Transverse NMR Relaxation of Water in Wood*

M. T. RIGGIN, A. R. SHARP, and R. KAISER, *Department of Physics, University of New Brunswick, Fredericton, N.B., Canada,* and M. H. SCHNEIDER, *Department of Forest Resources, University of New Brunswick, Fredericton, New Brunswick, Canada*

Synopsis

The transverse NMR relaxation times of hydrogen nuclei of water absorbed in white spruce sapwood [*Picea glauca* (Meunch) Voss] were measured for moisture contents in the range from 5 to 176%. The spin echo amplitudes resulting from the Carr–Purcell sequence decay nonexponentially suggesting the possibility of at least two different relaxation times for water in wood. A simplified structural model of the wood–water mixture is used to estimate the rates of chemical exchange at room temperature of hydrogen nuclei between various sites in the system. The high-resolution NMR line shape is discussed briefly in terms of this proposed model.

INTRODUCTION

It is well known that the macroscopic properties of cellulose and similar polymers are influenced profoundly by the presence of water.[1-3] Thus, measurement of the moisture content of wood is of considerable importance, and numerous methods for determining the mass fraction of water in wood and pulp have been proposed.[3] Measurement of the nuclear magnetic resonance signal of hydrogen nuclei in cellulose–water mixtures is one possible technique.[4-7] Magnetic resonance also has played a significant role in understanding the wood–water relationship,[8-12] because the technique is sensitive to the microscopic environment and dynamics of molecules containing spin-bearing nuclei such as hydrogen. The wide-line NMR absorption spectrum of hydrogen nuclei in wood–water systems exhibits a relatively narrow line attributable to water, superimposed upon a much broader line resulting from hydrogen nuclei within the wood fiber.[10,12] The intensity of the narrow absorption line gives an accurate measurement of the amount of water present in a given sample,[5] but the line shape of this component was found to be much broader than that of pure water, possibly implying that water in wood is much less mobile than in the liquid phase.

The NMR evidence indicates that water in cellulosic materials takes at least two different forms[9]: water that is associated intimately with wood cell walls and water that is relatively free to move about in the cell cavities. Pulsed nuclear magnetic resonance techniques are quicker, easier, and more readily analyzed in terms of models for the molecular dynamics than steady-state absorption methods, but in spite of this, few such studies have been undertaken for water–cellulose systems. Therefore, as part of an ongoing program to investigate the properties of water and oils in wood, we have used pulsed NMR methods to measure the transverse relaxation time T_2 as a function of the moisture content of white spruce sapwood.

EXPERIMENTAL

Cylindrical samples 0.5 cm in diameter and 1.5 cm long were cut from a block of green white spruce [*Picea glauca* (Meunch) Voss], dried for varying lengths of time, and sealed in glass tubes with picine vacuum wax.[7] After the magnetic resonance experiments, moisture contents of the specimens were determined by weighing before and after drying at 105°C for 12 hr. The moisture contents ranged from 5 to 176% on an oven dry basis, and the density of the dry wood was about 0.4 g/cc.

The transverse NMR relaxation time T_2 was measured using the Gill–Meiboom[13] modification of the Carr–Purcell[14] pulse sequence. The Carr–Purcell pulse train is initiated by a $\pi/2$ pulse which flips the net magnetization of the spin system into a direction perpendicular to the static magnetic field H_0. A π pulse applied a time τ after the $\pi/2$ pulse leads to a rephasing of the total magnetization at time 2τ after the $\pi/2$ pulse to form the well-known spin echo.[15] Reapplication of π pulses at times $(2k + 1)\tau$ $(k = 1, 2, \ldots)$ results in a series of spin echoes at times $2k\tau$ the amplitude envelope of which is related to the transverse relaxation time for systems with a single Lorentzian absorption line.

The measurements were made at two frequencies, 17.13 MHz and 5.0 MHz, on a Spin-Lock Electronics Model CPS-2 pulsed NMR spectrometer, but the results were independent of frequency. The intensity of the $\pi/2$ rf pulse corresponded to 25 G, and the dead time of the receiver was 6 μsec. As noted previously,[7] the free induction decay (FID) following a single $\pi/2$ pulse lasted on the order of 300 msec in a sample of high moisture content. Thus, it was necessary to shorten the free induction decay artificially with a magnetic field gradient across the sample to prevent overlap of the π pulse with the FID of the $\pi/2$ pulse. A gradient of about 1 G/cm allowed separations between pulses as short as 100 μsec to be used. The result of fast pulse rates is to minimize the effects on the spin echo envelope of a distribution of chemical shifts (i.e., resonance frequencies) in the spin ensemble and also of diffusion of the spin-bearing molecules in the magnetic field gradient.[14] If this latter phenomenon is important, T_2 as measured by the Carr–Purcell sequence decreases as the separation between π pulses increases. However, for the moist samples investigated here, T_2 was independent of τ for $\tau \lesssim 300$ μsec indicating that diffusion is unimportant in this regime. In addition to these measurements, high-resolution NMR spectra of the water absorption line in moist spruce were recorded on a Varian 4300B spectrometer operating at 56.44 MHz.

Electron spin resonance spectra of a few moist spruce samples were recorded at 9.11 GHz. Six absorption lines separated by 96 G and centered about $g = 2$ presumably were due to the Mn^{3+} ion, and an unidentified free-radical line at $g = 2$ also was observed. Typically, about 10^{15} Mn^{3+} ions were detected, but this number varied considerably from sample to sample. However, the NMR measurements seemed independent of Mn^{3+} concentration.

RESULTS AND DISCUSSION

We have noted previously[7] that the free induction decay (FID) following a single $\pi/2$ pulse clearly exhibits two different relaxation times T_2 which can be ascribed to hydrogen nuclei in the wood and in water. The T_2 of hydrogen nuclei

in the wood is about 7 μsec and increases slightly with increasing moisture content, in agreement with previous results that showed a decrease in the width of the broad, solid-like absorption line when water was added.[12] For moisture contents (MC) below about 30%, the FID due to water is nearly exponential, having time constants that increase from about 80 μsec (5% MC) to 0.9 msec (30% MC). Above about 33 ± 6% MC, the portion of the FID which is attributed to water has at least two different relaxation times.

This can be seen from curve (a) in Figure 1, where the logarithms of the water proton echo amplitudes of a typical moist spruce sample are plotted versus the time measured from the $\pi/2$ pulse of the Carr–Purcell sequence. It should be emphasized that the wood component of the signal with an apparent relaxation time of about 7 μsec is not plotted in Figure 1. Normally a single relaxation time T_2 leads to a straight line with slope $-1/T_2$ in such a plot, but it is clear from the figure that at least two different time constants, one long and one short, are required to describe the experimental data. Samples with low moisture contents exhibit only the shorter of the two relaxation times shown in Figure 1. Because the fiber saturation point[3] is near 33% MC, it seems possible that the shorter relaxation time is associated with water molecules that are adsorbed in the cell walls and the longer relaxation time, with more mobile molecules in the cell cavity.

Resing[16] has shown that water molecules preferentially occupy adsorption sites with high enthalpies, so we would expect water molecules adsorbed on the wood cell walls to have relatively short relaxation times and to constitute the
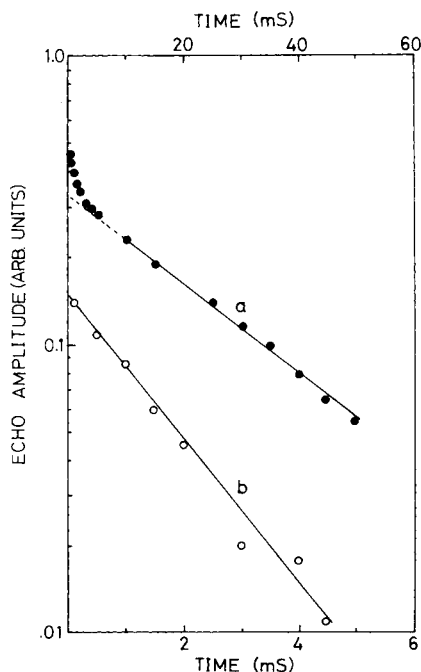

Fig. 1. In curve (a) the spin echo amplitude S of the Carr–Purcell B sequence is plotted as a function of time (upper abscissa) from the $\pi/2$ pulse. Curve (b) is proportional to ln $(S - P'_c\, e^{-t/T'_c})$ the slope of which is $-1/T'_b$. The lower abscissa is the time axis for curve (b). Moisture content was 96%, while $T'_c = 28.5$ msec and $T'_b \approx 1.6$ msec.

largest proportion of water at low moisture contents. Within this model, free water would be prevalent when all of the adsorption sites with high enthalpies were occupied. In addition, Nanassy's very careful measurements of the broad component of the NMR absorption show that about 38% of the hydrogen nuclei in wood are exchangeable with hydrogen nuclei in the water.[11] This seems convincing evidence that most noncrystalline hydroxyl protons are accessible to exchange with water protons, while the fact that separate NMR absorption lines are observed for hydrogen nuclei in wood and in water indicates that this exchange is relatively slow.

Hence, it appears realistic to analyze our results in terms of a three-phase model of the wood–water mixture in which the hydrogen nuclei may be in the wood, in water adsorbed on the wood cell wall, and in water that is not bound to wood. These three "phases" of hydrogen nuclei are denoted a, b, and c, respectively, while the measured transverse relaxation times associated with them are written as T'_a, T'_b, and T'_c and the fractional population of the three phases are P_a, P_b, and P_c. The apparent relaxation times T'_a, T'_b, and T'_c are equal to the true relaxation times T_a, T_b, and T_c only when exchange among the three phases is negligible (see Appendix).

The response of a three-phase system such as this to the Carr–Purcell sequence has been discussed in detail previously,[17–20] but for completeness the development is reviewed briefly in the Appendix, where it is shown that the spin echo envelope often is given by

$$S = P'_a \, e^{-t/T'_a} + P'_b \, e^{-t/T'_b} + P'_c \, e^{-t/T'_c} \qquad (1)$$

where t is the time measured from the $\pi/2$ pulse and the amplitudes P'_a, P'_b, and P'_c, the relative contributions of phases a, b, and c to the spin echo envelope, are related to P_a, P_b, and P_c and to the relaxation and exchange rates by considerations given in the Appendix. Because $T'_a \ll T'_b$, T'_c, the first term in eq. (1) may be neglected for $t \gg T'_a \approx 7 \ \mu\text{sec}$ and the resulting expression fitted to the experimental results to obtain the parameters P'_b, P'_c, T'_b, and T'_c as functions of moisture content. The apparent relaxation times T'_c and T'_b describe the slopes of the two parts (at long and short times, respectively) of curve (a) in Figure 1, while P'_c and P'_b are determined by the intercepts on the ordinate of the straight lines with slopes $-1/T'_c$ and $-1/T'_b$, respectively. T'_b is obtained from the slope of curve (b) in Figure 1, which is proportional to $S - P'_c \, e^{-t/T'_c}$.

The apparent relaxation times T'_b and T'_c are shown as functions of moisture content in Figure 2, while the ratios $P'_c/(P'_c + P'_b)$ obtained from our experimental results at high moisture contents are shown in Figure 3. Although plots analogous to Figure 1 are nonexponential above about 30% MC, only above about 50% MC can separate values of T'_b and T'_c be determined with reasonable confidence.

The analysis outlined in the Appendix can easily be adjusted to fit our experimental measurements using a few simplifying approximations. We assume that the bound water molecules are associated on a one-to-one basis with noncrystalline cellulosic hydroxyl protons and that all possible such sites on the wood cell surface are occupied before water molecules are "free" or able to move about in the wood cell cavity. Thus, P_c and P'_c are zero for moisture contents below 33%. We further assume that the hydroxyl protons are able to undergo chemical exchange with protons on the bound water molecules but not with unbound water
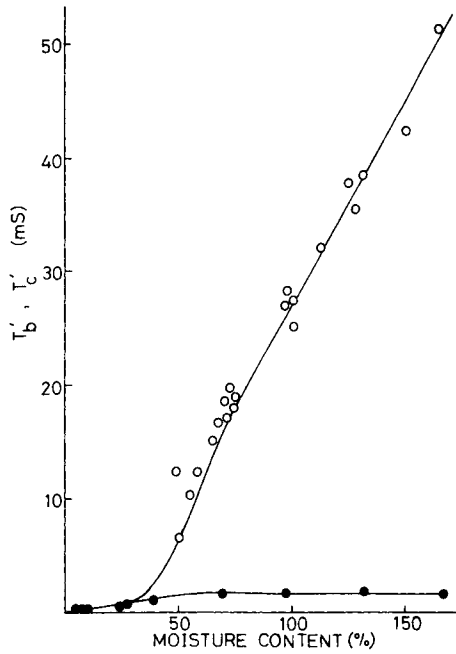
Fig. 2. Parameters T'_b (●) and T'_c (O) obtained from results like those shown in Fig. 1 are plotted vs. moisture content. The significance of the solid lines is discussed in the text.
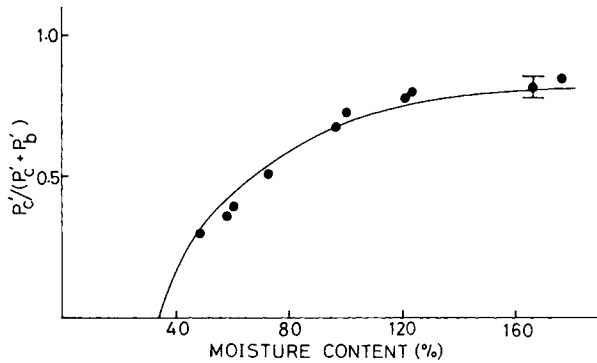

Fig. 3. Ratio $P'_c/(P'_c + P'_b)$ obtained from application of eq. (1) to the experimental results is shown as a function of moisture content of spruce. The significance of the solid line is given in the text.

protons. The possibility of chemical exchange between adsorbed and free water is allowed in this model. Denoting the rate of chemical exchange from phase i to phase j by C_{ij}, we therefore take $C_{ac} = C_{ca} = 0$ and suppose that C_{ab} and C_{bc} are independent of moisture content with

$$C_{ab} = (P_b/P_a)\, C_{ba} \tag{2}$$

and

$$C_{bc} = (P_c/P_b)\, C_{cb} \tag{3}$$

This analysis with $C_{ab} = 350\ \text{sec}^{-1}$, $C_{bc} = 90\ \text{sec}^{-1}$, $T_b^{-1} = 100\ \text{sec}^{-1}$, $T_c^{-1} = 0$, and $T_a^{-1} = 1.43 \times 10^5\ \text{sec}^{-1}$ yields the solid lines in Figure 2, which are seen to be in good accord with experiment. For pure water,[14] T_2 is about 2.4 sec at 25°C, so

the relative values of the relaxation times $T_c^{-1} > T_b^{-1} > T_a^{-1}$ are in agreement with *a priori* expectations, but for the phase model chosen here the calculations are more sensitive to $C_{ab} + T_b^{-1}$ than to individual values of either C_{ab} or T_b^{-1}. However, above 33% MC, T_c' is quite dependent on the rate of exchange of water between phases b and c. Hence, the value obtained for C_{bc} is regarded as somewhat more reliable than that quoted for C_{ab}. We also find that to a reasonable approximation the parameters P_b' and P_c' in eq. (1) are nearly equal to the fractional populations of the two phases (i.e., $P_b' \approx P_b$ and $P_c' \approx P_c$). Therefore, if all of the water in wood samples with moisture contents below the fiber saturation point were in the cell walls, then P_c, the fraction of water in the wood cell cavities, would be given by

$$P_c = [(M - 33)/M] (P_c + P_b) \qquad (4)$$

where M is the moisture content and the fiber saturation point[3] is 33%. This relation is shown by the solid curve in Figure 3 and is also in good agreement with experiment.

The steady-state NMR line shapes[18,21,22] of the water component of the wood–water system are nearly Lorentzian in shape and vary in full width at half-maximum from about 2450 Hz at 6% MC to 160 Hz at 155% MC. This dependence of linewidth on moisture content agrees qualitatively with previous results,[6,8] but the linewidth is considerably greater, particularly at high moisture contents, than predicted by the theory of chemical exchange[18] using exchange rates and relaxation times inferred from the Carr–Purcell experiment. This would seem to imply that the NMR proton absorption line shapes are inhomogeneously broadened due to a broad distribution of chemical shifts of the protons in many different magnetic environments within the wood–water mixture and that the linewidths do not reflect the real relaxation times of the system. Indeed, a displacement of the proton absorption maximum of water in wood from the corresponding maximum of pure liquid water has been observed previously.[6] Because chemical shifts do not affect the Carr–Purcell echo train for fast-pulse repetition rates, it therefore seems likely, in view of the very broad steady-state lines, that the relaxation times reported here actually represent complicated ensemble averages over many different "phases" of the system.

CONCLUSIONS

The wood–water system is an extremely complex one, so that it would be naive to suggest that the three-phase model used in this paper is anything better than a very crude approximation to reality. Nevertheless, the estimated rates of exchange between hydroxyl protons and protons on bound water and between bound and unbound water seem to be the right order of magnitude for such physical processes. Similar pulsed NMR techniques may be used to investigate other dynamic properties of water in wood. Measurement of the transverse relaxation times and the relative amounts of bound and free water in wood and pulp might be used to study the nature of the so-called fiber saturation point[23] in more detail than has been possible heretofore, but this would prove difficult near fiber saturation where the apparent relaxation rates in the adsorbed and free phases are about equal and hard to separate experimentally.

Appendix

In this Appendix we consider the spin echo envelope resulting from application of the Carr–Purcell B pulse sequence to a system having three phases, a, b, and c, each with different relaxation times T_a, T_b, and T_c with resonance frequencies ω_a, ω_b, and ω_c, respectively. The equilibrium populations of the phases are taken as P_a, P_b, and P_c, respectively, while the rate of chemical exchange from phase i to phase j is denoted by C_{ij} $(i, j = a, b, c)$. A generalization of Abragam's density matrix formulation[17,18] normally is used to calculate the spin echo amplitudes in a Carr–Purcell pulse experiment. The magnetization of the spin system at the $2n$th $(n = 1, 2, \ldots)$ echo is[19,20]

$$S(4n\tau) = 1 \cdot \mathbf{E}^{2n} \cdot \mathbf{W} \tag{A1}$$

where τ is the spacing between the $\pi/2$ and first π pulse,

$$1 = (1, 1, 1) \tag{A2}$$

$$\mathbf{W} = \begin{pmatrix} P_a \\ P_b \\ P_c \end{pmatrix} \tag{A3}$$

and $\mathbf{E}^{2n}$ is a matrix operator that describes the effect of the pulses on the spin system.[19] If the spacing between pulses is small, differences among ω_a, ω_b, and ω_c resulting from different chemical shifts cancel and

$$\mathbf{E}^{2n} \approx e^{4\mathbf{A}n\tau} \tag{A4}$$

where the relaxation matrix $\mathbf{A}$ is given by

$$\mathbf{A} = \begin{pmatrix} -\dfrac{1}{T_a} - C_{ab} - C_{ac} & C_{ba} & C_{ca} \\[2mm] C_{ab} & -\dfrac{1}{T_b} - C_{ba} - C_{bc} & C_{cb} \\[2mm] C_{ac} & C_{bc} & -\dfrac{1}{T_c} - C_{cb} - C_{ca} \end{pmatrix} \tag{A5}$$

Introducing $\mathbf{A}$ and $\mathbf{E}^{2n}$ into eq. (A1) after some algebraic manipulation, we obtain[17]

$$S = P'_a E^{-t/T'_a} + P'_b e^{-t/T'_b} + P'_c e^{-t/T'_c} \tag{A6}$$

for the even echo (i.e., echoes occurring at $t = 4n\tau$) decay envelope where the constants $(T'_a)^{-1}$, $(T'_b)^{-1}$, and $(T'_c)^{-1}$ are the eigenvalues of the relaxation matrix $\mathbf{A}$. A similar equation applies to the odd echoes at times $(2n - 1)2\tau$ $(n = 1, 2, \ldots)$ from the $\pi/2$ pulse. The eigenvalue equation,

$$\det(\mathbf{A} - \mathbf{I}/T') = 0 \tag{A7}$$

where $\mathbf{I}$ is the identity matrix, is cubic in $(1/T')$ and has three real unequal roots, $(T'_a)^{-1}$, $(T'_b)^{-1}$, and $(T'_c)^{-1}$, which easily are obtained either numerically or analytically. The analytic solutions of eq. (A7) are too complex to be given here, but it is clear from (A5) and (A7) that the apparent relaxation times T'_a, T'_b, and T'_c measured in the Carr–Purcell sequence are identically equal to the real relaxation times T_a, T_b, and T_c when all C_{ij} $(i, j = a, b, c)$ are zero. In general, amplitudes P'_a, P'_b, and P'_c are related to the relative populations of phases a, b, and c and to the eigenvalues of $\mathbf{A}$. However, for the special case of no exchange $(C_{ij} = 0)$, $\mathbf{A}$ is a diagonal matrix whose eigenvalues are the inverses of T_a, T_b, and T_c and the amplitudes P'_a, P'_b, and P'_c are equal to the equilibrium relative populations P_a, P_b, and P_c.

References

1. A. J. Panshin and C. H. deZeeuw, *Textbook of Wood Technology,* 3rd ed., McGraw Hill, New York, 1970.

2. U.S. Forest Products Laboratory, *Wood Handbook,* U.S. Agriculture Handbook No. 72 (rev.), U.S. Department of Agriculture, 1974.

3. C. Skaar, *Water in Wood,* Syracuse University Press, Syracuse, 1972.

4. T. M. Shaw and R. H. Elsken, *J. Chem. Phys.,* **18,** 1113 (1950).

5. A. J. Nanassy, *Wood Sci.,* **5,** 187 (1972).

6. J. E. Carles and A. M. Scallan, *J. Appl. Polym. Sci.,* **17,** 1855 (1973).

7. A. R. Sharp, M. T. Riggin, R. Kaiser, and M. H. Schneider, *Wood and Fibre,* **10,** 1 (1979).

8. A. Odajima, *J. Phys. Soc. Japan,* **14,** 308 (1959).

9. M. Sasaki, T. Kawai, A. Hirai, T. Hashi, and A. Odajima, *J. Phys. Soc. Jpn.,* **15,** 1652 (1960).

10. T. Swanson, E. O. Stejskal, and H. Tarkow, *Tappi,* **45,** 929 (1962).

11. A. J. Nanassy, *Wood Sci.,* **7,** 61 (1973).

12. R. A. Pittman and V. W. Tripp, *J. Polym. Sci.,* **8,** 969 (1970).

13. S. Meiboom and D. Gill, *Rev. Sci. Instr.,* **29,** 688 (1958).

14. H. Y. Carr and E. M. Purcell, *Phys. Rev.,* **94,** 630 (1954).

15. E. L. Hahn, *Phys. Rev.,* **80,** 580 (1950).

16. H. A. Resing, *Adv. Mol. Rel. Proc.,* **1,** 109 (1968).

17. R. Kubo, *J. Phys. Soc. Jpn.,* **9,** 935 (1954).

18. A. Abragam, *Principles of Nuclear Magnetism,* Oxford University Press, London, 1961.

19. M. Bloom, L. W. Reeves, and E. J. Wells, *J. Chem. Phys.,* **42,** 1615 (1965).

20. H. S. Gutowsky, R. L. Vold, and E. J. Wells, *J. Chem. Phys.,* **43,** 4107 (1965).

21. H. S. Gutowsky and A. Saika, *J. Chem. Phys.,* **21,** 1688 (1953).

22. T. J. Swift and R. E. Connick, *J. Chem. Phys.,* **37,** 307 (1962).

23. J. E. Stone and A. M. Scallan, *Tappi,* **50,** 496 (1967).