An Investigation of the Drying Rate of Water in Wood at Different Relative Humidities Studied by Time Domain Nuclear Magnetic Resonance

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The wood drying rate was determined at five different relative humidities (RHs) using time domain nuclear magnetic resonance (TD-NMR). The objective of this study was to obtain the drying rate of bound water and free water, and to also build a relation between RH and drying rate. Two kinds of wood species, Qingpi poplar (*Populus platyphylla* var. *glauca*) and *Pinus sylvestris* var. *mongolica* Litv. were employed for the spin-spin relaxation time (T2) measurement. The mass of free water and bound water during drying were obtained at the same time. The results indicated that the poplar specimens had a higher fiber saturation point (FSP). For both wood species, free water decreases quickly, which contributes to the main drying, especially at the beginning of drying, and still exists even when the moisture content (MC) is below the FSP. Bound water decreases slowly, and its equilibrium content ranges from less than 10% to more than 20%, in the order from lower RH to higher RH. In addition, the drying rate decreases linearly with increasing RH.

Keywords: Drying rate; Relative humidity; Bound water; Free water; TD-NMR

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INTRODUCTION

There are two different water states in wood, free water and bound water. Free water can move from one place to another in big pores, such as cell lumens, yet bound water combines tightly with hydroxyl groups in smaller pores, such as cell walls. Normally, wood should be dried before it is used for all applications. Wood drying is a process of energy absorption and moisture removal. It is widely recognized that the drying process improves the mechanical characteristics of wooden components and protects them from biological attack (Reuss *et al*. 1997; Ouertani and Azzouz 2011). It is an essential step in wood products processing.

Many drying methods have been applied in industry, such as conventional drying, microwave drying, high-frequency drying, and hot-air drying. However, one of the most commonly used methods is still conventional drying because of its low-tech and low-cost characteristics. Unfortunately, the temperature and moisture content gradients caused by the heat and mass transfer processes easily generate defects, which include cracking, bowing, warping, twisting, collapse, surface checking, and splitting (Ouertani *et al*. 2015). Therefore, to avoid these defects, the drying process needs to be adjusted. Increasing the heat and humidity during wood drying has been used to reduce these defects (Pang and Pearson 2004; Srinivas and Pandey 2012). Because an appropriate increase in temperature and relative humidity can effectively balance the temperature gradient and moisture content

gradient of wood, thus ensuring a fast and uniform drying rate, the probability of drying stress generation is greatly reduced, and hence the drying defects can be effectively reduced.

Assuredly, the RH plays an important role in the wood drying process. In the early stages of kiln drying, low temperatures (below 45 °C) and high RH (above 75%) are recommended in the presence of liquid water (Ciniglio 1998; Andrade 2000). Möttönen (2006) investigated the variation in drying behavior and final moisture content of *Betula pendula* during conventional low-temperature drying. The results indicated that the variation in RH clearly affected the drying rate during the first steps of the drying process (Möttönen 2006). Recently, the effect of the desorption rate on the wood shrinkage under different RHs has been studied, and it turns out that the shrinkage from 58% to 0% RH was not affected by the desorption rates (Passarini and Hernández 2016). Moreover, some researchers have studied the relationship between heat treatment temperature and equilibrium moisture content (EMC) at different RHs, and the results show that the difference in EMC among samples treated at each temperature was larger at lower RH conditions (Miyoshi *et al*. 2015).

Although the influences of RH on wood drying have been studied, the traditional methods failed to separately evaluate the free water and bound water at the same time. The most popular method for investigating moisture content in wood is the nuclear magnetic resonance (NMR) technique; as a nondestructive and effective determination, it has been used for the determination of moisture content for some time (Nanassy 1976; Sharp *et al*. 1978). Moreover, the free water and bound water NMR relaxation properties can be identified simultaneously using NMR (Schmidt 1991; Araujo *et al*. 1992). Generally, free water connects with wood loosely and has spin-spin relaxation time (T2) values from tens to more than 100 ms. The bound water connects with wood tightly and has short T2 values with a few milliseconds (Menon *et al*. 1987; Araujo *et al*. 1992).

The previous publications concerning water in wood during drying studied by NMR primarily focused on the water state and moisture distribution (Thygesen and Elder 2009; Zhang *et al*. 2013). To our knowledge, only a few references have been published investigating the influence of RH on drying rate (Awoyemi 2004; Sova *et al*. 2016), but they failed to achieve the drying rate of free water and bound water simultaneously. Hence, the main motivation in the present study is to examine the drying rate of free water and bound water during drying under different RHs and to determine its significance for wood drying.

EXPERIMENTAL

Saturated Salt Solution Preparation

In the present study, five saturated salt solutions, including magnesium chloride ($MgCl_2$), sodium bromide (NaBr), sodium nitrate ($NaNO_3$), potassium chloride (KCl), and potassium sulfate (K_2SO_4), were used in the construction of the drying conditions at various RHs. The RH values are listed in Table 1. The five metal salts were purchased from Tianjin Beilian Fine Chemicals Development Co. Ltd., in China, and all salt purities were greater than 99%. The procedure for preparing a hydrostatic solution was followed according to the OIML R121 standard (OMIL 1996). Moreover, five drying vessels were arranged for the saturated salt solutions. The cap edges of the vessels were smeared with Vaseline to generate an enclosed space. All vessels were heated in an oven to ensure the temperature

in the vessels remained stable at approximately 40±1 °C, the same as the unmodifiable temperature in the probe of the NMR spectrometer.

Sample Preparation

Cylindrical sapwood samples, with diameters of approximately 12 mm and lengths (longitudinal direction) of 20 mm, were cut from green Qingpi poplar and *Pinus sylvestris*, respectively. Both of the wood species were harvested in Hohhot, China.

Five samples of each species were first immersed in distilled water for water-saturation, in a vacuum (-0.084 MPa) for 24 h at room temperature. Secondly, they were wiped, removing excess water on the sample surface, and were wrapped with parafilm to prevent moisture evaporation. Furthermore, both ends of the samples were sealed with Loctite® M-31CL adhesive (Henkel, Germany) to prevent water evaporation in the axial direction. It has been confirmed that the adhesive used in the present study has a very short T2 relaxation time and does not provide an effective nuclear relaxation for the NMR measurement. Finally, the samples were left at room temperature for 12 h, until the adhesive was cured, then placed in a refrigerator (2 °C) to prevent moisture evaporation at room temperature.

Method

Before NMR measurements, the samples were taken from the refrigerator and numbered as ①, ②, ③, ④, and ⑤, which corresponded to the drying humidity from low to high. The samples were first thawed at room temperature for 40 min; after that, the parafilm was removed and the samples were weighed before the NMR experiment.

The T2 measurements for each sample were conducted with a Bruker Minispec mq20 NMR spectrometer (Bruker, Germany). The console operated at 19.95 MHz inside the magnetic body, and the dead time for the probe was 4.5 μs. The T2 measurements were carried out using the CPMG (Carr-Purcell-Meiboom-Gill) sequence with 16 scans. An echo time of 0.2 ms was always used, and 3000 echoes were set for initial measurement; in reality, however, the echoes decreased discreetly during the actual drying process. Furthermore, all samples were weighed before and after the measurements until reaching moisture equilibrium at each RH; by that time, all samples had been oven-dried at 105 °C for 24 h.

The T2 decay curves were fitted using a three-order/two-order/first-order exponential decay function, depending on the specific data, with Origin® Pro 9.1 (Version 91E; Origin Lab Corporation, Northampton, MA).

RESULTS AND DISCUSSION

Table 1 lists the information about drying condition, initial MC, and EMC of the poplar and *Pinus sylvestris*. It can be seen that the poplar had a higher initial MC and EMC. Hence, it was concluded that the *Pinus sylvestris* was easier to dry.

Generally, there are three water states in wood. The water in the cell walls connected with hydroxyl groups is restricted in movement and is considered to be bound water. Ordinarily, the T2 relaxation time is less than 10 ms. Moreover, there are two different types of free water. One is the free water in large cell lumens, and the other is the free water in small cell lumens.

The different pore sizes affect water molecule movement and nuclear magnetic properties. Normally, free water in large pores has a longer NMR T2 relaxation time of more than 100 ms, but the fraction in the small pores had a shorter T2 of approximately 50 ms (Menon *et al*. 1989).

Table 1. Initial MC and EMC of Poplar and *Pinus sylvestris* Dried at Various RHs

Wood	Saturated salt solutions	Temperature (°C)	RH (%)	Initial MC (%)	EMC (%)
Poplar	$MgCl_2$	40	31.6	170.1	8.9
	NaBr		53.2	172.2	9.6
	$NaNO_3$		71	173.5	14.1
	KCl		83.2	168.2	20.5
	K_2SO_4		96.4	167.1	26.8
Pinus sylvestris	$MgCl_2$	40	31.6	132.6	7.8
	NaBr		53.2	122.1	8.5
	$NaNO_3$		71	107.2	12.4
	KCl		83.2	120.0	15.4
	K_2SO_4		96.4	123.2	17.4

In this study, the original T2 decay curves were inversed by the following exponential function (Eq 1),

$$S = \sum_{i=1}^{n} [A_i \times \exp(\frac{X}{T_{2i}})], n = 1,2,3 \quad (1)$$

where S is the signal intensity; $T2_i$ is the T2 relaxation time of the i^{th} water component; generally, n=3 was assigned at high MC, especially during the first several hours of drying, and n=1 was assigned at low MC, normally at the end of drying. A_i is the proportion of the i^{th} water component. X is the interval between two 180° pulses in the CPMG sequence. Both $T2_i$ and A_i were obtained for the subsequent analysis.

Figure 1 shows the change in total water, bound water, and free water in Qingpi poplar during drying at five RHs. It can be seen that higher RH prolonged the drying time. In addition, it should be noted that the EMC increased with higher RH, which indicates that the moisture evaporation becomes increasingly limited with higher RH.

The initial bound water content was calculated to be approximately 25% to 30%, which is close to the average FSP of 30%. The initial free water content ranged from 140% to 150%, and it had a similar drying tendency compared with the drying of total water, which indicated that water drying mostly derives from free water. Additionally, free water still existed when the MC was below the FSP. It can be completely evaporated at the first three RHs, yet there was still a residual at the latter two RHs, which is corroborated by previous research (Passarini *et al*. 2015; Passarini and Hernández 2016). Different from free water, bound water has a slower drying rate, and the drying was continuous during the whole process. The EMC of bound water was less than 10% at 31.6% and 53.2% RH, 14% and 20% at 71% and 83.2% RH, and more than 25% at 96.4% RH.

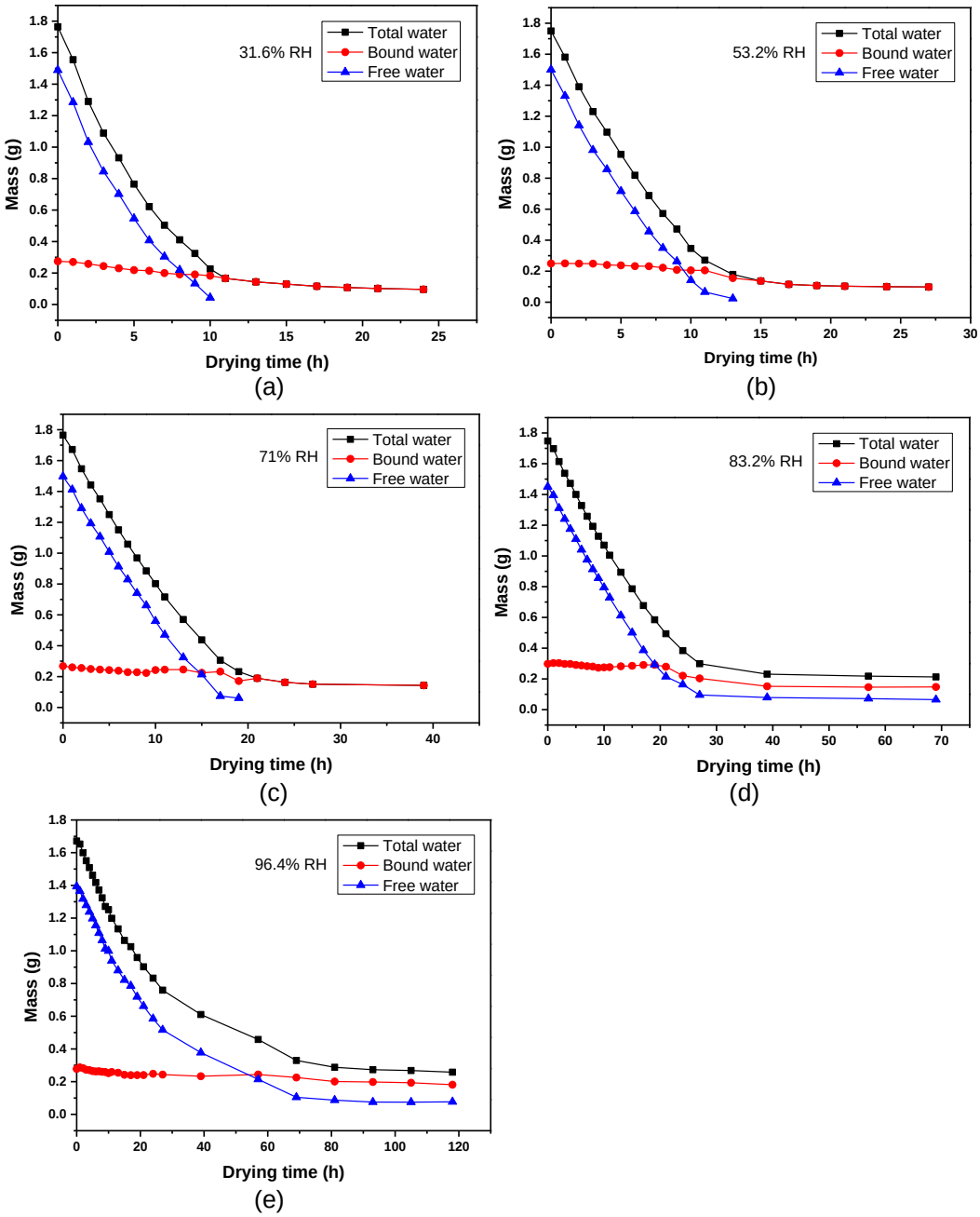

Fig. 1. The change of total water, bound water, and free water in poplar during drying: a, b, c, d and e are the water changes in the order from low to high in RH

Figure 2 shows the drying of total water, bound water, and free water in *Pinus sylvestris* at five different RHs. The MC calculation results revealed that *Pinus sylvestris* had a lower FSP (about 20%) compared with poplar, and its EMC was less than 10% at 31.6% and 53.2% RH, 12.4% at 71% RH, and more than 15% at 83.2% and 96.4% RH. Moreover, the initial free water content ranged from approximately 90% to 110%. Similarly, there also was free water present when the MC was below the FSP, but different from poplar, it could be totally evaporated at all five RHs.

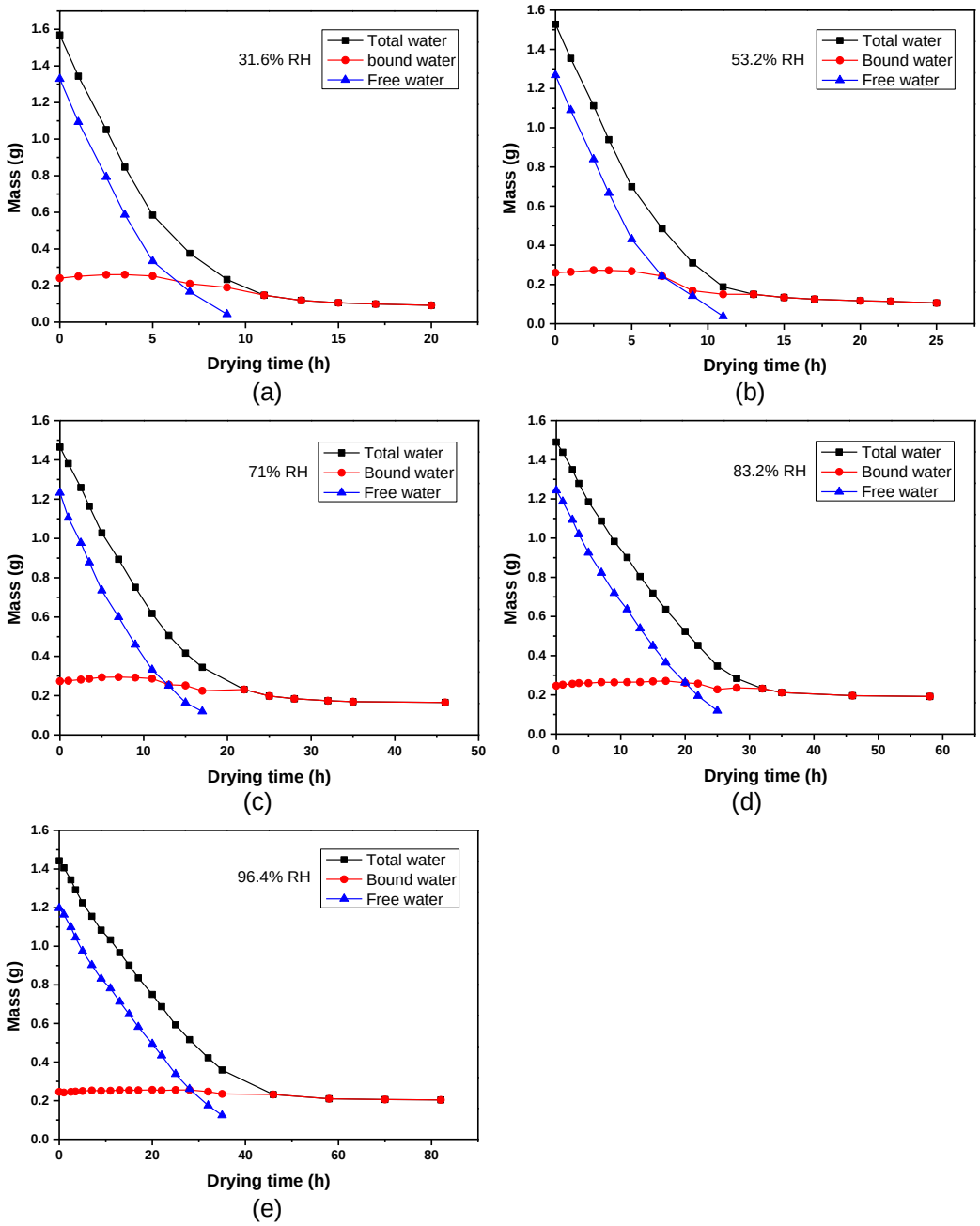

Fig. 2. The change of total water, bound water, and free water in *Pinus sylvestris* during drying: a, b, c, d and e are the water changes in the order from low to high in RH

It was observed that free water has a faster drying rate and linearly decreases during the drying process, except for the two exceptions at 83.2% and 96.4% RH, as shown in the last two graphs in Fig. 1. In this study, the last three and five data points were removed from the free water drying curve of 83.2% and 96.4% RH, respectively, because they had little effect on the drying curves, making a linear fit reasonable. In addition, all free water drying curves in Figs. 1 and 2 were fitted with linear functions as follows (Eq. 2):

$$y = a + b * x \quad (2)$$

where y is the water mass and x is the drying time; b is the average drying rate of free water.

Bound water decreased slowly, and its drying curves were more appropriately fitted by a logistic function as follows (Eq. 3),

$$y = A_2 + \frac{A_1 - A_2}{1 + \left(\frac{x}{x_0}\right)^P} \quad (3)$$

where A_1 is the initial bound water mass and A_2 is the final bound water mass, x_0 is the drying time taken to reach 50% of the initial water mass, P is the power and it is no physical meaning.

The drying rate can be calculated by taking the derivative of Eq. 3:

$$y' = \frac{(A_2 - A_1) * P * \left(\frac{x}{x_0}\right)^{P-1}}{\left(1 + \left(\frac{x}{x_0}\right)^P\right)^2} \quad (4)$$

Figure 3 shows the relationship between the drying rate and RH, and Table 2 lists the fitting functions. It can be seen that RH had a larger influence on the drying rate of free water than bound water. In addition, the slope of the linear functions reveals that the change in RH had a larger influence on poplar than on *Pinus sylvestris*.

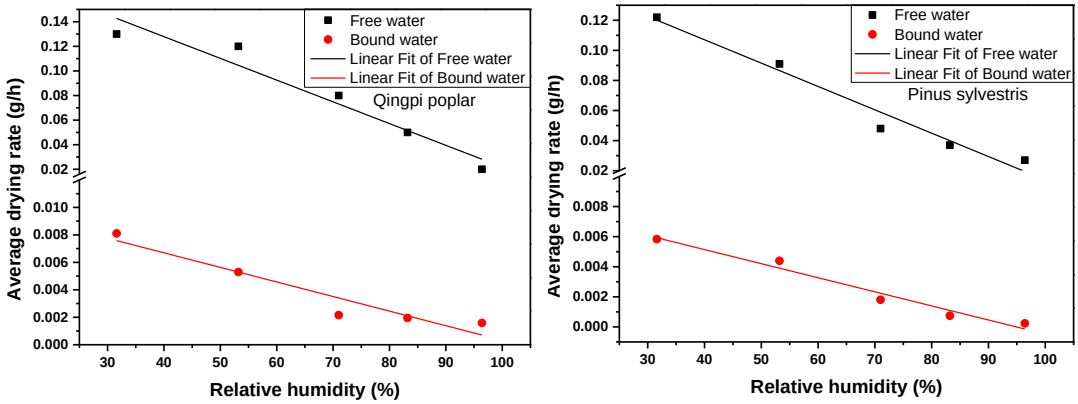

Fig. 3. Relationship between drying rate and RH

Table 2. Fitting Functions of Average Drying Rate and RH

Wood	Free water	R^2	Bound water	R^2
Qingpi poplar	y=0.20-0.002*x	0.92	$y=0.01-1.06*10^{-4}*x$	0.89
Pinus sylvestris	$y=0.17-1.55*10^{-3}*x$	0.96	$y=0.01-9.36*10^{-5}*x$	0.96

CONCLUSIONS

1. The use of TD-NMR established the possibility of mass determination of free water and bound water during the whole drying process, at the same time.
2. Free water contributes to the drying during the first few hours of the drying period, and it still exists when the MC is below the FSP.
3. Moreover, free water cannot be totally evaporated at 83.2% and 96.4% RH for poplar, but it was totally evaporated in *Pinus sylvestris*. Basically, free water has a faster drying rate and it decreased linearly with dying.
4. Bound water has a smaller drying rate and it decreased following a logistic function. Moreover, there was a gap of approximately 10% in initial MC between the two wood species.
5. Higher RH reduces the wood drying rate, and there was a linear relationship between them. Compared with bound water, free water drying was more easily affected by a change in RH.

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