WATER STATE STUDY OF WOOD STRUCTURE OF FOUR HARDWOODS BELOW FIBER SATURATION POINT WITH NUCLEAR MAGNETIC RESONANCE

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Abstract. Nuclear magnetic resonance (NMR) is a useful, powerful, and noninvasive technique to study the dynamics of wood–water relations, both quantitatively and qualitatively. The main objective of this study was to use NMR to characterize the state of water below the FSP. Two tropical hardwood species, huayruro (*Robinia coccinea* Aublet) and cachimbo (*Cariniana domesticata* [*C. Martius*] Miers), a plantation-grown eucalyptus species (*Eucalyptus saligna* Smith), and a temperate species, red oak (*Quercus rubra* L.), were studied. These species were chosen for their diversity in terms of anatomical and physical properties. Desorption tests were carried out at 21°C in a single-step procedure from full saturation state for huayruro, cachimbo, and red oak and from green condition for *E. saligna*. Discrete T_2 times were obtained for each species and equilibrium moisture content (EMC). The results showed that even under EMC, there was a region in the hygroscopic range in which the loss of bound water takes place before all liquid water was drained. This region varies according to wood species. Furthermore, variation in the fast T_2 values among the different wood species gives an indication of how bound water is distributed and arranged in sorption sites.

Keywords: Nuclear magnetic resonance, T_2 relaxation, water state, water–wood relations, fiber saturation point.

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INTRODUCTION

Wood is one of the most important and versatile engineering materials used worldwide. It is a complex biological material growing in a saturated environment in the living tree. This condition makes water omnipresent in wood structure before harvesting. Wood needs to be dry until it reaches adequate equilibrium moisture content (EMC) in a new environment, ie atmospheric air, to achieve an improved and stable performance as a finished product.

Moisture content has a significant effect on almost all physical properties of wood. As the bound water content increases, wood swells, mechanical strength decreases, thermal and electrical conductivities increase, and the rate of bound water diffusion increases (Siau 1984). For this reason, it is very important to understand and characterize the water state in wood at different EMCs and how it is related to the anatomical structure of wood.

Water exists in the wood structure in three states. Liquid water or capillary water is present in the micropores of cell walls, in the lumens of cells, and in the intercellular spaces. This water is subjected to the action of capillary pressure and thus differs from ordinary liquid water. A second form of water is the bound or hygroscopic water, which is adsorbed by free sorption sites or by hydroxyl groups. These groups are present mainly in the macromolecules of hemicellulose and amorphous cellulose and, to a lesser extent, associated with lignin and with the surface of crystalline parts of the cellulose. Water may also be present as vapor in the lumens and in the micropores of cell walls (Stamm 1964; Navi and Heger 2005).

The FSP is an important concept of wood hygroscopicity. Tiemann (1906) defined it as the moisture content at which the cell walls are saturated with bound water and the lumens are free of liquid water. In other words, the FSP is a transition point between the bound and liquid water (Stamm 1971). Since 1906, several studies on this concept have been advanced (Barkas 1935; Stone and Scallan 1967; Menon et al 1987; Skaar 1988; Hernández and Bizoň 1994; Babiak and Kúdela 1995; Siau 1995; Almeida and Hernández 2006a, 2006b; Hernández and Pontin 2006; Hernández 2007; Hernández and Cáceres 2010; Hoffmeyer et al 2011). FSP is a very useful concept for understanding the influence of bound water on physical and mechanical properties of wood, because below this point, these properties are affected by changes in moisture content (Skaar 1988; Siau 1995).

However, liquid water may still be entrapped in the wood even below FSP (Menon et al 1987; Araujo et al 1992; Hernández and Bizoň 1994; Hernández and Pontin 2006; Almeida and Hernández 2006a, 2006b; Hernández and Cáceres 2010). This water could be entrapped in the less permeable cells, probably those of radial parenchyma, since, according to different authors, these are the least permeable flow paths in hardwoods (Wheeler 1982; Siau 1984). In the case of sugar maple, liquid water seemed to be entrapped principally in the lumina of the least accessible libriform fibers (Hernández and Cáceres 2010).

Nondestructive evaluation of wood allows studying wood properties, performance, and condition of the material without changing its end-use capabilities (Ross et al 1998; Bucur 2003). Nuclear magnetic resonance (NMR) can provide detailed information of wood both at the microscopic and macroscopic levels, especially in the study of wood-water relations. This tool permits to study the distribution and the various states of water in wood (Araujo et al 1992; Araujo et al 1993; Hartley et al 1996) from changes in the magnetization of the nuclei hydrogen in the material. In this technique, a phase of excitation is followed by a relaxation of the protons (^{1}H) to a lower energy state, through the phenomena of longitudinal (T_1) and transverse (T_2) relaxations (Kastler 2011).

However, the T_1 and T_2 relaxations of the water in wood are very different from that of pure water. In this last case, the decay of the magnetization of the nuclei is characterized by a single exponential decay with a time constant of the order of a few seconds. Conversely, for water in a biological system, as water in wood cells, this

relaxation is a multi-exponential phenomena produced in a milliseconds or tens of milliseconds (Brownstein 1980). This behavior is a consequence of the size and shape of the cells (Brownstein and Tarr 1979). The NRM signal from green wood may be distinguished into three main components from different T_2 values: solid wood, bound water, and liquid water (Araujo et al 1993). In this manner, the solid-wood signal disappears in tens of milliseconds, allowing an easy way to separate from the cell-water signal, whose T_2 values ranges from one to a few milliseconds. The third component, the liquid water located in cell lumina, is characterized by a T_2 value in order of tens to hundreds of milliseconds (Hsi et al 1977; Menon et al 1987; Araujo et al 1992; Araujo et al 1993; Thygesen and Elder 2008).

Almeida et al (2007) used the NMR technique to separate the components of water in wood of two temperate and one tropical species at different EMCs. Three different water components were observed from T_2 relaxation times analyses: slow T_2 (liquid water located in vessel elements), medium T_2 (liquid water located in fiber and parenchyma tissues), and fast T_2 (associated to bound or cell wall water). Further, their results showed that, even at equilibrated conditions, during a certain range of moisture content, cell walls lost bound water even in presence of liquid water in the cell lumina. This range of moisture content varied according to each species. Therefore, they found liquid water at an EMC below FSP, contradicting this concept.

The main objective of this work was to use the NMR technique to study the state of water below FSP in wood samples whose EMCs were reached from full saturated and green conditions. Four wood species were chosen in order to better understand the effects of the anatomical structure on wood-water relations.

MATERIALS AND METHODS

Two hardwood species of economic importance from Peru, namely huayruro (*Robinia coccinea* Aublet) and cachimbo (*Cariniana domesticata* [*C. Martius*] Miers), a plantation grown eucalyptus species (*Eucalyptus saligna* Smith) from Brazil and a temperate species red oak (*Quercus rubra* L.) were used for this study. The wood species were selected considering their diversity in terms of anatomical and physical properties.

Two boards of each tropical species were taken for the preparation of samples. These boards were stored for a long period in a conditioning room at 20°C and 60% relative humidity (RH). The eucalypt samples were obtained from a board stored in green condition (never-dried) at −4°C and wrapped in polyethylene for preventing moisture loss. The red oak board was selected from a batch of kiln-dried boards conditioned at 20°C and 40% RH. All boards were without crook, visible decay, with a minimum of knots and grain distortion. The average basic density (BD, oven dry mass to green volume) of huayruro was 627 kg/m^3 (coefficient of variation [CV] of 2.4%), while that of cachimbo, eucalyptus, and red oak were 569 kg/m^3 (CV of 2.2%), 515 kg/m^3 (CV of 2.6%), and 490 kg/m^3 (CV of 1.7%), respectively.

For NMR studies, small cylinders samples of 3.6 mm in diameter (transverse to the grain) by 20 mm in length (parallel to the grain) were prepared from the selected boards of each species using a small lathe mounted with a freshly sharpened knife.

Experiments

Three groups of ten matched samples were obtained for each species. These groups of samples were destined for three desorption conditions (Table 1). The desorption tests were carried out in a single step procedure from full saturation state for all samples, except those of eucalyptus, which started from their initial green condition. In order to avoid internal defects in wood structure due to a fast full saturation process, the re-wetting treatment was done in three steps (Naderi and Hernández 1997). The samples were initially placed over a KCl saturated salt solution (86% RH) for 11 da, followed by 14 da over

Table 1. Characteristics of the moisture sorption conditions used in this experiment.

State of sorption	Saturated salt solution	Nominal RH at 21°C (%)
Desorption	$ZnSO_4$	90
Desorption	NaCl	76
Desorption	NaBr	58

distilled water (100% RH). Finally, they were immersed in water and underwent two 24 h cycles of vacuum and atmospheric pressure.

Samples of all groups were then conditioned in desorption over saturated salt solutions inside glass desiccators. These small sorption chambers were placed for long periods in vats kept at 21 ± 0.01°C, allowing a precise RH control. A similar procedure has been previously described by Hernández and Bizoň (1994). For each desorption condition, ten samples, one for NMR experiments and nine for EMC assessment, were weighed periodically without being removed from the desiccator until a constant value was reached. To minimize moisture content (MC) exchange during NMR tests, the NMR tubes were placed inside the desiccators at the beginning of the sorption test.

Once the EMC was reached, the specimen destined to NMR experience was placed in the NMR tube (200 mm long, 5 mm outside diameter). A Teflon dowel (180 mm long, 4 mm in diameter) was also inserted in the tube in order to minimize the air space and consequently reduce MC changes during NMR tests. A tight screw cap sealed the tube. Finally, the NMR tube was put in a 25 mm thick Styrofoam box to protect it against any hygrothermal changes during the transportation to the University of Montreal where the NMR tests were done. The tube was weighed before transportation, at the beginning and at the end of the NMR test to detect any MC variation in the sample.

NMR Analysis

The NMR tests were done at 21°C on a 14.1 T Bruker Avance 600 WB spectrometer equipped with a Micro 5 probe, operating at a ^{1}H frequency of 600 MHz. The T_2 relaxation times were calculated by the Carr-Purcell Meiboom-Gill (CPMG) pulse sequence: 90 – [τ – 180 – τ]$_n$-acquire. The ^{1}H spectral width was 20 kHz and an acquisition time of 100 ms. The ^{1}H pulses were applied at field strength of 29 kHz, with a recycle delay of 1 to 2 s.

The global T_2 values of the samples having three different MCs were obtained from the relationship between decay intensity (magnetization decrease) and the echo-time. This relationship is graphically shown for the four species having three different MCs (Fig 1). Once this relationship obtained, discrete global T_2 values could be obtained by fitting the data to the following equation:

$$I(\tau) = I(0)_I \, exp\left(-\frac{2\tau n}{T_{2_I}}\right) + I(0)_{II} \, exp\left(-\frac{2\tau n}{T_{2_{II}}}\right) + I(0)_{III} \, exp\left(-\frac{2\tau n}{T_{2_{III}}}\right) \quad (1)$$

where I is the signal intensity, τ is the echo-time, n is the number of loops or the number of echoes, and I, II and III are the component 1, 2 and 3, respectively.

Equation 1 illustrates a tri-exponential fitting of data. In this case, one, two or three components of water in wood may be involved in the fitting. The estimation of parameters in a nonlinear regression model is not a straightforward process. It is an iterative process that demands good starting values in order to obtain fast and realistic results (Draper and Smith 1998). The Simfit software estimated values for the parameters of the equation 1 that minimized the residual sum of squares (RSS). The RSS provides a measure of the discrepancy between the real data and the values predicted by an estimation model. Usually the smaller the RSS values can explain the model better. The RSS can be written as:

$$RSS = \sum_{i=1}^{N} (y_i - \hat{y}_i)^2 \quad (2)$$

where y_i is the y value of the i^{th} observation, and $\hat{y}_i$ is the predicted y value of the i^{th} observation.

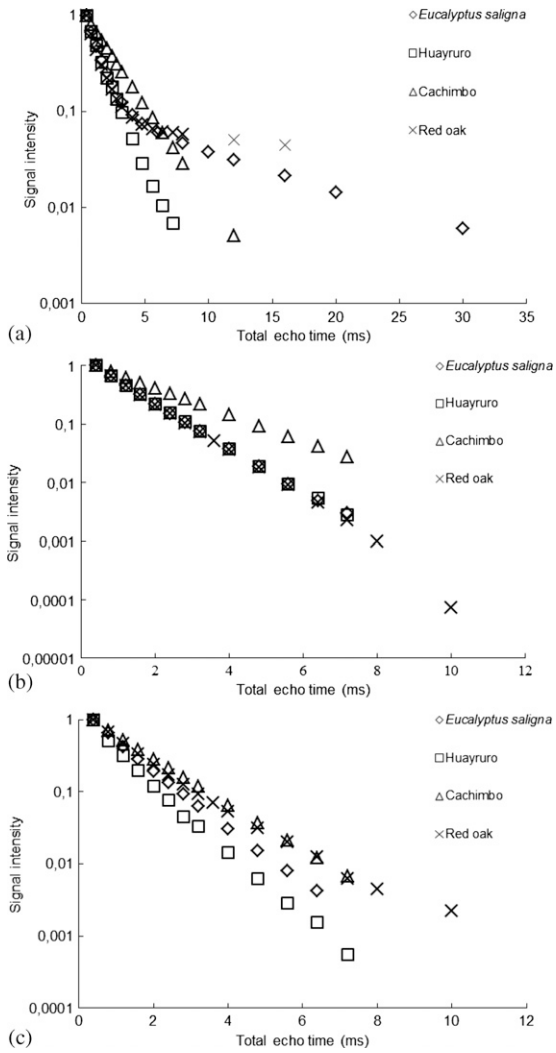

Figure 1. Signal intensity (arbitrary units) as a function of total echo time. (a) Specimens equilibrated in desorption at 90% RH. (b) Specimens equilibrated in desorption at 76% RH. (c) Specimens equilibrated in desorption at 58% RH.

The RSS cannot be decreased to zero because of the noise contaminating the measures of the signal nuclear magnetic resonance (NMR) (Whittall and MacKay 1989).

In this manner, Simfit software was able to decide the best model, ie if data were best described by a monoexponential equation, biexponential equation, or a triexponential equation.

RESULTS AND DISCUSSION

The relationship between EMC and RH for the three desorption conditions and for the four species studied is shown in Fig 2. Because the experiments were carried out from the full-saturated state for huayruro, cachimbo, and red oak, the maximum EMC for each RH was obtained for such species. In this case, the term boundary desorption curve is used to describe this feature. For *Eucalyptus saligna*, there was not a boundary curve given because the desorption was conducted from the green state. At 58% RH, the EMC was slightly higher for *Eucalyptus saligna* (13.3%), similar for huayruro (12.4%) and cachimbo (12.3%), and slightly lower for red oak (11.8%). As RH increased, the differences of EMC among species, especially for *Eucalyptus saligna*, became more evident. This behavior has been previously found elsewhere (Almeida and Hernández 2007; Hernández 2007). The difference in EMC observed at 90% RH could have been greater if desorption of *Eucalyptus saligna* was carried out from the full-saturated state as was done for the other three species. The low extractive content of *Eucalyptus saligna* may explain this behavior. In this case, low extractive content allowed greater availability of sorption sites in *Eucalyptus saligna* wood compared with the other three species, especially at higher moisture content (Nzokou and Kamdem 2004; Hernández 2007).

The results of the global T_2 times and their proportions obtained for each species and RH condition are shown in Table 2. The T_2 signal from solid wood material was not considered, because it was too fast to be measured adequately by the CPMG pulse sequence used in this study.

The separation and characterization of water in wood from different T_2 times have already been performed by several authors. Initially, only softwood species, whose anatomical structure is simpler and more homogeneous than hardwood species, were considered (Brownstein and Tarr 1979; Menon et al 1987; Araujo et al 1992, 1993). Later, a similar study was performed by Almeida et al (2007) with hardwood species. The main difference between these two kinds of wood is

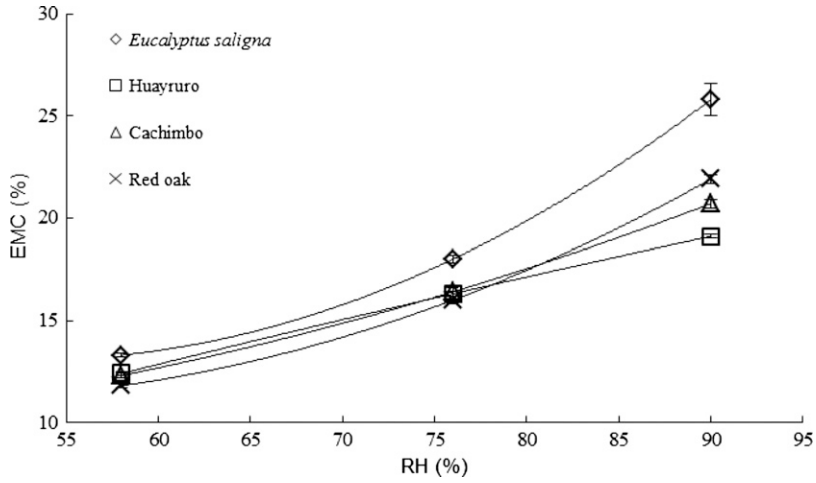

Figure 2. Equilibrium moisture content (EMC) obtained in desorption as a function of RH at 21°C for the four species studied (standard errors are shown only when it exceeds the symbol size).

the presence of vessel elements (large capillary tubes responsible mainly for sap transportation) in hardwoods. Thus, water in hardwoods may be separated into three parts: bound water or cell wall water with faster T_2 times, liquid water with medium T_2 times, and liquid water presenting slower T_2 times. Depending on the size of cell cavities, the medium and slow T_2 could correspond to the parenchyma, fibers, or vessels present in hardwoods. For some hardwood species, the large proportion of longitudinal parenchyma can also play a particular role (Almeida et al 2007).

The absence of slow T_2 values in Table 2 indicates that vessels of all species were already empty at 90% RH. Similar results were found by Almeida et al (2007) for huayruro and for two temperate species at the same RH as this study. These authors did not find any slow T_2 values in wood structure for all species studied even at 96% RH.

However, at this RH, huayruro showed a medium T_2 value (34 ms) four times higher than for the other two species, even if its EMC was lower. According to these authors, the high proportion

Table 2. Equilibrium moisture content (EMC) and T_2 values as a function of RH at 21°C for the four hardwoods studied.

			T_2 times (ms)			T_2 proportions (%)		
	RH (%)	EMC (%)	Fast	Medium	Slow	Fast	Medium	Slow
Eucalyptus saligna	90	25.8	0.9	8.2	—	94	6	0
	76	18.0	1.1	—	—	100	0	0
	58	13.3	1.0	—	—	100	0	0
	90	19.1	1.2	—	—	100	0	0
Huayruro	76	16.3	1.0	—	—	100	0	0
	58	12.4	0.7	—	—	100	0	0
	90	20.7	2.1	—	—	100	0	0
Cachimbo	76	16.4	1.8	—	—	100	0	0
	58	12.3	1.3	—	—	100	0	0
	90	21.9	0.9	22	—	94	6	0
Red oak	76	16.0	1.0	—	—	100	0	0
	58	11.8	1.1	—	—	100	0	0

of axial parenchyma in huayruro wood could explain this discrepancy.

The presence of two T_2 times for *Eucalyptus saligna* and red oak at 90% RH may be seen in Fig 1a from the curve representing the decreasing signal intensity as a function of total echo time. This curve is composed of two distinct parts: one from 0 to nearly 5 ms, representing fast T_2 times, and another from 5 ms, representing medium T_2 times. Thus, only these two species showed evidence of having liquid water, which is confirmed by the presence of medium T_2 values at 90% RH in Table 2 for *Eucalyptus saligna* and red oak. Medium T_2 was higher in red oak (22 ms) than in *Eucalyptus saligna* (8 ms). Scanning electron microscope images of *Eucalyptus saligna* and red oak (not shown) showed that the diameters of fiber and parenchyma lumens were smaller for *Eucalyptus saligna* than for red oak. This smaller area allows for a more efficient relaxation (less mobile) and consequently a shorter T_2 time for *Eucalyptus saligna* compared with red oak (Menon et al 1987; Araujo et al 1992). According to Thygesen and Elder (2008), during the T_2 relaxation measurement, if cell lumen is small enough to allow a considerable portion of water molecules to collide with the cell wall, these molecules will exhibit a faster T_2 time than unconfined water.

The drainage of liquid water was completed between 90 and 76% RH for *Eucalyptus saligna* (between 25.8 and 18% EMC; Table 2) and for red oak (between 21.9 and 16% EMC; Table 2). The T_2 proportion at 90% RH (both for fast and medium T_2 times) was the same for both species despite the higher EMC of *Eucalyptus saligna*. The percentage of bound water at 90% RH was 24.6% for *Eucalyptus saligna* (94% of 25.8% EMC; Table 2) and 20.6% for red oak (94% of 21.9% EMC; Table 2). For huayruro and cachimbo woods, the drainage of all liquid water occurred above 90% RH, ie above 19.1 and 20.7% EMC, respectively (Table 2). Similar results were found for huayruro wood by Almeida et al (2007). Huayruro and cachimbo are tropical hardwoods with special anatomical characteristics. Axial parenchyma represents 33.5% of the volume in huayruro wood (Almeida et al 2007), whereas in cachimbo wood, this tissue is classified as reticulate-apotracheal type. These tissues could therefore play a significant role in the liquid water drainage for these woods.

Within the studied RH range, huayruro and cachimbo woods presented close EMC values (Table 2). As EMC decreased, fast T_2 also decreased, especially for cachimbo wood. Many authors have reported this same tendency for softwoods (Menon et al 1987; Flibotte et al 1990; Araujo et al 1994; Cox et al 2010) and for hardwoods (Almeida et al 2007; Elder and Houtman 2013; Zhang et al 2013). According to Elder and Houtman (2013), the relaxation behavior of water molecules in wood is affected by the physical and chemical environments and can therefore reveal changes in structure and composition of wood. In other words, different T_2 times of bound water can reveal the way in which bound water is held in the cell wall. The T_2 relaxation process depends on magnetic field fluctuations in any direction, and the principal source of fluctuating magnetic fields is molecular motion (Reich 2013). The tighter the water molecules are held by the wood polymers, the shorter their T_2 times will be. Below FSP, as EMC decreases, wood loses water molecules sorbed to hydroxyl groups by hydrogen bonding in the cell wall. This allows a more intimate contact and a tighter energy bind between water and cell wall polymers, decreasing water molecular motion (shorter T_2 times) (Thygesen and Elder 2008, 2009; Elder and Houtman 2013; Zhang et al 2013).

Within all RH ranges, huayruro wood presented shorter T_2 times than cachimbo wood. This indicates that bound water was less mobile for huayruro than for cachimbo for the same RH. At the same time, both woods showed similar EMC (Table 2). Hartley et al (1992) and Hartley and Avramidis (1993) studied adsorption and desorption isotherm characteristics by means of the cluster theory. According to this theory, water molecules interact with each other and with available hydroxyl groups within the cell wall (Rawat and Khali 1998). As the clusters grow in size, the forces attaching them to the

sorption sites should weaken. Consequently, the clusters should become more mobile (Hartley et al 1992; Hartley and Avramidis 1993), which should increase T_2 times. This led us to infer that huayruro wood had more available sorption sites than cachimbo wood. In this way, a higher amount of water molecules might be held by strong sorption forces with low mobility. On the other hand, cachimbo wood could have less available sorption sites, where water molecules were held in larger clusters with higher mobility than huayruro wood clusters. Therefore, both woods can retain a similar amount of water molecules but these molecules are arranged differently. Thus, it might appear reasonable to assume that clusters in cachimbo wood were larger than in huayruro wood. Further studies are needed to investigate these hypotheses in more detail.

CONCLUSIONS

Water state in wood was studied with NMR at three EMCs below FSP. Desorption experiments from a full-saturated state and from green condition were carried out at 21°C on four hardwood species to better understand how their variable anatomical and physical features may influence water–wood relations. Even in small samples, liquid water may be found entrapped in wood structures below FSP in equilibrated conditions. In this case, wood lost bound water in the presence of liquid water, contradicting the concept of FSP. The range of EMCs in which it takes place will vary according to wood species. The wood elements that entrap liquid water below FSP could also vary according to wood species. Finally, the variation observed in fast T_2 times shows that the mechanisms for how sorption sites keep bound water are also species-dependent.

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