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Time-domain NMR study of the drying of hemicellulose extracted aspen (*Populus tremuloides* Michx.)

Abstract: The effect of hot water on aspen chips has been evaluated using time-domain low-field nuclear magnetic resonance (NMR) spectroscopy. At moisture contents above fiber saturation point, treated chips exhibit relaxation times of free water longer than for the control. This is consistent with the removal of hemicelluloses given the hydrophilicity of these polysaccharides. The rate of decrease in free water upon drying is greater for the pretreated samples. These results indicate that hot water treatment modifies both the chemical and physical properties of the chips and may therefore impact product manufacture and performance.

Keywords: aspen, moisture content, nuclear magnetic resonance (NMR), pretreatment

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Introduction

The extraction of hemicelluloses before a principal processing step has been proposed for various applications in recent years mainly in context of the biorefinery concept (Paredes et al. 2008; Hörhammer et al. 2011; Hosseinaei et al. 2011; Houtman and Horn 2011; Schütt et al. 2011; Testova et al. 2011) and the effect of such treatments on material properties of the wood has been reported (Paredes et al. 2009; McConnell and Shi 2011). Of late, the rationale for such work is that the sugars derived can be readily hydrolyzed for fermentation to ethanol, providing an additional revenue stream for a manufacturing facility. The focus of the present article is concerned with the quantity and quality of bound and free water (water population) in hot water-treated wood as a function of treatment parameters.

Working with aspen, spruce, and pine, Houtman and Horn (2011) report that pretreament with oxalic acid reduces the energy required for the production of thermomechanical pulp, with the removal 1–3% of the polysaccharides, the main constituent of which was arabinose. In the referenced study, a removal of large amounts of xylose by water treatment of aspen resulted in considerably larger mass losses compared with oxalic acid treatment. In another work on oxalic acid pretreatment, Li et al. (2011) found that loblolly pine chips needed less energy for refining and the medium density fiberboard prepared had increased dimensional stability but decreased internal bond strength.

In a work on oriented strand board (OSB) (Paredes et al. 2008), maple furnish was treated with water at 160°C at 620 kPa for 45 and 90 min. During the extraction, the strands lost 16–17% of their weight, and the moisture content (MC) (after conditioning to equilibrium moisture content at 21°C and 65% relative humidity) of the resultant panels was markedly lower than that of commercial controls. As might be expected, the longer treatment time resulted in generally poorer mechanical and physical properties. Paredes et al. (2009) investigated similarly treated strands and evaluated the fundamental properties of the material. Microscopic observations revealed the presence of surface deposits, which were subsequently removed by acetone extraction. Porosity increased with treatment severity as did cellulose crystallinity. Contact angles for various liquids were generally very low for the treated strands, indicating increased permeability, which may result in overpenetration of resin in OSB applications. Finally, it was found by inverse gas chromatography that both dispersive surface energy and acid-base characteristics are elevated with increasing treatment severity.

Related research has examined pine strands treated in water at temperatures from 140°C to 170°C for reaction times of 30 and 60 min (Hosseinaei et al. 2011). The mass loss ranged from 6.4% to 24.6%, with concomitant increases in sugar concentration and degradation products in the hydrolysate. As in the work by Paredes et al. (2008), microscopy revealed spherical deposits on the wood surfaces, which are proposed to be made up of lignin that softened and flowed with treatment. Infrared spectroscopy showed an increase of carbonyl oxygen,

although acetyl groups are removed from the hemicelluloses by the pretreatment. This finding is interpreted as the incorporation of such groups into lignin. In contrast to the work on maple strands, the contact angle for water in this work increased after treatment, indicating an increase in the hydrophobicity of the surface, which resulted from the removal of hemicelluloses. Lastly, both the elastic modulus and the hardness values, as determined by nanoindentation, decreased with treatment severity.

The foregoing literature illustrates that hot water extraction can have a distinct effect on the material properties of wood and therefore products made of it. Although hemicellulose extraction may be advantageous from a bioenergy standpoint, the level of removal must be balanced to avoid degrading the properties of the principal products, and as such, the process needs to be understood.

Nuclear magnetic resonance (NMR) methods are well suited for studying the wood/water relation beginning with simple water content determination (Merela et al. 2009) ending up with multinuclear magnetic resonance imaging of bound water concentration (Dvinskikh et al. 2011). However, in the present article, the low-field time-domain NMR spectroscopy will be in focus. This method is not appropriate for frequency domain experiments but permits the study of relaxation time behavior of various nuclei including [1]H. In wood, the protons associated with the structural polymers of the cell wall relax very rapidly and are not detected due to the dead time of the receiver in the instrument, whereas the protons in water exhibiting much longer relaxation times can be readily observed. Furthermore, the relaxation times of the water protons vary with the physical and chemical environment and can therefore be indicative of changes in structure and composition of wood. Depending on the experiment, spin-lattice (T_1) or spin-spin (T_2) relaxation times can be determined, the latter of which have been mainly applied to the study of water in wood. In addition, the magnetization decay curve can be subjected to an inverse Laplace transform, providing continuous distributions of relaxation times.

The earlier literature on the application of time-domain NMR to softwoods has been summarized by Thygesen and Elder (2008), in which the assignments of relaxation times to bound water and free water are described. The impact of modification on relaxation time has been reported for polymer-impregnated wood (Thygesen and Elder 2008, 2009; Thygesen et al. 2010), thermally degraded or treated material (Hietala et al. 2002; Elder et al. 2006; Kekkonen et al. 2010), biologically degraded wood (Todoruk et al. 2011), and enzymatically hydrolyzed cellulose (Felby et al. 2008).

In the present work, the distribution of T_2 relaxation times will be determined as a function of pretreatment conditions with hot water, as the samples dry from a saturated state to MCs below the fiber saturation point (FSP). These data will be compared with chemical analyses to evaluate changes in the interaction between water and the pretreated material.

Materials and methods

Aspen (*Populus tremuloides* Michx.) wood was treated at the Forest Products Laboratory in Madison, WI, USA, in a PREX (Sunds Defibrator, Metso, Helsinki, Finland) pilot-scale system, at a feed rate of 1.2 kg (od) min⁻¹. The system was modified with a second plug-screw feeder on the discharge of the pressure vessel, allowing liquid to be expressed as the chips exit the reactor, providing chips at 65% solids. The resultant pulps were subjected to one stage of pressurized refining at 206 kPa, followed by one or two stages of atmospheric refining, to give a target freeness of 150 ml CSF kg (Houtman and Horn 2011). In addition to an untreated control, the chips were subjected to hot water extractions under conditions of 207 kPa/135°C, 276 kPa/142°C, and 379 kPa/151°C for 120 min, corresponding to severity factors (SFs) of 3.11, 3.31, and 3.58, respectively (Table 1). The SFs were calculated as in Paredes et al. (2008):

$$SF = \log\left(\int_0^t \exp\left[\frac{Tr\text{-}Tb}{14.75}\right]dt\right)$$

where *Tr* is the reaction temperature (in °C), *Tb* is the base temperature (in °C), and 14.75 is the energy of activation (in kJ kg⁻¹ mol⁻¹). The

Treatment	Severity factor	Mass removal (%)	Concentration of monomeric sugars (g l⁻¹)				
			Ara	Gal	Glc	Xyl	Man
207 kPa/135°C	3.11	8.9	2.35	1.10	2.18	9.52	2.46
276 kPa/142°C	3.31	18	3.02	2.15	2.55	25.03	3.34
379 kPa/151°C	3.58	35	2.89	2.34	2.71	51.08	3.45

Table 1 Hot water extraction of three aspen samples: treatment parameters and monosaccharide concentration in the acid hydrolysates of the treated samples (Houtman and Horn 2011).
Ara, arabinan; Gal, galactan; Glc, glucan; Xyl, xylan; Man, mannan.

mass loss percentage (ML%) was estimated by determining the total volume of extract removed and measuring the carbohydrate content, based on the od weight of the wood. The sugar content of extract solutions (in g l^{-1}), after filtering and acid hydrolysis, was determined by HPLC with pulsed amperometric detection (Davis 1998). The chemical composition of the raw material was 45.6% glucan, 16.3% xylan, 1.41% mannan, 0.35% arabinan, and 0.46% galactan (Zhu et al. 2011).

For the NMR experiments, the chips were saturated under vacuum with deionized water for 2 h, after which they were blotted dry to remove excess water and placed in 18-mm NMR tubes. An initial experiment was done in the saturated condition, after which the samples were dried at 40°C for 2 h, with weight loss and NMR determinations performed every 15 min.

The NMR instrument was a Bruker mq20-Minispec analyzer, with a 0.7-T permanent magnet for a 20-MHz proton resonance frequency, operating at 40°C. The T_2 (spin-spin) relaxation times were determined with the Carr-Purcell-Meiboom-Gill (Carr and Purcell 1954; Meiboom and Gill 1958) pulse sequence, with pulse separation of 0.5 ms, 1000 echoes collected, and 32 scans with a 5-s recycle delay. The electronic gain of the instrument was held constant for all determinations of a given sample. The relaxation time distributions were calculated from the decay curves with CONTIN (Provencher 1982).

Results and discussion

Table 1 shows the results the ML% and the carbohydrate composition of the solubilized material for each treatment. In general, the ML% and sugar levels in the hydrolysate increase with severity. Expectedly, xylose shows the strongest response because of the prevalence of xylans in hardwoods.

Figure 1 shows the MC% (dry basis) taken at each of the 15-min intervals during drying. At saturation, the untreated control has an MC% content of 143%, whereas the treated samples all have initial MC% of ca. 100%, which is consistent with the chemical results indicating
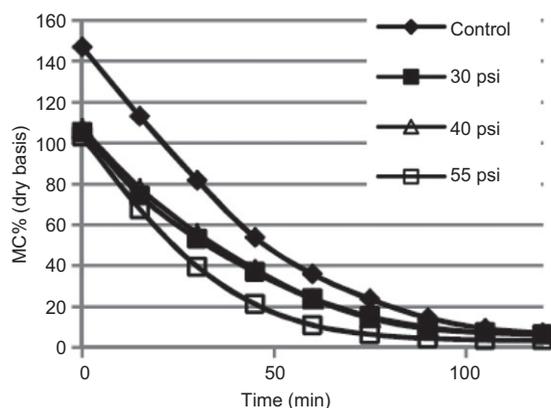

Figure 1 MC% as a function of drying time for three aspen samples treated with hot water. The numbers 3.11, 3.31, and 3.58 are the SFs of treatments (Table 1).

the selective removal of the hygroscopic hemicelluloses. Furthermore, while at saturation the MC of the sample treated at SF 3.58 is similar to the other treatments, the rate of its drying is more rapid.

Figure 2 is a compilation of the T_2 relaxation time distributions [intensity vs. time (in ms)], for each sample at 15-min drying intervals with the corresponding MC%. In the control (Figure 2a), several peaks are visible with varying levels of resolution and amplitude, which is consistent with other results obtained for hardwoods (Elder et al. 2006). In the present work, the distribution calculation generally reveals the presence of four peaks in the samples. The peak with the shortest relaxation time, on the order of 1–2 ms, is assigned to bound water in the cell wall. This is rationalized based on the intimate contact between water in the cell wall and the chemical constituents thereof, resulting in a high degree of interaction between these components. The longer relaxation times (~10–100 ms) are assigned to the free water present in the cell lumens. The appearance of multiple large peaks in this region is due to the differences in cell diameter associated with tracheids and vessels. Expectedly, softwoods exhibit a single large peak at about 100 ms, corresponding to free water in the cell lumens, whereas some smaller peaks may appear at longer relaxation times (Labbé et al. 2002, 2006; Thygesen and Elder 2008). For comparison, pure water has a T_2 of ~2000 ms, so that even at the longest relaxation times observed for water in wood, there is some level of perturbation of the water, which leads to an interaction between wood and water and is responsible for reducing the T_2 below 1000 ms.

The saturated control at 143% MC reveals the bound water peak at ~2 ms and a relatively large, well-resolved free water peaks at about 13 and 138 ms. There also is a less well-resolved peak at 37 ms, which has been subsumed into the free water peak with shorter relaxation time after the first drying interval. At 80% MC, all three of the free water peaks are fairly well-resolved. Qualitatively, the amplitude of the free water peaks decrease with drying and the resolution increases. As the MC goes below the FSP (MC ~30%), the amplitude of the bound water peak is still unchanged and begins to decrease remarkably at MC 11%. It might be surprising that at MCs below FSP, free water peaks continue to be observable. This is no doubt due to the drying regime that was utilized and the fact that at these intervals the wood is not at equilibrium, resulting in small amounts of residual free water even below FS.

The relaxation time distributions of the treated samples (Figure 2b–d) are similar at saturation, with well-resolved peaks at ~2 and 10 ms but with less well-resolved peaks at the longer relaxation times. These samples also
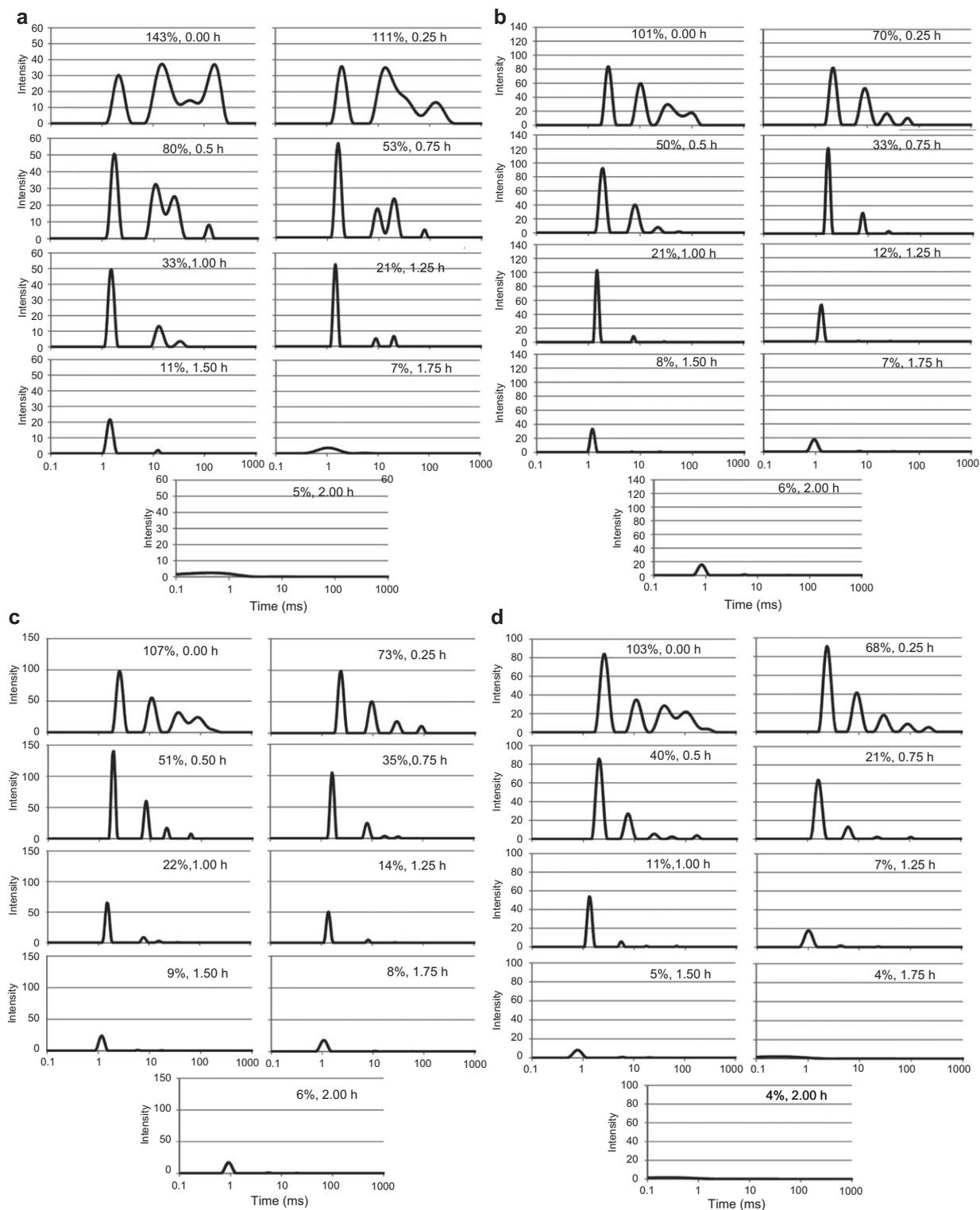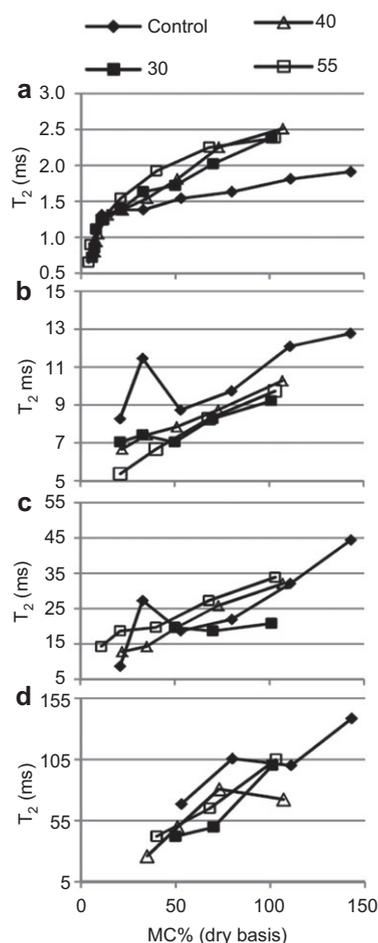
Figure 2 T$_2$ distributions aspen samples [peak intensity vs. relaxation time (in ms)]. The MC% data noted are on dry basis. (a) Distribution of the untreated control. (b), (c), and (d) Data of the hot water-treated samples with SFs of 3.11, 3.31, and 3.58, respectively (see Table 1).

differ from the control in that the amplitude of the longest relaxing peak at ~100 ms is considerably smaller, although a more appropriate comparison may be with the control at 111% MC, in which this peak exhibits a marked decrease,

apparently due to free water that is readily removed. Among the treated samples at about 70% MC, the free water peaks have become quite well separated, generally showing the profile with three peaks. The exception to

this is the sample treated at SF 3.58 (Figure 2d), with an MC of 68%, in which a fourth free water peak is detected at approximately 180 ms. This peak is still visible at 40% MC. The fourth peak may be an artifact due to the somewhat smaller particle size of this sample, which may entail changes in the surface area and therefore water holding capacity of the sample SF 3.58. A comparison of the sample with SF 3.11 at the MC level of 33% with the control is puzzling. In the former, the third peak at ~100 ms disappears, whereas it continues to be discernible, especially in the sample with SF 3.58, in which the MCs are quite low.
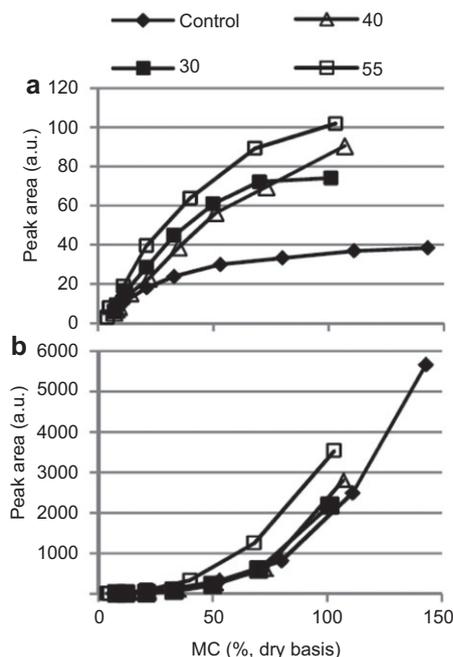
Figure 3 shows the relaxation times associated with maxima for each of the identified peaks in Figure 2 as a function of MC. In Figure 3a, the bound water peaks have obvious differences, with the control sample exhibiting much more rapid relaxation times, down to the FSP. The longer relaxation times of the treated samples are consistent with the removal of the hydrophilic hemicelluloses. In the untreated control, water interacts quite strongly with these polysaccharides and therefore relaxes more rapidly. In all treated samples, the magnitude of T_2 slowing down was very similar, even though the levels of hemicellulose removal differed with treatment SF. This generalization notwithstanding, the sample with SF 3.58 had somewhat longer T_2 values than the other treatments. The sharp T_2 decrement of bound water below FSP is expected due to intensified interaction with the cell wall constituents. Figure 3b–d are the relaxation times for the three free water peaks. In general, the T_2 values decrease with MC, and the relaxation times in Figure 3b and d are generally longer for the control samples, whereas the treated samples are quite similar to each other. This could perhaps be interpreted as physical changes such as compression or collapse of cells upon treatment. Beyond the systematic T_2 decrement at lower MCs, the data of the treated samples are mixed without a clear relation to the SF of the treatment.

The peak areas for the bound water and free water are presented in Figure 4a and b, respectively. Owing to the overlapping nature of the free water peaks, they are not presented separately but are rather combined into a single area. The comparability of the peak areas is limited to a "within-sample comparison" due to the lack of an internal standard (Thygesen and Elder 2008). Expectedly, the peak areas for all samples decrease with MC, albeit at different rates. In agreement with Figure 3a, the peak area

Figure 3 (a) T_2 values (in milliseconds) for bound water peak as a function of MC%. (b), (c), and (d) T_2 values for free water peaks as a function of MC%. The SFs of the hot water treatment are 3.11, 3.31, and 3.58.

Figure 4 (a) Peak areas for bound water as a function of MC%. (b) Peak areas for free water as a function of MC%. The SFs of the hot water treatment are 3.11, 3.31, and 3.58.

of the control bound water changes quite gradually and the plots are flat at higher MCs, whereas the peak areas of treated samples are changing more rapidly even in the range of higher MCs. The free water (Figure 4b) of the SF 3.58 sample decreases more rapidly than that of the control and the samples with SF 3.11 and 3.31, which exhibit very similar rates of change. The observed changes in relaxation times of the treated samples are related to the chemical and physical changes of the cell wall effectuated by the hot water treatment. Modifications of this type result in alterations in the way bound water is held in the cell wall. The interpretation of the changes in relaxation time and peak areas is not always straightforward, as chemical and physical changes upon treatment occur simultaneously.

Conclusions

The presented results are in reasonable agreement with those of the literature, in which several peaks were assigned to free water with longer relaxation times

(T_2) in the range 15–150 ms, whereas bound water has a relaxation time in the range of 1–2 ms. Drying leads to T_2 distribution profiles showing increased resolution of peaks. Accordingly, the isolation between the populations of water is improved, the interaction with the chemical constituents is increased, and the mobility of water in void spaces is affected. The removal of hemicelluloses, as evidenced by the sugar analyses of the hydrolysate, results in lower MCs at saturation and longer T_2 for the bound water. These data are all consistent and can be explained with the removal of a part of the hygroscopic hemicelluloses during hot water treatment. There are differences in both the quantity and the nature of the water upon pretreatment. This may have impacts on the performance or processing of the principal products, whether they are fiber or panel based, and may be of use in guiding the degree of pretreatment that should be performed.

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