WATER STATES IN YELLOW POPLAR DURING DRYING STUDIED BY TIME-DOMAIN NUCLEAR MAGNETIC RESONANCE

Minghui Zhang†
Professor
E-mail: zhangminghui@imau.edu.cn

Ximing Wang
Professor
College of Materials Science and Art Design
Inner Mongolia Agricultural University
Hohhot, P.R. China, 010018
E-mail: wangximing@imau.edu.cn

*Rado Gazo**†
Professor of Wood Processing–Industrial Engineering
Department of Forestry and Natural Resources
Purdue University
West Lafayette IN, 47907-2083
E-mail: gazo@purdue.edu

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Abstract. The time-domain nuclear magnetic resonance (NMR) technique can easily distinguish water states according to spin–spin relaxation time and can give more quantitative information on water in wood than any other method. In this study, water states in yellow poplar were investigated with a time-domain NMR technique. Water migration during drying was also analyzed. The results of this study show that yellow poplar has five components in water states (bound and free water) according to spin–spin relaxation time at moisture contents greater than 100%. The number of different water states decreased with decreasing moisture content. The longest spin–spin relaxation time was about 400 ms for free water, and the shortest was about 1 ms for bound water. With the NMR resonance technique, water states in yellow poplar drying are distinguished easily and migration from one water state to another can be analyzed quantitatively. This technique can benefit wood drying modeling and simulation.

Keywords: Water state, migration, NMR, relaxation time.

INTRODUCTION

Wood is a natural polymer material whose physical properties are decided not only by its chemical composition and lignocellulosic structures, but also by the amount of moisture contained within it. Water in wood was extensively studied by many researchers in past decades. Most of them studied bound and free water separately, because it was difficult to identify these two water states simultaneously (Skaar 1988). That is why some studies of moisture adsorption below the FSP ignored free water transformation into bound water during water migration (Zhang et al 2006, 2007). Today, time-domain nuclear magnetic resonance (TD-NMR) can provide more quantitative information on water in wood than any other method (Araujo et al 1992). Recently, Engelund et al (2013) provided a detailed review of research on water states in wood, including the TD-NMR method.

Nuclear magnetic resonance (NMR) relaxation is a powerful tool for understanding wood structure and dynamics of water in wood because abundant hydrogen nuclei in both wood chemical

* Corresponding author
† SWST member

composition and water can be detected by TD-NMR techniques. The hydrogen nucleus is composed of a single proton. It has a positive charge and a property known as nuclear spin. The combination produces a magnetic moment (μ). The spin–spin interaction causes individual magnetic moments to have different magnetic environments and this can be detected by an NMR instrument. Two important pieces of information can be obtained from a TD-NMR signal: 1) more NMR signals from free induction decay (FID) curves means more nuclei in the sample; and 2) the rate of decay (spin–spin relaxation time) is related to mobility of molecules. That is why liquids have longer decay times than solids. TD-NMR techniques are widely used in wood studies because they are quick, nondestructive, and quantitative. Most of these studies are related to moisture content determination (Nanassy 1976; Sharp et al 1978; Hartley et al 1994; Thygesen 1996; Casieri et al 2004; Merela et al 2009) and characterization of water in wood (Menon et al 1987; Araujo et al 1992; Labbe et al 2006; Cox et al 2010).

The loss of bound and free water in wood during drying is studied independently from each other, because it is difficult to identify these two water states simultaneously with traditional methods. TD-NMR can easily distinguish among the water states based on spin–spin relaxation times. It can also give more quantitative information on water in wood because bound water has short T2 (spin–spin relaxation time) values with a few milliseconds, whereas free water has T2 values from tens to more than 100 ms (Menon et al 1987). The continuous distribution of relaxation times instead of the limited sum of discrete T2 values is better explained by the continuous distribution of the wood cell sizes (Araujo et al 1992; Li and Odberg 1993). Because the amplitude of the magnetization is proportional to the number of protons, the amount of different water components as well as the percentage can be determined from the signal integrals, and thereafter, we can use this approach to investigate water states and migration during yellow poplar drying.

MATERIALS AND METHODS

A cylindrical sample of approximately 10-mm diameter and 20-mm length (longitudinal direction) was cut from the heartwood of a fresh yellow poplar disk. The sample was then weighed. FID and spin–spin relaxation time data were collected every hour automatically with a Bruker Minispec mq20 NMR (Billerica, MA) console operating at 22.6 MHz and using a custom-built magnetic body. Spin–spin relaxation time was measured using the Carr Purcell Meiboom Gill sequence with an echo time of 0.4 ms, and the data were acquired with a setting of 3000 echoes. The dead time was 10 μs. The experiment was performed at 40°C. Change in the sample weight was recorded at regular time intervals during drying. After the magnetic resonance experiment was completed, the sample was put into a 105°C oven for 24 h to obtain oven-dried weight, thus enabling us to obtain the relationship between moisture content determined gravimetrically and by NMR signal amplitude. Because a moisture gradient was present during drying, the reported sample moisture content values were average values.

RESULTS AND DISCUSSION

Water States during Drying

Figure 1a-b shows continuous spin–spin relaxation time distribution during drying at two different moisture contents, representing different components in water states.

At the initial moisture content of 112%, the sample displayed five components in water states. At 7.1% MC, the sample displayed only one component in the bound water state. According to Cox et al (2010), spin–spin relaxation time for bound water was between 1 and 10 ms and for free water was 10 ms and greater, whereas wood proton relaxation time was about 10-15 μs. Figure 1b shows a much shorter bound water component than 1-10 ms. That means the bound water became more restricted in motion. This component did not exist when the sample was at higher moisture content levels.

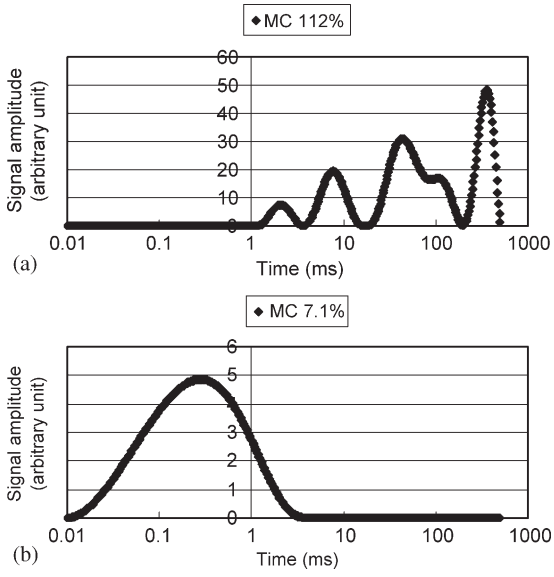

Figure 1. Spin–spin relaxation profile at (a) 112% average MC; (b) 7.1% average MC.

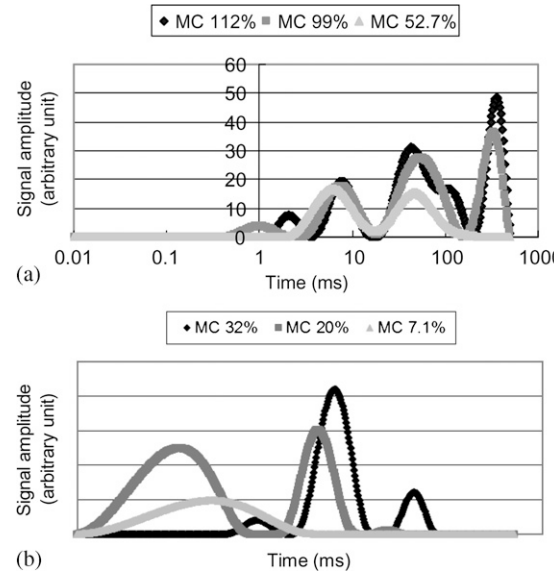

Figure 2. Spin–spin relaxation time profile during drying at different average moisture content from (a) 112 to 52.7%; and (b) 32 to 7.1%.

Table 1 shows the spin–spin relaxation time distribution for yellow poplar at 112% MC and 40°C temperature during drying.

From Fig 2a-b, the water state distribution changes are apparent. The relaxation times became shorter with decreasing average moisture content. The free water components were lost quickly from 112 to 32% average MC, especially for long relaxation times. Although the relaxation times below 10 ms change in this average moisture content range, the amount of change was small and basically stayed constant, whereas the amount of change for bound water components was obvious from 32 to 7.1% average MC.

The number of water components during drying was related to moisture content, and it changed with time. Figures 1a-b and 2a-b show that there were five water components at 112% MC, four at 99% MC, three at 32% MC, two at 52.7 and 20% MC, and one at 7.10% MC.

Water Migration during Drying

Figure 3 is a typical FID curve for the sample with 4% MC. The steep-sloped portion of the curve was associated with fast magnetic decay of wood protons, whereas the slow decaying portion of the curve was associated with water protons. The water signal starts to decay from 60 to 70 μs (Xu et al 1996).

Because signal amplitude is proportional to the number of protons, it is reasonable to calculate moisture content through NMR signal amplitude. Figure 4 shows the relationship between moisture content determined gravimetrically and NMR signal amplitude. This is a highly linear relationship with $R^2 = 0.998$. Therefore,

Table 1. Spin-spin relaxation time distribution for yellow poplar at 112% MC.

Bound water		Free water		
Component A	Component B	Component C	Component D	Component E
1.15–3.56	3.72–16.62	18.12–72.59	73.46–176.59	180.46–499.99

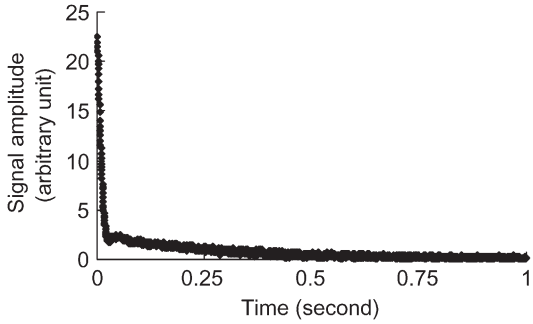

Figure 3. Yellow poplar free induction decay curve for 4% MC.

we can obtain an average moisture content of a sample anytime during drying through this regression line.

Figure 5a shows the yellow poplar sample average moisture content changes with drying time at 40°C. Moisture is lost very quickly at the beginning of drying and begins to slow down at about 20% average MC. It appears that the curve can be divided into two parts: one part apparently follows a linear function, and the other apparently follows an exponential function. The transition point is at 20% average MC. The drying time at that point is 150 h.

The regressions for these two parts are made separately to verify the previous statements. Results from Fig 5b-c show that it is highly linear between moisture content and drying time for the first 150 h with $R^2 = 0.9994$ followed by an exponential function after 150 h with $R^2 = 0.9665$.

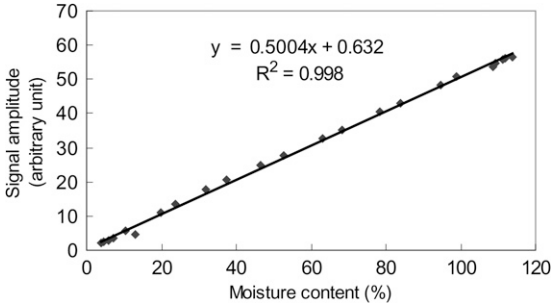

Figure 4. Relationship between moisture content determined gravimetrically and nuclear magnetic resonance signal amplitude.

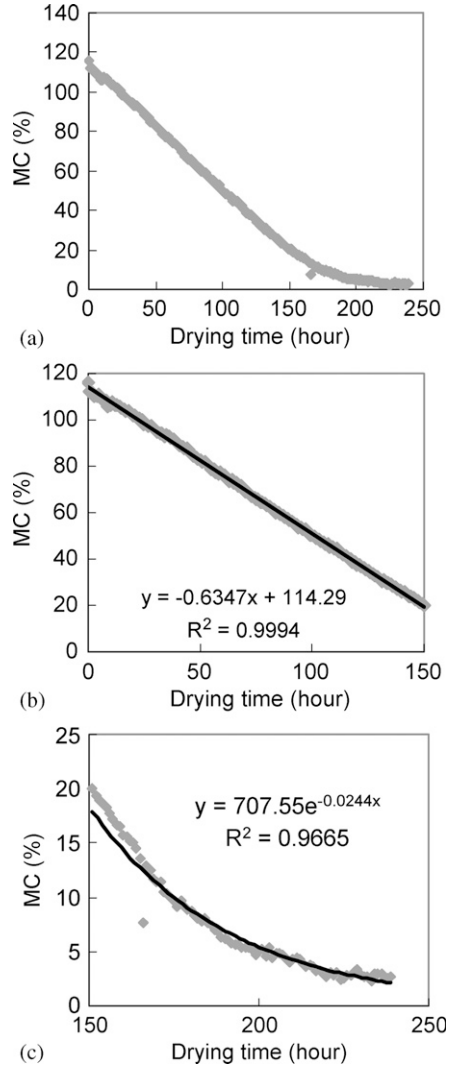

Figure 5. Yellow poplar sample average moisture content change (a) with drying time, (b) during the first 150 h, and (c) after the first 150 h.

Free water is mostly lost during the first 150 h. This can also be seen from Fig 2b because the T2 values are all less than 10 ms. Because 20% average MC is lower than FSP, some bound water is also lost during this time. Relaxation times became shorter with decreasing average moisture content. This means that the hydrogen bond between a water molecule and the wood substance was becoming tighter, which resulted in more restricted molecular motion.

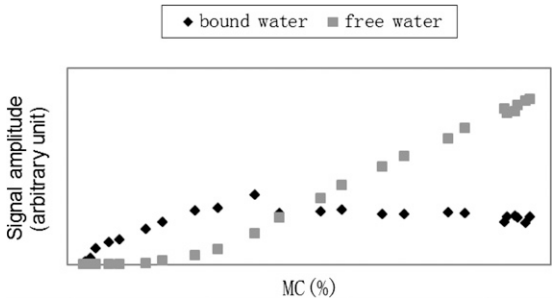

Figure 6. Signal integrals change of free and bound water during drying.

Because the amplitude of the magnetization is proportional to the number of protons, the signal integrals according to relaxation time distributions reflect the amount of different water states as well as the percentage. Figure 6 shows the change in the signal integrals of free and bound water during drying. Apparently, bound water does not change very much above 50% MC. Between 46 and 50%, the bound water increases with decreasing moisture content. One explanation for this could be the Barkas effect, a process during which the stress resulting from the drying process decreases the amount of bound water quickly because of cracks developing in the sample (Simpson and Skaar 1968). The bound water amount starts to drop below about 46% average MC.

CONCLUSIONS

It has been shown that the TD-NMR technique is a powerful tool for distinguishing water states through spin–spin relaxation times during wood drying. Based on this study, the following conclusions can be made about water states and migration in yellow poplar samples during drying at 40°C:

1. Yellow poplar has five components in water states (bound and free water) according to spin–spin relaxation time values at moisture contents greater than 100%.
2. Water states in wood will change with drying time. The relaxation times will get shorter with decreasing moisture content.
3. Water migration in yellow poplar drying can be divided into two phases; one follows linear function and the other an exponential function.
4. The amount of bound water does not change significantly above 50% average MC.

ACKNOWLEDGMENTS

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