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Effect of oxalic acid pretreatment of wood chips on manufacturing medium-density fiberboard

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Abstract

The main objective of this study was to evaluate the effect of oxalic acid (OA) wood chips pretreatment prior to refining, which is done to reduce energy used during the refining process. Selected mechanical and physical performances of medium-density fiberboard (MDF) – internal bonding (IB), modulus of elasticity (MOE), modulus of rupture (MOR), water absorption (WA) and thickness swelling (TS) – made from this OA-pretreated wood were tested and the effect of the OA treatment on carbohydrates investigated. The results showed that the OA treatment significantly reduced refining energy usage, and improved MDF dimensional stability and lightness. However, the OA treatment had a negative effect on the internal bonding strength of MDF panels. The amount of extracted carbohydrates was dramatically increased, up to 24 times, by the OA pretreatment. Carbohydrates extracted from wood chips could be a potential sustainable resource for biofuel or bio-based chemicals. This paper is a contribution to the so-called ''value prior to pulping (VPP)'' concept.

Keywords: cellulosic biofuel; fiber refining; internal bonding; medium-density fiberboard; modulus of elasticity; modulus of rupture; oxalic acid pretreatment; thickness swelling; water absorption.

Introduction

Medium-density fiberboard (MDF) has become one of the most popular wood-based composite materials due to its numerous advantages. Typically, there are three major steps in processing MDF panels. First, logs or other wood residuals are chipped. The wood chips are soaked and softened in a digester and then refined into fibers by means of a pressurized steam refiner. Finally, the fibers are mixed with resin, wax and other additives and hot pressed into MDF panels. The thermo-mechanical refining process is effective and widely used. However, the process is energy intensive and thus the product efficiency is low. With recent renewed interest in ethanol production from cellulosic materials, the pulp and paper industry proposed the concept of ''value prior to pulping'' (VPP) to compensate for the energy-intensive refining process (Thorp and Raymond 2004; Liu et al. 2006; Van 2006; Huang 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. The advantages are: energy savings in refining, production of new chemical feedstocks and reduced hygroscopicity of the pretreated wood fibers (Winandy et al. 2008).

Early studies indicated that oxalic acid (OA) or its derivatives are suitable for pretreatment of wood chips to reduce energy consumption and improve MDF performance (Swaney et al. 2003; Akhtar et al. 2007; Kenealy et al. 2007a). Essential steps of the pretreatment are: heating wood chips with atmospheric steam, impregnating the chips with OA and/or its chemical derivatives and heating the system for an effective extraction of the carbohydrates. The chips with diminished carbohydrate content are converted into fibers (Kenealy et al. 2007a; Akhtar et al. 2008; Winandy et al. 2008). Paper products are not adversely affected by the pretreatment; on the contrary, handsheet strength and brightness are increased under optimized conditions (Kenealy et al. 2007a). Similar results at lower temperatures have been reported for poplar (*Populus trichocarpa*) (Pinson et al. 2004). MDF made of pretreated chips has improved water repellency properties (Akhtar et al. 2008). Increasing the chemical levels, reaction time and temperature improved the carbohydrate removal. Approximately 50% of extracted carbohydrates were monosaccharides, which are suited to fermentation without additional treatment (Kenealy et al. 2007b). Some pulp and paper research organizations throughout the world are conducting various forms of VPP research work (Zhu and Pan 2010). However, only limited research on this subject has been reported so far.

Wood-plastic composites based on OA-pretreated fibers have similar mechanical performance to that of composites made of untreated fibers (Winandy et al. 2008). As a continuation from earlier works, the main objective of this study is to evaluate the effects of the OA pretreatment prior to refining, focusing on energy saving in refining and on select-

ed mechanical and physical performances of MDF panels. In addition, the pretreatment effect on mass loss and carbohydrate release from wood is investigated.

Materials and methods

Commercial loblolly pine (*Pinus taeda* L.) wood chips were provided by Flakeboard Inc. (Albany, NY, USA). The chips were stored frozen in plastic bags. The initial moisture content (MC) of the chips was about 65% before pretreatment. Oxalic acid (OA) was purchased from Sigma-Aldrich chemical company (St Louis, MO, USA). The concentration of the OA solution for pretreatment was 0.33%. Temperatures for pretreatment were: 120°C, 140°C, and 160°C for 10 min. For the control, wood chips were processed with hot water (160°C) for 10 min without chemicals (Table 1). The source of urea-formaldehyde (UF) resin was: Hexion Speciality Chemicals Inc. (Springfield, OR, USA). The resin was water dispersed (60% solids content). The reactor configuration and pretreatment procedure has been described by Winandy et al. (2008).

Following pretreatment, the hemicellulose extracts and extracted wood chips were collected and weighed. The wood chips mass and MC were measured before and after pretreatment. The carbohydrate and Klason lignin contents of the chips were analyzed according to Davis (1998) and Effland (1977), respectively. Hemicellulose content was determined by subtracting the glucan content from total carbohydrate content (Yildiz et al. 2006). The analysis of carbohydrates in aqueous extracts (Shuai et al. 2010) was performed by a Dionex HPLC system (ICS-3000, Sunnyvale, CA, USA) equipped with an integrated amperometric detector.

The extracted wood chips (OA-treated chips and control samples) and raw control chips (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, Muncy, PA, USA) was applied with 300 mm diameter plates, D2B505 plate pattern, and 0.1778 mm (0.007 in) refiner gap. Energy consumption during each refining run was recorded by a wattmeter connected directly to the refiner motor. During the thermo-mechanical refining process, the wood chips were placed into a presteaming tube and pressurized with steam to 0.62 MPa (90 PSI) for 10 min prior to defibration. The refining feed rate was approximately 1 kg min^{-1} on the dry weight basis. These fibers were collected separately and dried at 103±2°C to 2–3% MC. The refined fiber was kept in a cold storage room for three days before drying. The dried fibers were bagged prior to MDF fabrication.

A resin content of 12% (o.d. basis) was uniformly sprayed onto the wood fibers while they were circulating in a tube blender system. The mat was hand formed after resin application. The MDF panels were pressed by means of ''a 91.4-by 91.4-cm Nordberg hot press'' with a PressMAN control system (Alberta Research Center, Alberta, Canada) at 180°C platen temperature. The boards measured: 508 mm by 508 mm (20 in by 20 in) and 12.5 mm (0.5 in) thick. The target density was 0.70 g cm^{-3}. The total hot press time of 340 s (60 s closing, 190 s at the target thickness and 90 s opening) ensured the complete curing of the resin. Three replicate boards were made for each condition.

Table 1 Experimental variables of oxalic acid (OA) pretreatment.

Sample	Temp. (°C)	Time (min)	Conc. of OA (%)
Control	160	10	0
120	120	10	0.33
140	140	10	0.33
160	160	10	0.33

The surface color of all panels was determined using a Minolta Chroma CR-400 colorimeter (Konica Minolta, Inc., Ramsey, NJ, USA). Five areas (one in each corner and one in the center) were selected for the color evaluation. Internal bonding (IB), modulus of elasticity (MOE), modulus of rupture (MOR), water absorption (WA) and thickness swelling (TS) of the samples were prepared and tested in accordance with ASTM D 1037-06a (2006). Nine 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) were measured according to Material Testing System 634.11F-24 and the IB values were determined on a universal testing machine (Instron 555, Norwood, MA, USA). The WA and TS properties were measured after 24-h immersion in distilled water at 20°C.

Results and discussion

The mass loss (ML) of wood chips was considerable during the pretreatments. For the control sample (hot water treatment only) the ML was 5.6%, while the three OA-treated samples pretreated at 120°C, 140°C and 160°C revealed ML of 6.6%, 6.8% and 10%, respectively. Wood chips treated with OA at 160°C lost more than 70% mass compared with the control sample. Obviously, OA treatment leads to wood chip degradation and high mass losses. Higher treatment temperatures also resulted in elevated mass losses. The ML of OA-treated chips increased by about 50% when steam

Table 2 Chemical analysis of loblolly pine chips.

Sample	KL (%)	[a]Ara (%)	[b]Gal (%)	[c]Glc (%)	[d]Xyl (%)	[e]Man (%)	[f]Sum (%)	[g]Hemicelluloses (%)
Raw control	30.2	1.1	2.5	41.81	6.51	9.54	61.71	19.91
Control	30.0	1.1	2.2	39.10	6.07	8.95	57.59	18.49
120	30.3	0.6	2.0	40.90	6.19	8.91	58.63	17.73
140	31.3	0.3	1.7	39.93	5.82	9.04	56.78	16.85
160	31.7	0.1	1.5	41.99	5.22	7.50	56.51	14.53

[a–e]Monomeric sugar obtained by total hydrolysis.

[f]Total monomeric sugars.

[g]Hemicelluloses: sum of Ara, Gal, Xyl and Man.

KL, Klason lignin; Ara, Arabinan; Gal, Galactan; Glc, Glucan; Xyl, Xylan; Man, Mannan.

temperature was increased from 120 to 160°C. Similar results were found in pretreatment studies of reed and wheat straw (Han et al. 2001).

The chemical components of wood chips before and after pretreatment are listed in Table 2. The glucan contents of chips treated with OA (samples 120, 140, and 160) or hot water (control) are similar to those of untreated chips, which can be interpreted to mean that heat and OA pretreatments do not cause cellulose degradation. Kenealy et al. (2007b) reported similar results for southern yellow pine chips treated with OA and diethyl oxalate (DEO). In the present study, the hemicellulose content of chips decreased by the addition of OA in hot water or at elevated temperatures during OA treatment. In general, the same tendency was observed on the relative contents of arabinan, galactan, xylan and mannan in wood. Compared with the untreated specimens, the control specimens had a 7% reduction in hemicellulose content and OA-treatment led to a 27% decrease of hemicelluloses compared to the control (at 160°C). Accordingly, the OA pretreatment has a larger effect on hemicelluloses degradation than elevated pretreatment temperatures. Lignin proved to be most stable during thermal degradation (Yildiz et al. 2006; Kartal et al. 2008) and the slight increase in the relative lignin content is due to the hydrolysis loss of hemicelluloses during pretreatment.

The main carbohydrates extracted from the wood chips were arabinose, galactose, glucose, xylose and mannose (Table 3). The OA-treatment at 160°C led, for example, to 24 times more carbohydrate extraction compared to the control. Also in this context the temperature played a pivotal role: a temperature increase from 120 to 140°C entailed 3.7 times more carbohydrate extraction. The predominant carbohydrate removed from the chips at 120°C is arabinose. Chips treated with OA solution at 140°C and 160°C released mainly mannose. Kenealy et al. (2007b) observed the same effect by treating spruce, aspen, maple and southern yellow pine with diluted OA solutions prior to refining.

Pretreated wood chips, especially those subject to OA-pretreatment, exhibited considerably less total energy consumption in the refining process compared to the raw control (Figure 1a). At 160°C, for example, the total energy consumption in the refining process is reduced up to 50%. The influence of temperature was comparatively moderate: temperature increment from 120 to 160°C caused only 15.6% energy savings. A possible interpretation of these results is that OA treatment elevates the carboxylic acid content of the carbohydrates which leads to swelling, thereby diminishing the number of strong hydrogen bonds within the cell wall leading to lower energy consumption during the refining process (Kenealy et al. 2007a). In addition, removal of hemicelluloses as internal adhesive layers between cellulose and lignin in the microfibrils also entails energy saving during refining.

The major color parameters including lightness (L*) and the chromatic coordinates on the green-red (a*) and on the blue-yellow (b*) axis were tested on panels manufactured with different treatment parameters (Table 4). The pretreatment tends to increase (i.e. improve) the L* values. The F-test statistical analysis and two-tailed pair-wise t-test confirmed the significance of L* improvement at the 95% con-

Table 3 Sugar analysis of aqueous extracts of pretreated wood chip.

	Content (g kg^{-1} oven-dried wood)					
Sample	[a]Ara	[b]Gal	[c]Glc	[d]Xyl	[e]Man	[f]Sum
Control	0.63	0.36	0.18	n.d	n.d	1.17
120	3.53	1.10	0.49	0.49	0.48	6.09
140	4.87	3.78	2.57	4.27	8.38	23.88
160	4.38	5.25	4.75	4.83	9.45	28.66

[a–e]Monomeric sugar obtained by total hydrolysis.
[f]Total monomeric sugars.

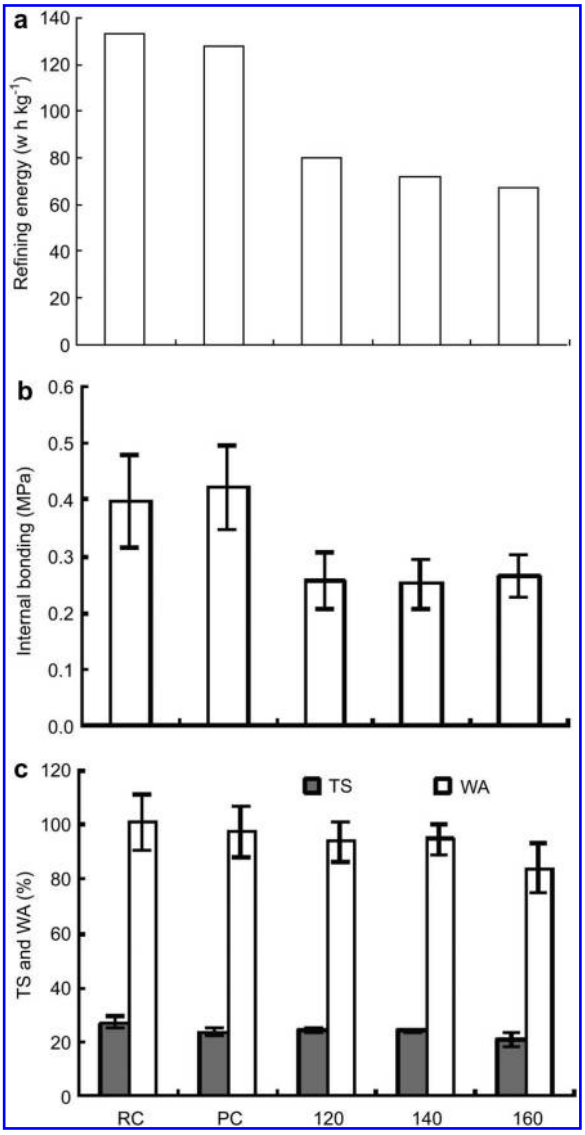

Figure 1 The effect of pretreatment conditions on refining energy consumption (a) and internal bonding (IB) (b) and thickness swelling (TS) and water absorption (WA) (c) of MDF panels. RC: raw control (without any pretreatment). PC: control (with hot water pretreatment). The numbers 120, 140, and 160 refer to the pretreatment temperature in °C.

Table 4 Color measurements in the CIEL*a*b* system on MDF panels.

Sample	L*	a*	b*
Raw control	60.78 (0.41)	7.43 (0.09)	27.21 (0.27)
Control	61.50 (0.36)	6.71 (0.06)	25.56 (0.24)
120	63.02 (0.47)	7.56 (0.14)	27.92 (0.38)
140	63.83 (0.47)	7.43 (0.10)	27.97 (0.18)
160	63.24 (0.29)	7.25 (0.11)	26.82 (0.65)

Each value is the mean of 15 replicates. Standard deviation is indicated in parentheses.

fidence level. However, the values of parameter a* of the OA-treated specimens are apparently slightly decreased with increasing temperature and are slightly higher than those of control specimens. A similar tendency was recorded concerning parameter b*. However, the F-test statistical analyses have not confirmed the significance of these observations.

Figure 1b shows the effect of pretreatment on the IB strength of MDF panels. In Figure 1b and c, the height of each bar represents a mean value under a certain condition and the maxima and minima of standard deviations are also indicated. The OA pretreatment decreases the specimen's IB strength by about 37% in comparison with the raw control, while the pretreatment temperature has little effect on the IB performance. The result of F-test statistical analysis and the two-tailed pair-wise t-test confirmed that the OA treatment did have significant effect on the IB strength at the 95% confidence level and there is no significant difference with this regard among the three OA specimens. The IB strength decrease is due to the loss of hemicelluloses with high contribution to the internal bond strength (Winandy et al. 2008). At the same time, residual OA in wood chips may lower the pH and lead to a self-condensation of UF resin and contribute to the reduction of IB strength. However, the process of OA pretreatment still has a high optimization potential to mitigate the effects of IB loss.

The effects of the steam and OA treatment on the static bending properties of MDF panels are presented in Table 5. The MOE and MOR values increased by 14% and 24%, respectively, when the temperature increased from 120 to 160°C during OA pretreatment. According to the F-tests, the effect of pretreatment temperature on the MOR of OA-treated panels is significant (95% confidence level). This is not true for MOE. The two-tailed pair-wise t-tests also confirm the significance of MOR change at the 95% confidence level

Table 5 Effect of pretreatment on MOE and MOR of MDF panels.

Sample	MOE (MPa)	MOR (MPa)
Raw control	1563 (192)	14.8 (2.6)
Control	1524 (69)	15.9 (0.9)
120	1304 (180)	12.2 (1.7)
140	1377 (215)	13.6 (1.8)
160	1487 (93)	15.1 (0.7)

Each value is the mean of six replicates. Standard deviation is indicated in parentheses.

when pretreatment temperature is increased from 120°C to 140°C or from 140°C to 160°C. In general, the static bending MOE and MOR of OA-treated panels are slightly lower than that of the control. Winandy et al. (2008) reported similar experiences when wood-plastic composites were prepared with variously pretreated TMP wood fibers. The observed effects could be due to physical changes of the fibers (i.e. fiber length reduction), or to chemical changes in the cell wall resulting from the hemicellulose extraction that might make the pretreated wood fiber and UF resin less compatible; or a combination of physical and chemical changes (Winandy et al. 2008).

Figure 1c shows the various pretreatment effects on WA and TS of specimens. Compared with the raw control specimens, the control specimens reduced their WA and TS about 3.7% and 12.7%, respectively. OA pretreatment leads to decreased WA and TS data up to 16.9% and 23.8%, respectively. Statistical analysis confirmed the significance of these observations at the 95% confidence level. The reduction in WA and TS implies that the dimensional stability of MDF panels could be improved by the OA pretreatment of wood chips prior to the refining process. Pretreatment temperature also affected the dimensional stability of MDF specimens. The WA and TS of the MDF specimen decreased by about 10.4% and 15.0%, respectively, when the OA pretreatment temperature was increased from 120 to 160°C.

Hemicelluloses are more water soluble and more hydrophilic than cellulose and lignin. Certainly, the improvement of dimensional stability is mainly attributable to the partial removal of hemicelluloses by the pretreatment. Other studies confirm this view (Garcia et al. 2006; Winandy and Krzysik 2007; Korkut and Guller 2008). Paraffin waxes (0.5–1.5% b.o. the oven-dried weight of the fibers) are currently used in the MDF panel industry to delay water absorption. Physical-chemical treatments, such as OA treatment prior to the refining process, could have the same effect, i.e. decrease the hygroscopicity of MDF fibers and improve the dimensional stability of panels in the longer term.

Conclusions

OA treatment prior to refining resulted in less refining energy consumption, better MDF dimensional stability, and improved panel lightness. However, OA pretreatment had a negative effect on IB strength. Extracted carbohydrates increased by a factor of 24 upon OA pretreatment. The OA process described in this paper shows promising potential to improve water repellency properties, reduce energy consumption during refining, and increase profitability by utilization of extracted carbohydrates for biofuel or bio-based chemicals.

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