

Primary properties of MDF using thermomechanical pulp made from oxalic acid pretreated rice straw particles

Xianjun Li^{a,b}, Yiqiang Wu^a, Zhiyong Cai^{b,*}, Jerrold E. Winandy^c

^a Material Science and Engineering School, Central South University of Forestry and Technology, Changsha 410004, China

^b USDA Forest Service, Forest Products Laboratory, Madison, WI 53726-2398, USA

^c University of Minnesota, St. Paul, MN 55108, USA

ARTICLE INFO

Article history:

Received 9 January 2012

Received in revised form 7 April 2012

Accepted 22 April 2012

Keywords:

Rice straw

Pretreatment

Thermo-mechanical defibration

MDF panel

Primary properties

ABSTRACT

The main objective of this study is to evaluate the effect the oxalic acid (OA) and steam pretreatment on the primary properties of rice straw medium-density fiberboard (MDF). The results show the IB strength increased about 9.6% and 13.4% for steam-treated MDF (PC) and OA-treated MDF compared with raw control panels, while OA pretreatment has a slight negative effect on the bending properties of MDF. Generally, the steam-treated and OA-treated panels exhibit a slightly improved dimensional stability, but the difference is not significant compared with raw control panels. The thermo-mechanical defibration process is the main factor to improve the bond-ability between UF resin and rice straw, which resulted in good quality rice straw MDF. The mechanical strength of rice straw MDF can meet ANSI standard for interior MDF, but the LE and TS of MDF without paraffin wax addition is lower than the minimal requirement of the ANSI standard. MDF is one of the most feasible products for utilizing rice straw.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Medium-density fiberboard (MDF) has become one of the most popular wood-based composite materials due to its numerous advantages including in uniform, dense, smooth, free of knots and grain patterns, and wonderful machining properties. The primary lignocellulosic material used in the MDF industry is wood. Faced with worldwide shortages of forest resources, many attempts have been conducted to produce MDF or other composite panels using other lignocellulosic materials. Globally, wheat and rice are the most important food grains ranking second and third in terms of the total cereal production (Halvarsson et al., 2008), and seem to be the most promising agriculture residues for manufacturing composite panels. At present, most of these residues are burnt in situ after harvest. The field burning of rice straw and other agriculture residues in wide areas not only results in serious environment issues, but also wastes precious resources. Therefore, there has recently been a revival of interest in using agriculture residues to produce MDF and other composite panels due to competition for wood raw materials as well as environmental and economic considerations (Halvarsson et al., 2008; Zheng et al., 2007; Ye et al., 2007; Copur et al., 2008; Mobarak et al., 1982; Zou et al., 2010; Yang et al., 2003; Hizioglu et al., 2008; Lee et al., 2006; Grigoriou, 1998; Mo et al., 2001).

In general, straw materials have lower cellulose and lignin content, but higher hemicellulose content compared to wood. Furthermore, the straw contains hydrophobic waxy cuticle layers and a high amount of inorganic silica and extractives (Pan et al., 1999; Pan and Sano, 2000; Hammerr et al., 2001; Han et al., 2010). In addition, the curing of pH-sensitive urea-formaldehyde (UF) resin was inhibited by the high pH and buffer capacity of the rice straw, which results in very low mechanical performance, especially for internal bonding strength within UF resin bonded panels (Han et al., 2001a; Boquillon et al., 2004; Li et al., 2010). Many attempts have been undertaken to improve the bondability between the straw materials and UF resin through raw material pretreatment (Han et al., 1999; Zhang et al., 2003), but the production of high-performance UF-bonded straw particleboards is still impracticable due to the high resin addition and the free formaldehyde emission level, and the poor internal bonding strength. MDF using thermo-mechanical pulp seems to be a viable alternative for the utilization of straw resources. During processing, the wax layer on straw surfaces is damaged and the inorganic silica and extractives in straw are also reduced by steam treatment during the thermal-mechanical refining process which resulted in good quality straw fiberboard (Han et al., 2001b; Halvarsson et al., 2008). However, the thermo-mechanical refining process is energy intensive and the product efficiency is low.

With recent renewed interest in ethanol products from cellulosic material, the pulp and paper industry put forth the concept of “value prior to pulping” (VPP) which was proposed to compensate for the energy-intensive refining process (Liu et al., 2006;

* Corresponding author. Tel.: +1 608 231 9446; fax: +1 608 231 9582.
E-mail addresses: lxjmu@yahoo.cn (X. Li), wuyq0506@126.com (Y. Wu),
Zcai@fs.fed.us (Z. Cai), jwinandy@umn.edu (J.E. Winandy).

Ragauskas et al., 2006; Huang et al., 2010; Walton et al., 2010). Instead of converting all the woody biomass into a single product, specific hemicelluloses are either partially or completely extracted through a prehydrolysis process and in this way a raw material is obtained for bio-ethanol or other chemical feedstocks. The remaining solid (cellulose, residual hemicelluloses and lignin) is then the raw material for pulp or fiber products (Zhu and Pan, 2010). Recently, the pretreatment of wood chips using a dilute OA solution prior to refining has been identified as an innovative means to reduce energy consumption during refining, extract carbohydrates for the production of cellulosic ethanol and other chemical feedstocks, and improve MDF water repellency properties and paper strength (Kenealy et al., 2007; Akhtar et al., 2008). The rice straw has higher hemicelluloses and extractives contents, and looser structure compared to woody biomass. The VPP pretreatment using dilute OA solution may be result in more extracted carbohydrates and improved physical performance of rice straw MDF. However, similar research on rice straw utilization is scarce so far.

In our previous research, the effect of OA- and steam pretreatment on the carbohydrates released from rice straw particles and primary properties of UF-bonded rice straw particleboards was investigated (Li et al., 2011). As a continuation from earlier works, the main objective of this study is to evaluate the feasibility of manufacturing MDF using UF resin and thermo-mechanical fibers made from OA treated rice straw particles, and to investigate some primary properties of rice straw MDF as affected by various treatment conditions.

2. Materials and methods

Rice straw was obtained from California, United States. Its variety number was Calrose M-206. It was approximately one meter tall at harvest and cut above the water line leaving the lower third as stubble in the field. This rice was also harvested with a conventional straw walker combine rather than a rotary, which optimizes straw quality by retaining much longer stalk sections for baling. The average moisture content of the straw was about 8.1%. After received, the rice straw was broken down into particles in a hammer mill, in which a perforated metal plate with opening size of 19.05 mm (3/4 in.) was used.

The reactor configuration and pretreatment procedure has been described previously (Winandy et al., 2008). Rice straw particles were treated with 0.33% OA solution at four temperature levels (100 °C, 120 °C, 140 °C and 160 °C). The treatment times for each temperature level were 5 and 10 min. For the control, rice straw particles were processed at the same 160 °C heating conditions for 10 min as the OA pretreatment, but no chemical was added to the hot water. These rice straw particles would be used as the positive control (PC) or steam-treated sample, which would be compared with the eight different OA-pretreatments. After pretreatments, the pressure in the digester was released and the rice straw particles were flooded with 70 °C hot water, which was circulated for 30 min to rinse the hemicellulosic sugar from the treated rice straw. The mass ratio of added hot water to rice straw particles (oven dry weight) is 8:1 in this process. Following pretreatment, the hemicelluloses extracts and extracted rice straw particles were collected and weighted separately. The treated particles were then washed with water for 15 min to bring the pH of the samples near to the level of untreated control samples.

The extracted rice straw particles (OA-treated and PC samples) and raw control particles (RC) without OA or steam pretreatment were processed separately through the thermo-mechanical refiner to produce MDF fibers. A laboratory pressurized refiner (Sprout-Bauer, model #1210P) was applied with 300 mm diameter plates, D2B505 plate pattern, and 0.508 mm (0.020 in.) refiner gap. During

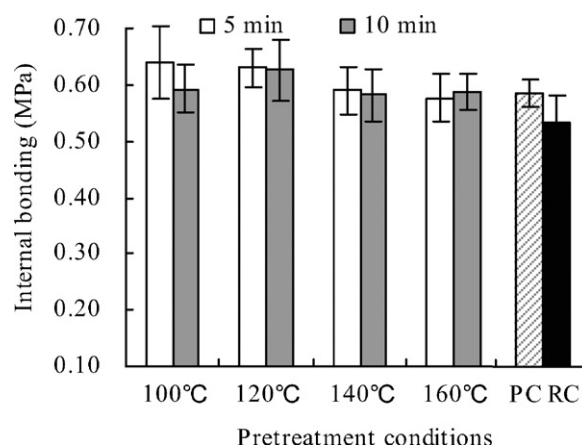


Fig. 1. Effects of pretreatment conditions on IB strength of rice straw MDF.

the thermo-mechanical refining process, the particles were placed into a presteaming tube and pressurized with steam to 0.62 MPa (90 PSI) for 10 min prior to defibration. These fibers were collected separately and dried at 103 ± 2 °C to 2–3% MC. The dried fibers were bagged prior to MDF fabrication.

The commercial UF resin used in this study was acquired from Arclon Corporation (281 Wallace Road, North Bay, Ontario, Canada). The UF resin was water dispersed with a solid content of 65%. A resin content of 15% (oven-dried weight basis) was uniformly sprayed onto the rice straw fibers while they were circulating in a tube blended system. The mat was hand formed after resin application. The MDF panels were pressed by means of a 914 mm × 914 mm (36 in. × 36 in.) Nordberg hot press with a PressMAN control system (Alberta Research Center, Alberta, Canada) at 170 °C platen temperature. The boards measured: 508 mm × 508 mm (20 in. × 20 in.) and 12.5 mm (0.5 in.) thick. The target density was 0.75 g/cm³. The total hot press time of 470 s (60 s closing, 320 s at the target thickness, and 90 s opening) ensured the complete curing of the resin. Three replicate boards were made for each condition.

Internal bonding (IB), modulus of elasticity (MOE), modulus of rupture (MOR), linear expansion (LE), water absorption (WA), and thickness swelling (TS) of the samples were prepared and tested in accordance with ASTM D 1037-06a (2006). Twelve specimens for IB testing and six specimens for other mechanical and physical properties testing, including MOE, MOR, WA and TS, were cut from three replicate boards prepared under different conditions. Static bending (MOE and MOR) was measured according to Material Testing System (634.11F-24) and the IB values were determined on a universal testing machine (Instron 555), respectively. The WA and TS properties were measured after 24-h immersion in distilled water at 20 °C.

3. Results and discussion

It is well known that IB strength is very low within UF resin bonded straw particleboards because of poor compatibility between straw and water soluble UF resin. As expected, the results shown in Fig. 1 clearly indicate that all MDF panels have high IB strength, which can meet the requirement of American national standard for interior MDF (ANSI A208.2-2009). The superior IB properties of MDF are thought to be attributed to the defibration process, in which the wax layer on the surface of rice straw was probably damaged, and non-polar extractives in rice straw are partly removed. In comparison with the RC specimens, an improvement in IB properties was observed within treated rice straw MDF, where IB increased about 9.6% and 13.4% for steam-treated MDF (PC) and OA-treated MDF, respectively. The reason for these

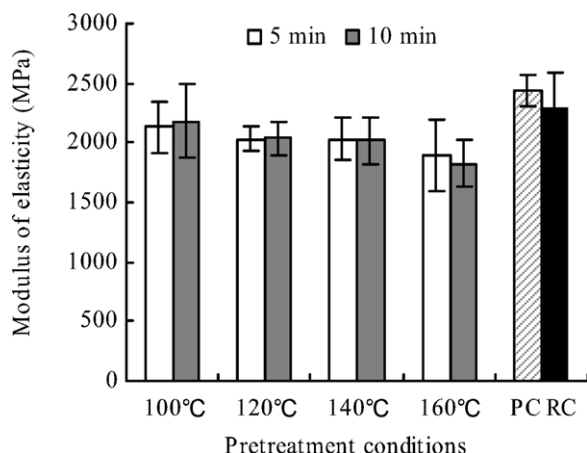


Fig. 2. Effects of pretreatment conditions on MOE of rice straw MDF.

increases is mainly due to higher extraction levels of wax-like substance from rice straw during pretreatment. In general, the effect of pretreatment temperature and time on the IB strength of OA-treated panels is not significant, and IB difference between OA- and steam-treated panels is also minimal. The *F*-test statistical analysis and two-tailed pair-wise *t*-test also confirms the observation at the 99% confidence level. The results means that thermo-mechanical defibration process is the main factor to improve the bond-ability between UF resin and rice straw compared with steam and OA-treatment.

The effects of the steam and OA treatment on the static bending properties of rice straw MDF are shown in Figs. 2 and 3. Compared with RC samples, the MOE and MOR increased by 6.0% and 13.9% for steam-treated panels, while they decreased by 9.9% and 8.6% for OA-treated panels. Generally, the effect of pretreatment time and temperature on the static bending properties of OA-treated panels is not significant in this study. The increase of bending properties within steam-treated panels is probably due to their higher IB strength. However, slightly higher IB strength does not result in higher bending properties within OA treated panels in comparison with the RC sample. Except for the IB strength, the geometry of fiber is also a very important factor affecting the bending properties of the panel. Other studies of natural fiber-reinforced composites have shown that MOR and MOE are widely influenced by the fiber form factor, such as length/diameter ratio (Boquillon et al., 2004; Li et al., 2010). The reason for the slight reduction of bending properties during OA pretreatment is not yet entirely understood, but it could

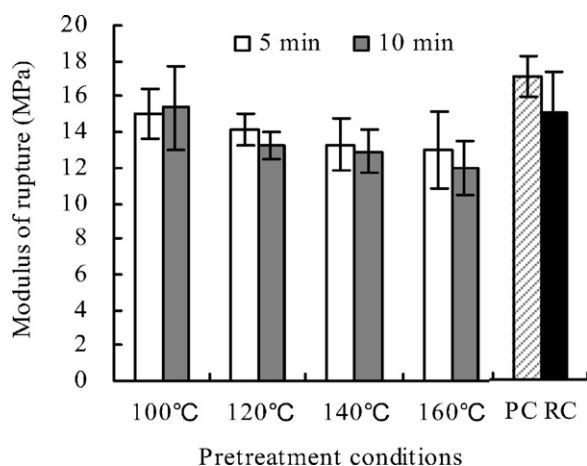


Fig. 3. Effects of pretreatment conditions on MOR of rice straw MDF.

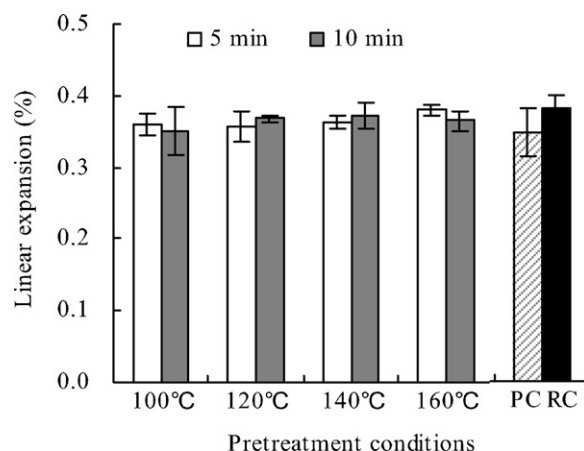


Fig. 4. Effects of pretreatment conditions on LE of rice straw MDF.

be a result of physical changes, such as the formation of more short fibers with lower length/diameter ratio during refining process, resulting from the reduction in strength of fiber during OA treatment. A similar result was also observed in previous studies where wood-plastic composites were produced from thermo-mechanical pulp made from OA pretreated wood chips (Winandy et al., 2008). The statistical analysis shows the effect of steam and OA treatment on the bending properties of MDF is not significant. The bending properties of all rice straw MDF, except for the panel made from OA treated rice straw at 160 °C and 10 min, can meet ANSI Standard for interior MDF.

LE and TS are key parameters in describing dimensional stability of wood composites. Particularly, LE is considered as the control factor in qualifying the behavior of wood panels exposed to moisture (Cai et al., 2004). The influence of various pretreatment on the dimensional stability (including in LE, TS and WA) of rice straw MDF was examined and presented in Figs. 4–6. In comparison with RC panels, the average value of LE, TS and WA decrease by 8.6%, 4.4% and 1.4% for steam-treated panels, and 3.5%, 1.9% and 0.1%, respectively, for OA-treated panels. Generally, the steam-treated and OA-treated panels exhibit a slightly better dimensional stability than RC panels. But unexpectedly, the difference of the dimensional stability among all MDF samples is not significant, which also indicate that the addition of OA in pretreatment or increase of pretreatment time and temperature has not evidently positive effect on improving the dimensional stability of MDF panel. The statistical analysis revealed that the effect of OA or steam

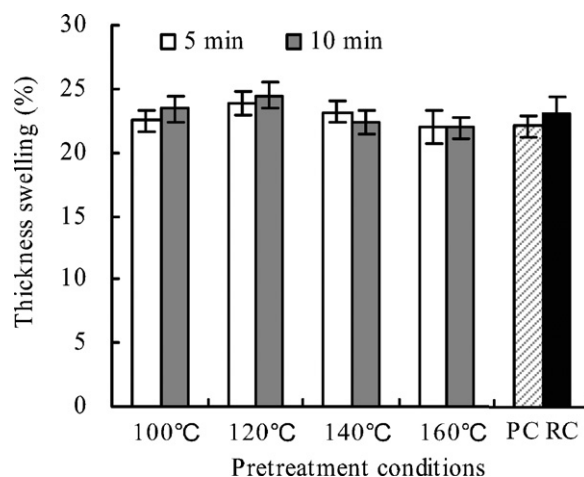


Fig. 5. Effects of pretreatment conditions on TS of rice straw MDF.

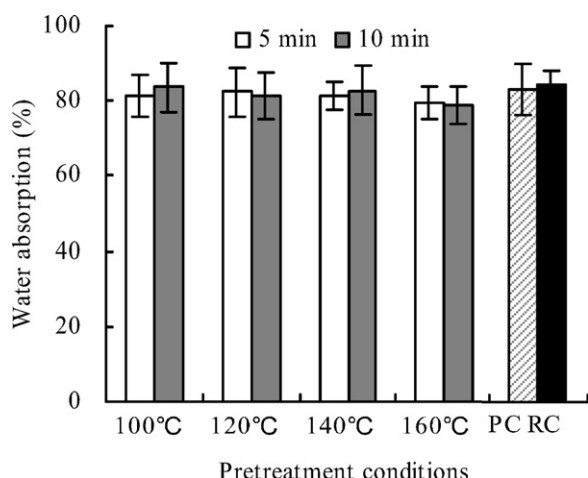


Fig. 6. Effects of pretreatment conditions on WA of rice straw MDF.

pretreatment on the LE, TS and WA of panels was not significant. The reason for this could be the fact that most wax-like substance was removed from rice straw by the thermo-mechanical defibration process. Compared with thermo-mechanical defibration process, the OA and steam pretreatment to remove partial hemicellulose in rice straw particles has a negligible effect on the improvement of the dimensional stability of rice straw MDF panels.

The mechanical properties of rice straw MDF without any pretreatment (PC) can meet ANSI Standard for interior MDF. However, the LE and TS of the rice straw MDF is lower than the requirement of the ANSI standard. Compared with woody materials, rice straw has higher moisture adsorption and much higher water absorption. In our previous research, the moisture content of wood treated at similar conditions is below 200%, while the moisture content of rice straw after pretreatment is above 400%. The higher adsorption or absorption properties of rice straw are believed to be a main reason why the dimensional stability of rice straw MDF cannot meet the ANSI standard. Here, it must be mentioned that no additive wax was used in the manufacturing of the MDF in this study. The addition of paraffin wax could delay moisture adsorption and water absorption, reduce LE, TS and WA, and improve the dimensional stability of MDF substantially. Therefore, it is thought that MDF is one of the most feasible products for utilizing rice straw bio-resource based on the comprehensive considerations of economy and environment.

4. Conclusions

The results show that the mechanical strength of rice straw MDF can meet ANSI Standard for interior MDF, but the LE and TS of MDF without paraffin wax addition is lower than the minimal requirement of the ANSI standard. The IB strength increased about 9.6% and 13.4% for steam-treated MDF (PC) and OA-treated MDF compared with raw control panels, while OA pretreatment has a slight negative effect on the bending properties of MDF. Generally, the steam-treated and OA-treated panels exhibit a slightly improved dimensional stability, but the difference is not significant compared with raw control panels. Compared with steam and OA-treatment, thermo-mechanical defibration process is thought to be a main factor to improve the bond-ability between UF resin and rice straw, which resulted in good quality rice straw MDF. MDF is one of the most feasible products for utilizing rice straw.

Acknowledgements

The authors thank Mr. Eric Horn of Biopulping International Inc., Madison, WI, USA, for his kind support and help with the rice straw

pretreatment process in this research. Thanks for the support of Chinese Education Program for New Century Excellent Talents.

References

- Akhtar, M., Kenealy, W.R., Horn, E.G., Swaney, R.E., Winandy, J., 2008. Method of making medium density fiberboard. US Patent No: US 2008/0,264,588 A1.
- ASTM, 2006. Standard Test Methods for Evaluating Properties of Wood-based Fiber and Particle Panel Materials. ASTM D 1037-06a. American Society for Testing Materials, West Conshohocken, PA.
- Boquillon, N., Elbez, G., Schonfeld, U., 2004. Properties of wheat straw particleboards bonded with different types of resin. *Journal of Wood Science* 50, 230–235.
- Cai, Z.Y., Wu, Q.L., Lee, J.N., Hiziroglu, S., 2004. Influence of board density, mat construction, and chip type on performance of particleboard made from eastern red-cedar. *Forest Products Journal* 54 (12), 226–232.
- Copur, Y., Guler, C., Tascioglu, C., Tozluoglu, A., 2008. Incorporation of hazelnut shell and husk in MDF production. *Bioresource Technology* 99 (5), 7402–7406.
- Grigoriou, A.H., 1998. Straw as alternative raw material for the surface layers of particleboards. *Holzforchung* 50 (2), 32–33.
- Halvarsson, S., Edlund, H., Norgren, M., 2008. Properties of medium-density fiberboard (MDF) based on wheat straw and melamine modified urea formaldehyde (UMF) resin. *Industrial Crops and Products* 28, 37–46.
- Hammerr, A.L., Youngs, R.L., Sun, X.F., Chandra, M., 2001. Non-wood fiber as an alternative to wood fiber in China's pulp and paper industry. *Holzforchung* 55 (2), 219–224.
- Han, G.P., Umemura, K., Kawai, S., Kajita, H., 1999. Improvement mechanism of bondability in UF-bonded reed and wheat straw boards by silane coupling agent and extraction treatments. *Journal of Wood Science* 45, 299–305.
- Han, G.P., Umemura, K., Wong, E.D., Zhang, M., Kawai, S., 2001a. Effects of silane coupling agent level and extraction treatment on the properties of UF-bonded reed and wheat straw particleboards. *Journal of Wood Science* 47, 18–23.
- Han, G.P., Umemura, K., Zhang, M., Honda, T., Kawai, S., 2001b. Development of high-performance UF-bonded reed and wheat straw medium-density fiberboard. *Journal of Wood Science* 47, 350–355.
- Han, G.P., Deng, J., Zhang, S., Bicho, P., Wu, Q.L., 2010. Effect of steam explosion treatment on characteristics of wheat straw. *Industrial Crops and Products* 31, 28–33.
- Hiziroglu, S., Jarusombuti, S., Baichongkol, P., Fueangvivat, V., 2008. Overlaying properties of fiberboard manufactured from bamboo and rice straw. *Industrial Crops and Products* 28, 107–111.
- Huang, H.J., Ramaswamy, S., Dajani, W.W.A., Tschirner, U., 2010. Process modeling and analysis of pulp mill-based integrated biorefinery with hemicellulose pre-extraction for ethanol production: a comparative study. *Bioresource Technology* 101, 624–631.
- Kenealy, W., Horn, E., Houtman, C., 2007. Vapor-phase diethyl oxalate pretreatment of wood chips. Part 1. Energy savings and improved pulping. *Holzforchung* 61, 223–229.
- Lee, S., Shupe, T.F., Hse, C.Y., 2006. Mechanical and physical properties of agro-based fiberboard. *Holz als Roh-und Werkstoff* 64, 74–79.
- Li, X.J., Cai, Z.Y., Winandy, J.E., Basta, A.H., 2010. Selected properties of particleboard panels manufactured from rice straws of different geometries. *Bioresource Technology* 101 (12), 4662–4666.
- Li, X.J., Cai, Z.Y., Winandy, J.E., Basta, A.H., 2011. Effect of oxalic acid and steam pretreatment on the primary properties of UF-bonded rice straw particleboards. *Industrial Crops and Products* 33 (3), 665–669.
- Liu, S.J., Amidon, T.E., Francis, R.C., Ramarao, B.V., Lai, Y.Z., Scott, G.M., 2006. From forest biomass to chemicals and energy. *Industry Biotechnology* 2 (2), 113–120.
- Mo, X.Q., Hu, J., Sun, X.S., Ratto, J.A., 2001. Compression and tensile strength of low-density straw-protein particleboard. *Industrial Crops and Products* 14, 1–9.
- Mobarak, F., Fahmy, Y., Augustin, H., 1982. Binderless lignocellulose composite from bagasse and mechanism of self-bonding. *Holzforchung* 36 (3), 131–135.
- Pan, X.J., Sano, Y., Ito, T., 1999. Atmospheric acetic acid pulping of rice straw. II. Behaviour of ash and silica in rice straw during atmospheric acetic acid pulping and bleaching. *Holzforchung* 53 (1), 49–55.
- Pan, X.J., Sano, Y., 2000. Comparison of acetic acid lignin with milled wood and alkaline lignins from wheat straw. *Holzforchung* 54 (1), 61–65.
- Ragauskas, A., Nagy, M., Kim, D.H., Eckert, C.A., Hallett, J.P., Liotta, C.L., 2006. From wood to fuels integrating biofuels and pulping production. *Industry Biotechnology* 2 (1), 55–65.
- Walton, S., Heiningen, A.V., Walsum, P.V., 2010. Inhibition effects on fermentation of hardwood extracted hemicelluloses by acetic acid and sodium. *Bioresource Technology* 101, 1935–1940.
- Winandy, J.E., Stark, N.M., Horn, E., 2008. Wood-plastic composites using thermo-mechanical pulp made from oxalic acid pretreated red pine chip. In: *The 7th Global WPC and Natural Fiber Composites Congress and Exhibition*. University of Kassel, Kassel, Germany, pp. A16.1–A16.7.
- Yang, H.S., Kim, D.J., Kim, H.J., 2003. Rice straw-wood particle composite for sound absorbing wooden construction materials. *Bioresource Technology* 86 (2), 117–121.
- Ye, X.P., Julson, J., Kuo, M., Womac, A., Myers, D., 2007. Properties of medium density fiberboards made from renewable biomass. *Bioresource Technology* 98 (5), 1077–1084.

- Zhang, Y., Lu, X., Pizzi, A., Delmotte, L., 2003. Wheat straw particleboard bonding improvements enzyme pretreatment. *Holz als Roh-und Werkstoff* 61, 49–54.
- Zheng, Y., Pan, Z.L., Zhang, R.H., Jenkins, B.M., Blunk, S., 2007. Particleboard quality characteristics of saline jose tall wheat grass and chemical treatment effect. *Bioresource Technology* 98 (6), 1304–1310.
- Zou, Y., Huda, S., Yang, Y., 2010. Lightweight composites from long wheat straw and polypropylene web. *Bioresource Technology* 101, 2026–2033.
- Zhu, J.Y., Pan, X.J., 2010. Woody biomass pretreatment for cellulosic ethanol production: technology and energy consumption evaluation. *Bioresource Technology* 101, 4992–5002.