at a temperature of 180°C to 250°C, pressure 40 kgf/cm² or more, where the weight ratio small plants (a) and carboxylic acids (b) in the form of a solution of 1:4 to 1:8. The patent also states that a small part of the plant (a) can be added with carboxylic acid (b) and saccharide (c) in the form of a solution, and by heat treatment at a temperature of 180°C to 250°C, pressure 40 kgf/cm² or more, where the ratio of the weight of a small part of the plant (a) with carboxylic acid (b) and saccharide (c) in the form of a solution of 1:6 to 1:14.

In our study, sugarcane bagasse particles were mixed with citric acid solution then being preheated. The pre-pressuring stage was conducted to reduce the trapping of water vapor in sugarcane bagasse particles during the hot-pressed process and avoid the risk of failure of particleboard formation due to blister (particleboard disruption due to trapped-water vapor pressure). The aim of this study was to provide alternative raw materials for the particleboard industry with bonding agents that are environmentally friendly, not harmful to health, with the result of high quality particleboards.

2. Materials and Methods

2.1. Materials

Sugarcane bagasse (Saccharum officinarum) was collected from sugarcane juice seller around Pakansari Stadion, Cibinong, West Java. Sugarcane bagasse stalks were cut into 40 cm length then processed using ring flaker. Afterward, sugarcane bagasse particles were screened to obtain particles
that passed through a 4-mesh and retained on a 14-mesh screen. All of the particles were dried in oven of 60°C to a moisture content of around 5%.

Citric acid (anhydrous) of technical grade was used without further purification. Citric acid was dissolved in water at a concentration of 59 wt%, and this solution was used as the binder. No other chemical compounds were used.

2.2. Methods

2.2.1. Manufacture of particleboard

Citric acid solution was sprayed onto dried particles to achieve various citric acid contents, i.e., 15, 20 and 25 wt%. Particles that had been sprayed with citric acid solution were dried at 80°C for 6 h and were called pre-dried particles. Subsequently, these particles were formed into mats using a forming box with the size of 300 × 300 mm.

The particle mat was hot-pressed at 180°C, and 200°C for 10 min. To produce particleboard with target density of 0.8 g/cm³, a 9-mm steel-thick bar was used to control the board thickness during the hot-pressing process. The maximum pressing pressure was 2.5 MPa when the upper side of pressing plate reached the steel-thick bar.

2.2.2. Evaluation of particleboards properties

2.2.2.1. Physical properties

Characterization of sugarcane bagasse particleboards physical properties were included thickness swelling (TS) and water absorption (WA) analysis. After conditioning for 1 week at room temperature, the boards were tested according to the Japanese Industrial Standards for particleboards (JIS A 5908:2003). The specimen size for TS and WA evaluation was 50 x 50 x 9 mm. Specimens were immersed in water for 24 h. The thickness and weight difference before and after immersion were calculated.

To observe particleboards thickness swelling in severe condition, specimens were subjected to a cyclic aging treatment (drying at 105°C for 10 h, warm-water immersion at 70°C for 10 h, drying at 105°C for 12 h, hot water immersion at 80°C for 10 h, and drying at 105°C for 12 h). The thickness and weight changes of the specimens that occurred throughout the treatment were evaluated. Each experiment was performed in five replications, and the average values and standard deviations were calculated. The thickness swelling (TS) and water absorption (WA) values of board after each cycle of treatment were measured.

2.2.2.2. Evaluations of functional groups in sugarcane bagasse-citric acid particleboards.

The edge of particleboard was scratched to obtain particles. The particles were ground into a powder, and the powder obtained was dried in a drying oven at 60°C for 16 h. Infrared (IR) spectral data were obtained with a FTIR spectrophotometer (Spectrum Two, Perkin Elmer) using the Universal Attenuated Total Reflectance (UATR) method and were recorded by an average of 16 scans at a resolution of 4 cm⁻¹.

2.2.2.3. Mechanical properties.

Characterization of sugarcane bagasse particleboards mechanical properties were included modulus of elasticity, modulus of rupture, and internal bond, according to the Japanese Industrial Standards for particleboards (JIS A 5908:2003). The bending properties of the boards, i.e., the modulus of rupture (MOR) and the modulus of elasticity (MOE), were evaluated by conducting a three-point bending test on a 200 × 50 × 9 mm specimen of board under dry conditions using Universal Testing Machine
(UTM 50kN Autograph, Shimadzu). The loading speed and effective span were 10 mm/min and 150 mm, respectively. The internal bonding (IB) strength was investigated using a 50 × 50 × 9 mm specimen of board.

3. Results and Discussion

3.1. Physical properties of sugarcane bagasse particleboards bonded with varied citric acid content

The challenge of using particleboards for furniture application in tropical countries is how to resolve the particleboards thickness swelling because of high humidity throughout the year. Moisture could cause particleboards to be swollen, particularly, particleboard bonded with urea formaldehyde, which is the most common adhesive used in particleboard industries. Beside susceptible to moisture, particleboards bonded with urea formaldehyde also brought problem to human health due to formaldehyde emission during its application. This research uses citric acid as bonding agent in sugarcane bagasse particleboards, as an alternative adhesive with no formaldehyde emission.

Particleboard physical properties explained by thickness swelling and water absorption characteristics. Figure 1, shows particleboards thickness swelling and water absorption after 24 h immersion in water. All types of sugarcane bagasse particleboards were fulfilled JIS standard that required particleboards thickness swelling lower than 12%. Sugarcane bagasse particleboard bonded with 25% citric acid and pressed at 200°C shows the best thickness swelling property, which was 4.43%. While sugarcane bagasse particleboard bonded with 15% citric acid and pressed at 180°C shows the worst thickness swelling property, which was 11.47%. The water absorption of sugarcane bagasse particleboards in this research were varied in range of 29.48% up to 48.57%.

![Figure 1](image)

**Figure 1.** Effect of citric acid content and pressing temperature on particleboard thickness swelling and water absorption.

Physical properties of sugarcane bagasse particleboards in this research were superior compare to alang-alang particleboards bonded with 15% citric acid, which the thickness swelling was 13.32 % [10]. The physical properties related to bondability between sugarcane lignocellulosic materials and citric acid. Chemical compound in sugarcane bagasse particles reacted with citric acid more effectively compare to chemical compound in alang-alang particles. Sugarcane bagasse contain cellulose in range of 38.4 - 45.5% and hemicellulose in range of 22.7 – 27.0% [3], on the other hand, alang contain 40.22% cellulose, 18.40% hemicellulose and 31.29% lignin [11]. Another data of lignocellulose component in alang [12], shows that alang contain 42.50% cellulose, 15.69% hemicellulose, 21.76% lignin and 7.49% ash. Hemicellulose content in sugarcane bagasse was higher than in alang fibers. The carboxyl groups of citric acid reacted with hydroxyl groups in hemicellulose of sugarcane bagasse to form ester linkages, then produced particleboards with superior physical properties.

To prove the superiority of sugarcane particleboards physical characteristics, we conducted cylic aging treatment. The change in particleboards thickness after several cycles of immersion and drying
was illustrated in Figure 2. The expanded of thickness change of the particleboard decreased with increasing of citric acid content. The thickness changes of the particleboard bonded with 25 wt% citric acid and pressed at 200°C after boiling treatment were lower than that of the other types of the particleboard. The thickness changes of all particleboards produced by pressing temperature of 200°C, were lower than 12%. The thickness swelling of sugarcane bagasse particleboards bonded with 15%, 20% and 25% citric acid after cyclic aging treatment were 8.27%, 7.31% and 6.03%, respectively. On the other hand, particleboards thickness change produced by pressing temperature of 180°C could reach higher than 12%, which were 15.12%, 11.38%, 12.38%, when bonded with 15%, 20% and 25% citric acid, respectively. These data show that citric acid content of 25 wt% and pressing temperature at 200°C, produce high quality dimensional stability of sugarcane particleboard even after a severe treatment.

![Figure 2](image)

**Figure 2.** Thickness change of particleboards with 15%, 20%, 25% citric acid content and 180°C, 200°C pressing temperature, during cyclic aging treatment.

### 3.2. Functional groups in sugarcane bagasse particleboards bonded with varied citric acid content

The infrared (IR) spectra of sugarcane particleboards with varied citric acid content is presented in Figure 3. An absorption peak at 1716 cm\(^{-1}\) appeared clearly in FTIR spectra of sugarcane particleboards bonded with 15% and 25% citric acid. Then the absorption peak was shift to 1721 cm\(^{-1}\) in FTIR spectra of sugarcane particleboards bonded with 20% citric acid. The peak at 1716 cm\(^{-1}\) and 1721 cm\(^{-1}\) were typically assigned to C=O stretching due to carbonyl groups and/or the C=O ester groups [13], [14]. The appearance of ester groups in the IR spectra indicates that the carboxyl groups of citric acid reacted with hydroxyl groups of sugarcane to form ester linkages.

The lignocellulosic materials contain abundant hydroxyl groups derived from lignocellulosic components such as cellulose, hemicellulose and lignin [15]. The sugarcane particleboards bonded with increased citric acid content showed more intense ester linkage. The consequent formation of ester linkages would improve the adhesiveness. As the result, physical and mechanical properties of sugarcane particleboards bonded with citric acid were improved.

The vibration at 3341 cm\(^{-1}\) was assigned to intra-molecular hydrogen bonding of cellulose C(3)OH·O(5) [16]. The region of IR spectra of sugarcane particleboards bonded with 15% citric acid contains vibrations at 2901 cm\(^{-1}\), which is assigned to CH\(_2\) asymmetrical stretching of the methoxyl groups [16], [17], [18]. That peak at 1034 cm\(^{-1}\) was corresponding to C-O vibration in hemicellulose
Figure 3 shows that absorption peak appeared at 1031 cm\(^{-1}\) in strong intensity, indicate a quite high hemicellulose content in sugarcane bagasse.

![Figure 3. Fourier transform infrared spectra of sugarcane bagasse particleboards with varied citric acid content (15%, 20%, 25%) and pressing temperature (180°C, 200°C) after cyclic aging treatment.](image)

3.3. Mechanical properties of sugarcane bagasse particleboards bonded with varied citric acid content

The sugarcane bagasse modulus of rupture and modulus of elasticity, were illustrated in Figure 4. Particleboards made from sugarcane bagasse particles with 25% citric acid, pressed at 200°C shows the highest modulus of rupture (MOR) among other particleboards in this study, which was 21.88 N/mm\(^2\). The MOR of sugarcane bagasse particleboards was higher than that of alang-citric acid particleboards (7.82 MPa) [10]. The particleboard modulus of elasticity (MOE) made from sugarcane particle bonded 25% citric acid, pressed at 200°C (3944 N/mm\(^2\)) was higher than that of sugarcane particleboards, bonded with 15% and 25% citric acid, which were 3429 N/mm\(^2\) and 3361 N/mm\(^2\), respectively.

In the previous study, the tensile strength of wheat straw hemicellulose film decreased, but its MOE increased as the citric acid content increased up to 20 wt%, because citric acid acting as a flexible cross linker [20]. The same phenomenon was observed in this study. Citric acid was also acting as cross-linking agent in sugarcane particleboards. The citric acid causes the material to stiff and brittle, therefore the particleboards elasticity was improved but the particleboards tensile strength was decreased.

![Graphs showing modulus of rupture and modulus of elasticity](image)
Particleboards internal bond (IB) properties (Figure 5) was also confirmed that citric acid successfully acting as bonding agent in sugarcane particleboards. The internal bond of particleboards made from sugarcane bagasse particle bonded 25% citric acid, pressed at 200°C, which was 1.03 N/mm², was higher than that of sugarcane particleboards made from sugarcane bagasse particles bonded with 15% citric acid (0.73 N/mm²) or 20% citric acid (0.98 N/mm²).

The internal bond (IB) strengths of sugarcane particleboards produced by pressing temperature of 200°C were higher than that of particleboards produced by pressing temperature of 200°C (Figure 4). Particleboards IB values produced by pressing temperature of 180°C were 0.68 MPa (CA 15%), 0.86 MPa (CA 20%), 0.63 MPa (CA 25%). The increment of citric acid amount introduced into sugarcane particles, could not enhanced the particleboards internal bond strength, when pressing temperature was 180°C. Although chemical reaction between sugarcane lignocellulosic material and citric acid was occurred as presented in Figure 3, it seems some substance in sugarcane materials could not reacted with citric acid at temperature of 180°C. All the sugarcane particleboards bonded were fulfilled the internal bond values requirement of JIS A 5908 for particle boards type 18 (IB min 0.3 N/mm²).

Although physical properties, modulus of elasticity and internal bond of sugarcane particleboards bonded with citric acid and pressed at 200°C in this study were fulfilled the requirement of JIS 5908:2003 for particleboards type 18, only sugarcane particleboards bonded with 20% citric acid pressed at 180°C and sugarcane particleboards bonded with 25% citric acid pressed at 200°C which were fulfilled the requirement of screw withdrawal value according to JIS 5908:2003 for particleboards type 8 (Figure 5). One of the disadvantage of particleboard bonded with citric acid is the brittleness [21].

4. Conclusion
The thickness swelling properties of sugarcane bagasse particleboards bonded with 15%, 20% or 25% citric acid were 5.32%, 5.18%, 4.43%, respectively, fulfilled the requirement of the JIS A 5908:2003. After cyclic aging treatment, thickness swelling of sugarcane bagasse particleboards pressed at 200°C were lower than 9%, indicate that citric acid successfully performed as bonding agent to produce high quality particleboards. The sugarcane particleboards bonded with 25 wt% citric acid and pressed at 200°C, fulfilled the JIS 5908:2003 for particleboards type 18 on modulus of rupture, modulus of elasticity, internal bond and screw withdrawal characteristics, emphasized that the high-quality particleboards were produced. The infrared (IR) spectral analysis showed the presence of ester linkage, representing that the carboxyl groups of citric acid had reacted with the hydroxyl groups of the sugarcane bagasse particles.
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Acknowledgments
Authors wishing to acknowledge assistance from Ambarwati Fauziah on producing sugarcane particleboards. Authors also very thankful for financial support from SATREPS project for producing biomass energy and material through revegetation of alang-alang (Imperata cylindrica) fields.