Jurnal Ilmu Kehutanan
Journal of Forest Science
https://**jurnal**.ugm.ac.id/jikfkt

Binderless MDF from Hydroxymethylated Kenaf Pulp

MDF Tanpa Perekat dari Pulp Kenaf Terhidroksimetilasi

Nyoman J Wistara[1]*, Wulan Starini[1], Fauzi Febrianto[1], & Gustan Pari[2]

[1]Department of Forest Products, Faculty of Forestry, Bogor Agricultural University (IPB), Kampus Dramaga IPB. Dramaga Bogor, Bogor 16680
Email: nyomanwis@gmail.com
[2]Forest Products Research Center, Ministry of Environment and Forestry, Republic Indonesia, Jl. Gunung Batu, Ciomas. Bogor, 16610

RESEARCH PAPER

Article history:
Received (masuk): 24 Mei 2017
Accepted (diterima)): 9 November 2017

KEYWORDS
Hibiscus cannabinus L.
hydroxymethylation
lignin
MDF
chemical modification

ABSTRACT

Modified lignin with improved reactivity can be a potential alternative for synthetic phenol formaldehyde resin for the adhesive of wood composite. Direct hydroxymethylation of kenaf in the present experiments was intended to increase lignin reactivity, and therefore was expected to result in satisfying properties of binderless MDF. The stem of kenaf was refined in a disk refiner and the refined fibers were hydroxymethylated in various levels of alkalinity. The concentration of NaOH during hydroxymethylation was of 3%, 6% and 12%. Wet process was applied to produce MDF (30 cm x 30 cm x 1 cm) with target density of 0.65 g/cm³. Physical and mechanical properties of MDF were measured in accordance with the standard procedure of JIS A 5905: 2003. Chemical changes in the surface of pulp and the change of board crystallinity were evaluated by FTIR-KBr method and X-Ray Diffractometry (XRD), respectively. Density, moisture content, and screw withdrawal of the board increased with increasing of NaOH concentration. Thickness swelling, water absorption, MOE and MOR increased up to 3% concentration of NaOH. The IB and heat conductivity of MDF were not influenced by NaOH concentration. Increasing OH groups due to hydroxymethylation was thought to be the origin of high water absorption and thickness swelling of the resulting boards. Higher alkalinity during hydroxymethylation stage was likely increasing cellulose crystallinity that brought about increasing board density. However, chemical modification of the fiber was thought to be more influential to the bending strength and stiffness of the resulting fiberboard. Hydroxymethylation of kenaf pulp was successfully improved board properties. Except for the moisture content, thickness swelling and internal bonding (at 0% and 3% NaOH concentration), all properties of the MDF satisfied the requirement of JIS A 5905: 2003 (type 5) standard.

KATA KUNCI
Hibiscus cannabinus L.
hidroksimetilasi
lignin
MDF
modifikasi kimia

INTISARI

Lignin yang telah ditingkatkan reaktifitasnya dapat menjadi bahan alternatif perekat resin sintetis fenol formaldehida. Reaktivitas lignin dapat diperbaiki melalui hidroksimetilasi. Dalam penelitian ini, batang kenaf digiling menggunakan *disk refiner*, dan selanjutnya dilakukan hidroksimetilasi pada beragam alkalinitas. Konsentrasi NaOH yang digunakan dalam hidroksimetilasi bervariasi dari 3%, 6% dan 12%. Proses basah diterapkan untuk membuat MDF (30 cm x 30 cm x 1 cm) dengan target kerapatan 0,65 g/cm^3. Sifat fisis dan mekanis MDF diukur mengikuti prosedur standar JIS A 5905: 2003. Perubahan gugus fungsi permukaan pulp dan tingkat kristalinitas papan masing-masing dievaluasi menggunakan FTIR-metode KBr dan difraksi sinar X (XRD). Hasil penelitian menunjukkan bahwa konsentrasi NaOH tidak mempengaruhi IB dan konduktivitas panas MDF. Kerapatan, kadar air, dan kuat pegang sekrup cenderung meningkat dengan meningkatnya konsentrasi NaOH. Pengembangan tebal, daya serap air, MOE, dan MOR meningkat sampai dengan hidroksimetilasi dalam NaOH konsentrasi 3%. Peningkatan gugus OH serat akibat hidrosimetilasi diduga meningkatkan penyerapan air dan pengembangan tebal papan yang dihasilkan. Alkalinitas hidroksimetilasi yang lebih tinggi meningkatkan gugus cincin aromatik yang menunjukkan bahwa reaksi formaldehida berlangsung dengan lebih baik. Peningkatan alkalinitas dalam hidroksimetilasi meningkatkan kristalinitas selulosa. Peningkatan kristalinitas selulosa diduga berkontribusi dalam meningkatkan kerapatan, namun perubahan gugus kimia serat diduga lebih berpengaruh terhadap MOR dan MOE dari papan serat yang dihasilkan. Hidroksimetilasi pulp kenaf berhasil meningkatkan sifat papan. Kecuali untuk kadar air, pengembangan tebal dan IB (pada hidroksimetilasi dalam 0% dan 3% NaOH), semua sifat-sifat dari MDF yang dihasilkan memenuhi persyaratan standar JIS A 5905: 2003 (tipe 5).

© *Jurnal Ilmu Kehutanan-All rights reserved*

Introduction

Lignin is a natural product of plants along with cellulose and hemicelluloses. It is the most abundant natural polymer after cellulose with its content varied from 15–30% dependent on plant species (Mansouri & Salvado 2006). Lignin constituting structural units determine its reactivity (Capraru et al. 2012). The presence of phenolic and aliphatic hydroxyl at C-α and C-γ of its side chain bring about lignin can be used for partial phenol substitution in phenol formaldehyde adhesive (Benar et al. 1999; Malutan et al. 2008). Convenience of collection, non-toxic nature, and cheaper procurement of lignin also support its potential for phenol substitution in PF adhesive (Vázquez et al. 1997).

Technical lignins of pulping process (Çetin & Özmen 2003) such as that of kraft lignin and lignosulfonate have been used to substitute part of phenol in phenolic resin or directly used as natural adhesive for fiber board preparation (Alonso et al. 2005; Velásquez et al. 2003). Arias (2008) further reported that lignin can be used as adhesive without the need of pretreatment. However, the reactivity of adhesive from technical lignin is lower than that of phenolic adhesive because of its low phenolic hydroxyl content, high ring substitution, and the presence of steric hindrance in lignin (Vázquez et al. 1999). Less reactive nature of technical lignin render its limited capacity to replace phenol in phenolic adhesive (Nimz 1983). The drawback of lignosulfonate

based adhesive for wood products adhesion could be brought about by insignificant cross linking ability of lignosulfonate with PF resin, for instance (Pizzi 1994).

Increasing substitution of phenol with lignin can be done through lignin modification that increases its reactivity (Benar et al. 1999; Arias 2008). Lignin can be modified through methylolation, phenolation, demethylation and fractionation (Malutan et al. 2008). Benar et al. (1999) and Malutan et al. (2008) have shown that hydroxymethylation is a very relevant method for lignin modification. Hydroxymethylation is carried out by reacting lignin with formaldehyde in alkaline media (Malutan et al. 2008).

During the initial stage of hydroxymethylation, hydroxyl group reacts with lignin preferably at ortho position. At elevated temperature, hydroxymethyl groups react with other lignin units or its phenolic group to form methylene bridge (Benar et al. 1999). When the reaction temperature is decreased, cross linked chemical bonds are formed resulting in a hardened adhesive (Pizzi 1994).

Hydroxymethylated technical lignin can be used for adhesive substitution at various proportion (Benar et al. 1999). However, Pizzi (1994) indicates that the resulting adhesion product of technical lignin was not satisfying due to the insignificant reactivity of lignin to formaldehyde and the limited presence of free aromatic groups. Lignin reactivity resulted from hydroxymethylation is determined by the nature of raw material (softwood, hardwood and non wood), pulping condition of the raw material (pH, temperature and pressure), and other reaction conditions (Gonçalves & Benar 2001). Upon hydroxymethylation with formaldehyde, non-wood based lignin is more reactive than that of lignin from wood (Karina et al. 1994).

Kenaf is non-wood lignocellulosic materials with lignin content of approximately 16 % (Pande et al. 2000). Therefore, it is a potential raw material for the production of binderless composite board (Xu et al. 2006). Extensive researches have been done to produce binderless composite boards based on kenaf fibers (Okuda & Sato 2004; Xu et al. 2004; Widyorini et al. 2005). However, physical and mechanical properties of non-wood lignocellulosic based fiber board (Eroglu et al. 2001) is inferior to that of fiber board produced from softwood (Ye et al. 2007). Board properties could be improved through various method of chemical activation, such as that of steam-pressed pretreatment on kenaf core carried out by Widyorini et al. (2005).

In the present research, endeavors for the improvement of kenaf binderless fiber board properties was carried out by direct hydroxymethylation of kenaf pulp. The effect of hydroxymethylation on the physical and mechanical properties of binderless medium density fiber board was specifically examined.

Materials and Methods

The present research was mainly emphasizing on the hydroxymethylation of kenaf pulp, chemical analysis, functional group analysis of lignin, and physical and mechanical properties testing of the resulted MDF. Analysis was done on control (unmodified) pulp and modified pulp. Kenaf stem (bast fiber and core) was crushed into a 10 mesh particles. The particles were then refined by a disc refiner.

Lignin content and hydroxymethylation of pulp

Lignin content was determined according to the standard procedures of TAPPI T 222 om-22. Hydroxymethylation was carried out on pulp with predetermined lignin content following the method applied previously by Malutan et al. (2008). In this case, 100 mL NaOH and 25 mL formaldehyde (CH_2O) 37 % was added into a flask contained pulp of equivalent amount with 8 g lignin. The slurry was then stirred for 2 min and heated at 50 ^{o}C in a waterbath for 1 h, and then reheated at 90 ^{o}C for three hrs. The pH of

the treated slurry was reduced to two with HCl 1N and centrifuged at 2500 rpm for 10 min. The residue (pulp) was washed with distillated water until neutrality, and finally dried in an oven at 40–60 °C for 24 hours. Concentration of NaOH during hydroxymethylation was varied at 3%, 6%, and 12%. The properties of MDF produced from hydroxymethylated pulp were compared to the properties of MDF prepared from untreated pulp.

Binderless MDF preparation

The boards were prepared by wet process in a deckle box with the size of 30 cm x 30 cm x 1 cm (L x W x T) and targeted density of 0.65 g/cm^3. The mat was cold pressed and then hot pressed at 160 °C for 25 minutes with 20 kg/cm^3 of pressing load. Preceeding the physical and mechanical properties testing, the boards were conditioned for 14 days at 27 °C and relative humidity of 70%.

Functional groups analysis

Functional groups analysis of the board was carried out by Fourier Transformed Infrared Spectroscopy (FTIR). As much as 2 g of pulp were refined (kneaded) and mixed with 200 mg of KBr. The mixture was then peletized in a die and vacuum ovened overnight. The spectra were generated with 16 scans and analyzed within the range of 4000 to 400 cm^{-1}.

Physical and mechanical properties of binderless MDF

Physical and mechanical properties of the boards were tested in accordance with JIS A 5905: 2003 standard. Thermal conductivity of the MDF was carried out by Netzch 436 Heat Flow Meter Thermal Conductivity conditioned at 23 ± 2 oC and ± 50% relative humidity.

MDF crystallinity

Crystallinity degree measurement of the MDF was carried out by X-ray diffractometer Shimadzu XRD-700 MaximaX. Samples were scanned and recorded from 10-50º of 2θ with Cu-Kα radiation generated at 30 mA and 40 kV. Crystallinity degree was calculated following the equation of Focher et al. (2001).

Results and Discussion

Chemical properties of fiber surface

Functional groups analysis of the FTIR spectrogram was carried out in accordance with George and McIntyre (1987). It can be seen from the

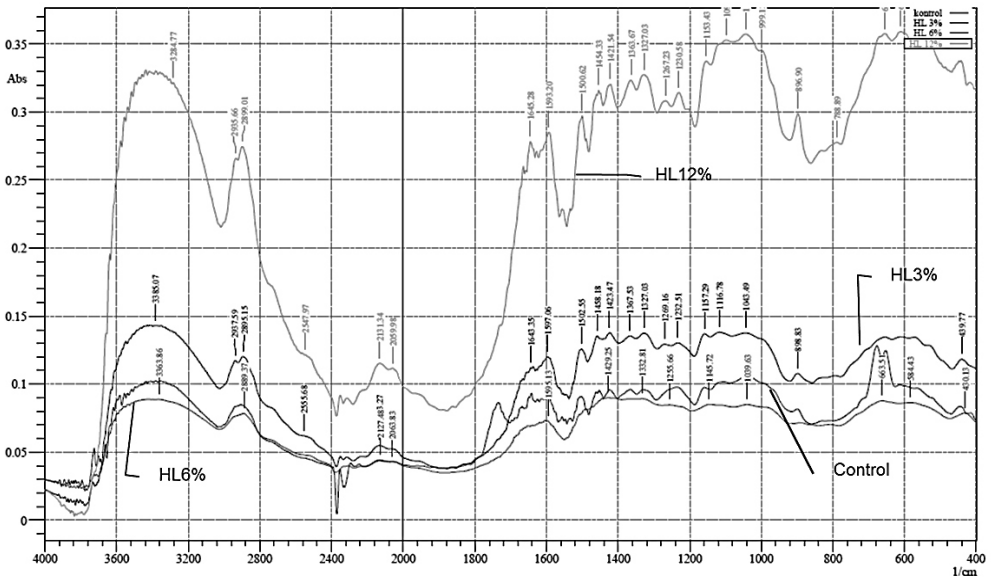

Figure 1. FTIR spectra of hydroxymethylated and non-hydroxymethylated pulp
Gambar 1. Spektrograf FTIR pulp tanpa- dan dengan perlakuan hidroksimetilasi

FTIR spectrogram in Fig. 1 that all fibers, regardless of its treatment, containing similar functional groups such as benzene, alcohol, phenol, ether, and carboxylic acid. Halogen element such as C-Cl and C-F was also presence in the fibers.

Band absorbance in the area of 3430 cm^{-1} is typical characteristic of OH group in lignin (Nada et al. 1997). The spectrogram indicates that hydroxymethylation of the fibers changed the bound OH in untreated fiber into free OH group. The increasing number of free OH groups increased fiber affinity and consequently increased thickness swelling and water absorption of the resulting MDF.

Absorbance in the range of 2949 cm^{-1}-2930 cm^{-1} indicates the C–H bond in lignin (Nada et al. 1997). Absorbance of the C – H groups in the present results appeared in the range of 2937.59 cm^{-1} –2906.73 cm^{-1} and its intensity tended to increase with hydroxymethylation. The increase of C–H peak intensity is indicative of the increase of $–CH_2OH$ substituent in lignin resulted from hydroxymethylation reaction between lignin and formaldehyde. The absorbance of C=O appears in the wave length range of 1727 cm^{-1} - 1690 cm^{-1} (Nada et al. 1997). In the untreated fibers, the present of C=O was indicated by the wave length absorbance at 1734 cm^{-1}. Upon hydroxymethylation, the C=O peak absorbance disappeared. Malutant et al. (2008) has previously found that hydroxymethylation removed the C=O absorbance.

Absorbance bands in the wave number of 1600 cm^{-1} and 1500 cm^{-1} are the characteristic of aromatic ring's C – H vibration of the lignin (Nada et al. 1997). In the presence results, aromatic ring of lignin appeared between 1643.35 and 1500.62 cm^{-1}. Hydroxymethylation in the increasing concentration of NaOH increased the content of CH_2OH groups in the aromatic ring, as indicated by the increasing intensity of band from 1643–1500 cm^{-1}. Arias (2008) also assumed that increasing intensity of this band as increasing possibility of formaldehyde reaction to lignin aromatic ring.

Crystallinity measurement

Cellulose crystallinity indicates the intensity of hydrogen bonds in crystalline zone of cellulose, and thus may represent the physico-chemical properties of the fiber. Measurement of board crystallinity in the present research indicated that the crystallinity of board prepared from fibers hydroxymethylated at 12% concentration of NaOH was higher than that of board prepared from untreated fibers (control) (Fig. 2). The crystallinity of board produced from hydroxymethylated fibers at 12 % concentration of NaOH and that of board prepared from untreated fibers was of

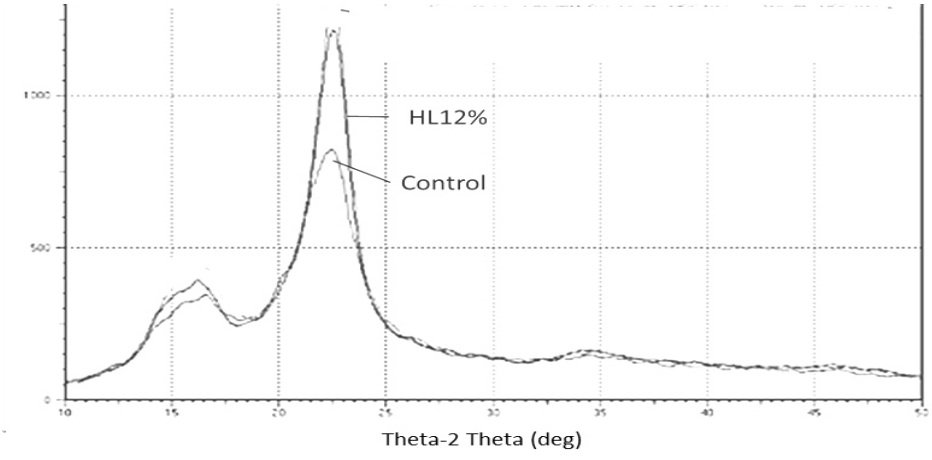

Figure 2. The crystallinity of MDF prepared from fibers hydroxymethylated at 12% concentration of NaOH and untreated fibers

Gambar 2. Kristalinitas MDF yang dibuat dari serat tanpa perlakuan dan serat yang dihidroksimetilasi pada konsentrasi NaOH 12%

43.21% and 34.89%, respectively. Tensile strength, stiffness, density, and dimension stability increase with increasing of cellulose crystallinity (Chen et al. 2011).

Binderless MDF properties

Statistical evaluation indicated that NaOH concentration during hydroxymethylation influenced all physical properties and mechanical properties except for the internal bond (IB). Heat conductivity was also not influenced by the concentration of NaOH.

The density of MDF produced from non hydroxymethylated pulp (control) was of 0.51 g/cm^3 and that produced from pulp with 12% concentration of NaOH during hydroxymethylation was of 0.71 g/cm^3. MDF density increased with increasing NaOH concentration during hydroxymethylation process (Fig. 3). Density requirement for MDF by JIS A 5905:2003 is in the range of 0.35 g/cm^3 ρ 0.80 g/cm^3. Therefore, the resulted MDF achieved the requirement of JIS A 5905:23. Activation of lignin by increasing the number of hydroxyl groups through hydroxymethylation, as indicated by FTIR spectra (Fig. 1), was thought to increase interfiber contact in the board, thus increase its density. The increase of board crystallinity was also possibly increased board density (see Fig. 2). A more flexible fiber is also possible by increasing delignification of the cell wall because of increasing concentration of NaOH during hydroxymethylation. A better board formation with fewer gaps can be resulted from more flexible fibers.

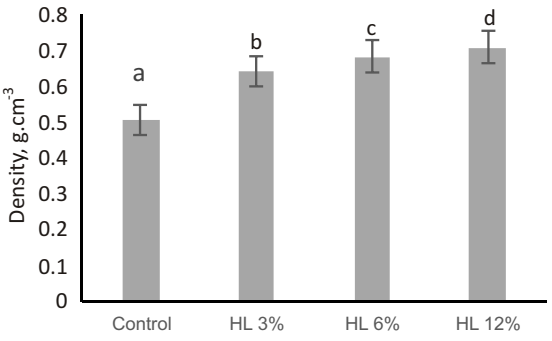

Figure 3. The effect of NaOH concentration during hydroxymethylation on the MDF density (different label letter indicates a significant difference)

Gambar 3. Pengaruh konsentrasi NaOH saat hidroksimetilasi terhadap kerapatan MDF (label huruf yang berbeda menunjukkan perbedaan signifikan)

Moisture content of the resulting MDF increased with increasing of NaOH concentration in hydroxymethylation processes (Fig. 4). The moisture content of the MDF produced from hydroxymethylated fibers with 3% concentration of NaOH reached as much as 12.15% and that produced from fibers hydroxymethylated with 12% concentration of NaOH was of 22.28%. Hydroxymethylation increases the number of hydroxyl groups in phenolic ring of lignin (Malutan et al. 2008). The increase of hydroxyl group upon hydroxymethylation of the pulp is clearly indicated by the FTIR analysis (Fig. 1). Furthermore, fiber swelling due to increasing concentration of NaOH during hydroxymethylation process facilitates the penetration of water into fiber cell wall. The increase of hydroxyl group increases the affinity of the fibers to water (Sjostrom 1993), and along with swelling of fibers by NaOH solution increased the moisture content of the MDF. MDF produced from untreated fibers was the only board that satisfied the moisture content requirement of JIS A 5905:2003 (5% ≤MC ≤13%).

Thickness swelling of the resulted MDF was over that required by JIS A 5905: 2003, i.e. maximum of 12%.

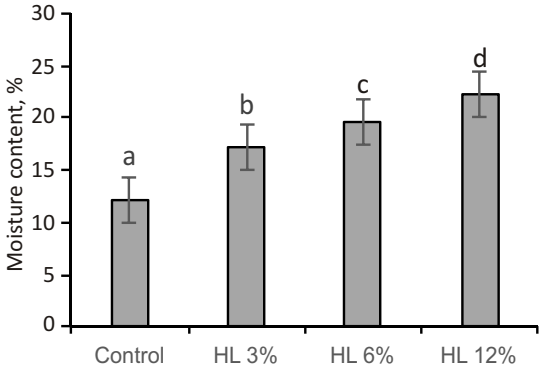

Figure 4. The effect of NaOH concentration during hydroxymethylation on the moisture content of MDF (different label letter indicates a significant difference)

Gambar 4. Pengaruh konsentrasi NaOH saat hidroksimetilasi terhadap kadar air MDF (label huruf yang berbeda menunjukkan perbedaan signifikan)

MDF produced from untreated fibers retained the lowest thickness swelling (15.08%), and that produced from pulp hydroxymethylated at 3% concentration of NaOH was the highest (22.06%), as indicated by Fig.5. In particleboard, the absence of external adhesive makes the thickness swelling of the board is influenced by chemical nature of the treated particles (Widyorini et al. 2005). Chemical component (lignin, cellulose, and hemicelluloses) and physical properties such as crystallinity and board density influence swelling properties of wood based panels. While hemicelluloses are the most hydrophilic among structural chemical component of natural fibers, lignin is a relatively hydrophobic polymer. In the present finding, it seemed that chemical factor was more influential to these of physical properties in determining thickness swelling. Highest lignin content of control board indicated by Fig. 5 was thought to bring about its lowest thickness swelling. Removal of lignin, but retaining hemicelluloses at 3% concentration of NaOH consequently increased the hydrophilicity of the boards that brought about its highest moisture content. At 12% concentration of NaOH, hemicelluloses were also possibly dissolved, thus the affinity of board to water reduced and caused the reduction of thickness swelling. Even though, removal of lignin with the presence of NaOH during hydroxymethylation process increased the crystallinity of cellulose upon hot pressing of the produced MDF (as shown by XRD spectrogram in Fig. 2), its influence on thickness swelling was inferior compared to the influence of chemical composition. Quintana et al. (2009) has confirmed that the differences of hemicellulose content in treated fibers could lead to different swelling behavior of the resulting MDF. Furthermore, Sjostrom (1993) also mentioned that chemical treatment influences longitudinal shrinkage and swelling of fibers.

Similar to that of thickness swelling, water absorption is also influenced by the chemical content of raw material. High hemicellulose content of wheat straw (Eroglu et al. 2001) and peanut shell (Akgül & Tonzluoglu 2008) have been found to increase water absorption of their fiber board. Information on MDF water absorption value is important to determine whether the board is suitable for exterior or interior use (Sarumaha 2008). Figure 6 indicates that hydroxymethylation increased the water absorption of the board. MDF from untreated fiber (control) has the lowest water absorption (81.94%) and that from fiber hydroxymethylated at 3% concentration of NaOH has the highest water absorption value. However, when the concentration of NaOH increased to 12 %, water absorption value significantly decreased (significantly lower than that of hydroxymethylation with 3 % concentration of NaOH). As for the thickness swelling, the nature of chemical components

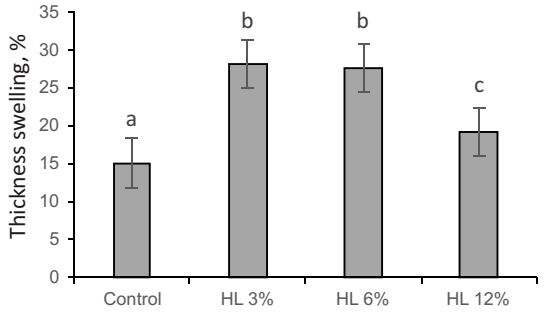

Figure 5. The effect of NaOH concentration during hydroxymethylation on the thickness swelling of MDF (different label letter indicates a significant difference)

Gambar 5. Pengaruh konsentrasi NaOH saat hidroksimetilasi terhadap pengembangan tebal MDF (label huruf yang berbeda menunjukkan perbedaan signifikan)

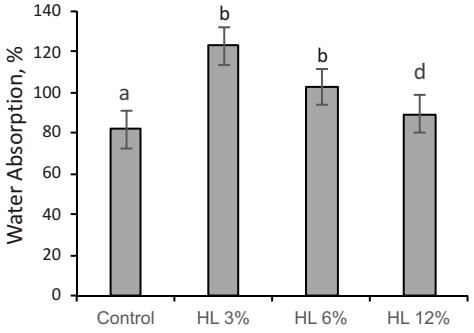

Figure 6. The effect of NaOH concentration during hydroxymethylation on the water absorption of MDF (different label letter indicates a significant difference)

Gambar 6. Pengaruh konsentrasi NaOH saat hidroksimetilasi terhadap daya serap air MDF (label huruf yang berbeda menunjukkan perbedaan signifikan)

modification on hydroxymethylated fiber was also thought to bring about the trend of water absorption properties depicted by Fig. 6.

MOE of the resulted MDF was in the range of 752.96 – 1431.33 N/mm^2. Hydroxymethylation of fibers in 3% NaOH produced the highest MOE and untreated fibers giving the lowest MOE, as shown by Fig. 7. Only MOE of MDF from untreated fibers was below the JIS A 5905: 2003 type 5 requirement, i.e. with the minimum value of 800 N/mm^2. The effect of alkaline treatment of biomass such as rise husk on mechanical properties is a competition between better mechanical properties due to better surface properties and inferior mechanical properties due to cell wall degradation (Ciannamea et al. 2010). NaOH is capable of degrading cell wall component of biomass (Sjöström 1993) and thus could decrease the mechanical properties of composites produced from it. Hydroxymethylation at 3% concentration of NaOH was thought to improve bonding properties of kenaf fibers because of more polar groups exposed on the surface. However, further increasing of the concentration of NaOH degraded the cell wall and consequently decreased the mechanical properties of the resulted MDF. Previous results of Ramli et al. (2002) also indicate that increasing concentration of NaOH decrease the MOE of the resulting MDF. At high concentration, NaOH could degrade cellulose, which is the main source of lignocellulosic material strength (Widyorini et al. 2005).

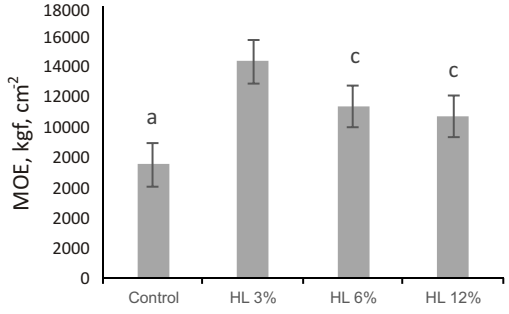

Figure 7. The effect of NaOH concentration during hydroxymethylation on the MOE of MDF (different label letter indicates a significant difference)

Gambar 7. Pengaruh konsentrasi NaOH saat hidroksimetilasi terhadap nilai MOE MDF (label huruf yang berbeda menunjukkan perbedaan signifikan)

Figure 8 indicates that MOR of the resulted MDF tended to be in a similar trend with that of the MOE. Eventhough the MOR of the MDF was relatively low, except for the untreated fibers (control), all values of MOR were satisfying the requirement of JIS A 5905: 2003 type 5. Thermal degradation of the lignocellulosic materials during hot pressing of board formation might also involve in the reduction of board strength. Han et al. (2009) assumed that depolimerization of polysaccharide and lignin occurred at high temperature. MOR is also influenced by fiber length. Increasing the amount of short fiber in the board has been reported to decrease the value of MOR (Ye et al. 2007). Reduction of composites strength due to the decrease of fiber length is brought about by the decrease of the effective fiber contact in the composites (Kumar et al. 2008). In the present experiment, kenaf fiber was refined. Therefore, fiber shortening possibly occurred and could be among the reason for low the MOR of MDF.

Internal bond of the resulted MDF was not influenced by the concentration of NaOH during

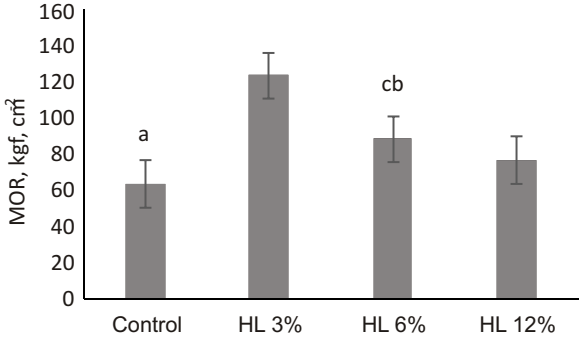

Figure 8. The effect of NaOH concentration during hydroxymethylation on the MOR of MDF (different label letter indicates a significant difference)

Gambar 8. Pengaruh konsentrasi NaOH saat hidroksimetilasi terhadap nilai MOR MDF (label huruf yang berbeda menunjukkan perbedaan signifikan)

hydroxymethylation (Fig. 9). Even though the concentration of NaOH did not influence the IB of the boards, the MDF prepared with fibers hydroxymethylated at 6% and 12% concentration of NaOH satisfied the requirement of JIS A 5905: 2003 type 5, i.e. at least of 0.2 N/mm^2. IB is determined by the

homogeneity of fiber surface to result in a better self-bonding (Kurokochi & Sato 2015). Increasing the concentration of NaOH during hydroxymethylation could make the fiber surface more homogen with more polar group on the surface and consequently increased interfiber bonding. Intense refining of the fibers is also capable of increasing the IB of board (Xue et al. 2006).

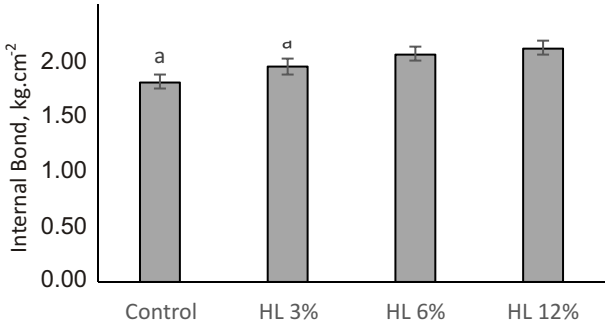

Figure 9. The effect of NaOH concentration during hydroxymethylation on the internal bond (IB) of MDF (different label letter indicates a significant difference)

Gambar 9. Pengaruh konsentrasi NaOH saat hidroksimetilasi terhadap *internal bond* (IB) MDF (label huruf yang berbeda menunjukkan perbedaan signifikan)

A similar trend of MOE and MOR are demonstrated by Fig. 7 and 8, and both are different from that of IB. Furthermore, statistical evaluation indicated that MOE and MOR of the boards were significantly influenced by the concentration of NaOH during hydroxymethylation. On the other hand, IB was not influenced by the concentration of NaOH. MOE and MOR are determined by interrelated factors such as compression, tension, and interfiber bonding (in the case of binderless composites), and IB is mostly determined by interfiber bonding. This was thought to bring about a different influence of the treatment on the mechanical properties of the boards.

In line with board density, screw withdrawal increased with increasing concentration of NaOH during hydroxymethylation (Fig. 10). Screw withdrawal of the resulted MDF satisfied the requirement of JIS A 5905: 2003 type 5, i.e. at least of 200 N or more. MDF prepared from untreated fiber and that prepared from fiber hydroxymethylated at 12% concentration of NaOH retained screw withdrawal of 236.15 N and 502.31 N, respectively.

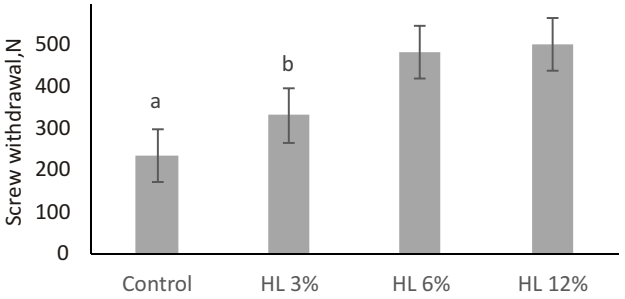

Figure 10. The effect of NaOH concentration during hydroxymethylation on the screw withdrawal of MDF (different label letter indicates a significant difference)

Gambar 10. Pengaruh konsentrasi NaOH saat hidroksimetilasi terhadap daya pegang skrup MDF (label huruf yang berbeda menunjukkan perbedaan signifikan)

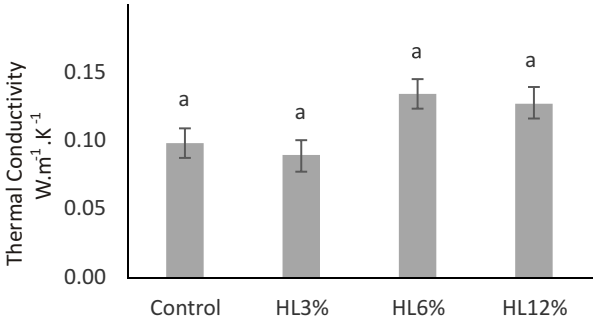

Figure 11. The effect of NaOH concentration during hydroxymethylation on the thermal conductivity of MDF (different label letter indicates a significant difference)

Gambar 11. Pengaruh konsentrasi NaOH saat hidroksimetilasi terhadap konduktifitas panas MDF (label huruf yang berbeda menunjukkan perbedaan signifikan)

Thermal conductivity of the resulted MDF was not influenced by the concentration of NaOH during hydroxymethylation (Fig. 11). Thermal conductivity of MDF prepared from fibers hydroxymethylated at 3% concentration of NaOH and that from fibers hydroxymethylated at 12% concentration of NaOH were of 0.089 $W.m^{-1}.K^{-1}$ and 0.134 $W.m^{-1}.K^{-1}$, respectively. As reported previously that thermal conductivity of board increased with increasing of its density (Okuda & Sato 2004). Lower thermal

conductivity in the lower board density was assumed due to the presence of void filled with air (a non-conductive substance) in board with low density (Xu et al. 2004).

Conclusions

Increasing concentration of NaOH during hydroxymethylation of kenaf fiber increased hydroxyl group and board crystallinity. The change in chemical properties such as increasing the magnitude of OH groups and crystallinity of the treated fiber were thought to influence the density, moisture content, thickness swelling, water absorption, MOE, MOR, and screw withdrawal of the MDF. Except for the moisture content and thickness swelling, the properties of binderless MDF from hydroxymethylated kenaf pulp satisfied the requirement of JIS A 5905: 2003 type 5 standard.

References

Akgól M, Tonzluoglu A. 2008. Utilizing peanut husk (*Arachis hypogae* L.) in the manufacture of medium density fiberboards. BioResource Technology **99**:5590-5594.

Alonso MV, Oliet M, Rodrìguez F, Garcia J, Gilarranz MA, Rodriguez JJ. 2005. Modification of ammonium lignosulfonate by phenolathion for use in phenolic resins. Bioresource Technology **96**: 1013-1018.

Arias CM. 2008. Binderless fiberboard production from *Cynara cardunculus and Vitis vinifera*. Dissertation. Tarragona-Spain: Departemen of Mechanical Engineering Universitat Rovira I Virgili.

Benar P, Gonçalves AR, Mandelli D, Schuchardt U. 1999. Eucalyptus organosolv lignins: Study of the hydroxymethylation and use in resols. Bioresource Technology **68**(1): 11-16.

Cypraru AM, Ungureanu E, Trincy LC, Myluώan T, Popa VI. 2012. Chemical and spectral characteristics of annual plant lignins modified by hydroxymethylation reaction. Cellulose Chemistry and Technology, **46**(9-10): 589-597

Çetin NS, Özmen N. 2003. Studies on lignin-based adhesives for particleboard panels. Turk Journal of Agriculture and Forestry **27**: 183-189.

Chen Y, Wan J, Zhang X, Ma Y, Wang Y. 2011. Effect of beating on recycled properties of unbleached eucalyptus cellulose fiber. Carbohydrate Polymers **87**(1):730-736. doi:10.1016/j.carbpol.2011.08.051.

Ciannamea EM, Stefani PM, Ruseckaite RA. 2010. Medium-density particleboards from modified rice husks and soybean protein concentrate-based adhesives. Bioresource Technology **101**:818–825

Eroglu H, Istek A, Usta M. 2001. Medium density fiberboard (MDF) manufacturing from wheat straw (*Triticum aestivum* L.) and straw wood mixture. Journal of Engineering Science **7**(2): 305-311.

George WO, McIntyre PS. 1987. Infrared spectroscopy: Analytical chemistry by open learning. John Wiley and Sons, London.

Gonçalves AR, Benar P. 2001. Hydroxymethylation and oxidation of organosolv lignins and utilization of the products. Bioresource Technology **79**:103-111.

Han G, Cheng W, Deng J, Dai C, Zhang S, Wu Q. 2009. Effect of pressurized steam treatment on selected properties of wheat straws. Industrial Crops and Products **30**:48-53.

Japanese Industrial Standard. 2003. JIS A5905-2003: Fibreboards. Japan.

Karina M, Indratmoko HP, Prasetya B, Subiyakto B. 1994. Pembuatan dan karakteristik perekat lignin-phenol-formaldehida (LRF). Prosiding Seminar Ilmiah Hasil-Hasil Penelitian dan Pengembangan Puslitbang Fisika Terapan-LIPI. pp. 85-98. Subang.

Kumar KSS, Nair CPR, Ninan KN. 2008. Effect of fiber length and composition on mechanical properties of carbon fiber-reinforced polybenzoxazine. Polymers for Advanced Technologies **19**(7): 895–904

Kurokochi Y, Sato M. 2015. Properties of binderless board made from rice straw: The morphological effect of particles. Industrial Crops and Products **69**:55–59. doi:10.1016/j.indcrop.2015.01.044

Malutan T, Nicu R, Popa VI. 2008. Lignin modification by epoxidation. BioResources **3**(4): 1371-1376.

Mansouri NEE, Salvado J. 2006. Structural characterization of technical lignins for the production of adhesives: Application to lignosulfonate, kraft, soda-anthraquinone, organosolv, and ethanol process lignins. Industrial Crops and Products **24**: 8-16.

Nada AMA, El-Sakhawy M, Kamel SM. 1997. Infra-red spectroscopic study of lignins. Polymer Degradation and Stability **60**: 247-251.

Nimz HH. 1983. Lignin-based wood adhesives. pp. 219-241 in Pizzi A, editor. Wood adhesives chemistry and technology. Marcell Dekker Inc., New York.

Okuda N, Sato M. 2004. Manufacture and mechanical properties of binderless boards from kenaf core. Journal of Wood Scince **50**:53-61.

Pande H, Roy DN, Kant S. 2000. Tear and tensile properties of soda pulp from kenaf bast fibers. TAPPI Journal **83**(6): 47.

Pizzi A. 1994. Advanced wood adhesives technology.Marcel Dekker Inc., New York.

Quintana G, Velasquez J, Betancourt S, Ganan P. 2009. Binderless fiberboard from steam exploded banana bunch. Industrial Crops and Product **29**:60-66.

Ramli R, Shaler S, Jamaludin MA. 2002. Properties of medium density fiberboard from oil palm empty fruit bunch fibre. Journal of Oil Palm Research **14**(2): 34-40.

Sarumaha PSH. 2008. Kualitas komposit kayu plastik dari limbah serat buah sawit dan polipropilena daur ulang. Skripsi (Tidak dipublikasikan). Universitas Sumatera Utara, Medan.

Sjöström E. 1993. Wood Chemistry: Fundamentals and Application 2nd Edition. Academic Press, Helsinki, Finland.

Velásquez JA, Ferrando F, Salvado J. 2003. Effect of kraft lignin addition in the production of binderless fiberboard from steam exploded *Miscanthus sinensis*. Industrial Crops and Production **18**: 17-23.

Vázquez G, Freire S, Rodriguez-Bona C, Gonzalez J, Antorrena G. 1999. Structures, and reactivities with formaldehyde of some acetosolv pine lignins. Journal of Wood Chemistry and Technology **19**(4): 357-378.

Vázquez G, Gonzáez J, Freire S, Antorrena G. 1997. Effect of chemical modification of lignin on the gluebond performance of lignin-phenolic resins. Bioresource Technology **60**:191-198.

Widyorini R, Xu J, Watanabe T, Kawai S. 2005. Chemical changes in steam-pressed kenaf core binderless particleboard. Journal of Wood Science **51**:26-32.

Xu J, Widyorini R, Yamauchi H, Kawai S. 2006. Development of binderless fiberboards from kenaf core. Journal of Wood Science **52**:236-243.

Xu J, Sugawara R, Widyorini R, Han G, Kawai S. 2004. Manufacture and properties of low-density binderless particleboard from kenaf core. Journal of Wood Science **50**:62-67.

Ye XP, Julson J, Kuo M, Womac A, Myers D. 2007. Properties of medium density fiberboard made from renewable biomass. Bioresource Technology **98**: 1077-1084.