CHAPITRE 4. An NMR study of water distribution in hardwoods at several equilibrium moisture contents

4.1 Résumé

L'état de l'eau a été déterminé pour trois espèces feuillues (une tempérée et deux tropicales) à différentes humidités durant des essais de désorption à 25°C. La méthode RMN a été utilisée pour séparer l'eau du bois en différentes classes. Les espèces étudiées ont des structures différentes, ce qui est devenu apparent lors de la mesure du temps de relaxation spin-spin T_2. Trois classes d'eau ont été aisément distinguées: l'eau liquide dans les vaisseaux (T_2 long), l'eau liquide dans les cellules de parenchyme et dans les fibres (T_2 moyen) et l'eau liée ou eau des parois cellulaires (T_2 court). Les résultats RMN montrent que, même à l'état d'équilibre, il existe un domaine d'humidité où la perte d'eau affecte à la fois l'eau liée et l'eau liquide. La plage d'humidité de ce domaine dépend de la structure du bois. Finalement, l'eau liquide est présente à des humidités d'équilibre plus basses que le point de saturation des fibres, ce qui est en opposition avec le concept de PSF.

4.2 Abstract

The water state of one tropical and two temperate hardwoods was determined at different equilibrium moisture contents during desorption at 25ºC. NMR technique was used to separate different components of water in wood. The species studied presented different structure which was apparent on the spin-spin relaxation T_2 values. Three different water components were easily separated: slow T_2 (liquid water in vessel elements), medium T_2 (liquid water in fiber and parenchyma elements) and fast T_2 (bound or cell wall water). The NMR results showed that, even at equilibrated conditions, a region exists where loss of liquid water and bound water takes place simultaneously. This region will vary according to the wood structure. Finally, liquid water was present at equilibrium moisture content values lower than the fiber saturation point, which contradicts the concept of this point.

4.3 Introduction

Wood is a hygroscopic material and the amount of water in the wood structure will affect its physical and mechanical properties. For this reason, the knowledge of the distribution and interaction of water in wood at different relative humidities of air is of great importance on the utilization of this material.

Several works used non-destructive analysis on the study of wood-water relationships. NMR technique is one of the most used for this purpose given that it can provide valuable information on the distribution and concentration of water in wood (Brownstein 1980; Menon et al. 1987; Araujo et al. 1993; Hartley et al. 1994; Rosenkilde and Glover 2002; Casieri et al. 2004).

In NMR measurements there are two main types of relaxation processes by which nuclei in upper energy states can relax to lower energy states. These are spin-lattice relaxation (or longitudinal relaxation), T_1, and spin-spin relaxation (or transverse relaxation), T_2.

The relaxation time for water molecules is qualitatively different for compartmented water than for bulk water. The relaxation for bulk water is a single exponential process with a time constant in the order of a few seconds. For compartmented water (such as for the water in a biological cell), one finds a multiexponential decay with time constants ranging from milliseconds to hundreds of milliseconds (Brownstein 1980). According to Araujo et al. (1993), NMR signal from green wood may be separated into three major components: solid wood, cell-wall water and lumen water. The T_2 signal of solid wood decays to zero in tens of microseconds, making it readily separable from the cell wall water signal, which has a T_2 from one to a few milliseconds. In contrast, the lumen water has a T_2 ranging from tens to hundreds of milliseconds (Menon et al. 1987; Araujo et al. 1993).

The fiber saturation point (FSP) was initially defined by Tiemann (1906) as the moisture content (MC) at which the cell walls are saturated with bound water with no free water in the cell cavities. According to Riggin et al. (1979), the measurements of the transverse relaxation times (T_2) and the relative amounts of bound and free water in wood might be used to study the nature of the so-called FSP. However, near the FSP the apparent

relaxation rates in the bound water (cell wall water) and liquid water (lumen water) are about equal and hard to separate experimentally.

Menon et al. (1987) studied the water location during drying in Douglas fir and western red cedar using NMR technique. Liquid water remained in the ray and tracheid compartments when bound water begins to leave the cell walls at 31% MC. The liquid water was all lost when the MC reached values as low as 9%. Even though their work was done under unequilibrated conditions, these researchers suggested that the concept of FSP should be reevaluated.

The spin-spin relaxation time (T_2) for water in the cell lumens has been found to be roughly proportional to the cell lumen diameter on different softwood species (Menon et al. 1987; Flibotte et al. 1990). NMR is also sensitive to differences in hydration as well as to cell size and cell wall thickness. Menon et al. (1987) observed that samples of fir sapwood with higher volume of latewood (thicker cell walls and smaller cell diameters) had cell wall T_2 component 60% shorter than samples with smaller volume of latewood. Fir in general has a cell wall T_2 (fast relaxation time) which is about 3.5 times shorter than that for cedar. As a result, the T_2 values in the cell voids are also shorter, due to the effect of surface states on the T_2 of the water in the lumina.

Most of the NMR studies in wood have been made using softwood species, which have simpler anatomical structure compared to hardwood species. The use of this technique on hardwood species would give useful information on the wood - water relationships for this type of wood.

The principal objective of this work was to use the NMR technique to separate the different types of water in wood obtained under equilibrated conditions during boundary desorption. Three hardwoods presenting different structure were selected in order to study the influence of the wood structure on the wood - water relationships.

4.4 Material and methods

Experiments were carried out on two temperate hardwoods, sugar maple (*Acer saccharum* Marsh.) and beech (*Fagus grandifolia* Ehrhart), and one tropical hardwood, huayruro

(*Robinia coccinea* Aublet). These species were chosen taking into account their different wood structures. A selected board of each species was equilibrated in a conditioning room at 20°C and 60% relative humidity (RH). Specimens were turned using a freshly sharpened knife to a final dimension of 4 mm in diameter and 20 mm in length. The long axis of the specimens was perpendicular to the fibers length.

The test material had an average basic wood density (oven-dry mass to green volume) of 616 kg m^{-3} for sugar maple (coefficient of variation (CV) of 4%); 507 kg m^{-3} for beech (CV of 1%) and 654 kg m^{-3} for huayruro (CV of 1%).

EXPERIMENTS

Sorption tests

Prior to the desorption tests, all samples were saturated until their maximum moisture content was reached. This was done in three steps in order to avoid internal defects caused by a rapid moisture adsorption (Naderi and Hernández 1997). Thus, specimens were conditioned over a KCl saturated salt solution (86% RH) for 10 days, then over distilled water for 9 days and finally they were immersed in distilled water until full saturation by cycles of vacuum and pressure.

The sorption experiments were carried out at 25°C. Six desorption conditions were performed over saturated salt solutions in a single step procedure (Table 4.1). These experiments were conducted in sorption vats that have been previously described by Hernández and Bizoň (1994). These vats provide a temperature control of ± 0.01°C during extended periods, thus allowing for precise RH control in the various desiccators serving as small sorption chambers. For each point of sorption, one desiccator containing three samples of each species was used (one sample per species was used to the NMR analysis and the other two samples to the equilibrium moisture content (EMC) determination). Specimens were weighed periodically, without being removed from the desiccator. In order to improve the control of RH during the NMR test, NMR tubes were also put inside each desiccator. Specimens at full saturation condition were also tested (Table 4.1). Each specimen was placed into a 20 cm long x 5 mm o.d. NMR sample tube (Screw Cap Tube). As made by Menon et al. (1987) a 17.5 cm long Teflon dowel, 4 mm in diameter was

inserted just above the wood in order to minimize the air space with which the wood could equilibrate.

NMR analysis

The specimens were analyzed by NMR once they reached the equilibrium moisture content. They were inserted into the NMR tubes, which were hermetically closed. All NMR experiments were done at 25°C on a Varian INOVA instrument operating at a ^{1}H frequency of 600 MHz. Samples at sorption conditions 1 to 4 (Table 4.1) were analyzed using a room-temperature XYZ-PFG triple-resonance probe. Sorption conditions 5 to 7 (Table 4.1) were analyzed using a cryogenic Z-PFG triple-resonance probe. T_2 relaxation times were measured using a Carr-Purcell Meiboom-Gill (CPMG) sequence: 90-[tau-180-tau]$_n$-acquire. The ^{1}H spectral width was 40 kHz, the acquisition time was 204.8 ms, ^{1}H pulses were applied at field strength of 42.3 kHz, and a recycle delay of 4 sec was used. For the condition 1, the delay tau was 2.0 ms and relaxation delays were: 8, 16, 24, 40, 64, 96, 136, 184, 240, 304, 360 and 440 ms. For the sorption conditions 2 to 7, the delay tau was 0.1 ms and relaxation delays were: 0.4, 0.8, 1.2, 1.6, 2.4, 3.2, 4.8, 9.6, 12.8, 25.6, 51.2 and 102.4 ms (for huayruro samples the maximum relaxation delay was 51.2 ms).

The decay intensity as a function of spin-spin relaxation time (T_2) for specimens having two different moisture contents is shown in Figure 4.1. The MatLab 7.0 software was used to fit the data to:

$$Y = A\exp^{(-Bt)} + C\exp^{(-Dt)} + E\exp^{(-Ft)} \qquad (4.1)$$

where: A, C and E are the populations of the three T_2 values; B, D and F are the inverse of the three T_2 times for the three components.

Equation 4.1 shows an example of triexponential fitting, where three types of water in wood are distinguished. The goodness of fit was determined using the graphical analysis and the Akaike Information Criterion (AIC) (Akaike 1974), which provides a statistical means to select an adequate model with a minimal estimate of the squared error from a set of competing models. The AIC value is calculated as follows:

Table 4.1. Characteristics of the moisture sorption conditions applied for each wood species.

State of sorption	Chemical or saturated salt solution	Nominal relative humidity (%)	Sorption condition
	Full saturation under distilled water		
Saturation	H_20	100	1
	Equilibration over saturated salt solutions at 25°C		
Desorption	K_2SO_4	96	2
Desorption	$ZnSO_4$	90	3
Desorption	KCl	86	4
Desorption	NaCl	76	5
Desorption	NaBr	58	6
Desorption	$MgCl_2$	33	7

$$AIC = N\ln(SSE) + 2NP \tag{4.2}$$

where: N is the number of data points fit to the model, P is the number of parameters estimated by the model, SSE is the summed square of residuals. The SSE is given by:

$$SSE = \sum_{i=1}^{N} w_i (y_i - \hat{y}_i)^2 \tag{4.3}$$

where: y_i is the y value of the i^{th} observation, $\hat{y}_i$ is the predicted y value of the i^{th} observation, and w_i are the weights (weights determine how much each response value influences the final parameter estimates).

This approach was applied in model discrimination, especially in deciding whether data are best described by a monoexponential equation, biexponential equation or a triexponential equation. The more appropriate model has the smallest AIC (the smallest sum of weighted squared deviation) (Wen et al. 1999).

4.5 Results and discussion

The desorption curves of the three species studied are shown in Figure 4.2. Since the desorption was carried out from the full saturated state, the curves obtained corresponds to the maximum EMC expected for each humidity condition. The term boundary desorption curve is therefore used to describe this feature. The species presented different boundary desorption curves, which can be principally explained by their different anatomical structure.

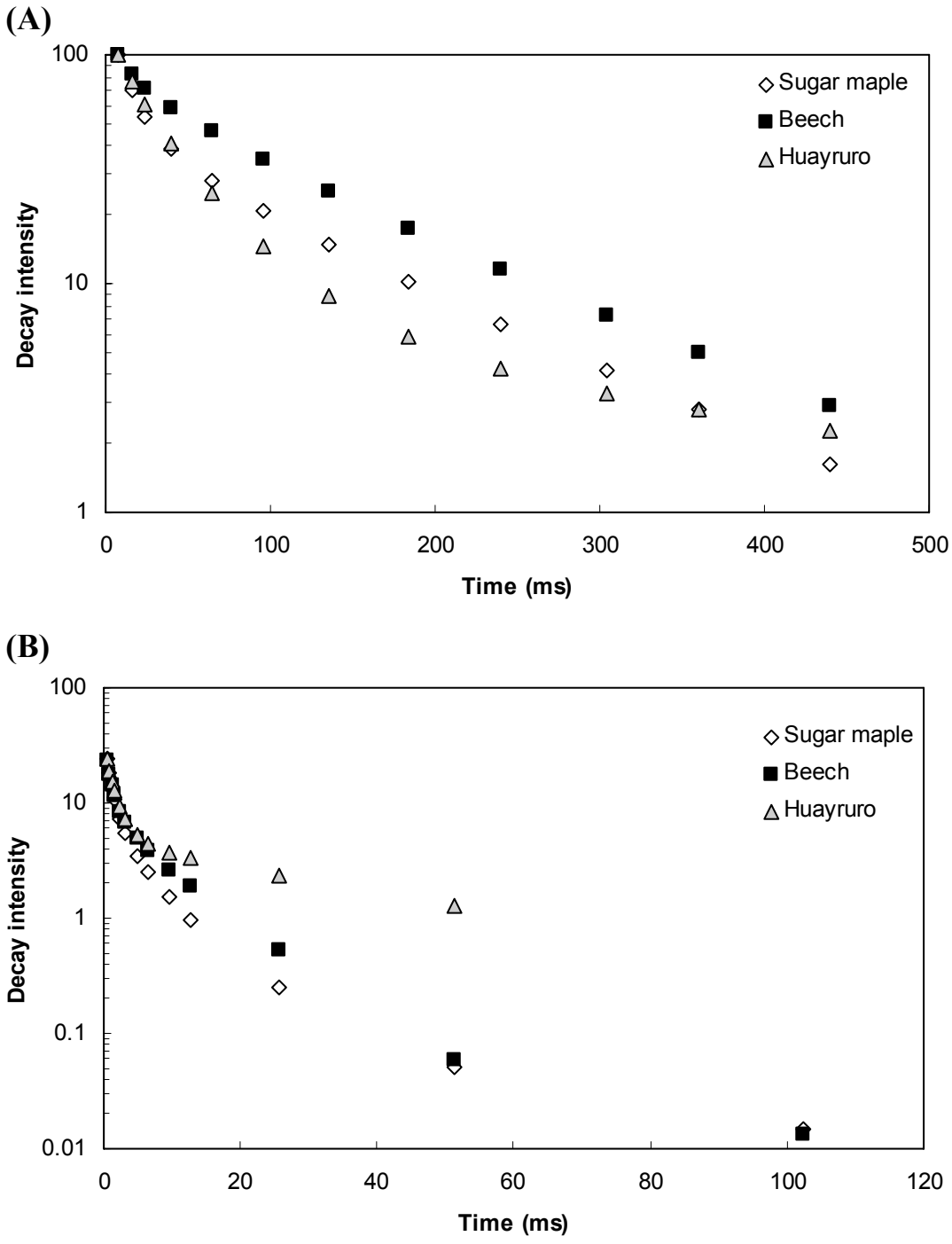


Figure 4.1. Decay intensity as a function of spin-spin relaxation time (T_2). (A) Full saturated specimens. (B) Specimens equilibrated in desorption at 96% RH and 25°C.

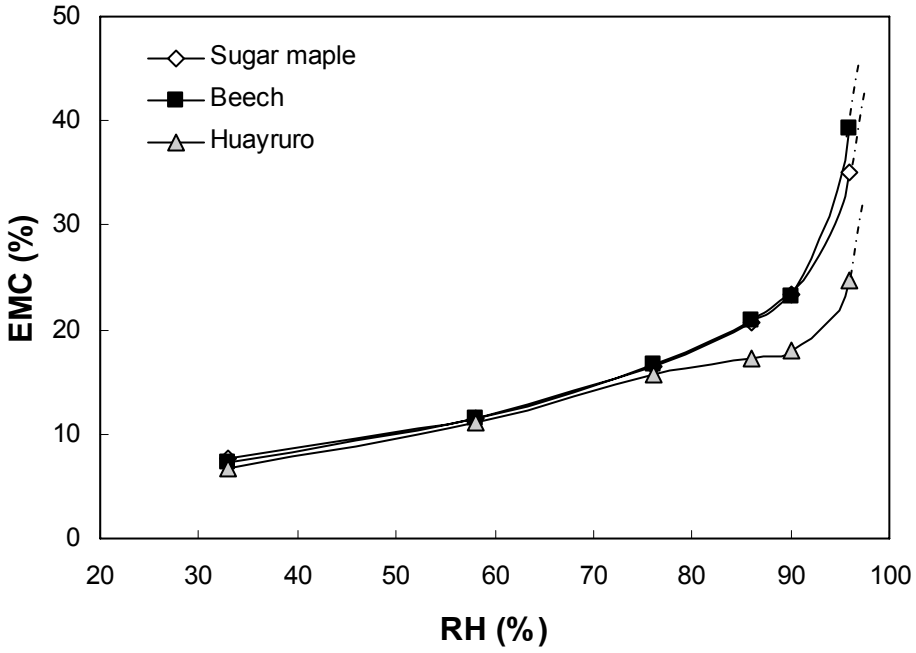


Figure 4.2. Equilibrium moisture content (EMC) obtained in desorption as a function of relative humidity at 25°C for the three hardwoods studied (standard errors did not exceed the symbol size).

The EMC values and the corresponding T_2 results for all species are shown on Tables 4.2 to 4.4 and Figures 4.3 and 4.4. In the present work, the solid wood component was not studied. The T_2 results show that the water in wood was distinctly divided on three types: "bound water" or "cell wall water" with fast relaxation times (less than 1.5 ms); "lumen or liquid water" with medium relaxation times (between 2.8 and 40 ms) and lumen water presenting slow relaxation times (more than 120 ms). As observed by Menon et al. (1987), the relaxation times are related to the wood anatomical structure, which explains the separation of liquid water on two distinct types. Menon et al. (1987) studied softwood species, which present a simpler structure than hardwoods. An important difference between softwoods and hardwoods is the vessel elements (large capillaries ensuring the sap rise in hardwood species). The slow relaxation times shown in Tables 4.2 to 4.4 represent the liquid water located in the lumina of these elements. The vessel elements of the three species studied exhibit several differences, which are reflected on slow T_2 results. Results presented on Table 6.3 and by Panshin and de Zeeuw (1980) show that huayruro vessels are

Table 4.2. Equilibrium moisture content (EMC) and T_2 results for sugar maple.

RH (%)	EMC (%)	T_2 times (ms)			T_2 populations (%)		
		Fast	Medium	Slow	Fast	Medium	Slow
100	103.8	-	12 (± 1) [1]	120 (± 9)	-	69	31
96	35.0	0.95 (± 0.06)	5.8 (± 0.7)	-	77	23	0
90	23.4	0.78 (± 0.05)	4.2 (± 0.8)	-	85	15	0
86	20.6	0.64 (± 0.04)	2.8 (± 0.7)	-	88	12	0
76	16.4	1.1 (± 0.2) / 0.53 (± 0.06)	-	-	33 / 67	0	0
58	11.5	0.64 (± 0.03)	-	-	100	0	0
33	7.7	0.37 (± 0.02)	-	-	100	0	0

[1] Values between parentheses indicate the confidence interval of T_2 times at 95% confidence level.

Table 4.3. Equilibrium moisture content (EMC) and T_2 results for beech.

RH (%)	EMC (%)	T_2 times (ms)			T_2 populations (%)		
		Fast	Medium	Slow	Fast	Medium	Slow
100	117.5	-	13 (± 3) [1]	125 (± 7)	-	40	60
96	39.2	0.97 (± 0.06)	8.3 (± 0.8)	-	73	27	0
90	23.1	0.85 (± 0.07)	5 (± 1)	-	86	14	0
86	20.8	0.71 (± 0.09)	3 (± 1)	-	84	16	0
76	16.6	1.5 (± 0.3) / 0.6 (± 0.2)	-	-	38 / 62	0	0
58	11.4	0.67 (± 0.03)	-	-	100	0	0
33	7.2	0.37 (± 0.02)	-	-	100	0	0

[1] Values between parentheses indicate the confidence interval of T_2 times at 95% confidence level.

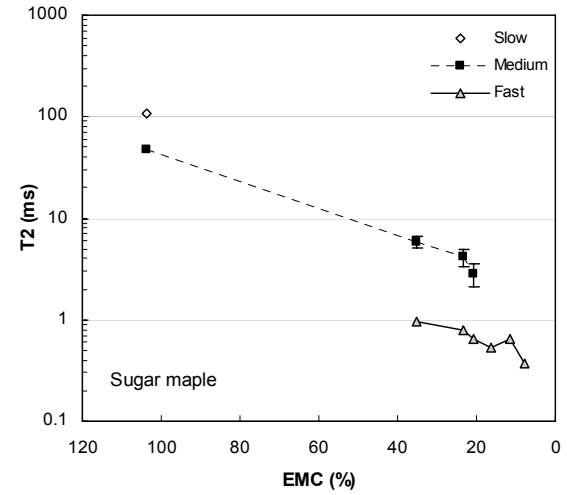
Table 4.4. Equilibrium moisture content (EMC) and T_2 results for huayruro.

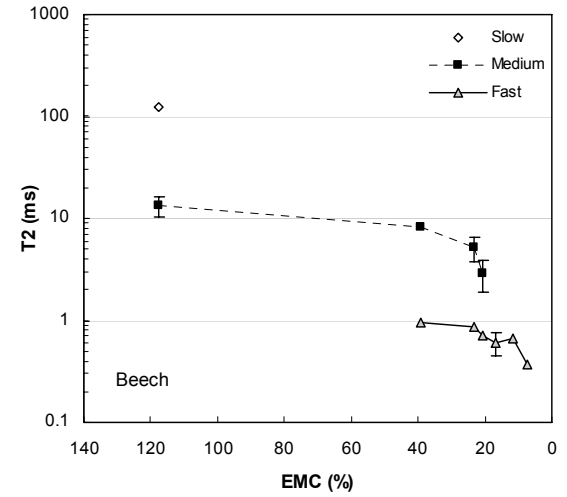
RH (%)	EMC (%)	T_2 times (ms)			T_2 populations (%)		
		Fast	Medium	Slow	Fast	Medium	Slow
100	84.7	-	11 (± 2) [1] / 40 (± 3)	311 (± 58)	-	30 / 64	6
96	24.8	1.40 (± 0.06)	34 (± 6)	-	83	17	0
90	18.0	1.43 (± 0.06)	-	-	100	0	0
86	17.2	1.38 (± 0.05)	-	-	100	0	0
76	15.8	1.26 (± 0.04)	-	-	100	0	0
58	11.0	0.90 (± 0.03)	-	-	100	0	0
33	6.8	0.44 (± 0.02)	-	-	100	0	0

[1] Values between parentheses indicate the confidence interval of T_2 times at 95% confidence level.

4 times larger than beech and sugar maple vessels. As a result, the slow T_2 values are shorter for the temperate species, due to the higher surface effect on the water inside the lumina. On the other hand, the vessel proportion in the wood volume of beech is about 5 times higher than that of huayruro (Table 6.3). This results in a higher proportion of slow T_2 time for beech than for huayruro (Tables 4.3 and 4.4).

The medium T_2 values represent the liquid water located in the lumina of fiber and parenchyma elements. The results obtained on full saturated samples also reflect the anatomical differences among species. Huayruro has a large proportion of axial parenchyma (33% of wood volume) (Table 6.3). The cavities of this tissue are larger than those of fibers and radial parenchyma. Consequently, the T_2 exponential fit of huayruro resulted in two distinct medium times: lumen water of axial parenchyma (40 ms) and lumen water of fiber and radial parenchyma (11 ms) (Table 4.4). In contrast, sugar maple and beech presented only one medium T_2 (Tables 4.2 and 4.3) given that their proportion of axial parenchyma is very low, 0.1% and 3%, respectively (Panshin and de Zeeuw 1980). Given the precision of the measure, it was not possible to distinguish the bound water portion on the full saturated samples.





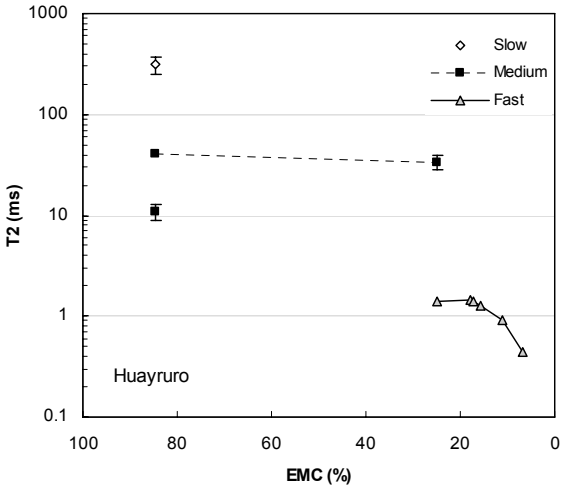


Figure 4.3. T_2 values (ms) as a function of equilibrium moisture content for the three hardwoods studied. The confidence interval (95% confidence level) of T_2 is shown only when it exceeds the symbol size.

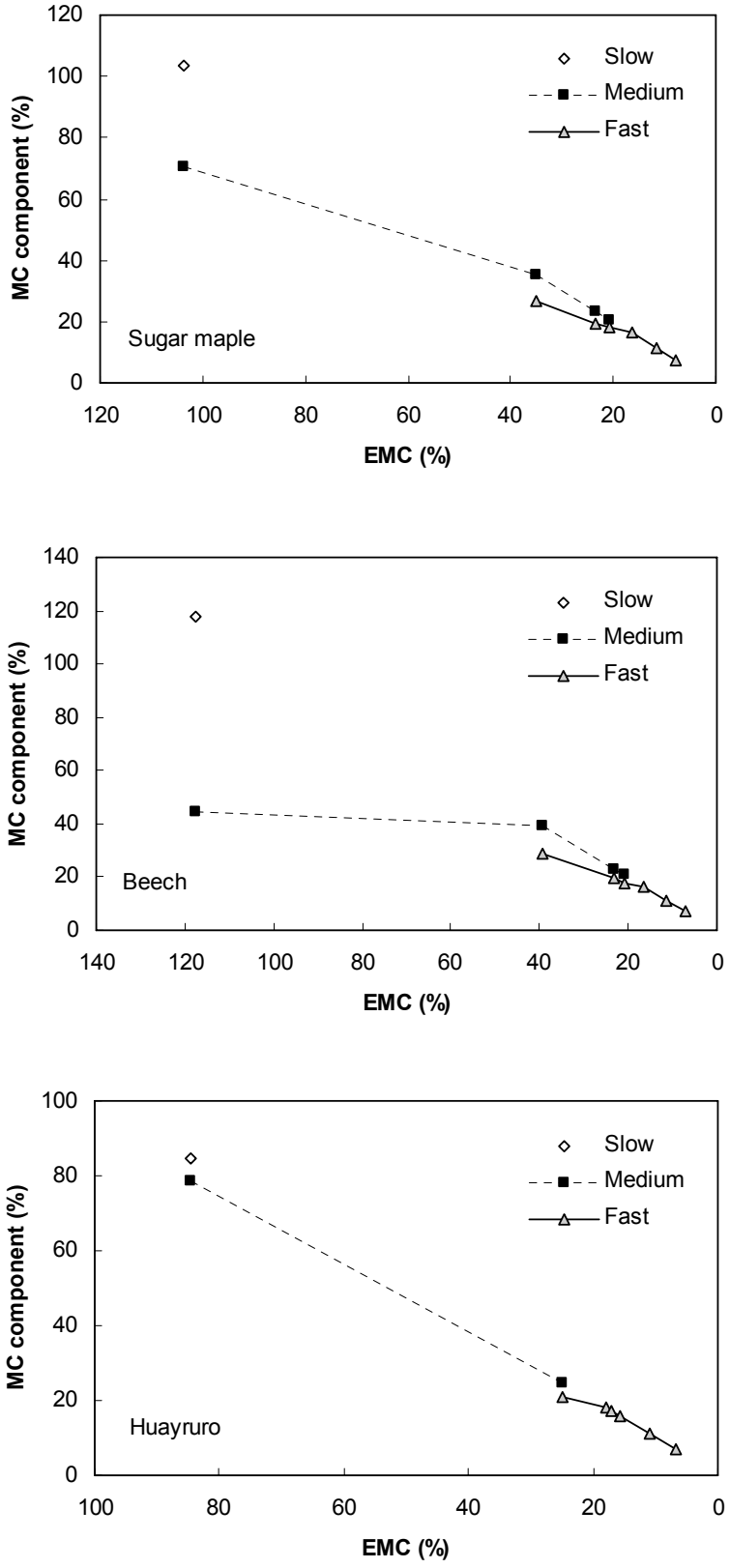


Figure 4.4. Moisture content of each water component as a function of equilibrium moisture content for the three hardwoods.

The results obtained in desorption at 96% RH (Tables 4.2 to 4.4, Figures 4.3 and 4.4) show the absence of the slow T_2, which indicates that the vessel elements are already empty at this level of RH. A faster relaxation time becomes evident, which is related to the cell wall water component. The EMC at 96% RH was lower for huayruro than for sugar maple and beech. This results in a smaller proportion of lumen water (medium T_2) for huayruro (Table 4.4) than for the other two wood species (Tables 4.2 and 4.3). Important differences are observed between the medium relaxation time of huayruro and that of temperate hardwoods, where T_2 of the first one was more than 4 times larger than the other species. The influence of the axial parenchyma of the tropical species as mentioned above can also explain this result.

At 90% RH, the temperate hardwoods presented similar EMC and T_2 results (Tables 4.2 and 4.3). Huayruro wood still had smaller EMC values and this fact was manifested on the T_2 results, with the absence of liquid water (medium T_2 value) (Table 4.4). Several works have reported the ray parenchyma as being the least permeable tissue in the wood structure (Hart et al. 1974; Gonzalez and Siau 1978; Siau 1995). As a result, temperate species presenting rays elements surrounded by fibers could still have liquid water inside ray parenchyma. The fact that rays elements are surrounded by axial parenchyma in huayruro may explain the easier drainage of liquid water. This liquid water can be considered in a metastable state given that it could be eliminated by diffusion at a very long term.

For sugar maple and beech woods, the medium T_2 values (liquid water) were not observed anymore at RH values lower than 76% (Tables 4.2 and 4.3). This means that, at equilibrium conditions, the full drainage of liquid water had already achieved at 76% RH for these two species and at 90% RH for huayruro wood. These results corroborate early studies made on sugar maple wood by Djolani (1970). Thus, figure 4.5 shows that desorption in presence of liquid water and desorption starting from the FSP had similar values at about 76% RH, showing the absence of liquid water at this state of desorption.

At 76% RH the exponential fit of temperate woods showed two different relaxation times of bound water (Tables 4.2 and 4.3). The faster T_2 time can be assigned to the water content more strongly bonded by hydroxyl groups (monomolecular water) whereas the slower T_2 time shows the weakly bound water (polymolecular water). Figure 4.6 shows only the

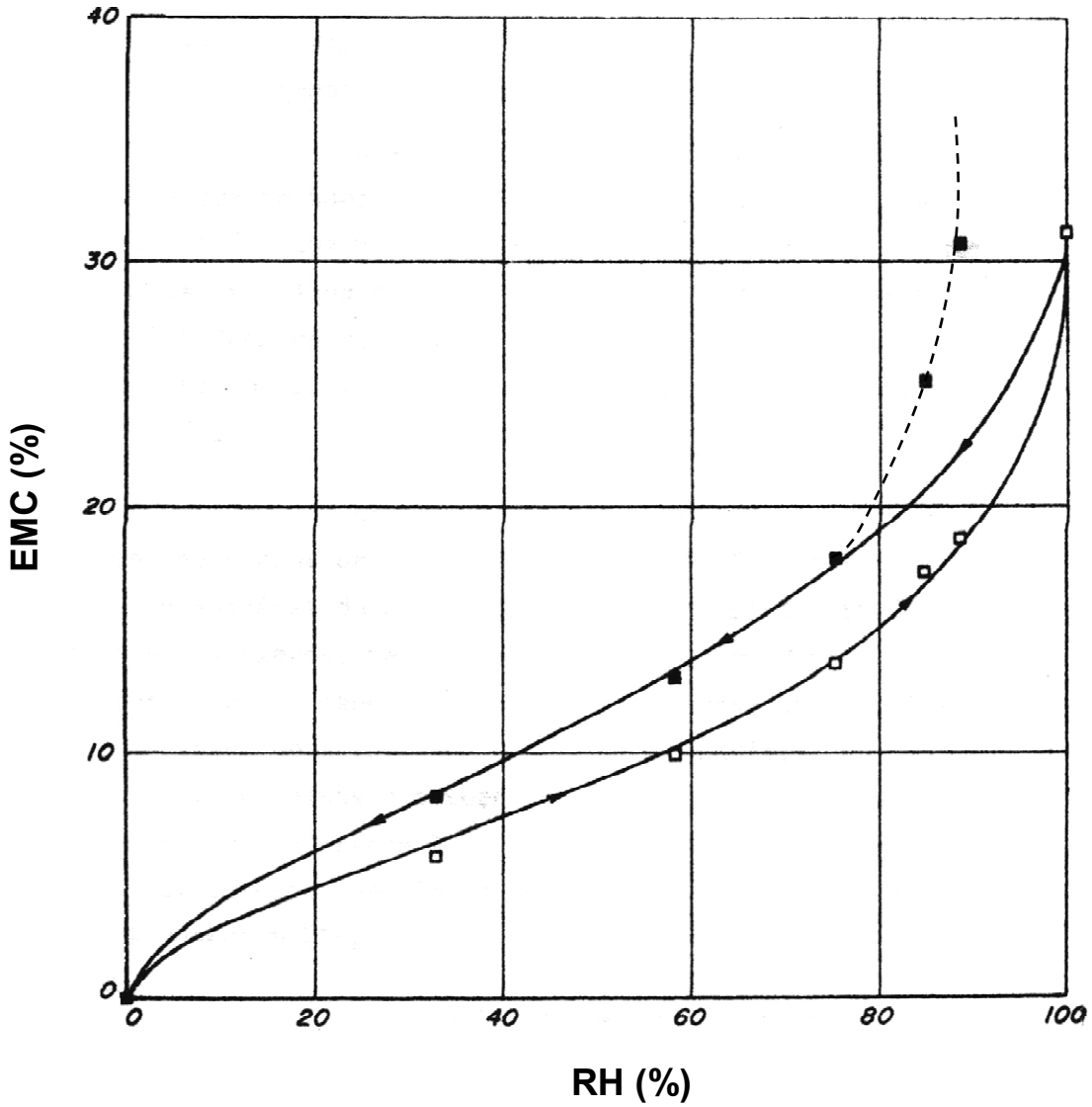


Figure 4.5. Sorption isotherms of sugar maple wood at 21°C (Djolani 1970). Discontinuous layer indicates desorption in presence of liquid water.

bound water with faster T_2 for the values of temperate woods at 76% RH.

One objective of this work was to study the liquid water distribution on the region of FSP. As cited before, the FSP is the MC at which the cell walls are saturated with bound water, with no free water in the lumens (Tiemann 1906). In the present work, the bound water content of samples equilibrated at 96% RH was considered as the FSP determined by NMR. This was the higher level of RH where the total bound water could be estimated. However, previous works have reported that a loss of bound water can occur at EMC above

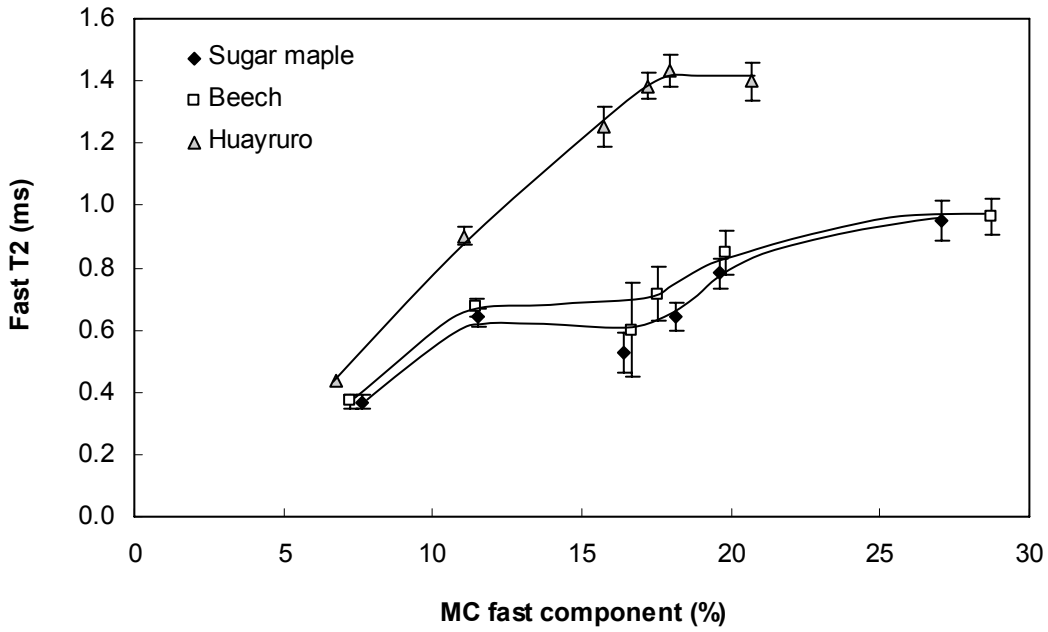


Figure 4.6. Fast T_2 relaxation times (cell wall water or bound water) as a function of equilibrium moisture content for the three hardwoods (confidence interval is shown only when it exceeds the symbol size).

the FSP: at about 42% EMC for sugar maple (Hernández and Bizoň 1994), 40% EMC for beech (chapter 3) and 77% EMC for huayruro (Hernández and Pontin 2006). Consequently, the bound water content determined at 96% RH can not be considered as total given that a loss of this water occurs at early states of desorption. The FSP values determined by NMR were 27%, 29% and 21% for sugar maple, beech and huayruro, respectively. These values were hence lower than those of 31% EMC determined by the volumetric shrinkage intersection method for sugar maple (Hernández and Bizoň 1994) and beech (chapter 3). However, the two methods gave a similar FSP for huayruro wood (Hernández and Pontin 2006). As a consequence of the high axial parenchyma proportion of huayruro wood, the high EMC at which the physical properties started to change was probably caused by a localized collapse on the thin cell walls of axial parenchyma rather than by a loss of bound water at early states of desorption. The results of FSP estimated by NMR tend to confirm this hypothesis.

NMR results of samples at equilibrium conditions showed that liquid water (medium T_2) was not gone from the void volume until EMC values of 21% for sugar maple and beech, respectively (Tables 4.2 and 4.3). These results confirm the hypothesis of Hernández and Bizoň (1994) that a region exists where the loss of bound water takes place in the presence of liquid water. These authors observed that, at equilibrium state, wood properties starts to change at EMC values well above the FSP and that the remaining liquid water could be entrapped within the least permeable wood tissues. In the case of huayruro wood, the EMC obtained does not allow us to confirm the above hypothesis, since liquid water was present at 25% EMC and absent at 18% EMC (Table 4.4). These results show that the range of the region where loss of bound water takes place in the presence of liquid water will depend on the size distribution of wood capillaries and, as a result, this will vary among wood species.

Araujo et al. (1994) showed that the bound water fraction (fast component) in lodgepole pine heartwood increased from about 0.2 ms to a plateau value of 1 ms as the moisture content goes above the FSP, which was determined by NMR tests as 26.7%. Figure 4.6 also shows that bound water T_2 values increase as EMC increases. This result was expected since the mobility of the bound water has a positive correlation with the EMC. The fast T_2 values of the three hardwoods become similar at lower EMCs.

As mentioned above, different bound water T_2 values were observed between the temperate and tropical species (Tables 4.2 to 4.4 and Figure 4.6). Huayruro exhibits a higher proportion of axial parenchyma (thin cell wall) which resulted in a larger relaxation time of bound water than that of the other species (Tables 4.2 to 4.4). Menon et al. (1987) also observed the influence of cell wall thickness on T_2 values, where the fir samples with higher percentage of latewood (thicker cell walls) had 60% shorter T_2 for the bound water component.

4.6 Summary and conclusions

NMR technique was used to separate different components of water in wood at equilibrium state. One tropical and two temperate hardwoods were studied during desorption at 25ºC in order to determine the influence of wood structure on the wood - water relationships. The principal conclusions are listed below:

1. Three different water components were easily separated: slow T_2 (liquid water of vessel elements), medium T_2 (liquid water of fiber and parenchyma elements) and fast T_2 (bound or cell wall water).

2. The different structure of the three hardwoods was manifested on the spin-spin relaxation T_2 values. The largest difference was observed between the tropical and the temperate species.

3. Even in equilibrated conditions, a region exists where the loss of liquid water and bound water takes place simultaneously. Liquid water is present at EMC values lower than the fiber saturation point, which contradicts this concept.

4. The region where the loss of liquid water and bound water takes place simultaneously depends on the wood species.

5. At equilibrium conditions, the loss of liquid water is already accomplished at 16% EMC (76% RH), 17% EMC (76% RH) and 18% EMC (90% RH), for sugar maple, beech and huayruro, respectively.