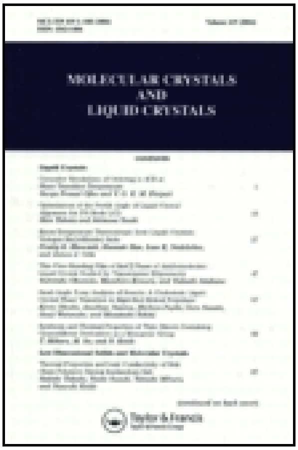

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Heat Treatments of Wood Fibers for Self-Bonding and Stabilized Fiberboards

Roger M. Rowell [a] & James D. McSweeny [a]

[a] USDA, FS, Forest Products Laboratory and Biological Systems Engineering, University of Wisconsin, Madison, WI, USA

Version of record first published: 16 Jun 2008

To cite this article: Roger M. Rowell & James D. McSweeny (2008): Heat Treatments of Wood Fibers for Self-Bonding and Stabilized Fiberboards, Molecular Crystals and Liquid Crystals, 483:1, 307-325

To link to this article: http://dx.doi.org/10.1080/15421400801918179

Mol. Cryst. Liq. Cryst., Vol. 483, pp. 307–325, 2008
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400801918179

Heat Treatments of Wood Fibers for Self-Bonding and Stabilized Fiberboards

Roger M. Rowell and James D. McSweeny
USDA, FS, Forest Products Laboratory and Biological Systems
Engineering, University of Wisconsin, Madison, WI, USA

Heat treatment of wood fibers in a closed press for 4 and 8 minutes and pressed into fiberboards greatly reduces moisture regain and increases dimensional stability of the boards. Part of the hemicellulose sugars are lost during the steam treatment and furan intermediates were detected. Mannose, galactose, xylose, arabinose and rhamnose were partially lost during the steaming process. The steam treated boards have lower strength as compared to adhesive added boards but they do not fall apart when placed in water.

Keywords: closed press; dimensional stability; EMC; furans; heat treatments; MOE; MOR; steam

INTRODUCTION

The treatment of wood with heat dates back into the oral history of Africa. Long straight wooden sticks destined to become spears were heat treated to harden and sharpen them. The treatment involved several steps including placing the end of the stick under hot coals, withdrawing after a certain time and then hitting the burned stick end with a rock. This process was repeated many times until the end was hard and sharp. The mechanism of this process is quite simple. Heating wood in the absence of oxygen caused the wood to undergo pyrolysis converting some of the hemicellulose and cellulose sugars to furan resins and some of the wood substance to charcoal. Pounding the pyrolyzed stick end with a rock drove the furans and charcoal into the interface/interphase of the charred-undegraded wood. Repeating this process and shaping the end resulted in a furan

Address correspondence to Roger M. Rowell, USDA, FS, Forest Products Laboratory and University of Wisconsin, One Gifford Pinchot Dr, Madison, WI, USA 53705. E-mail: rmrowell@wisc.edu

impregnated, carbon hardened point. Other historical references are made to burning the outside of wooden ships for both decay resistance and fire proofing.

In the 1930's, Stamm and coworkers started a long series of studies on heat stabilization of wood [1]. Stamm's work was based on earlier research of Tiemann [2] who showed that high-temperature kiln drying of wood decreased the hygroscopicity and subsequent swelling and shrinking of lumber. Heating wood in a vacuum at high temperatures caused lignin to flow and the hemicelluloses to decompose producing water-insoluble polymers. This treatment increased stability but decreased strength. One such treatment was known as Staybwood [3]. Staybwood was made by heating wood at temperatures between 100–160°C in a bath of molten metal (50% tin, 30% lead and 20% cadmium) with a melting point of about 150°C. This alloy did not stick to the wood surface. Sand circulated with dry nitrogen was also used to heat veneers with similar results. Heating times ranged from a few minutes at high temperatures to a few hours at lower temperatures. Dimensional stability of Staybwood increased as both heating time and treating temperatures were increased, whereas strength decreased. Under conditions that reduced swelling and shrinkage by 40% resulted in a reduction in toughness to less than half that of untreated wood. Abrasion resistance was also reduced. The hygroscopicity of Staybwood was greatly reduced and resistance to decay was improved.

The use of high levels of heat alone to improve dimensional stability of wood can cause extensive damage to the cellular structure. For this reason, researchers also looked at heat stabilization using both heat and moisture. Seborg *et al.* compressed wood while heating moist wood to form a heat stabilized product known as Staypak [4]. Staypak was made by compressing thin veneers that had been conditioned to 30 to 65% relative humidity at temperatures between 170–177°C. The compressed veneers had a specific gravity of about 1.3. The compressed product sorbs water at a slower rate than uncompressed wood and was more dimensionally stable. It was not more resistant to biological attack. Strength properties were much higher than untreated wood. Strength increased almost proportionally to the amount of compression. Tensile strength both parallel and perpendicular to the grain, modulus of rupture, and elasticity in bending were increased. The greatest increase was in impact bending strength. Other products similar to Staypak were produced in Germany called Lignostone and Lignofol and in England Jicwood and Jablo [5].

Burmester [6] also observed that swelling could be reduced in wood based on heating wood in a sealed system under pressure.

He compressed oak, beech, spruce and pine with moisture contents ranging from 20 to 30% and found 52–75% reductions in deformation due to moisture regain. Similar results were found for particleboard.

Giebeler [7] treated wood at 180 to 200°C in the presence of moisture and found that these treatments resulted in a large reduction in the resistance to shock, modulus of elasticity (MOE), modulus of rupture (MOR) and compression strength. Hillis [8] also studied the effects of high temperature and chemicals on wood stability. Hsu [9,10] published data on a new process using high pressure steam digestion of aspen and pine flakes and fiber before board production. Flakes or fiber was hot pressed at 177°C for 9 minutes followed by 4 hours at 138°C in a forced air oven. During the process, he found that the xylan content was reduced, free xylose was formed, water solubles increased, and both lignin and cellulose content remained unchanged using aspen flakes. Skaar [11] reported that heating wet wood degraded 10 times faster than heating dry wood.

Viitaniemi and Jamsa [12] also studied heat treatments of wood to improve dimensional stability. Inoue *et al.* [13,14] used a high pressure, high temperature treatment to stabilize solid wood and Rowell *et al.* [15] used a similar process to stabilize fiberboards made using jute fiber. In both of the research of Inoue and Rowell, the team used in the process is generated from moisture in the wood or fiber during the hot pressing and contained in the hot press by means of a rubber gasket which contains the wood or fiber during the process. Also, in both of these approaches the wood or fiberboard produced is cooled in the press under pressure [15].

In 1997, Honda [16] patented a process where wood, below the fiber saturation point is heated, under pressure, to a temperature above the softening temperature (Ts) of cellulose with decompression followed by recompression. A similar process of compression, decompression and recompression at high temperatures except applied to dry wood was patented by [17].

Another process has been reported called the PLATO process (Proving Lasting Advanced Timber Option) [18]. In this three step process, green wood is heated under pressure between 160 to 190°C, it is then dried to below 10% moisture by conventional drying and then cured between 170 and 190°C at atmospheric pressure in the absence of air. The final product has a lower hygroscopicity and improved dimensional stability as compared to controls.

Negi and Chawla [19] studied the heat treatment of rice straw, grasses and pine needles over a wide range of temperature and treatment times. They showed that lower temperatures could be used to form fiberboards using heating as compared to wood.

MECHANISM OF BONDING

Since wood contains cell wall polymers that are susceptible to hydrolysis, dehydration, and oxidation upon heating, understanding the bonding mechanisms may lie in the understanding of the chemistry of wood thermal degradation. Wise and John [20] report a wide range of thermal degradation products from wood. It is well known from pulping technology that the hemicelluloses are much less stable to heat and undergo thermal degradation more rapidly than cellulose and lignin [21]. In the early stages of heat stabilization, the hemicelluloses depolymerize to form free sugars which degrade to form various simple organic compounds. Mitchell *et al.* [22] reported that the hemicelluloses in Douglas fir decomposed at 220°C faster than alpha-cellulose, which was faster than lignin. Interestingly, decomposition was faster and occurred to a greater extent in a closed system as compared to an open system. They also found that, under these conditions, the hemicelluloses decomposed mainly to carbon dioxide and water with the formation of very little condensation products. Melcer *et al.* [23], however, found that the hemicelluloses degraded the fastest but that lignin was degraded faster than cellulose in beech wood at 120°C. Sondermann and Augustin [24] reported pentosan degradation varied from 8% at 170°C to 100% at 350°C. A review of the thermal degradation of wood has been published by [21,25,26].

Fengel and Wegner [26] reported that organic acids were formed as reaction products from the non-hydrolytic degradation of hemicelluloses. Kosik *et al.* [27] reported that acetaldehyde, methyl acetate, propyl aldehyde, acetone, acetic acid, methanol and furfural were formed from the thermal decomposition of 4-0-methylgluconoxylan. Aoyama [28] reported that a large percentage of the hemicelluloses from bamboo were solubilized at temperatures between 170 and 206°C. The extent of degradation was dependent on moisture content, temperature and time of treatment. Schmidt *et al.* [29] reported that there were differences in the degradation of the hemicelluloses in the steam treatment of wheat straw as compared to birch wood. It was found that the optimum conditions for degrading hemicelluloses, by steam, from straw were significantly different than those used for wood.

Several researchers have shown that the yield of free sugars formed from hemicelluloses during steaming of lignocellulosics increase and undergo a maximum in concentration and then decrease with increasing time of steaming [30–33]. This would indicate that free sugars released from the degradation of the hemicellulose then undergo further reactions to other products. Pectic polysaccharides have also been shown to influence the production of free sugars upon heating [32,33].

Research done by the Masonite Corporation also provides useful information on the possible bonding mechanism [34,35]. Fiberization was done at high temperatures and under steam pressure. The yield of fiber from this process was approximately 80 to 85% [36]. The fiber then went through three counter current washing cycles to remove soluble sugars. The additional fiber weight loss after washing was 10 to 15%. If the concentration of sugars in the fibers before pressing was too high, the fiberboards would stick in the press. If the sugar content was too low, the fiberboards would not stick together. During the counter current wash cycles, furfural could be detected by smell; however, no analytical determination of the exact amount generated was ever carried out. The weight loss during refining was assumed to be mainly due to degradation of the hemicellulose polymers producing both free sugars and other degradation products, including furfural. During the hot pressing in the production of fiberboards, the free sugars underwent reversion reactions under the high temperature acidic conditions giving rise to complex, highly branched polysaccharides. The hygroscopicity of the reversion-derived polysaccharides was lower than the other cell wall polymers resulting in a reduced hygroscopicity of the final fiberboard. The counter current washing removed most of the soluble sugars. Inoue *et al.* [13] and Norimoto [37] also reported the formation of furfural during the heating of moist wood.

Shen [38] describes another process for degrading part of the hemicelluloses using a steam explosion process of wood chips to produce fiber. He claims, but does not prove, that furan monomers are formed in the process. Using this process, Brooks has shown that heating wood at 208°C for 1 to 3 minutes and exploding in a Stake Digester results in the release of most of the pentosans in the hemicelluloses [39]. Using only the fibers from the digester, boards were made which showed less than 9% thickness swelling after a 2 hour boiling test. Approximately half of the fiberboard strength properties remain after this boiling test.

It is well known that lignin and the hemicelluloses are amorphous polymers. Cellulose, on the other hand, is mainly crystalline but does contain regions with amorphous character within the crystalline lattice. Amorphous polymers undergo changes in physical characteristics upon heating resulting in transitions to glassy and rubbery states [40]. The temperature where this happens is referred to as the glass transition temperature or Tg. Transitions from one state to another depend on sufficient energy input to overcome the intermolecular attractive forces with in the polymer and allow a greater degree of flow. Chawla and Sharma [41] showed that once the temperature exceeded 160°C, there was sufficient flow of lignin to block pores within the wood structure to restrict the reentry of moisture. Hillis and Roza [42] found that a minimum heating of 2 hours at 100°C plasticized the hemicellulose-lignin matrix.

It is also well recognized that moisture lowers the Tg of an amorphous polymer [43]. Goring [43] examined the softening temperatures for dry and wet lignin, hemicellulose and cellulose and found that the sorption of water greatly decreased the Tg of both lignin and hemicellulose while the Tg for cellulose only varied slightly from dry to wet. The Tg for dry lignin is approximately 155–160°C depending on the chemical structure. High syringyl content lignins have a lower Tg as compared to other lignins [44]. Inoue and coworkers [14] showed that at temperatures between 180 and 200°C, the lignin-hemicellulose matrix became plasticized and underwent thermoplastic flow. All of this data shows that under heat and pressure, the lignin-hemicellulose matrix becomes thermoplastic and will deform to a different stable matrix. If the compressed matrix is cooled under pressure, the newly formed matrix has little memory of its pre-compressed form [15].

Chawla and Sharma [41] published results suggesting that during the heating process crosslinking of polysaccharide chains could occur. They also suggested that some of the thermal degradation products recombined during heating. Norimoto [37] and Dwianto *et al.* [45] also suggested the formation of interlinkages between wood polymers during the heat treatment of wood. Boostra *et al.* [46] suggested that degradation products from the hemicelluloses and lignin form reactive intermediates that cross link during the curing stage in the PLATO process (see above).

It has also been shown that the thick-walled latewood cells are compressed less than the thinner walled earlywood cells [47]. The compression of void space in the compressed wood restricts the re-entry of moisture.

Finally, it has been shown that heating wood under pressure resulted in an increase in cellulose crystallinity [48]. This could also have an influence on re-wetting of the cell wall polymers after compression.

Several people have studied steam explosion of wood chips and other agro-resources to produce a binderless fiberboard. Mobarak *et al.* [49] worked on a binderless composite from bagasse. Their board has greatly reduced water sorption (less than 19%) and bending strength up to 130 N/mm^2. They concluded that it was not clear whether secondary valency forces, particularly hydrogen bonding, predominate in the linkages formed during pressing, or whether covalent bonds also play a part in this connection. The high self-bonding capacity of bagasse particles may be partly attributed to degradation products of hemicelluloses acting as an adhesive, e.g., short-chain polysaccharides, condensation products of furfural.

Hsu *et al.* [50] studied the dimensional stability of wood-based composites using a steam pretreatment of aspen chips. He used a mild steam pretreatment of 1.55 MPa for 3 to 4 minutes that resulted in a significant reduction of the xylans. He used either phenol-formaldehyde or urea-formaldehyde as an added adhesive but the fact that he found a large reduction in the hygroscopic hemicelluloses is significant.

Kawai and his team in Japan [51–56] studied the chemical changes in steam-pressed kenaf core to produce a binderless particleboard. They used steam-injection pressing at 0.6 to 1 MPa and found a decrease in hemicelluloses (up to 28%), cellulose (up to 20%) and lignin (up to 18%) and produced a board with greatly improved dimensional stability. They did not determine the mechanism of bonding but did detect furfural in the off gasses from the pressing. They also studied degradation products from lignin [55].

Okuda and Sato [57] also studied the manufacturing and mechanical properties of binderless boards made form kenaf core. They treated the kenaf at 180°C for 10 min and then pressed at 5.3 MPa to give fiberboards with a board density of 1.0 g/cm^3. The dry and wet MOR values were 36.1 MPa and 9.3 MPa respectively; dry MOE 5.5 GPa, IB 5.7 MPa and TS 19.6%. They concluded that mechanical properties (MOR, MOE) exceed the minimum requirements for MDF based on the Japanese standards.

Sekino *et al.* [58] also studied the mechanism of improved dimensional stability of steam-pretreated particles for particleboard production. They treated veneers of Japanese Sugi at different steam temperatures (160 to 220°C) and then converted the treated veneers into different types of particles. The particles were compressed into particleboards and changes in thickness under different conditions were determined. The veneers treated at 220°C gave the most stable boards.

Based on the literature review, it is not possible to make any conclusions on the exact mechanism associated with the reduction in hygroscopicity, the increase in dimensional stability and the bonding mechanism derived from heat and steam treatment of lignocellulosics. The effects of the treatments depends on many variables such as temperature, time of treatment, moisture content, chemical composition of the lignocellulosic, and probably other factors which are not yet understood. Common to all of the mechanisms discussed in past work include matrix softening, loss of hemicellulose sugars, weight loss during treatment and improvements in hygroscopicity and dimensional stability with other properties such as decay resistance and mechanical strength affected.

From the research the Forest Products Laboratory has done to date, however, we speculate that the mechanisms of the increased dimensional stability and reduced hygroscopicity achieved from high temperature treatment of wood is a combination of one or more factors [59]. These include: (1) degradation of the hygroscopic hemicelluloses to form soluble sugars which may undergo reversion reactions to form less hygroscopic, highly branched polysaccharides, (2) degradation of the hemicelluloses to form free sugars which, in turn, form furan intermediates that can undergo polymerization during hot pressing resulting in the formation of an adhesive, (3) thermal softening of the cell wall matrix, mainly lignin, to allow reformation of a new less stressed matrix after pressing, (4) degradation of the hygroscopic hemicelluloses to form volatile break down products that are lost during hot pressing, (5) crosslinking between carbohydrate polymers and/or between lignin and carbohydrate polymers takes place, (6) densification of the wood results in a reduction of pore size and void volume which restricts the flow of moisture back into the pressed wood, and/or (7) an increase in cellulose crystallinity during high temperature compression. While no definitive mechanism has been published, there are clues in the literature to support one or more of the above theories.

EXPERIMENTAL

The closed pressing system used in this research is shown in Figure 1 [15]. A flat silicone ring 5 cm on each side with a 23 cm center cut out.

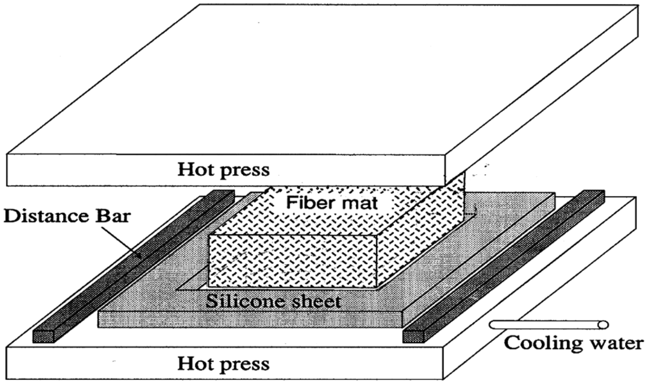

FIGURE 1 The closed press system used in this research.

The rubber ring was placed in a 35 by 35 cm press heated by oil and cooled by water.

Steam Stabilized Fiberboards

Aspen fiber was dried over night at 105°C and weighed. A water spray was used to bring the fiber moisture content to 15%. A hand formed fiber mat was formed inside the pressing ring and then placed in the press. The press was then closed to come into contact with the rubber ring to contain the steam generated from the moisture in the fiber. The fibers were pressed at 200°C for either 4 or 8 minutes to form fiberboards with a specific gravity of either 0.64 or 1.0. A known amount of fiber was used for each board and the press was closed to metal stops to give the desired specific gravities. After pressing, the fiberboards were cooled, under pressure, in the press, removed, weighed and cut into test specimens.

Control Fiberboards

Similar fiberboards were made as given above except the rubber ring was not used in the press. These boards were pressed for 4 or 8 minutes at 200°C to give fiberboards with a specific gravity of wither 0.64 or 1.0. After cooling in the press, under pressure, the fiberboards were removed, weighed, and cut into test specimens.

Equilibrium Moisture Content (EMC)

Ovendried, weighed specimens (5 by 5 cm) were placed in constant humidity rooms at 30%, 65% and 90% relative humidity at 27°C. The specimens were left until reaching a constant weight, then the specimens were weighed to determine the EMC and the thickness was measured to determine thickness swelling (TS). Equilibrium moisture content (EMC) was determined based on oven dry specimen weight. Five specimens of each set of fiberboards were tested and the results averaged.

Water-Soaking and Thickness Swelling Tests

Ovendried, weighed and thickness measured specimens (5 by 5 cm) were placed in a container, distilled water was added and the board thickness was recorded as a function of time. Measurements were taken every 15 minute for the first hour, every hour for the first 5 hours, then once a day for 4 days. After 4 days each specimen was re-ovendried for 24 hours at 105°C weighed and its thickness determined. Five specimens of each set of recycled boards were tested and the results averaged.

Strength Tests

Static bending tests were conducted on board specimens (5 by 20 cm) conditioned to 65% relative humidity according to ASTM standard D 1037 [60]. Modulus of rupture (MOR) and modulus of elasticity (MOE) were determined. Ten specimens from each board were tested and the results averaged.

Leaching, Chemical Analyses and Mass Balance

To determine the effect of temperature on cell wall carbohydrate polymer degradation, specimens were milled (<1 mm particle size) and subsamples analyzed for carbohydrate composition. To determine the effect of temperature on the solubility of surviving carbohydrates, subsamples were leached using essentially the ASTM Standard Test Method for the cold-water solubility of wood. Briefly, *ca.* 500 mg was extracted with 5 mL of water, with 0.05% sodium azide as a preservative, for 48 hr at 23°C using a rotating tumbler shaker set at 14 revolutions per minute. Masses extracted were determined gravimetrically, and both extracts and residues were analyzed for carbohydrate composition.

To determine sugar composition, fibers were hydrolyzed using a two-step procedure: a primary hydrolysis with 1.00 ml 72% (w/w) H_2S USDA, Forest Service, General Technical Report, FPL-GTR-55, Forest Products Laboratory, Madison, V.A., Effects of heat-pressure-treatments of semi-dry wood on its dimensional stability, Holz Roh-Werkst. 31:237–243 (1973).

Davis, M.W. A Rapid Modified Method for Compositional Carbohydrate Analysis of Lignocellulosics by HPAEC/PAD, J Wood Chem O_4 for 1 hr at 30°C, followed by a secondary hydrolysis with 4% (w/w) H_2SO_4 for 1 hr at 121°C [61]. Aqueous extracts were hydrolyzed using only the secondary hydrolysis step. To control for sugar degradation during secondary hydrolysis, a standard mixture of sugars was hydrolyzed in parallel with the samples. Losses during primary hydrolysis are minimal and were ignored. Hydrolysate sugar contents were determined by anion exchange high performance liquid chromatography using pulsed amperometric detection [62]. The chromatographic system consisted of a 738 autosampler (Alcott Chromatography, Norcross, GA), a GP40 quaternary gradient high pressure pump (Dionex Corporation, Sunnyvale, CA), and a pulsed amperometric detector (Dionex). Sugar separation was achieved with Carbo-Pac PA1 guard and analytical columns (Dionex) connected in series. Sugars were eluted with water (>17.8 mOhm/cm) at a flow rate of 1.2 ml/min. For detection, 300 mM NaOH was added as a post-column reagent at a flow rate of ca. 0.5 ml/min. Prior to each injection, the anion exchange columns were conditioned with 170 mM $NaC_2H_3O_2$ in 200 mM NaOH, then equilibrated with distilled water.

Results are reported as the percentage of glycan, relative to the glycan content of the non-steamed, non-extracted sample that was lost to steam treatment, lost to aqueous extraction, or remained as water insoluble polysaccharide in the wood residue. Because bulk mass losses attributable to the steam pressing per se were difficult to measure, the assumption was made that no mass was lost to this process. To the extent that this assumption is in error, carbohydrate contents steam-pressed samples will be overestimates. In fact, analytical yields of glucan in samples treated for 4 and 8 min was calculated to be 103% and 109%, respectively, indicating that some mass loss did occur.

Furan Determination

Volatile furan compounds were collected from the closed press after steaming the 8 minute run and analyzed by GC-MS.

RESULTS AND DISCUSSION

Because of the limited number of specimens per individual test, statistical analysis of the data was not appropriate. The results presented here should be considered as indicative of trends that a larger, statistically valid experiment should confirm.

Chemical Analysis

The glycan composition of the control material was fairly typical for a hardwood. Glucan and xylan were by far the most abundant carbohydrates, comprising 43.5% and 16.4% of the mass of the wood, respectively. The mass contributions of mannan, galactan, arabinan and rhamnan were 1.65%, 0.60%, 0.53% and 0.32%, respectively. The percentage of these components that were destroyed by steam treatment, that were removed by aqueous extraction, and that remained in the wood (residue) following these treatments is shown in Figures 1–3. In the control sample (Fig. 1), extraction losses of

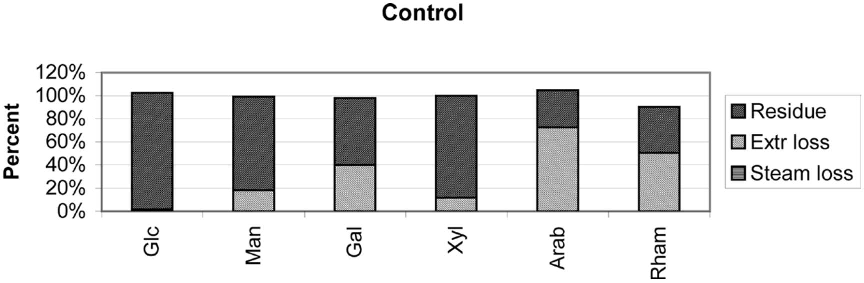

FIGURE 2 Sugars present in a non-treated sample.

hemicelluloses from wood ranged from 12% to 73% of the original component mass, following the pattern arabinan > rhamnan > galactan > mannan > xylan. Interestingly, in the 4 min treatment sample (Fig. 2), losses of hemicelluloses attributable to the steam pressing per se followed the same pattern, with the exception that xylan losses exceeded those of mannan. Steam pressing losses for this treatment ranged from 7% to 84%. No changes in water solubility as a result of steam pressing of hemicelluloses that survived the treatment were observed, with the exception of that of xylan, whose aqueous extraction increased from 12% to 29% following a 4 min treatment. Steam pressing for 8 min (Fig. 3) resulted in progressive losses of all hemicellulosic components. Essentially all of the arabinan and rhamnan were destroyed, and the trace that survived was removed by aqueous extraction.

In neither the 4 min nor the 8 min steam pressing treatment (Fig. 4) was measurable glucan destroyed or rendered extractable. Small losses associated with degradation of glucomannans are apparently masked by the abundance and stability of the cellulosic portion of the wood.

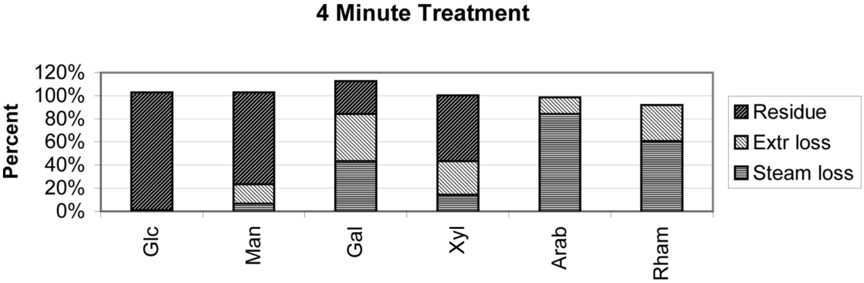

FIGURE 3 Sugars present in a 4 minute steam treated sample.

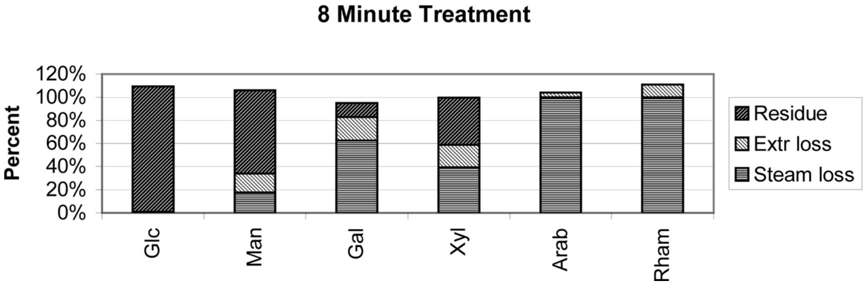

FIGURE 4 Sugars present in an 8 minute steam treated sample.

These results do not appear to support the hypothesis that the formation of less hygroscopic polysaccharides plays a significant role in the increased dimensional stability and reduced hygroscopicity associated with the process. One would expect less hygroscopic polysaccharides to be less extractable by water, but results indicate that extractability of hemicellulosic components was either unchanged or increased by steam treatment. Of course, this finding does not disprove the hypothesis, as one could still argue that less hygroscopic reversion products that are no longer covalently bound to the insoluble matrix are still more extractable than are the covalently bound but more hygroscopic moieties of non-steam treated wood.

In neither the 4 min nor the 8 min stream pressing treatment (Fig. 4) was measurable glucan destroyed or rendered extractable. Small losses associated with degradation of glucomannans are apparently masked by the abundance and stability of the cellulosic portion

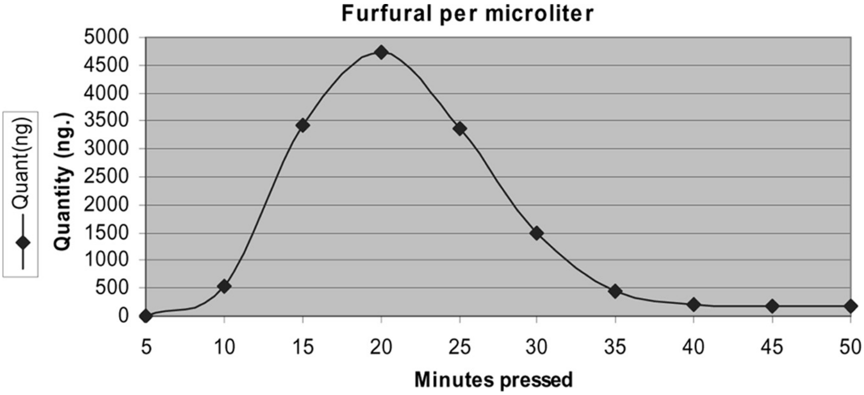

FIGURE 5 Determination of furan compounds by GC-MS.

of the wood. These results are consistent with the hypothesis that degradative losses of hemicelluloses per se play a role in the reduction of the wood's bulk hygroscopicity upon steam treatment. In terms of total hemicellulosic mass, treatment for 4 min or for 8 min destroyed 17% or 41% of the total hemicellulosic mass of 195 mg/g wood. It is also quite likely that these bulk figures, while impressive, may underestimate the potential impact of hemicellulose destruction on wood hygroscopicity. Structural aspects must also be considered. For instance, the removal of sugars that form short side chains would be expected to substantially decrease a polysaccharide's hygroscopicity, whereas removal of sugars incorporated into its linear backbone would have a less pronounced effect. In this context, although the absolute mass loss attributable to destruction of arabinan, galactan and rhamnan seems small at 12 mg/g wood, the effect of these losses might well be more in line with the 63–100% percentage losses of these typically side-chain constituents. However, it is also true that aqueous extraction of control wood removed substantial quantities (40–73%) of these side-chain sugars. If the loss of such side chains plays a significant role in the hygroscopic and dimensional stability changes associated with the steam pressing process, then similar changes should be obtainable by an aqueous extraction procedure. This prediction has not yet been tested. Figure 5 shows the concentration of furan compounds collected from the closed press after steaming for 8 minutes as determined by GC-MS. The major compound was furfural.

It is also possible that dimensional stability might be positively impacted by liberation of oligosaccharides from the cell-wall matrix of wood. In effect, this hypothesis posits that the "memory" of the compressed fiber's original configuration is broken with the breakage of the covalent bonds that hold together the hemicellulosic portion of this matrix. To the extent that this mechanism is relevant, hygroscopicity per se of the bulk wood sample might be little changed, because the liberated oligosaccharides are still physically present in the wood. However, because they are no longer covalently attached to the larger hemicellulosic matrix, it is theorized that the hydration of these liberated oligosaccharides does not confer upon the matrix the physical stresses that drive the swelling response. Losses from the matrix can be assessed by the sum of destructive and extractive losses of sugars that make up the backbone of the hemicellulosic matrix. In hardwoods, xylan is by far the predominant matrix polymer. Xylan losses from the cell wall matrix to both outright destruction and to the soluble pool were 71 mg/g wood (43%) and 96 mg/g wood (59%) after 4 min and 8 min of steam pressing, respectively. In control wood, only 19 mg/g wood (12%) of the xylan was lost upon aqueous extrac-

TABLE 1 Equilibrium Moisture Content (EMC) and Thickness Swelling (TS) of Fiberboards made from Control and Steam Stabilized Fiber

	EMC and TS at 27°C					
	30%RH		65% RH		90% RH	
Fiber	EMC (%)	TS (%)	EMC (%)	TS (%)	EMC (%)	TS (%)
			%			
Control fiber	4.7	—	10.3	—	18.9	—
Steam 4 min, LSG	2.6	<1	5.8	<1	10.2	2.6
Steam 4 min, HSG	2.9	< 1	6.2	<1	10.3	2.8
Steam 8 min, LSG	2.4	< .25	5.4	<1	9.2	4.4
Steam 8 min, HSG	2.3	1.1	5.4	<1	9.3	3.4
Control 4 min, LSG	2.8	3.1	6.4	6.5	13.9	27.4
Control 4 min, HSG	2.8	3.1	6.5	8.3	14.1	31.3
Control 8 min, LSG	2.7	2.3	6.3	5.4	14.0	23.3
Control 8 min, HSG	2.8	1.6	6.2	7.1	13.1	21.3

LSG = low specific gravity, HSG = high specific gravity.

tion. The glucomannan content of the wood used in the present was about 15% that of xylan. This polymer appears to be more stable to the process than is xylan: 34% was liberated by an 8 min treatment as compared to 18% by aqueous extraction of the control sample. If the proposed mechanism plays a significant role in dimensional stability, this finding would suggest that the relatively greater abundance of the mannose-based polymer might result in a less pronounced

TABLE 2 Rate and Extent of Thickness Swelling in Liquid Water of Fiberboards made from Control and Steam Stabilized Fiber

	Percent thickness swelling at					
	Minutes		Days			
Board	15	60	1	4	After oven drying (%)	Weight loss (%)
Steam 4 min, LSG	6.8	6.9	8.5	9.6	1.9	7.2
Steam 4 min, HSG	8.4	9.4	10.4	11.6	3.3	6.0
Steam 8 min, LGS	4.9	6.0	6.7	7.8	1.4	8.1
Steam 8 min, HSG	7.8	8.4	9.4	10.0	1.9	10.0
Control 4 min, LSG	82.9	90.2	102.2	111.6	118.7	8.8
Control 4 min, HSG	96.8	103.7	118.8	127.1	143.4	6.2
Control 8 min, LSG	59.1	64.6	71.4	75.6	66.6	6.6
Control 8 min, HSG	67.3	70.3	82.4	86.4	74.9	5.7

TABLE 3 Modulus of Rupture (MOR), and Modulus of Elasticity (MOE) for Control and Steam Treated Aspen Fiberboards

Board	MOR (MPa)	MOE (GPa)
Steam 4 min, LSG	4.9	0.9
Steam 4 min, HSG	9.6	1.6
Steam 8 min, LSG	6.7	1.1
Steam 8 min, HSG	7.8	1.6
Control 4 min, LSG	3.3	0.9
Control 4 min, HSG	6.3	1.6
Control 8 min, LSG	3.9	1.1
Control 8 min, HSG	6.4	1.7
ANSI Standard	31.0	—

dimensional stability effect upon treatment of softwoods than that observed for hardwoods. Finally, it should be noted that a corollary to this hypothesis is that washing to remove the water soluble fraction of steam pressed wood should result in a decrease in hygroscopicity with little effect on dimensional stability. This corollary has not yet been tested.

Table 1 shows the equilibrium moisture content (EMC) and thickness swelling (TS) of control and steam stabilized fiberboards. The data show that the EMC for all types of fiberboards are about the same at 30% RH, however, the TS is much higher for the non-steamed boards. The EMC for all types of boards at 65% RH are about the same but TS is higher in control boards. The results at 90% RH show that the EMC is lower and TS much lower for steamed boards than the control boards. There are some minor differences in the data for low specific gravity boards as compared to high specific gravity boards but the differences are not significant.

Table 2 shows the rate and extent of swelling of all board types in liquid water. Fiberboards made using steam swell at a slower rate and to a lesser extent than control fiberboards. Table 3 shows the modulus of rupture (MOR) and modulus of elasticity (MOE) of all types of fiberboards used in these experiments. Values for MOR, for all types of boards, were lower in the low specific gravity fiberboards as compared to the high specific gravity fiberboards. After drying, the steam treated fiberboards were about 2% thicker than the original fiberboard before the test. The control boards remained in a greatly swollen state after drying as compared to their original oven dry thicear e did greatly increase strength properties.

REFERENCES

[1] Stamm, A. J. & Hansen, L. A. (1937). Minimizing wood shrinkage and swelling: Effects of heating in various gases. *Ind. Eng. Chem.*, *29*(7), 831–833.

[2] Tiemann, H. D. (1920). *Effect of Different Methods of Drying on the Strength and Hygroscopicity of wood. The Kiln Drying of Lumber*, 3rd edition, J.P. Lippincott Co.: Philadelphia, PA, Chapter 11, 256–264.

[3] Stamm, A. J., Burr, H. K., & Kline, A. A. (1946). Staybwood – A heat stabilized wood. *Ind. Eng. Chem.*, *38*(6), 630–634.

[4] Seborg, R. M., Millett, M. A., & Stamm, A. J. (1945). Heat stabilized compressed wood (Staypak). *Mec. Eng.*, *67*(1), 25–31.

[5] Rowell R. M. & Konkol, P. (1987). Treatments that enhance physical properties of wood, USDA, Forest Service, Forest Products Laboratory Gen. Technical Report FPL-GTR-55, Madison, WI.

[6] Burmester, V. A. (1973). Effects of heat-pressure-treatments of semi-dry wood on its dimensional stability. *Holz Roh-Werkst*, *31*, 237–243.

[7] Giebeler, E. (1983). Dimensional stabilization of wood by moisture-heat-pressure. *Holz Roh-Werkst.*, *41*, 87–94.

[8] Hillis, W. E. (1984). High temperature and chemical effects on wood stability. *Wood Sci. Technol.*, *18*, 281–293.

[9] Hsu, W. E. (1986). Method of making dimensionally stable composite board produced by such method. Canadian Patent 1215510.

[10] Hsu, W. E. (1988). Steam pretreatment of wood fibers. In: *Proceedings, Stabilization of the Wood Cell Wall*, Suchsland, O. (Ed.), Michigan State University: East Lansing, MI, 65–71.

[11] Skaar, C. (1976). Effect of high temperature on the rate of degradation and reduction in hygroscopicity of wood. In: *Proceedings: High Temperature Drying Effects on Mechanical Properties of Soft-Wood Lumber*, Gerhards, C. C. & McMillen, J. M. (Eds), USDA, Forest Service, Forest Products Laboratory: Madison, WI, 113–127.

[12] Viitaniemi, P. & Jamsa, S. (1996). Modification of wood with heat treatment. VTT Julkaisuja, Publication number 814, Espoo, Finland.

[13] Inoue, M., Morooka, T., Norimoto, M., Rowell, R. M., & Egawa, G. (1992). Permanent fixation of compressive deformation of wood. In: (II) *Mechanisms of Permanent Fixation*, Forest Research Institute Bulletin No. 176, Plackett, D. V. & Dunningham, E. A. (Eds.), Rotorua: New Zealand, 181–189.

[14] Inoue, M., Norimoto, M., Tanahashi, M., & Rowell, R. M. (1993). Steam or heat fixation of compressed wood. *Wood and Fiber Sci.*, *25*(3), 224–235.

[15] Rowell, R. M., Lange, S., Todd, T., Das, S., Saha, A. K., Choudhury, P. K., & Inoue, M. (1998). Steam stabilization of jute-based composites. In: Proceedings, International Seminar on Jute and Allied Fibers: Changing Global Scenario, Compiled by Mitra, B. C. Calcutta, February, 97–108.

[16] Honda, T. Japanese Patents, JP 09174511 A2. (1997). Compressed wood material with densified surface and its manufacture. Japanese Patents JP 09174512 A2.

[17] Hasegawa, R. & Tomita, M. (1997). Japanese Patent, JP 09267309 A2. Improved method for compressing in manufacture of surface densified wood.

[18] Tieerdsma, B. F., Boonstra, M., & Militz, H. (1998). Thermal modification of non-durable wood species. 2. Improved wood properties of thermal treated wood. IRG document IRE/WP 98-40123, 3–13 and RG/WP 98-40124, 1–10.

[19] Negi, J. S., Chawla, J. S., Negi, J. S., & Chawla, J. S. (1993). Heat treatment of Fiberboards. *Research and Industry (New Delhi)*, *38*(12), 248–253.

[20] Wise, L. & John, E. (1952). Wood Chemistry, Reinhold Pub. Corp.: New York, Vols. 1 and 2.

[21] Stamm, A. J. (1964). *Wood and Cellulose Science*, The Ronald Press Co.: New York, NY.

[22] Mitchell, R. L., Seaborg, R. M., & Millett, M. A. (1953). Effect of heat on the properties and chemical composition of Douglas-Fir wood. *J. For. Prod. Res. Soc.*, *3*(4), 38.

[23] Melcer, I., Melcerova, A., Kacik, F., Sindler, J., Vargicova, K., & Sertic, V. (1990). Changes in the properties of beech wood. *Drevo (Praha then Bratislava)*, *45*(9), 255–260.

[24] Sondermann, W. & Augustin, H. (1964). Chemical investigation of the thermal decomposition of wood, Part III, Chemical investigation of the course of the decomposition. *Holz als Roh-und Werkstoff*, *22*, 377–386.

[25] Shafizadeh, F. (1984). The chemistry of pyrolysis and combustion. In: *The Chemistry of Solid Wood*, Rowell, R. M. (Ed.), Advances in Chemistry Series No. 207, American Chemical Society: Washington, DC, 489–529.

[26] Fengel, D. & Wegner, G. (1984). *Wood: Chemistry, Ultra Structure, and Reactions*, De Gruyter: New York.

[27] Kosik, M., Geratova, L., Rendos, F., & Domansky, R. (1968). *Holz. Und Holzverw.*, *20*, 15–19.

[28] Aoyama, M. (1996). Steaming treatment of bamboo grass. II Characterization of solibilized hemicellulose and enzymatic digestibility of water-extracted residue. *Cellulose Chemistry and Technology*, *30*, 385–393.

[29] Schmidt, A. S., Puls, J., & Bjerre, A. B. (1996). Comparison of wet oxidation and steaming for solubilisation of the hemicellulose fraction in wheat straw and birch wood. Biomass Energy Environ., Proc. Ninth European Bioenergy Conf., Vol. 3, 1510–1515.

[30] Oji, U. I. & Mowa, D. N. (1978). Nutritive value of steam-treated corn stover. *Canadian Journal of Animal Science*, *58*, 177–181.

[31] Rangnekar, D. V., Badve, V. C., Kharat, S. T., Sobale, B. N., & Joshi, A. L. (1982). Effect of high-pressure steam treatment on chemical composition and digestibility in vitro of roughages. *Animal Feed Science and Technology*, *7*, 61–70.

[32] Overend, R. P. & Chornet, E. (1987). Fractionation of lignocellulosics by steam-aqueous pretreatments, *Phil. Trans. R. Soc. London, A321*, 523–536.

[33] Lawther, M., Sun, R.-C., & Banks, W. B. (1996). Effect of steam treatment on the chemical composition of wheat straw. Holzforschung, *50*(4), 365–371.

[34] Mason, W. H. (1926). United States Patent 1578609. Process and apparatus for disintegration of wood and the like.

[35] Boehm, R. M. (1940). United States Patent 2224135. Making board products and recovering water solutions from fibrous lignocellulose material.

[36] Turner, D. (2000). Personal communication, March.

[37] Norimoto, M. (1994). Heat treatment and steam treatment of wood. *Wood Industry*, *49*, 588–592.

[38] Shen, K. C. (1985). Composite products from lignocellulosic materials. United States Patent 0161766.

[39] Brooks, H. (1982). Personal communication August (2000). AHA American National standard. Basic Hardboard. ANSI/AHA 135.4, (reaffirmed January 1988) American Hardboard Association, Palatine, IL.

[40] Irvine, G. M. (1985). The significance of the glass transition of lignin in thermomechanical pulping. *Wood Sci. Technol.*, *19*, 139–149.

[41] Chawla, J. S. & Sharma, A. N. (1972). *In.* Acad. Wood Sci., *3*, 70.

[42] Hillis, W. E. & Rozsa, A. N. (1978). The softening temperature of wood. *Holzforschung*, *32*, 68–73.

[43] Goring, D. A. I. (1963). Thermal Softening of Lignin, Hemicellulose and Cellulose Pulp and Paper Magazine of Canada, 64, T517–T527.

[44] Olsson, A.-M. & Salmen, L. (1993). Cellulosics: Chemical, Biochemical and Material Aspects. Kennedy, J. F., Phillips, G. O., & Williams, P. A. (Eds.), Ellis Horwood Ltd.

[45] Dwianto, W., Morooka, T., & Norimoto, M. (1998). The compressive stress relaxation of Albizia wood during heat treatment. *Mokuzai Gakkaishi*, *44*, 403–409.

[46] Boostra, M. J., Tjeerdsma, B. F., & Groeneveld, H. A. C. (1998). Thermal modification of non-durable wood species. 1. The PLATO technology: Thermal modification of wood. *International Research Group Annual Meeting* (1998).

[47] Schrepfer, V. & Scheaingruber, F. H. (1998). Anatomical structures in reshaped press-dried wood. *Holzforschung*, *52*(6), 615–622.

[48] Inoue, M. & Norimoto, M. (1991). Heat treatment and steam treatment of wood. *Wood Industry*, *49*, 588–592.

[49] Mobarak, F., Fahmy, Y., & Augustin, H. (1982). Binderless lignocellulose composite from bagasse and mechanism of self-bonding. *Holzforschung*, *36*, 131–135.

[50] Hsu, W. E., Schwald, W., Schwald, J., & Shields, J. A. (1988). Chemical and physical changes required for producing dimensionally stable wood-based composites. *Wood Sci. Technol.*, *22*, 281–289.

[51] Xu, J., Han, G., Wong, E. D., & Kawai, S. (2003). Development of binderless particle board from kenaf core using steam-injection pressing. *J. Wood Sci.*, *49*, 327–332.

[52] Xu, J., Sugawara, R., Widyorini, R., Han, G., & Kawai, S. (2004). Manufacture and properties of low-density binderless particleboard from kenaf core. *J. Wood Sci.*, *50*, 62–67.

[53] Xu, J., Widyrini, R., Yamauchi, H., & Kawai, S. (2006). Development of binderless fiberboard from kenaf core. *J. Wood Sci.*, *52*, 1–8.

[54] Widyorini, R., Xu, J., Watanabe, T., & Kawai, S. (2005a). Chemical changes in steam-pressed kenaf core binderless particleboard. *J. Wood Sci.*, *51*, 26–32.

[55] Widyorini, R., Higashihara, T., Xu, J., Watanabe, T., & Kawai, S. (2005b). Self-bonding characteristics of binderless kenaf core composites. *Wood Sci. Technol.*, *39*, 651–662.

[56] Widyorini, R., Xu, J., Umemura, K., & Kawai, S. (2005c). Manufacture and properties of binderless particleboard from bagasse I: Effect of raw material type, storage methods, and manufacturing process. *J. Wood Sci.*, *51*, 648–654.

[57] Okuda, N. & Sato, M. (2004). Manufacture and mechanical properties of binderless boards from kenaf core. *J. Wood Sci.*, *50*, 53–61.

[58] Sekino, N., Inoue, M., Mark Irle, & Adcock, T. (1999). The mechanisms behind the improved dimensional stability of particleboards made from steam-pretreated particles. *Holzforschung*, *53*, 435–440.

[59] Rowell, R. M., Lange, S., McSweeny, J., & Davis, M. (October 2002). Modification of wood fiber using steam. Proceedings: 6th Pacific Rim Bio-Based Composites Symposium, Portland, OR.

[60] American Society for Testing and Materials Standard D 1037-38. (1993). Standard methods for evaluating properties of wood-based fiber and particle panel materials, Philadelphia, PA.

[61] Saeman, J. F., Moore, W. E., Mitchell, R. L., & Millett, M. A. (1954). Techniques for the determination of pulp constituents by quantitative paper chromatography. *Tappi J*, *37*(8), 336–343.

[62] Davis, M. W. (1998). A rapid modified method for compositional carbohydrate analysis of lignocellulosics by HPAEC/PAD. *J. Wood Chem. & Technol.*, *18*, 235–252.