STUDY OF RESTRICTED DIFFUSION IN WOOD[1]

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ABSTRACT

An NMR study of restricted diffusion of water in Douglas-fir wood was undertaken using the pulsed field gradient method. The measurements were performed at 25 C and at two different moisture contents. Analysis of the results shows that the restricted diffusion of water molecules in this sample can be adequately described using a restricted diffusion model that considers diffusion to occur between infinite planar barriers. Two different barrier separations were incorporated into the model in order to obtain a good correspondence between the calculated and experimental results. Excellent agreement exists between parameters deduced from the NMR measurements and known anatomical data.

Keywords: Wood, nuclear magnetic resonance (NMR), restricted diffusion.

INTRODUCTION

Properties of wood are affected by moisture content. Moisture is dynamically associated with wood and therefore is usually nonuniformly distributed (macroscopically and microscopically). Predicting and controlling wood properties and behavior require understanding moisture behavior in wood at the molecular level.

A previous report (MacGregor et al. 1983) on the anisotropic diffusion of water in wood showed that water in wood undergoes restricted diffusion. Investigations of systems exhibiting restricted diffusion using the nuclear magnetic resonance (NMR) pulsed gradient spin-echo technique have been effective (Stejskal and Tanner 1965; Tanner and Stejskal 1968; Packer and Rees 1972; Lauffer 1974; Callaghan et al. 1979). In this study the pulsed gradient technique was applied to samples of Douglas-fir (*Pseudotsuga menziesii* (Mirb.) Franco) in order to determine its usefulness in gaining more understanding of the distribution and behavior of water in wood.

EXPERIMENTAL

Samples

Douglas-fir was chosen as an example of softwood with relatively uniform cell size and few rays.

Cylindrical samples of diameter 0.6 cm and length 1.5 cm were cut from larger blocks of wood. The cylinder axis of the sample was along the direction of the grain. Each sample contained earlywood and latewood—by volume, approxi-

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mately 45% earlywood and 55% latewood, as determined using a microscope. The Douglas-fir samples were immersed in water at room temperature for several months. They were then blotted to remove excess surface water, weighed, and flame sealed in 8 mm o.d. NMR sample tubes 5 cm in length. After sealing, each sample was allowed to equilibrate for several days prior to measurement. These were labelled the "partially saturated" samples.

After the NMR measurements, some of the samples were removed from the sample tube and again immersed in water. Vacuum pumping on the vessel containing the samples revealed that a certain amount of air was trapped in the wood. The vacuum was continued until no further air escaped from the wood. These samples were labelled "saturated." The saturated samples were blotted, weighed, and sealed in an NMR tube in a similar manner to the partially saturated samples.

Immersion of the Douglas-fir in water for extended periods of time is not sufficient to saturate it because bordered pits (interconnections) between tracheids aspirate. This aspiration (closure) severely restricts air and water mass flow. Mechanical aids (vacuum, pressure) are required to overcome the restrictions.

The moisture content of each sample was determined by oven drying at 105 C for 12 hours and reweighing. The moisture contents of the partially saturated and saturated Douglas-fir samples are $(82.3 \pm 0.5)\%$ and $(106.4 \pm 0.6)\%$, respectively.

NMR measurements

The pulsed field gradient spin-echo technique (Tanner and Stejskal 1968) is well suited for investigating restricted diffusion. The appropriate pulse sequence is the Hahn spin-echo pulse sequence (Hahn 1950), $90_x - \tau - 180_y$, where each of the two r.f. pulses is followed by a pulsed gradient g of duration δ in a direction parallel to the main magnetic field. For simplicity, consider diffusion bounded by two infinite planar barriers separated by a distance α. If the echo amplitudes in the absence and presence of the gradient pulse are $M(2\tau)$ and $M(2\tau, \delta, g)$, respectively, the spin-echo attenuation caused by restricted self-diffusion is given (Tanner and Stejskal 1968) by

$$\begin{aligned} R &= M(2\tau, \delta, g)/M(2\tau) \\ &= (2/\pi^2c^2)\{1 - \cos(\pi c) + 2 \sum_{n=1}^{\infty} \exp(-n^2\pi^2D(\tau - \delta/3)/\alpha^2) \\ &\qquad \times [1 - (-1)^n\cos(\pi c)]/[1 - (n/c)^2]^2\} \end{aligned} \tag{1}$$

where $c = \alpha \gamma \delta g/\pi$, γ is the nuclear gyromagnetic ratio and D is the self-diffusion coefficient. Information about α is obtained by measuring R as a function of τ and fitting Eq. (1) to the data.

NMR measurements were performed at 25 C and 40 MHz with a pulsed NMR spectrometer built in this laboratory. The pulsed field gradient was produced by a quadrupole coil (Assink 1976) powered by a Kepco Model BOP 15-20M operational power amplifier. This system is capable of providing any desired field gradient amplitude up to 100 G/cm.

The spin-echoes were recorded with a Nicolet 1170 signal averager. Up to 4,096

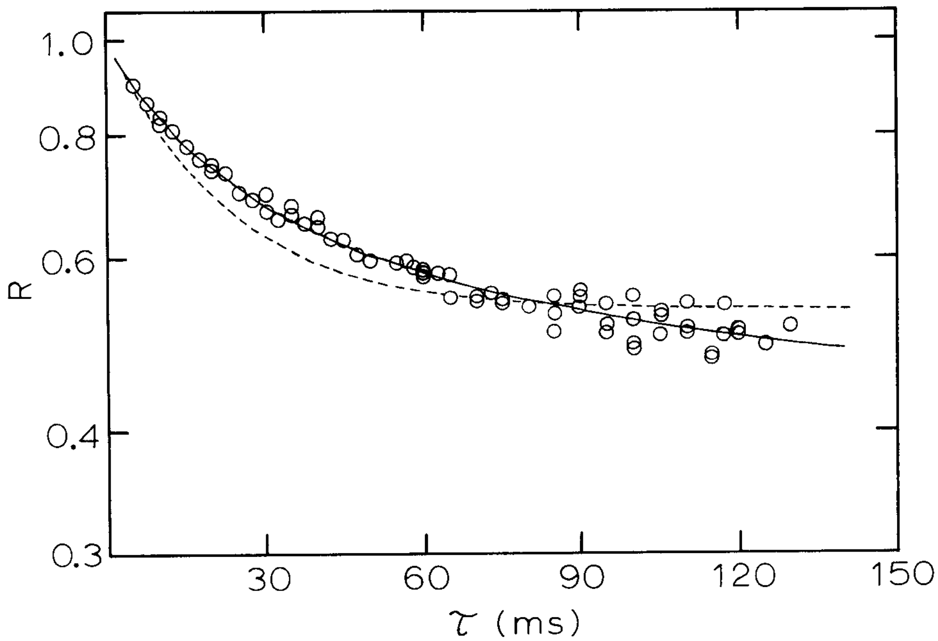

FIG. 1. Spin-echo attenuation R versus τ in partially saturated Douglas-fir wood. In this experiment g = 46.9 G/cm and δ = 1 msec. The dashed line represents a fit of the data to Eq. (1) with α = (21 ± 6) microns. The solid line is calculated from R_{OBS} = 0.46 R (9 microns) + 0.64 R (44 microns).

accumulations were used in the experiments in order to improve the signal-to-noise ratio of the echo.

The field gradients were calibrated using the method of Murday (1973) and have an uncertainty not exceeding ±2% associated with them. When the apparatus was used to measure the diffusion coefficient of pure water at 25 C, a value of $(2.2 \pm 0.1) \times 10^{-5}$ cm^2/sec was obtained. This is in agreement with published results (Simpson and Carr 1958).

RESULTS AND DISCUSSION

Partially saturated sample

Figure 1 shows a plot of R as a function of τ for the partially saturated sample of Douglas-fir. The sample was oriented such that the long axis of the wood cells was perpendicular to the field gradient direction. R appears to approach an asymptotic value at the larger values of τ shown. It has been pointed out (Tanner and Stejskal 1968) that such behavior can be due either to the presence of a fraction of water that has a much smaller diffusion coefficient than the remaining water fraction or the presence of water undergoing restricted diffusion. In a recent investigation (MacGregor et al. 1983) of the anisotropic diffusion of water in wood, it was concluded that water undergoes restricted diffusion in the direction perpendicular to the long axis of the wood cells in Douglas-fir. The results (Fig. 1) were analyzed using the simple model of diffusion between two parallel planes as described by Eq. (1).

TABLE 1. *Summary of NMR results for Douglas-fir.*

Sample	α_1 (μm)	f	α_2 (μm)	1 − f
Partially saturated Douglas-fir	9 ± 2	0.46 ± 0.07	44 ± 5	0.54 ± 0.07
Saturated Douglas-fir	9 ± 2	0.30 ± 0.05	52 ± 5	0.70 ± 0.05

The choice of g used in these experiments warrants a comment. The gradient strength is chosen such that values of R cover a reasonable range. For the partially saturated Douglas-fir sample, a g value of 47 G/cm appeared satisfactory (Fig. 1).

The dashed line in Fig. 1 was calculated from Eq. (1) using a least-squares curve fitting routine (Bevington 1969). The parameter α was adjusted to produce the best fit, and the final values are given in the figure caption. The bulk water value (Simpson and Carr 1958) for $D = 2.2 \times 10^{-5}$ cm^2/sec was used in the calculations. It has been shown previously (MacGregor et al. 1983) that this value is representative of the diffusion coefficient of water in wood (excluding the water in cell walls, which is not observed here due to its short T_2). Equation (1) does not provide a good fit for the partially saturated Douglas-fir (Fig. 1). The Douglas-fir sample consists of earlywood and latewood which are made up of longitudinal cells of considerably different diameters (Panshin and deZeeuw 1980). The poor fit of these data to the simple model, Eq. (1), appears to be a consequence of this.

The simple model, Eq. (1), can be improved by assuming that two different fractions of water, each undergoing restricted diffusion to a different extent, contribute to the observed signals. Assuming that the protons associated with each water fraction have the same spin-spin relaxation time (Riggin et al. 1979), the observed spin-echo attenuation becomes

$$R_{OBS} = fR(\alpha_1) + (1 - f)R(\alpha_2) \tag{2}$$

where $R(\alpha_1)$ is the echo attenuation of the water fraction f with effective barrier separation α_1, and $R(\alpha_2)$ is the echo attenuation of the remaining water with effective barrier separation α_2. The solid line in Fig. 1 represents the fit of the

TABLE 2. *Known anatomical data for Douglas-fir.*

	Earlywood	Latewood
Longitudinal cell diameter (microns)	35–60	7–15
Volume of longitudinal cells	45% of 92.4 ~42	55% of 92.4 ~51
Longitudinal cell-wall material (% of unit volume)	~2	~75
Ray cell diameter	7–12	
Volume of rays	7.2	
Ray cell-wall material (% of unit volume)	~40	

Note: Volumes are expressed as percent of total sample volume. Parameters in this table are taken from Panshin and deZeeuw (1980). A brief examination of these samples was also made under a microscope. No major deviation between values estimated this way and those given by Panshin and deZeeuw (1980) were observed.

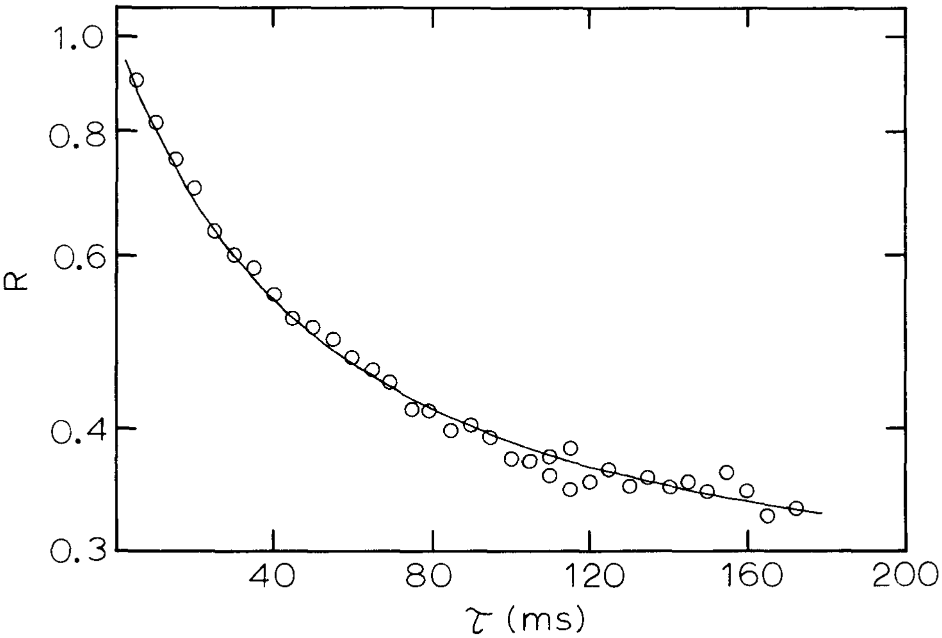

FIG. 2. R versus τ in saturated Douglas-fir wood. The experimental conditions are the same as in Fig. 1. The solid line was calculated using R_{OBS} = 0.30 R (9 microns) + 0.70 R (52 microns).

data to Eq. (2) in conjunction with Eq. (1). The fit is good. The parameters of the fit are given in the figure caption and in Table 1. A reasonable correspondence exists between α_1, α_2 and known Douglas-fir anatomical structure (Table 2). The parameters $\alpha_1 = (9 \pm 2)$ microns and $\alpha_2 = (44 \pm 5)$ microns can be associated with the tangential diameters of longitudinal tracheids of late- and earlywood, respectively (Table 1 and Table 2).

Saturated sample

R values plotted as a function of τ for saturated Douglas-fir are shown in Fig. 2. The R value at a particular value of τ is smaller than that obtained for the partially saturated sample. This is very noticeable at larger τ values. Thus, a major fraction of the water added to the sample, upon pumping, sees an effective barrier-to-barrier distance that is larger than the small spacing parameter (α_1) deduced for the partially saturated samples (Table 1). Immersion without vacuum, therefore, appears to fill the cells having smaller diameters (where capillary tension would be greatest) preferentially.

Upon pumping, it is expected that smaller wood cells already filled with water by immersion will remain filled and others, mainly larger ones, will also fill with water. This suggests that a reasonable approach for analyzing the data (Fig. 2) is to apply Eq. (2) but incorporate the information about the spacing parameters obtained from the partially saturated sample into the analysis. The accuracy with which a particular barrier separation can be obtained depends upon the size of the fraction of water that sees such a separation. The fraction of water with the small spacing parameter α_1 is less in the saturated samples than in the partially saturated samples (compare Fig. 2 with Fig. 1). Therefore the value of α_1 from the partially saturated sample is incorporated into the analysis of the saturated sample. The fitting routine is used to optimize α_2 and the new fraction f.

The solid line in Fig. 2 is a fit of the data to Eq. (2) where α_1 was taken from Table 1 (partially saturated Douglas-fir). Parameters obtained from the fit are given in the figure caption and Table 1. The fit is good. The value of $\alpha_2 = (52 \pm 5)$ microns corresponds well to that obtained from the analysis of the partially saturated sample and to the average diameter of the longitudinal tracheids in the earlywood of Douglas-fir.

The fractions f and $(1 - f)$ used in Eq. (2) do not correspond directly to the fractional volumes occupied by particular cell types in the saturated sample. This is because the fractional volume occupied by cell-wall material in a given unit volume of wood is different in the latewood compared to that in the earlywood. These fractional volumes were estimated for latewood and earlywood in Douglas-fir from data given by Panshin and deZeeuw (1980, Fig. 11-58) and are given in Table 2. Using the information in Table 2, the fractions f and $(1 - f)$ can be estimated from the known anatomical data.

Considering that water in latewood tracheids and ray cells in Douglas-fir contribute to the fraction f and water in the earlywood tracheids to $(1 - f)$, the estimate from Table 2 is that $f \sim 0.29$ and $(1 - f) \sim 0.71$. These values are in excellent agreement with the values derived from the NMR results, $f = 0.3$ and $(1 - f) = 0.7$, for saturated Douglas-fir in Table 1.

The good agreement between the NMR results and anatomical data requires comment. Although the longitudinal tracheids in latewood and earlywood each have relatively uniform tangential diameters, it is clear from data given by Panshin and deZeeuw (1980, Fig. 11-58) that a distribution of tracheid diameters exists in this wood. The good agreement obtained, using Eq. (2) in which the distribution is taken as the sum of two delta functions, suggests that the width of the distribution for early and late Douglas-fir wood is small compared to the average diameters.

CONCLUSIONS

Within experimental error, the cell diameters and volumetric fractions obtained by NMR of latewood and earlywood in Douglas-fir were found to correspond well to known anatomical data. It is clear from this study that the pulsed gradient approach can be used to obtain quantitative information about the water-containing compartments in wood. Presently, restricted diffusion studies in other kinds of wood are being undertaken in this laboratory in conjunction with nuclear spin relaxation analysis. Such a combined investigation has the potential of increasing understanding of the distribution of water and its dynamics in wood.

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