

Moisture Content and Extractive Materials in Maritime Pine Wood by Low Field ^1H NMR

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Summary

The low field ^1H NMR relaxometry technique has been shown to be effective in determining the qualitative and quantitative moisture content and the water state distribution in maritime pine wood (*Pinus pinaster* Ait). Further investigations on extractive materials in resin-rich samples evinced the presence of oleoresin components, which may disturb adhesion on pine wood boards.

Introduction

The ability of wood to adsorb and desorb water molecules in response to its surrounding atmospheric environment has, for a long time, constituted a crucial industrial issue. The physical and mechanical properties of wood are greatly affected by its moisture content, therefore a precise knowledge of the water amount is highly important in using wood as a raw material (Haygreen and Bowyer 1996). The significance of investigating wood-water interactions (and wood-extractive interactions) in basic and industrial research can hardly be overestimated, though its real utility is subordinated to the development of specific and useful analysis techniques. In order to better understand the mechanism by which water influences wood fibre properties, a great deal of work has been carried out to account for the mass fraction and the water states in wood (Nelson 1977; Rowell 1984; Scholz 1984; Skaar 1988; Chen *et al.* 1994; Hartley *et al.* 1996; Lindberg and Laanterä 1996). Hence, the need for a non-destructive NMR approach emerged rapidly. While the continuous wave NMR technique initially allowed measurement of the total wood moisture content (Shaw and Elskén 1950; Nanassy 1973, 1974, 1978; Sharp *et al.* 1978), the low field ^1H NMR tool came into prominence for effectively determining both the total amount and the distribution of water through the cell-walls and lumens (Hsi *et al.* 1977; Riggin *et al.* 1979; Hall and Rajanayagan 1986; Menon *et al.* 1989; Flibotte *et al.* 1990; Quick *et al.* 1990; Araujo *et al.* 1992, 1993; Hartley *et al.* 1994; Rutledge 1996; Harańczyk *et al.* 1999).

According to the type of NMR experiment implemented, the relaxation profiles contain information about the longitudinal relaxation time T_1 of the spin-lattice interactions (Vriesenga *et al.* 1983; Araujo *et al.* 1993; Xu *et al.* 1996) or the transversal relaxation time T_2 of the spin-spin inter-

actions (Monteiro-Marques *et al.* 1991; Araujo *et al.* 1994). While the T_1 relaxation times exhibit a rather complicated dependence on the temperature and moisture content, affording only a little insight into the water state distribution in wood, it has been demonstrated that the T_2 relaxation times provide more detailed and quantitative information. NMR evidence (Menon *et al.* 1987) indicates that the ^1H NMR signal from water in western red cedar may be separated on the basis of spin-spin T_2 relaxation times into solid wood, bound water (that is associated intimately with wood cell-walls) and lumen water (that is relatively free to move in the cell cavities).

The interpretation of NMR relaxation spectra in inhomogeneous systems involves analysis of the free induction decay (FID) signal as a function of time. As a rule, the solid-wood signal decays rapidly to zero in tens of microseconds after the 90° pulse and is therefore immediately differentiated from the water environment which extends over hundreds of milliseconds (Hsi *et al.* 1977; Riggin *et al.* 1979). Multiexponential profiles obtained from the CPMG sequence (Carr and Purcell 1954; Meiboom and Gill 1958) were fitted to a sum of exponential components and had to be decomposed into their different contributions. The water environment itself may be separated into three major components with different relaxation times: a signal with a short T_2 value of a few milliseconds is assigned to the bound water, a signal with an intermediate T_2 value can be assigned to the latewood water lumens and a signal with a large T_2 value of over 100 milliseconds is connected with the earlywood water lumens (Menon *et al.* 1987, 1989).

Owing to the continuous distribution of the wood cell sizes (Brownstein *et al.* 1979; Li and Ödberg 1993), the relaxation profiles have been shown to be best depicted as a continuous distribution of relaxation times (Whittall *et al.* 1989; Araujo *et al.* 1992) rather than a limited sum of dis-

Table 1. Continuous T₂ relaxation times distribution of a sapwood maritime pine wood sample versus temperature

Temperature °C	Liquid %*	T ₂ relaxation times distribution ms**					
25	59	0.003–0.011	0.23	0.75–0.95	3.04–3.84	18.4–29.5	60–122
15	58	0.003–0.011	0.29		1.51–1.9	18.4–23.3	96.2–122
5	58	0.003–0.011	0.29–0.37	1.19–1.51	3.84–4.85	18.4–23.3	96.2–122
0	58	0.003–0.011	0.29–0.37		1.51–1.9	18.4–23.3	96.2–122
-5	25	0.003–0.009	0.09–0.12	0.29–0.37	1.19–1.51	3.04–3.84	14.5–18.4
-11	26	0.003–0.011	0.18–0.23	0.95–1.19	2.41–3.04		

* free and bound water

** Standard error ±2 %

crete T₂ values. Computer implementation of the discrete approach is based on the optimization algorithm of Marquardt (Marquardt 1963) using the Table Curve 2D program (Jandel Scientific), while the continuous approach has been expressed by Contin, a Provencher's program (Provencher and Dovi 1979; Provencher 1982).

Materials and Methods

The NMR experiments were conducted on a low resolution impul-sional Bruker Minispec NMS 120 spectrometer operating at 20 MHz. The spectrometer is programmed for routine determinations of the solid/liquid ratio and for the measurement of T₂ relaxation times. Samples of about 40 mm in length (longitudinal) and 8 mm in diameter were placed in a 10 mm NMR glass tube. The 10 VTS-GRA NMR probe was thermostated between +25 and -11 °C using a HAAKE KIS cryostat. For a spectrometer operating at 20 MHz for protons, the typical dead time value was 7 μs. Samples having predetermined solid contents were used as calibration standards.

Analysis of the T₂ relaxation times does not depend on field inhomogeneity phenomena and was carried out using the Carr-Purcell Meiboom-Gill (CPMG) sequence (Meiboom and Gill 1958). Spectra were acquired setting 200 echoes at two τ values. Echo spacing of 10 μs allows observation of the shortest T₂ values while a τ value of 400 μs is needed to discriminate the longest T₂ values.

The xylem of maritime pine (*Pinus pinaster*) was studied, including the clear differences between sapwood and heartwood materials. Specimens were taken from a log slice in sapwood and juvenile heartwood samples, and from a plank's knot of *Pinus pinaster*.

Specimens were cut maintaining the overall fiber orientations parallel (longitudinal) or perpendicular (radial) to the longitudinal tracheids of the wood. Cylindrical blocks were equilibrated to different moisture levels in a moist environment (saturated saline solutions, 23 °C) for a period of one month (Table 2).

In order to compare the water distribution times before and after removal of extractive components and rehydration of the sample, the removal of extractives was carried out using successive extractions with acetone and ethanol in a Soxhlet extractor device. The samples were further oven-dried at 103 ± 2 °C for 24 h. The process does not affect bound water NMR data.

¹H and ¹³C high-resolution NMR experiments were performed on a Bruker DPX-400 spectrometer operating at 400.130 MHz for the proton and 100.613 MHz for the carbon. Materials were analysed without lock or rotation of the sample. Sapwood and heartwood samples were from the same wood specimen.

Results and Discussion

The aim of the present study is to quantify the distribution of water in samples of maritime pine wood, of which water states are not well known, in order to gain a better under-

standing of the properties affecting the drying process of this material. Since the maritime pine wood drying process has a direct connection with gluing properties, we further investigated wood-extractive systems in order to improve the adhesive properties of maritime pine wood rich in resinous products.

As a start, the moisture content and the relaxation time distribution of a sapwood and heartwood test sample were analysed at various temperatures. The solid/liquid ratio was evaluated by progressively lowering the temperature from 25 to -11 °C (Table 1). The data were collected between 0.0075 and 0.01 ms for the solid plus liquid signal intensity and between 0.047 and 0.088 ms for the liquid signal intensity. The total wood signal intensity was extrapolated from the signal zero-time intercept (Sharp *et al.* 1976; van den Enden *et al.* 1978; Araujo *et al.* 1992; Hartley *et al.* 1996). Measurement of the solid plus liquid ratio corresponds to the sample humidity at the given temperature.

The graphical representation of the evolution of the solid content ratio versus the temperature is shown in Figure 1 for sapwood, heartwood and knot specimens. What is noticeable as the temperature decreases is the appearance of a very marked point of inflexion in the sapwood sample curve slope at -5 °C (Fig. 1), while no sudden variation in

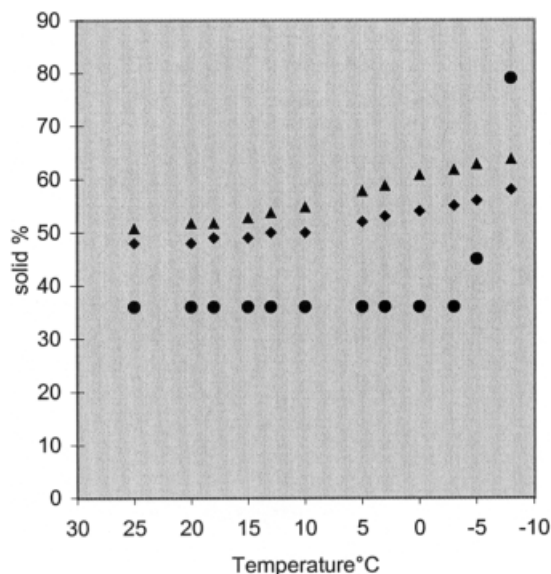


Fig. 1. Solid content ratio in sapwood (●), heartwood (▲) and knot (◆) samples versus temperature.

the shape of the heartwood and knot profiles occurs (Fig. 1). The observed temperature dependence of the sapwood curve corresponds to a solidification, at the inflexion point, of the lumen water component that is relatively free to move about in the sapwood cell cavities. This behaviour allows the quantitative determination of the sapwood free water.

In contrast, the comparable monotonic evolution observed for the heartwood and knot profiles versus temperature suggests the absence of pure free water. One possible hypothe-

sis could be the presence of a water/organic component (*e.g.* oleoresin) "mixture", increasing the viscosity of the medium as the temperature is reduced.

Structural identification of the sapwood, heartwood and knot components requires application of the high-resolution NMR spectroscopy (Fig. 2). At 400 MHz, the ^1H NMR spectra allow discrimination between the two kinds of materials. While the sapwood sample displays a sharp-lined water resonance (Fig. 2a), the heartwood and knot resin-rich samples

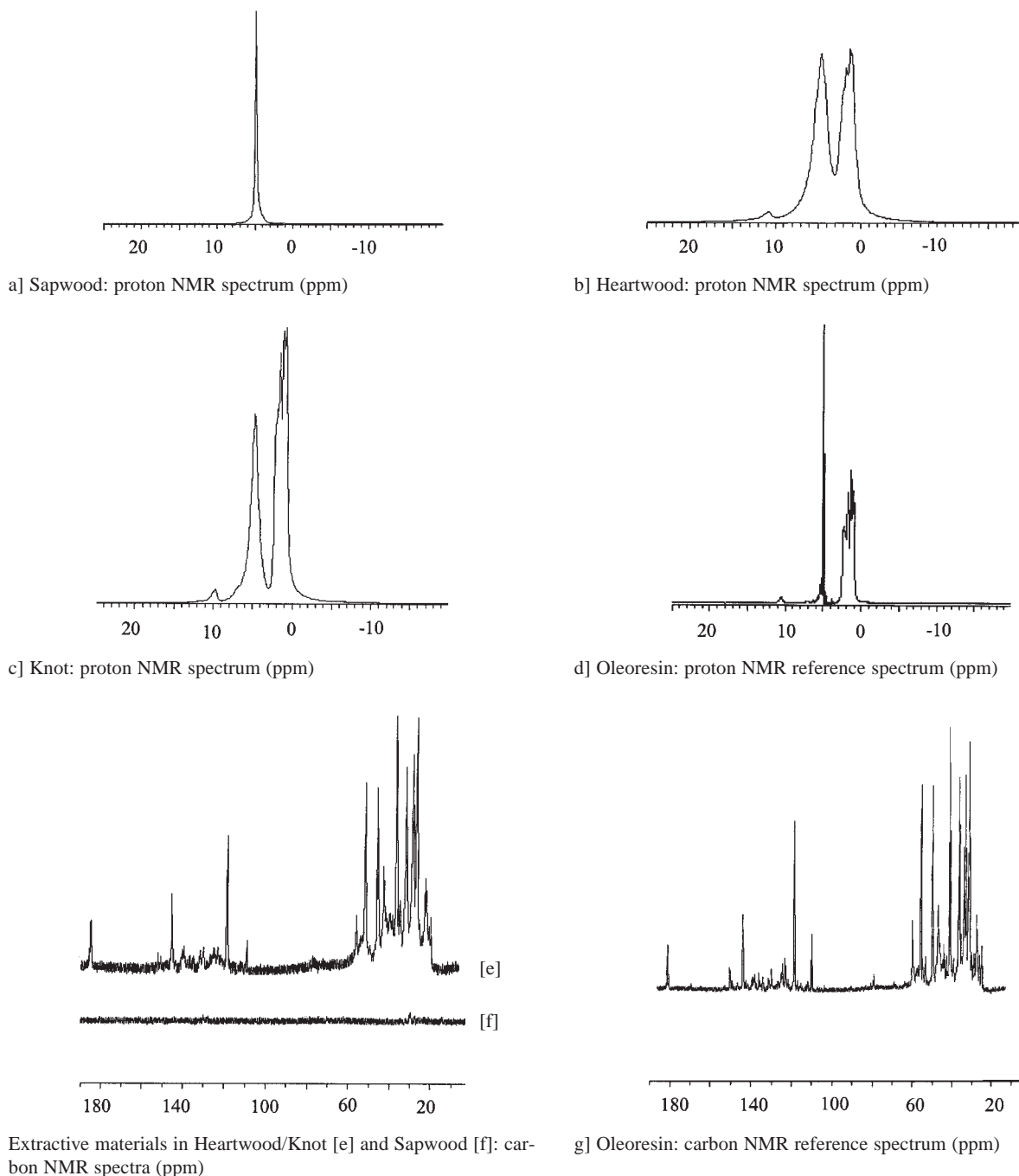


Fig. 2. 400 MHz ^1H and ^{13}C high-resolution NMR spectra of sapwood and heartwood maritime pine wood samples: a) ^1H NMR of the sapwood sample; b) ^1H NMR of the heartwood sample; c) ^1H NMR of the knot sample; d) ^1H NMR of the oleoresin reference; e) ^{13}C NMR spectra of the heartwood/knot (α - and β -pinene) samples; f) ^{13}C NMR spectrum of the sapwood sample; g) ^{13}C NMR spectrum of the oleoresin reference sample.

Table 2. Moisture content and continuous relaxation times distribution of a series of sapwood samples

Samples	Liquid %*	solid phase			bound water	free water	
		T _{2a} ***	T _{2b}	T _{2c}	T _{2d}	T _{2e}	T _{2f}
B5**	14	0.002–0.011	0.11–0.14	0.57–0.73	1.15–1.46		
B6**	14	0.002–0.007	0.14–0.18	0.92–1.15			
B7**	18	0.002–0.009	0.11	0.29–0.36	1.15–1.46		
B8**	18	0.002–0.009	0.09–0.11	0.73–0.92	1.46–1.84		
B9	20	0.002–0.007	0.11	0.72–0.91	2.31–2.92		
B10	37	0.002–0.009	0.11–0.14	0.45	1.08–1.73	14.5–18.4	47.2–59.8
B11	37	0.002–0.011	0.29	0.81–1.74		14.5	37.4–47.4
B12	57	0.003–0.011	0.29–0.37	0.75	2.2–9.07		37.4–195
B13	61	0.003–0.007	0.06–0.07	0.37–0.46	2.2–3.53		23.3–29.5

B5: radial fiber orientation sample equilibrated in a potassium carbonate saturated saline solution; B6: longitudinal fiber orientation sample equilibrated in a potassium carbonate saturated saline solution; B7: longitudinal fiber orientation sample equilibrated in a sodium nitrate saturated saline solution; B8: radial fiber orientation sample equilibrated in a potassium chloride saturated saline solution; B9: longitudinal fiber orientation sample; B10: longitudinal fiber orientation sample; B11: longitudinal fiber orientation sample; B12: longitudinal fiber orientation sample; B13: longitudinal fiber orientation sample.

* free and bound water

** equilibrated samples

*** in milliseconds (Standard error $\pm 2\%$)

Table 3. Moisture content and continuous relaxation times distribution of a series of longitudinal fiber orientation heartwood samples

Samples	% Liquid*	solid phase			bound water	free water		oleoresin		
		T _{2a} ms****	T _{2b}	T _{2c}	T _{2d}	T _{2e}	T _{2f}	T _{2g}	T _{2h}	T _{2i}
A1**	23	0.003–0.007	0.12–0.15	0.47–0.59	1.51–1.9		7.16–11.5		29.5–37.4	
A2**	2	0.003–0.011	0.15–0.18	0.47–0.59						
A3**	22	0.003–0.011	0.18–0.23	0.86–1.74	9.07–11.5		37.4–47.4			
A4**	39	0.003–0.011	0.29	0.75–0.95	2.41–3.04	11.5–18.4	37.4–47.4			
B1***	36	0.002–0.011	0.09–0.11	0.29–0.36	1.08–1.73		7.15		23.3–29.4	
B2***	1	0.003–0.011	0.18	0.47–0.53						
B3***	45	0.003–0.011	0.18–0.23	0.75–0.95	2.41–3.04	23.3–29.95	75.4–122			
B4***	58	0.003–0.011	0.23–0.29	0.75–0.95	1.37–2.79	47.4–75.9	195–313			
A5	48	0.002–0.014	0.11–0.14	0.72	0.85–2.2		4.46–7.15		18.4–23.3	75.7–95.8
C1 (knot)	48	0.003–0.009	0.072–0.09	0.37–0.47	1.18–1.5		5.66–11.5		60–75.9	313–396
C2 (heartwood)	51	0.003–0.014	0.23–0.29	0.94–1.19	1.37–1.74		7.17–9.07		37.4–47.4	122–154

A1: pine wood plank sample; A2: pine wood plank sample, after removal of extractive materials and drying; A3: rehydrated pine wood plank sample, after removal of extractive materials and drying; A4: rehydrated pine wood plank sample, after removal of extractive materials and drying; A5: pine wood plank sample (knot); B1: heartwood sample; B2: heartwood sample, after removal of extractive materials and drying; B3: rehydrated heartwood sample, after removal of extractive materials and drying; B4: rehydrated heartwood sample, after removal of extractive materials and drying; C1: heartwood sample (knot); C2: heartwood sample"

* bound water and/or free water + oleoresin

** sample A1 submitted to the A2/A3/A4 sequence of experiments

*** sample B1 submitted to the B2/B3/B4 sequence of experiments

**** in milliseconds (Standard error $\pm 2\%$)

display a more complicated signal pattern (Fig. 2b, 2c) which can be assigned to a mixture of aqueous and organic phase. Due to the intrinsic mobility of these phases, spectra could be directly obtained from the solid wood samples. The nature of the organic phase has been assigned on a firm basis to oleoresin materials (mostly α - β -pinene and resinic acids) by comparison of the heartwood/knot and sapwood ¹³C NMR spectra (Fig. 2e/2f) with an oleoresin reference spectrum (Fig. 2g).

The water state distribution was further determined from CPMG experiments, carried out at variable temperatures and using the optimized time parameters giving access to the whole T₂ sample distribution (see experimental section: $\tau = 10$ and 400 μ s). Continuous distribution profiles of relaxation times were extracted from the multiexponential curves, using the Contin program. Measured T₂ relaxation times are depicted in Table 1 together with the water content of the sample at the given temperature.

Table 4. Quantitative estimation of the water and oleoresin components (values in square brackets, %) with the corresponding discrete relaxation times in sapwood, heartwood and knot samples

Samples*	Liquid %**	bound water	free water		oleoresin		
		T _{2d} ms****	T _{2e}	T _{2f}	T _{2g}	T _{2h}	T _{2i}
A1	23	1.24 [15.8]			8.29	23.9 [7.2]***	115.26
A3	22	1.27 [19.9]	11.88 [1.9]	117.59 [0.2]			
A4	39	1.56 [27.8]	16.56 [10.3]	87.96 [0.8]			
B1	36	1.38 [21.7]			6.37	20.51 [14.5]***	
B3	45	1.43 [21.2]	23.69 [7.6]	81.86 [16.2]			
B4	58	2.13 [8.6]	52.28 [12.4]	108.39 [36.8]			
C1 (knot)	48	1.47 [22.6]			8.14	46.42 [25.3]***	221.29
C2 (heartwood)	51	1.31 [32.6]			7.4	36.8 [18.3]***	77.42
A5	48	1.56 [15.9]			6.67	26.48 [32.1]***	114.64
B5	14	1.07 [14]					
B6	14	0.96 [14]					
B7	18	1.39 [18]					
B8	18	1.21 [18]					
B9	20	2.73 [20]					
B10	37	1.32 [32.8]	14.87 [2.3]	50.92 [1.8]			
B11	37	1.2 [33]	12.61 [1.2]	39.37 [2.6]			
B12	57	5.01 [17.2]	45.29 [10.8]	100.34 [28.9]			
B13	61	2.73 [14.2]	31.51 [16.2]	89.04 [30.6]			

* samples A2/B2: liquid % about zero

** bound water and/or free water + oleoresin

*** quantitative estimation of the whole oleoresin contributions

**** Standard error $\pm 2\%$

Aside from the readily distinguishable solid wood contribution located at the 0.003–0.011 ms range, the problem which now arises is to assign the water distribution during freezing. As shown in Table 1, the prominent feature of these experiments is the disappearance of the longest time intervals upon decreasing temperature and the appearance of a short (0.09–0.12 ms) T₂ time domain at –5 °C. The presence of this short time domain is assumed to result from a partial solidification of the free water at –5 °C and is therefore absent at –11 °C. These observations account for a total freezing of the free water at –11 °C. The solid-liquid ratio therefore varies significantly during the water solidification from about 38–39% at 0 °C to 74.2% at –11 °C and the resulting shortening of the corresponding times makes them indiscernible from the solid content relaxation time. Keep-

ing in mind that the T₂ continuous distribution times of water from lumens reflect the continuous distribution of the lumen diameters (Brownstein and Tarr 1979; Menon *et al.* 1987), we assign the longest time intervals to the earlywood and latewood tracheid lumens.

To obtain further information about intermediate relaxation times (Table 1), the measurement of the moisture content and the relaxation times below the fibre saturation point (FSP) are required. First, experiments were conducted on samples equilibrated at different moisture levels. Results are presented in Table 2. As demonstrated by the absence of lumen-water T₂ times (T_{2e}/T_{2f} Table 2), the moisture content of equilibrated **B5–B8** sapwood samples stand below the fiber saturation point. Four T₂ relaxation times are present in the continuous spectra of these equilibrated samples.

The solid phase relaxes rapidly in the 0.002–0.011 ms T_{2a} time interval and the signal with the longest T_{2d} values of a few milliseconds (1.15 to 1.84 ms) is assigned to water bound to the cell walls. In addition, according to the cluster theory for water sorption in wood (Hartley *et al.* 1992; Hartley and Avramidis 1993), the relaxation time of the bound water should increase with the humidity degree of the sample. Such a behaviour is effectively observed, whatever the moisture content of the equilibrated sample (Table 2). Further experiments carried out on a series of non-equilibrated sapwood samples **B9–B13** are depicted in Table 2. Beside the four short T_2 times, samples having a moisture content higher than the fibre saturation point present two additional, large T_2 values which were assigned to the free water distribution in the lumens. The T_{2b} and T_{2c} relaxation times are not assigned.

As demonstrated by the non-destructive ^{13}C NMR experiments, heartwood and knot samples contain some amount of oleoresin components. The presence of this material is evidenced by the appearance of additional T_2 times (T_{2g} , T_{2h} and T_{2i}) in the spectra of a series of resin-rich samples (Table 3: **A1**, **A5**, **B1**, **C1** and **C2**). Experiments were conducted on samples of three different origins: sample A: maritime pine wood plank; sample B: maritime pine wood disk (tree 1); sample C: maritime pine wood disk (tree 2). Assignment of these times to oleoresin material rather than to water contributions results from the comparison between these distribution times, with the profiles obtained after removal of extractive materials and drying of the residue on the one hand (**A2** and **B2**), and the profiles obtained after rehydration of some dried samples (**A3**, **A4**, **B3** and **B4**) on the other hand.

After removal of extractive materials, the spectra of dried samples **A2** and **B2** point out the absence of $T_{2d}/T_{2e}/T_{2f}$ water signals (previously assigned to sapwood samples; see Table 2). The two unknown T_{2b} and T_{2c} contributions observed in the sapwood relaxation profiles are also present in the heartwood samples. These contributions turned out to be insensitive to the drying process and are thus not water-type contributions. Finally, spectra of rehydrated **A3/A4/B3** and **B4** residues (Table 3) denote the presence of bound and free water relaxation times (T_{2d} and T_{2e}/T_{2f} respectively), enabling the attribution of the characteristic resin-rich T_{2g}/T_{2h} and T_{2i} relaxation times to extractive materials (oleoresin, Table 3). A careful rehydration of the dried samples evidences both the appearance and/or the disappearance of each type of compartmentalized water.

Nevertheless, as shown in Table 3, the relaxation spectrum of an unknown material does not allow unambiguous distinction between sapwood or heartwood specimens despite the presence of an additional T_2 time (about 7 ms), due to the non-specificity of the observed lumen and oleoresin T_2 times. In this case, the answer is given by the presence (sapwood) or the absence (heartwood) of any significant point of inflexion in the thermal analysis of the sample (see Fig. 1).

A quantitative estimation of the water state distribution in the sapwood and heartwood samples is deduced from the analysis of CPMG profiles in terms of discrete distribution

of relaxation times, though this approach proved to be suitable only in a small number of discrete exponential component times and amplitudes (Whittall *et al.* 1989). Valuable information on the moisture content can be appraised from the non-linear treatment of the relaxation curve by the “Table Curve 2D” program. Since the amplitude of the magnetisation is proportional to the number of protons, the total amount of water as well as the percentage of the different water species and extractives can be determined from the signal integrals. The results of the discrete approach are depicted in Table 4.

Conclusion

The qualitative and quantitative moisture content as well as the water state distribution of a series of maritime pine wood samples have been appraised from discrete and/or continuous T_2 relaxation times. Analysis of the sapwood, heartwood and knot of plank samples at varying temperatures demonstrates, for the sapwood samples, the existence of a marked point of inflexion at low temperature, characteristic of a free water freezing. This behaviour allows a straightforward discrimination between the sapwood or heartwood origin of an unknown raw material. In the resin-rich heartwood and knot samples, some additional relaxation times ascribable to oleoresin materials emerge from the relaxation profiles. Identification of oleoresin materials results from ^{13}C high-resolution NMR studies at 400 MHz of the mobile organic phases, carried out directly on the solid wood samples. These results afford a further insight of the low field NMR relaxation technique into the parameters affecting the physical and mechanical properties of the maritime pine wood.

References

- Araujo, C.D., A.L. MacKay, J.R.T. Hailey, K.P. Whittall and H. Le. 1992. Proton magnetic resonance techniques for characterization of water in wood: Application to white spruce. *Wood Sci. Technol.* 26, 101–113.
- Araujo, C.D., A.L. MacKay, K.P. Whittall and J.R.T. Hailey. 1993. A diffusion model for spin-spin relaxation of compartmentalized water in wood. *J. Magn. Reson. B* 101, 248–261.
- Araujo, C.D., S. Avramidis and A.L. MacKay. 1994. Behaviour of solid wood and bound water as a function of moisture content: a proton magnetic resonance study. *Holzforschung* 48, 69–74.
- Brownstein, K.R. and C.E. Tarr. 1979. Importance of classical diffusion in NMR studies of water in biological cells. *Phys. Rev. A* 19, 2446.
- Carr, H.Y. and E.M. Purcell. 1954. Effects of diffusion on free precession in nuclear magnetic resonance experiments. *Phys. Rev.* 94, 630–638.
- Chen, Z., E.M. Wengert and F.M. Lamb. 1994. A technique to electrically measure the moisture content of wood above fiber saturation. *Forest Prod. J.* 44, 57–62.
- Flibotte, S., A.L. Menon, A.L. MacKay and J.R.T. Hailey. 1990. Proton magnetic resonance of western red cedar. *Forest. Prod. J.* 22, 362–376.
- Hall, L.D. and V. Rajanayagam. 1986. Evaluation of the distribution of water in wood by use of three dimensional proton NMR volume imaging. *Wood Sci. Technol.* 20, 329–333.
- Haranczyk, H., W.P. Weglarz and Z. Sojka. 1999. The investigation of hydration processes in Horse Chestnut (*Aesculus hippocas-*

- tanum*, L.) and Pine (*Pinus silvestris* L.) bark and bast using proton magnetic relaxation. *Holzforschung* 53, 299–310.
- Hartley, I.D. and S. Avramidis. 1993. Analysis of the wood sorption isotherm using clustering theory. *Holzforschung* 47, 163–167.
- Hartley, I.D., F.A. Kamke and H. Peemoeller. 1992. Cluster theory for water sorption in wood. *Wood Sci. and Technol.* 26, 83–99.
- Hartley, I.D., S. Avramidis and A.L. MacKay. 1996. H-NMR studies of water interactions in sitka spruce and western hemlock: moisture content determination and second moments. *Wood Sci. and Technol.* 30, 141–148.
- Hartley, I.D., F.A. Kamke and H. Peemoeller. 1994. Absolute moisture content determination of aspen wood below the fiber saturation point using pulsed NMR. *Holzforschung* 48, 474–479.
- Haygreen, J.G. and J.L. Bowyer. 1996. *Forest Products and Wood Science*. 3rd ed. Iowa State University Press, Ames, Iowa.
- Hsi, E., R. Hossfeld and R.G. Bryant. 1977. Nuclear magnetic resonance relaxation study of water absorbed on mill northern white-cedar. *J. Colloid. Interface Sci.* 62, 389–395.
- Li, T.-Q. and L. Ödberg. 1993. Determination of pore sizes in wood cellulose fibers by 2D and ^1H NMR. *Nordic Pulp and Paper Res. J.* 3, 326–330.
- Lindberg, J.J. and M. Laanterä. 1996. Hydrogen bonds and macromolecules. The interaction between wood cells and water. *Pure Appl. Chem.* A 33, 1385–1388.
- Marquardt, D.W. 1963. An algorithm for least-squares estimation of nonlinear parameters. *Soc. Indust. Appl. Math.* 11, 431–441.
- Meiboom, S. and D. Gill. 1958. Modified spin echo method for measuring relaxation times. *Rev. Sci. Instr.* 29, 688–691.
- Menon, R.S., A.L. MacKay, J.R.T. Hailey, M. Bloom, A.E. Burgess and J.S. Swanson. 1987. An NMR determination of the physiological water distribution in wood during drying. *J. Appl. Pol. Sci.* 33, 1141–1155.
- Menon, R.S., A.L. MacKay, S. Flibotte and J.R.T. Hailey. 1989. Quantitative separation of NMR images of water in wood on the basis of T_2 . *J. Magn. Reson.* 82, 205–210.
- Monteiro-Marques, J.P., D.N. Rutledge and C.J. Ducauze. 1991. Low resolution pulse nuclear magnetic resonance study of carrots equilibrated at various water activities and temperatures. *Sciences des Aliments* 11, 513–525.
- Nanassy, A.J. 1973. Use of wide line NMR for measurement of moisture content in wood. *Wood Sci.* 5, 187–193.
- Nanassy, A.J. 1974. Water sorption in green and remoistened wood studied by the broad-line component of the wide line NMR spectrum. *Wood Sci.* 7, 61–68.
- Nanassy, A.J. 1978. Temperature dependence of NMR measurement on moisture in wood. *Wood Sci.* 11, 86–90.
- Nelson, R.A. 1977. The determination of moisture transitions in cellulosic materials using differential scanning calorimetry. *J. Appl. Pol. Sci.* 21, 645–654.
- Provencher, S.W. and V.G. Dovi. 1979. Direct analysis of continuous relaxation spectra. *Bio. and Biophys. Math.* 1, 313–318.
- Provencher, S.W. 1982. A constrained regularization method for inverting data represented by linear algebraic or integral equations. *Comput. Phys. Comm.* 27, 213–227.
- Provencher, S.W. 1982. Contin: A general purpose constrained regularization program for inverting noisy linear algebraic and integral equations. *Comput. Phys. Comm.* 27, 229–242.
- Quick, J.J., J.R.T. Hailey and A.L. MacKay. 1990. Radial moisture profiles of cedar sapwood during drying: A proton magnetic resonance study. *Wood Fiber Sci.* 22, 404–412.
- Riggin, M.T., A.R. Sharp, R. Kaiser and M. Schneider. 1979. Transverse NMR relaxation of water in wood. *J. Appl. Polym. Sci.* 23, 3147–3155.
- Rowell, R. 1984. *The Chemistry of Solid Wood*. Vol. I. Chapter 1–6. American Chemical Society, Washington, D. C.
- Rutledge, D.N. 1996. Signal treatment and signal analysis in NMR, *Data Handling in Science and Technology*, Vol 18. Ed. D.N. Rutledge. Elsevier, New York. pp. 191–217.
- Shaw, T.M. and R.H. Elksen. 1950. Nuclear magnetic resonance absorption in hygroscopic materials. *Chem. Phys.* 18, 1113.
- Sharp, A.R., M.T. Riggin, R. Kaiser and M. Schneider. 1976. Determination of moisture content of wood by pulsed nuclear magnetic resonance. *Wood and Fiber.* 10, 74–81.
- Skaar, C. 1988. *Wood Water Relations*. Springer-Verlag, New York.
- Scholz, E., G.A. Rechnitz. 1984. *Karl Fischer Titration-Determination of Water*. Springer-Verlag, New York, Vol 20. p. 108.
- Table Curve 2D, Jandel Scientific 89–94, AISN Software.
- Van den Eenden, J.C., A.J. Haighton, K. van Putte, L.F. Vermaas and D. Waddington. 1978. A method for the determination of the solid phase content of fats using pulse Nuclear Magnetic Resonance. *Fette-Seifen-Anstrichmittel* 5, 180–186.
- Vriesenga, J.R., S. Chandrasekaran and P. Luner. 1983. Proton NMR of absorbed water in wood. *J. Appl. Polymer Sci.: Applied Polymer Symposium* 37, 911–921.
- Whittall, K.P. and A.L. MacKay. 1989. Quantitative interpretation of NMR relaxation data. *J. Magn. Reson.* 84, 134–153.
- Xu, Y., C.D. Araujo, A.L. MacKay and K.P. Whittall. 1996. Proton spin-lattice relaxation in wood – T_1 related to local specific gravity using a fast exchange model. *Magn. Reson. B* 110, 55–64.

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