Manufacture and Properties of Non-Wood Binderlessboard: Effect of Storage Method and Manufacturing Process on Chemical Composition of Bagasse Binderlessboard

Ragil Widyorini and Shuichi Kawai

Abstract

Effects of storage and pressing methods on the chemical composition of Sugarcane (*Saccharum officinarum* L.) bagasse binderlessboards were investigated by chemical and spectroscopic analyses. The inner layer (core/pith) and the outer hard fibrous layer (face/rind) of bagasse were used as raw materials. The result showed that effect of steam-injection pressing was higher than hot pressing treatment on the chemical composition of bagasse binderlessboards. Under steam-pressure of 1.0 MPa for 10 min, hemicelluloses of bagasse were more significantly degraded than α-cellulose and lignin. Decreasing of Syringyl/Guaiacyl (S/G) and Cinnamic acids/Guaiacyl (C/G) ratios indicated that modification of lignin had occurred during steam and heat treatments. Considering that the residual sugar in bagasse was still high, the storage method of Sugarcane bagasse was an important key for producing bagasse binderlessboards.

Key words: bagasse pith, bagasse rind, binderlessboard, storage method, chemical composition.

Introduction

Shen (1986) pointed out that wood/non-wood based fragment could be converted into boards by steam or heat treatments without using any resin adhesives. This phenomenon, called self-bonding, is improved by activating chemical components of the board constituents during steam or heat treatments. Effects of the steam/heat treatments depend on many variables, such as chemical composition of the lignocellulosics, pressing time, temperature, pretreatment, moisture content, and possibly many other factors that are still not yet understood.

Bagasse is the highly fibrous residue remaining after Sugarcane is pressed to remove sucrose. Large quantities of bagasse are now still left unused or burnt in developing countries. The surplus bagasse is usually used as a fuel source for sugar processing. Many researches have been done to utilize the bagasse for production of ethanol, animal feeds, paper, and composite products. Bagasse normally still contains residual sugars, depending on the cane variety, its maturity, harvesting method, and the efficiency of the sugar milling plant. The removal of pith and residual sugars is usually an important point to produce the good quality resin-bonded panel products (Shen 1986; Atchison and Lengel 1985). Pith, which has no structural strength, is very absorbent and can rob the boards much of applied resin. Residual sugars may not be chemically compatible with the conventional resin binders and may interfere the bonding. In our previous study (Widyorini *et al.* 2005b), bagasse pith showed higher board properties than bagasse rind binderless boards. Severe condition of steam-injection pressing caused delamination on the bagasse binderless boards, however, steam-pressed boards provided relatively higher board properties than hot-pressed boards.

This study is designed to investigate chemical changes of bagasse pith and bagasse rind binderless particleboards manufactured by steam-injection pressing and hot pressing systems. Considering that bagasse is a non-woody material that contains cinnamic acids, pyrolysis-gas chromatography-mass spectrometry with methylation using tetramethylammonium hydroxide (TMAH/Py-GC-MS) analysis is used to avoid the decarboxylation of polar moieties and yields phenolic derivatives, which are not observed during conventional analytical pyrolysis (Kuroda *et al.* 2002). Effects of pressing and storage methods on the chemical composition of bagasse binderless boards are studied and discussed.

Materials and Methods

Raw Materials

Raw materials in this research were same with our previous study (Widyorini *et al.* 2005b), which can be described as follows; Sugarcane (*Saccharum officinarum L.*) stalk was separated by a cane separator to get the inner layer (pith) and the outer layer (rind). The pith particles, was sent in the sugar milling process to extract the sugar juice. Bagasse rind was further processed into particles using hammer mill and then screened to pass 2 mm. Bagasse pith (C1) and rind particles (F1) were then air-dried.

In order to investigate effect of storage methods, other bagasse pith were also prepared as follows: After harvesting, the Sugarcane stalk was separated by the cane separator. The pith particles was sent in the sugar milling process to extract the sugar juice, and then kept in the refrigerator (for $\pm$ 5 month), to prevent the effect of fermentation process. The pith particles obtained were

then called C2. The other Sugarcane stalk was stored for 3 weeks before prepared by the cane separator. Then after, the pith particles were sent in the sugar milling process to extract the sugar juice, and then air-dried (C3).

Binderless boards from those particles (C1, C2, C3, and F1) were manufactured by steam-injection pressing at 1.0 MPa (183 °C) and hot pressing treatments at 190 °C for 10 min pressing time. The target densities of all binderless boards were 0.7 g/cm^3, with dimension size was 23 x 23 x 1.2 cm.

Chemical Analysis of Sugarcane Bagasse and the Binderless Boards

All bagasse particles (C1, C2, C3, and F1) and its binderless boards were cut and ground to pass through 30 mesh screen, were retained on 60 mesh screen, and were then air-dried. The samples were extracted successively with a mixture of ethanol and benzene (1:2, v/v) for 24 hours by refluxing, and then with distilled water at 85°C for 3 h. The analyses of extractives were carried out in duplicates. Lignin and holocellulose was determined by Klason method and Wise method, respectively. α-cellulose content was determined using the holocellulose by extraction with 17.5% NaOH as reported. All the chemical analyses were carried out in triplicate.

Neutral sugar composition of the water-soluble fraction was determined as an alditol acetate by a Gas Chromatogram, Shimadzu GC-17A (Kyoto, Japan) on ULBON HR-SS10 (0.25 mm x 25 m, ULBON, Kyoto, Japan) after acid hydrolysis. The acid hydrolysis was carried out with trifluoroacetic acid (TFA) at 100 °C for 3 h. All analyses were run in duplicate.

Bagasse lignin was analyzed by pyrolysis-gas chromatography-mass spectrometry with methylation using tetramethylammonium hydroxide (TMAH/Py-GC-MS). The samples (0.2 ± 0.01 mg) were placed on a 20 µm ferromagnetic pyrofoil. A solution of 1 mmol/ml 3-ethoxy-4-hydroxybenzaldehyde in methanol (1 µl) was added as internal standard (IS). Tetra methylammonium hydroxide (25% in methanol solution) as methylating agent was droped on the sample about 3 µl. Then, the mixture was air dried for 30 min. The samples were pyrolyzed at 500 °C for 6 s. The pyrolysis was performed on a Shimadzu GCMS-QP5050A Mass Spectrometer (Kyoto, Japan) equipped with a Frontier Lab Pyrolyser PY-2020D (Fukushima, Japan). Separation of compounds was done on a fused silica capillary column, CP-Sil 8 CB (50 m×0.25 mm i.d., Chrompack, Netherlands) using helium as a carrier gas (total flow rate, 27 ml/min). The temperatures of the injection and detector ports were kept at 280°C. The programming of the column oven temperature for GC-MS was synchronized with the temperature program of the pyrolyzer. The column temperature for GC-MS was kept at 50°C for 1 min, and then raised to 280°C at a rate of 5°C/min and after which was maintained for 10 min. Peak assignments were carried out by comparison of their mass spectra and relative retention times with compounds reported in the literature and standard compounds. The syringyl/guaiacyl ratio (S/G) was calculated by dividing the sum of peak areas from syringyl derivatives by the sum of peak areas from guaiacyl derivatives. The cinnamic acid/guaiacyl ratio (C/G) was calculated by dividing the sum of peak areas from cinnamyl derivatives (*p*-coumaric acid and ferulic acid) by the sum of peak areas from guaiacyl derivatives. A minimum of three-repeated TMAH/Py-GC-MS was done for each sample.

Results and Discussion

Chemical Composition of Bagasse and Its Binderless Boards

Figure 1 shows chemical composition of bagasse pith C1 and F1 particles as well as their binderless boards. Bagasse pith C1 and rind F1 particles contained a large amount of water extractives. It seemed that residual free sugar was still high, as desribed by Shen 1986. The amount of alcohol-benzene extractives of rind F1 particles was higher than that of pith C1 particles, indicating that some waxes and silica were still remained in the rind F1 particles. The presence of waxes inhibit bonding among particles, as the bonding properties of bagasse rind boards were lower than bagasse pith boards (Widyorini *et al.* 2005b). Figure 1 shows that hot-pressing system has no significant effects on the degradation of α-cellulose and

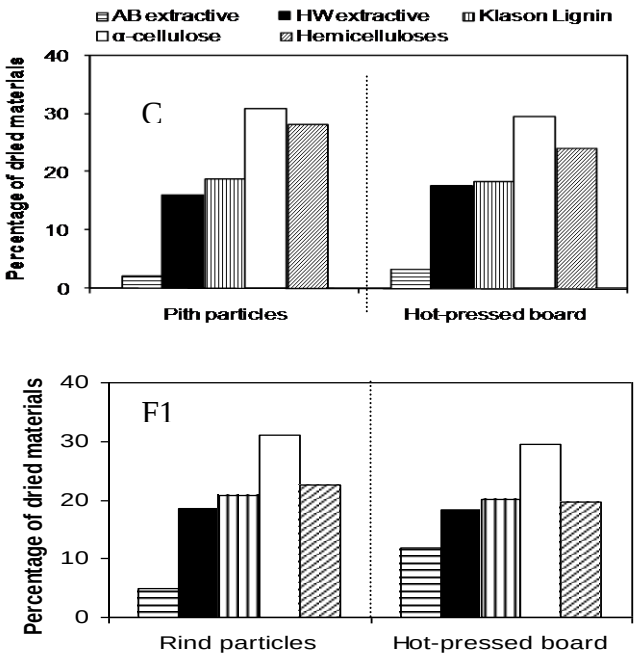

Figure 1. Effect of hot-pressing treatment on chemical composition of binderless boards. Pressing time was 10 min, corrected board density was 0.65 g/cm^3. AB, alcohol-benzene; HW, hot water.

lignin, but significant degradation on hemicelluloses in pith C1 board. It indicated that the pith particles were more easily degraded during treatments compared with rind particles.

Bagasse C3 particles contained higher water-soluble components, but lower hemicelluloses, lignin and cellulose than other bagasse particles as shown in Figure 2. It seemed that fermentation process had already occurred during storage time. The fermentation process occurs in an exothermic process, thus rapidly increasing the temperature, while at the same time the residual sugars ferments to acetic acid (Atchison and Lengel 1985). The combination caused in severe damage of hemicelluloses and cellulose fiber quality, as well as severe losses in storage. The color of bagasse pith C3 was pink, supporting this phenomenon. It was found that severe degradation of pith C3 components occurred during steam and heat treatments, producing poor quality of binderless boards. Thus, fermentation process has to be controlled to preserve the quality of bagasse and to minimize losses in storage.

Effect of steam-injection pressing was higher than hot pressing treatment on the chemical composition of bagasse binderless boards, as found in the kenaf core binderless boards (Widyorini *et al.*2005a). The surface of the steam-pressed boards was much darker than that of hot-pressed boards, indicating intensive changes in the chemical compositions of the lignocellulosic materials has occurred. The degradation of the chemical components and residual free sugars into low molecular weight compounds would release water during treatment. By

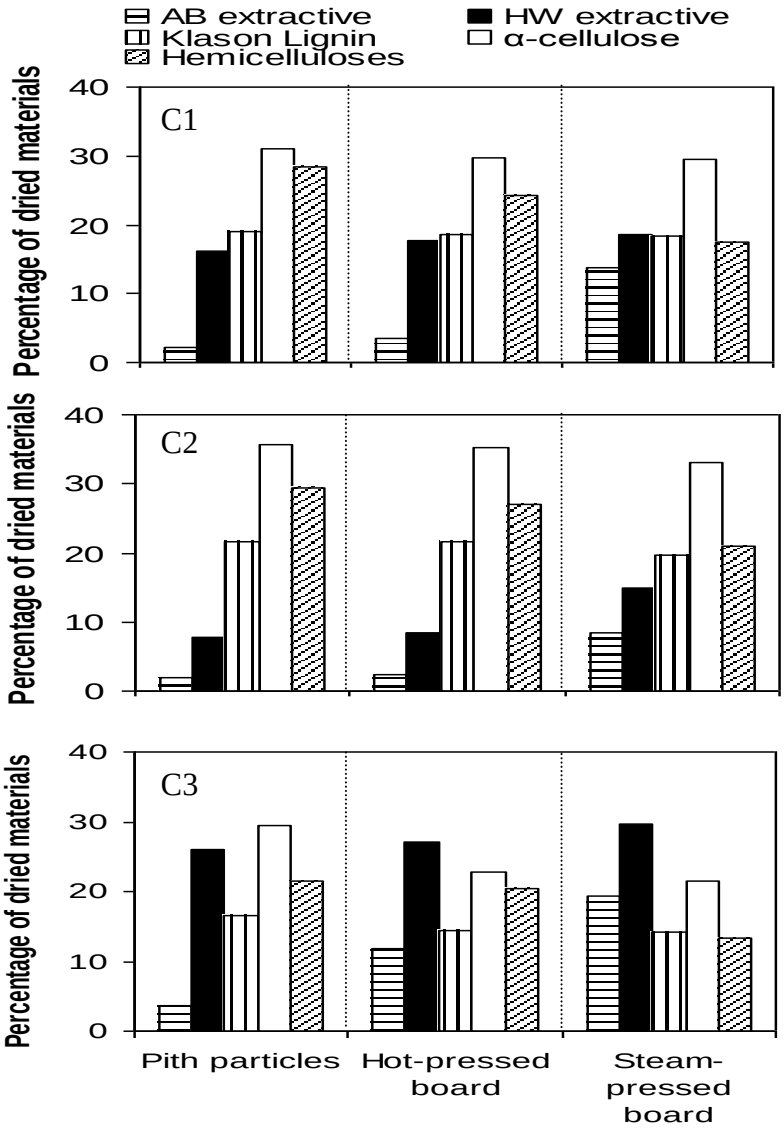

Figure 2. Effects of pressing and storage methods on chemical composition of binderless boards. Pressing time was 10 min, corrected board density was 0.65 g/cm^3. AB, alcohol-benzene; HW, hot water.

injecting the high-pressure steam at longer pressing time, the excessive of steam would be produced and a great degradation of the chemical components would occur in the board. It was well known that intensive degradation of chemical components during treatment would decrease the board properties. Therefore, a special attention in the steam-injection pressing must be given due to the delamination of binderless boards could be occurred during high steam-pressure and longer pressing time (Widyorini *et al.*2005b).

Result of this study showed that hemicelluloses of bagasse pith C1 and C2 were more significantly degraded than α-cellulose and lignin during steam/heat treatments. Okamoto *et al.* (1994) found that under steam-injection pressing in a pressure range of 0.6 ~ 1.1 MPa for 5 min, hemicelluloses and cellulose of softwood/hardwood decreased with increase in steam pressure, while the lignin component did not change significantly. On the other case, hemicelluloses, α-cellulose and lignin of kenaf core decreased significantly with increase in steam pressure and pressing time under mild steam treatment (0.6 ~ 1.0 MPa) (Widyorini *et al.*2005a).

Analysis of Water-soluble Polysaccharide

The hemicelluloses in bagasse are composed of a xylan polymer backbone onto which other groups are bonded-mainly glucuronic acid and arabinose (Lavarack *et al.* 2002). The hemicelluloses are associated with the cell wall, mostly soluble in alkali and easy hydrolyzed by an acid to simple sugars/sugar acids (Nagaty *et al.* 1982).

The neutral sugar composition of water-soluble polysaccharide from bagasse and their binderless boards is shown in Table 1. The amount of xylose in the hot water extract of the bagasse pith C1 boards after steam treatment at 1 MPa was 6.67%, based on the dry weight of the bagasse boards, while that obtained after hot pressing at 190°C was 0.05%. Thus, marked differences were found in the amount of soluble xylan between the steam-injecting and hot pressing treatments. Similar trend was found in the amount of soluble xylan of the other bagasse particles.

Hsu *et al.* (1988) reported that xylose content in water extract from aspen treated by steam at 1.55 MPa for 4 min was 0.35%. Whereas, the amount of xylose in the water extract of kenaf boards after steam-injection treatment at 1 MPa for 20 min was 3.0% (Widyorini *et al.* 2005a). Compared with those results, the hemicelluloses of bagasse seemed more easily susceptible to hydrolysis by steam. Kaar *et al.* (1998) found that processing optimums of steam explotion were highly raw materials dependent, since different carbohydrates composition dictated different condition. Materials with high in xylose content required milder conditions with shorter treatment times, than materials with lower in xylose or higher in glucose (Kaar *et al.* 1998).

High content of glucose in the water-soluble polysaccharide from untreated bagasse particles indicated the residual free sugars content. Glucose content of rind F1 much higher than pith C1 particles, it might due to the F1 particles were not extracted for its sugar juice. Water-soluble polysaccharide from bagasse pith C3 contained higher glucose content than other bagasse piths, which might also come from degradation of cellulose, considering that bagasse pith C3 has degraded during storage period, as mentioned before.

TMAH Pyrolysis GC-MS Analysis

It was known that the structural features of lignin, such as the ratio of syringyl nuclei to guaiacyl nuclei and the amount of ring-conjugated carbonyl groups, had a great influence on the rate of the delignification reaction and the quality of the final products in the pulping process (Sun *et al.* 2003). The combination of pyrolysis with high-resolution capilarry gas chromatography and mass spectrometry has been increasingly used for the determination of the chemical compositions of lignin in wood chemistry. The analysis required only small sample size and a simple sample preparation.

Table 1. Neutral sugar composition of water-soluble polysaccharide.*

	Rhamnose	Arabinose	Xylose	Mannose	Galactose	Glucose
C1	**	0.26	**	0.20	**	3.15
HPC1	**	0.45	0.05	0.28	**	4.88
SPC1	**	0.57	6.67	0.63	0.47	4.47
C2	**	0.25	0.04	0.30	0.09	1.89
HPC2	**	0.50	0.21	0.12	**	2.14
SPC2	**	0.75	6.08	0.56	0.50	2.62
C3	**	0.07	0.03	0.04	0.03	8.10
HPC3	**	0.29	0.15	0.31	**	8.64
SPC3	**	1.00	10.06	0.52	0.65	8.04
F1	**	**	**	**	**	6.46
HPF1	**	0.23	0.98	0.53	0.17	7.04

HP, hot pressing treatment (190°C, 10min); SP, steam-injection pressing (1 MPa, 10min)
* percentage of dried materials; ** not detected

The TMAH products from bagasse and its binderless boards consisted of methylated syringyl, guaiacyl and *p*-hydroxyphenyl derivatives. Figure 3 shows the chromatogram of the total ion current (TIC) for the TMAH/Py-GC-MS products for bagasse pith (C1) and rind (F1) particles, and the compounds notation are defined in Table 2. Result showed that S/G ratios of bagasse C1, C2, C3, and F1 particles were 1.73, 1.84, 1.60, and 1.42, respectively. The S/G ratios were decreased during steam and heat treatments, which steam-pressed boards had S/G ratios lower than hot-pressed boards. It showed that syringyl units were more reactive than guaiacyl units, due to the more highly condensed structures of the G units than those of the S units.

The presence of cinnamyl units (*p*-coumaric acid/P18 and ferulic acid/G18 supports their identification in non-woody plants (Kuroda *et al.* 2002; Clifford *et al.* 1995; Martin *et al.* 1995; Widyorini *et al.* 2005c). The presence of p-coumaric acid exists in greater amounts than ferulic acid, which is consistent with other researchers (Sun *et al.* 2003, Kato *et al.* 1984). Kato *et al.*(1984) reported that the cinnamic acids in the Sugarcane bagasse were considered to be esterified to the different moleculer species, polysaccharide and lignin nuclei, respectively. The result also showed that both linkages of lignin-carbohydrate and phenolic acid-carbohydrate were labile to alkali.

The S/G and C/G values of untreated bagasse pith C1 and its binderless boards are shown in Table 3. As the result of S/G ratios, bagasse steam-pressed boards provided lower C/G ratios than the hot-pressed boards. Steam-pressed boards had C/G ratios lower than hot-pressed boards. The obtained cinnamic acids in this study came from both linkages of lignin and carbohydrate. Quantitative analysis is required to make clear the cleavage of cinnamic acids. Nevertheless, based on those results, it could be suggested that some parts of ester-linked cinnamic acids were cleaved due to the degradation of hemicelluloses and lignin during steam/heat treatments. All these degradation products are supposed to contribute in the self-bonding formation of binderless boards.

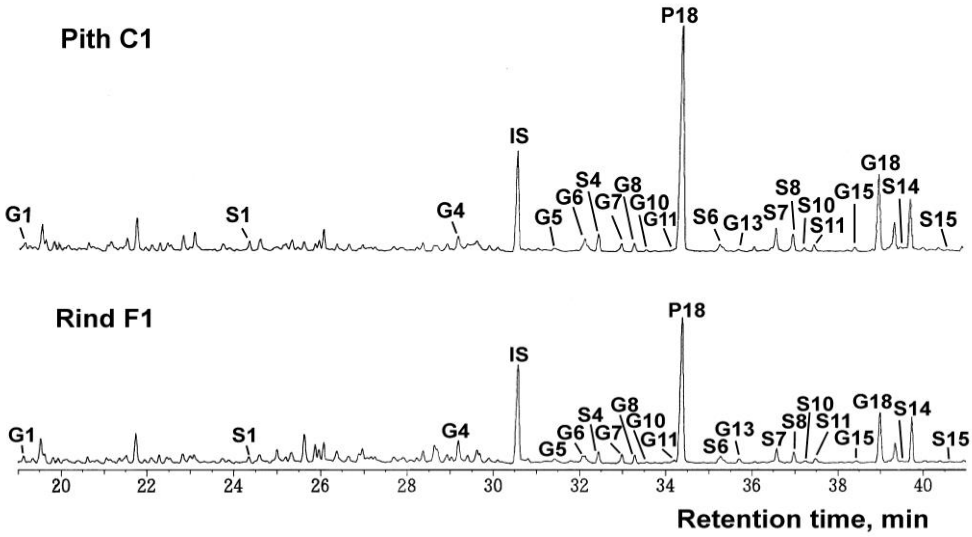

Figure 3. Chromatogram of the total ion current (TIC) for the TMAH Py-GC-MS products from bagasse pith C1 and rind F1 particles. Peak assignments are listed in the Table 2.

Table 2. List of products detected by TMAH Py-GC-MS analysis.

Notation	Assignment	Molecular weight
G1	1,2-dimethoxybenzene	138
S1	1,2,3-trimethoxybenzene	168
G4	3,4-dimethoxybenzaldehyde	166
IS	3-ethoxy-4-methoxybenzaldehyde	180
G5	3,4-dimethoxyacetophenone	180
G6	methyl 3,4-dimethoxybenzoate	196
S4	3,4,5-trimethoxybenzaldehyde	196
G7	cis-2-(3,4-dimethoxyphenyl)-1-methoxyethylene	194
G8	trans-2-(3,4-dimethoxyphenyl)-1-methoxyethylene	194
G10	cis-1-(3,4-dimethoxyphenyl)-1-methoxy-1-propene	208
G11	trans-1-(3,4-dimethoxyphenyl)-1-methoxy-1-propene	208
P18	4-methoxycinnamic acid, methyl ester	192
S5	3,4,5-trimethoxyacetophenone	210
S6	methyl 3,4,5-trimethoxybenzoate	226
G13	trans-1-(3,4-dimethoxyphenyl)-3-methoxy-1-propene	208
S7	cis-2-(3,4,5-trimethoxyphenyl)-1-methoxyethylene	209
S8	trans-2-(3,4,5-trimethoxyphenyl)-1-methoxyethylene	209
S10	cis-1-(3,4,5-trimethoxyphenyl)-1-methoxy-1-propene	223
S11	trans-1-(3,4,5-trimethoxyphenyl)-1-methoxy-1-propene	223
G14	threo/erythro-1-(3,4-dimethoxyphenyl)-1,2,3-trimethoxypropane	270
G15	threo/erythro-1-(3,4-dimethoxyphenyl)-1,2,3-trimethoxypropane	270
G18	3,4-dimethoxycinnamic acid, methyl ester	222
S14	threo/erythro-1-(3,4,5-trimethoxyphenyl)-1,2,3-trimethoxypropane	300
S15	threo/erythro-1-(3,4,5-trimethoxyphenyl)-1,2,3-trimethoxypropane	300

G, guaiacyl units; S, syringyl units; P, *p*-hydroxyphenyl units; IS, internal standar

Table 3. A S/G and C/G ratios* of the bagasse and its boards by TMAH Py-GC-MS.

Sample	Ratio S/G	Ratio C/G
C1	1.73	9.97
HPC1	1.52	9.89
SPC1	0.86	6.59

Remarks: G, guaiacyl units; S, syringyl units;
C, cinnamic acids (*p*-coumaric acid + ferulic acid) units.
HP, hot pressing treatment (190^{o}C, 10min); SP, steam-injection pressing (1 MPa, 10min)
*as relative percentage of total-ion areas of TMAH/Py-GC-MS products

Conclusion

Effects of pressing and storage methods on chemical changes of bagasse binderless boards were evaluated. The result showed that effect of steam-injection pressing was higher than hot pressing treatment on the chemical composition of bagasse binderless boards. It was found that under steam-pressure of 1.0 MPa for 10 min, hemicelluloses of bagasse were more significantly degraded than α-cellulose and lignin. Decreasing of S/G and C/G ratios indicated that modification of lignin had occurred during steam and heat treatments. It supposed that all these degradation products contributed in the self-bonding formation of non-woody binderless boards. Storage method of Sugarcane bagasse was one of the important keys for producing binderless boards, considering that the residual sugars in bagasse was still high.

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Ragil Widyorini
Forest Product Technology Department,
Faculty of Forestry, Gadjah Mada University
Jl. Agro no. 1, Bulaksumur Yogyakarta 55281
Telp. 0274-6491428/550541
Email: ragil_w@hotmail.com

Shuichi Kawai
Research Institute for Sustainable Humanosphere,
Kyoto University
Kyoto, Japan