

MODELING WOOD MOISTURE SORPTION HYSTERESIS BASED ON SIMILARITY HYPOTHESIS. PART II. CAPILLARY-RADII APPROACH

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(Received August 1997)

ABSTRACT

The applicability of Mualem's capillary-radii model to wood moisture sorption hysteresis is evaluated. The model further simplifies the prediction of sorption hysteresis in that scanning curves can be obtained from the moisture content and relative humidity data of the boundary isotherms, with no other intermediate parameters needed. A comparison of predicted moisture contents with actual experimental data points for yellow-poplar (*Liriodendron tulipifera*) indicates that the model consistently underestimates the primary desorption scanning isotherms, with errors ranging from -0.01 to -1.31 . These prediction errors are slightly larger than those obtained from an earlier model based on Mualem's direct similarity hypothesis.

Keywords: Modeling, sorption, adsorption, desorption, isotherm, hysteresis, yellow-poplar, *Liriodendron tulipifera*.

INTRODUCTION

In an earlier paper (Peralta and Bangi 1998), wood moisture sorption hysteresis was modeled after Mualem's direct similarity hypothesis, which accounts only for the irreversible component of the sorption process (Mualem 1973). In 1974, Mualem reported another model that is also based on the similarity hypothesis but uses capillary radii as similarity statement parameters to reflect both the reversible and irreversible sorption components. The latter model results in a more straightforward mathematical calculation requiring no intermediate parameters, just the moisture content and relative humidity data of the boundary isotherms to generate the scanning curves. It has been successfully applied to different soil media and holds promise as a tool for analyzing wood sorption data. The present paper investigates the validity of the capillary-radii model as applied to wood.

THEORETICAL CONSIDERATIONS

A capillary porous medium may be characterized in terms of two parameters ρ and r , defined as the radius of a pore and the radius of a pore's connection with other pores, respectively. In softwood's gross capillary structure, ρ and r may be thought of as the radii of the tracheid lumina and of the pit openings, respectively. In hardwoods, the assignment of ρ and r to the various openings is more difficult owing to the complex structure of this wood group. If it is assumed that free water is contained solely in vessel lumina and that communication between vessel elements is through perforation plates only, then ρ and r may be assigned to the radii of the vessel elements and perforation plates, respectively. If, in addition to the vessels, the fiber and parenchyma cell lumina also hold a substantial amount of water, then ρ may be thought of as

the radii of the vessels, fibers, and parenchyma cells, while r may be assigned to the radii of the pit openings between these different cell types.

The independent variables ρ and r can be normalized as follows:

$$\bar{\rho} = \frac{\rho - R_{\min}}{R_{\max} - R_{\min}} \quad \bar{r} = \frac{r - R_{\min}}{R_{\max} - R_{\min}} \quad (1)$$

where $\bar{\rho}$ and \bar{r} are the normalized radii ρ and r , respectively; $R = \beta/H$ is a parameter related to the relative humidity H by a constant β ; and R_{\min} and R_{\max} are the values of R at H_{\min} ($=0$) and H_{\max} ($=100$), respectively. The parameter R may likewise be normalized as follows

$$\bar{R} = \frac{R - R_{\min}}{R_{\max} - R_{\min}}. \quad (2)$$

Since ρ , r , and R vary between R_{\min} and R_{\max} , then $\bar{\rho}$, \bar{r} , and \bar{R} change within the range of zero to one.

According to Mualem (1974), the water distribution function (in terms of the normalized variables $\bar{\rho}$, \bar{r}) is a bivariate distribution that may be represented as a product of the two independent functions $h(\bar{r})$ and $l(\bar{\rho})$, as follows:

$$w(\bar{r}, \bar{\rho}) = h(\bar{r})l(\bar{\rho}). \quad (3)$$

This hypothesis differs from that of Mualem (1973) since it uses capillary radii instead of relative humidity as parameters in the similarity statement. During adsorption, when the relative humidity H changes from $H_{12}(\bar{R})$ to $H_{12}(\bar{R} + d\bar{R})$, all pores having radii $\bar{R} \leq \bar{\rho} \leq \bar{R} + d\bar{R}$ are filled. On the other hand, during desorption, when H decreases from $H_{21}(\bar{R})$ to $H_{21}(\bar{R} - d\bar{R})$, only the pores characterized by $\bar{R} - d\bar{R} \leq \bar{\rho} \leq \bar{R}$ and $\bar{R} \leq \bar{r} < 1$ are drained.

The use of capillary radii as similarity statement parameters makes it possible to take into consideration not only the capillaries that adsorb and desorb irreversibly but those that behave reversibly as well. The model's domain diagrams of the adsorption and desorption boundary curves are shown in Fig. 1b, d, respectively. Because of its reversible compo-

nent, the model defines the domains over a rectangle rather than the usual triangular representation. Triangle OBC in Fig. 1b, d, represents the reversible contribution, while triangle OAB represents the hysteretic contribution. Pores that behave reversibly are assumed to have radii \bar{r} greater than $\bar{\rho}$ and therefore are filled and drained at the same H , corresponding to the radius ρ of the pores only.

By defining the integral distribution functions $\lambda(\bar{R})$ and $\eta(\bar{R})$ as

$$\lambda(\bar{R}) = \int_0^{\bar{R}} l(\bar{\rho}) d\bar{\rho} \quad (4)$$

$$\eta(\bar{R}) = \int_0^{\bar{R}} h(\bar{r}) d\bar{r} \quad (5)$$

the relationship between the moisture content M and the relative humidity H may be derived. For the adsorption boundary isotherm,

$$M_a(\bar{R}) = \int_0^{\bar{R}} l(\bar{\rho}) d\bar{\rho} \int_0^1 h(\bar{r}) d\bar{r} = \lambda(\bar{R})\eta(1) \quad (6)$$

where M_a represents the adsorption boundary moisture content. For the desorption boundary isotherm,

$$\begin{aligned} M_d(\bar{R}) &= \int_0^{\bar{R}} l(\bar{\rho}) d\bar{\rho} \int_0^1 h(\bar{r}) d\bar{r} + \\ &+ \int_{\bar{R}}^1 l(\bar{\rho}) d\bar{\rho} \int_0^{\bar{R}} h(\bar{r}) d\bar{r} \quad (7) \\ M_d(\bar{R}) &= \lambda(\bar{R})\eta(1) + \eta(\bar{R}) \times \\ &\times \left[\int_0^1 l(\bar{\rho}) d\bar{\rho} - \int_0^{\bar{R}} l(\bar{\rho}) d\bar{\rho} \right] = \\ &= \lambda(\bar{R})\eta(1) + \eta(\bar{R}) \left[\lambda(1) - \lambda(\bar{R}) \right] \quad (8) \end{aligned}$$

where M_d is the desorption boundary moisture content.

For the sake of convenience, define $\eta(1) = 1$, so that Eq. (6) simplifies to the form

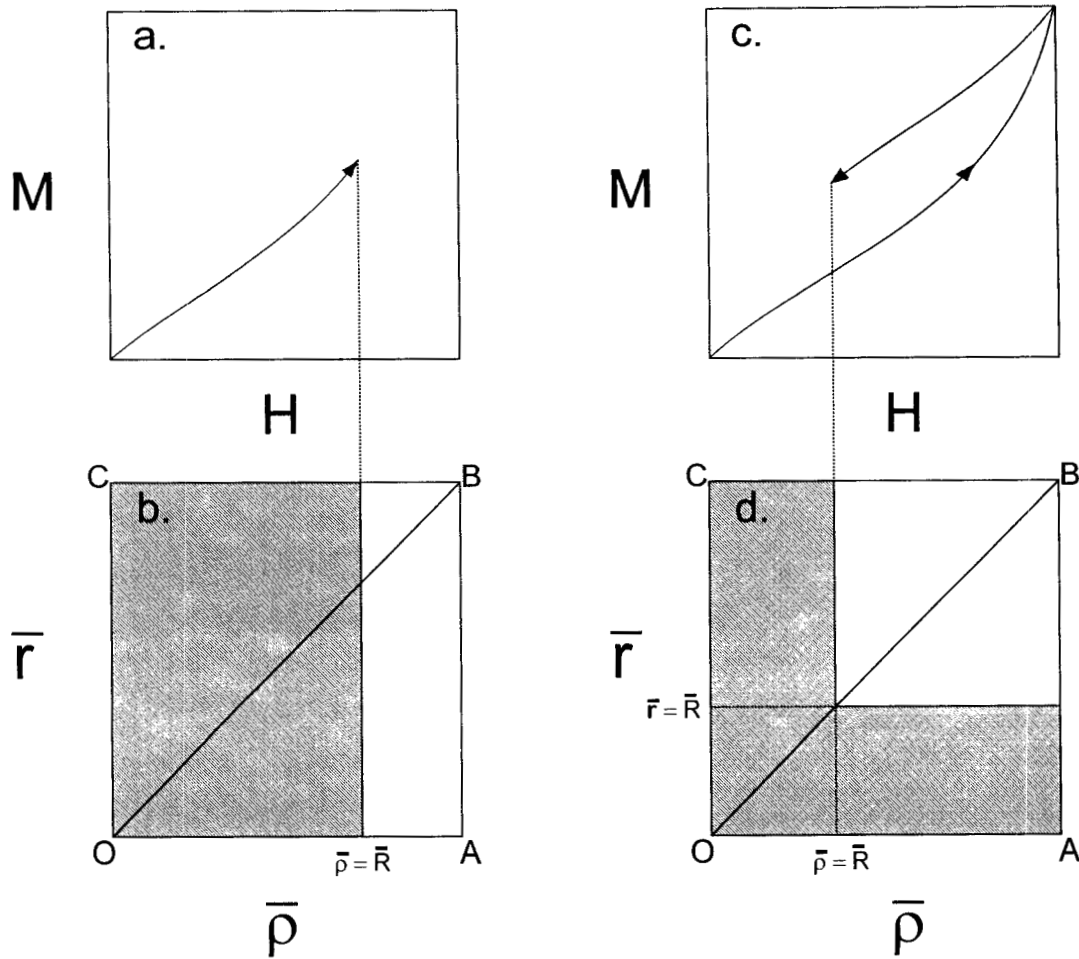


FIG. 1. Adsorption boundary (a) and desorption boundary (c) isotherms with their corresponding state-of-domains diagrams (b and d, respectively).

$$M_u(\bar{R}) = \lambda(\bar{R}). \tag{9}$$

For $\bar{R} = 1$,

$$M_u(1) = \lambda(1) = M_u \tag{10}$$

where M_u represents the maximum effective moisture content. Thus, incorporating Eqs. (9) and (10) into Eq. (8) results in the following relationship:

$$\eta(\bar{R}) = \frac{M_d(\bar{R}) - M_u(\bar{R})}{M_u - M_u(\bar{R})} \tag{11}$$

Since the $H-\bar{R}$ relationships is a univalued function, Eqs. (9) and (11) may be written in terms of H as follows:

$$\lambda(H) = M_u(H) \tag{12}$$

$$\eta(H) = \frac{M_d(H) - M_u(H)}{M_u - M_u(H)} \tag{13}$$

where H ranges from 0 to 100.

METHODOLOGY AND RESULTS

The reliability of the capillary-radii model was tested by comparing its mathematical predications with actual experimental sorption data for yellow-poplar (*Liriodendron tulipifera*). Scanning curves were derived from the moisture content and relative humidity data of the boundary curves. Using a notation sug-

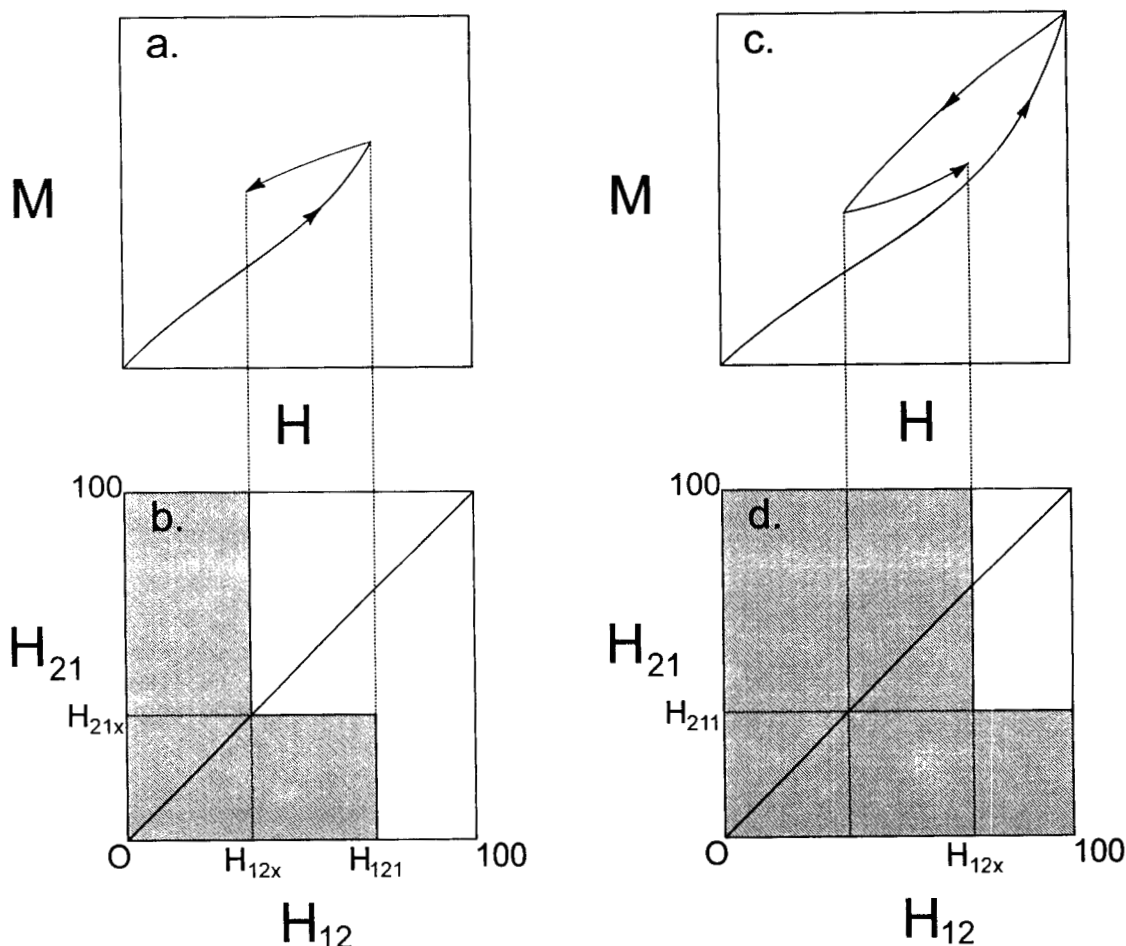


FIG. 2. Primary desorption (a) and primary adsorption (c) scanning isotherms with their corresponding state-of-domains diagrams (b and d, respectively).

gested by Enderby (1955), the primary desorption scanning isotherms were obtained using the equation:

$$\begin{aligned}
 M \left(\begin{matrix} \bar{R}_1 \\ 0 \\ \bar{R} \end{matrix} \right) &= \int_0^{\bar{R}} l(\bar{\rho}) d\bar{\rho} \int_0^1 h(\bar{r}) d\bar{r} + \\
 &+ \int_{\bar{R}}^{\bar{R}_1} l(\bar{\rho}) d\bar{\rho} \int_0^{\bar{R}} h(\bar{r}) d\bar{r} = \\
 &= M_a(\bar{R}) + [\lambda(\bar{R}_1) - \lambda(\bar{R})]\eta(\bar{R})
 \end{aligned}
 \tag{14}$$

which simplifies to the form:

$$\begin{aligned}
 M \left(\begin{matrix} H_{121} \\ 0 \\ H_{21x} \end{matrix} \right) &= \\
 &= M_a(H_{12x}) + [M_a(H_{121}) - M_a(H_{12x})] \times \\
 &\times \frac{M_d(H_{21x}) - M_a(H_{12x})}{M_u - M_a(H_{12x})}
 \end{aligned}
 \tag{15}$$

where M is the moisture content of interest; the notation in parentheses on the left side of the equation describes the dynamics of the sorption process, that is, H first increases from 0 to H_{121} and then decreases from H_{121} to H_{21x} (Fig. 2a, b); H_{121} the relative humidity corresponding to the reversal point of the given pri-

mary desorption scanning isotherm; H_{12x} the relative humidity corresponding to M during adsorption; and H_{21x} the relative humidity corresponding to M during desorption.

The primary scanning adsorption curves can similarly be generated using the equation:

$$\begin{aligned} M\left(\frac{1}{\bar{R}_1}, \bar{R}\right) &= \int_0^{\bar{R}} l(\bar{p}) d\bar{p} \int_0^1 h(\bar{r}) d\bar{r} + \\ &+ \int_{\bar{R}}^1 l(\bar{p}) d\bar{p} \int_0^{\bar{R}_1} h(\bar{r}) d\bar{r} = \\ &= M_a(\bar{R}) + [\lambda(1) - \lambda(\bar{R})]\eta(\bar{R}_1) \end{aligned} \quad (16)$$

which simplifies to:

$$\begin{aligned} M\left(\frac{100}{H_{211}}, H_{12x}\right) &= \\ &= M_a(H_{12x}) + [M_u - M_a(H_{12x})] \times \\ &\times \frac{M_d(H_{211}) - M_a(H_{121})}{M_u - M_a(H_{121})} \end{aligned} \quad (17)$$

where the notation in parentheses following M indicates that H decreases from 100 to H_{211} and then increases from H_{211} to H_{12x} (Fig. 2c, d); H_{211} is the relative humidity corresponding to the reversal point of the given primary adsorption scanning isotherm; the rest of the terms are as previously defined.

In using Eq. (14) to generate the primary desorption scanning curves of yellow-poplar, the Hailwood-Horrobin single-hydrate model was employed to calculate the values of the adsorption boundary moisture content M_a and desorption boundary moisture content M_d . The parameters (M_p , K_1 , and K_2) for this model are listed in Table 2 of Peralta (1995). (Note: M_p for the adsorption boundary isotherm should be 352.677 instead of 362.677). The boundary isotherms were extrapolated to 100% relative humidity to allow calculation of the maximum effective moisture content M_u , which was assumed to be equal to the average of the adsorption and desorption boundary moisture content at 100% relative humidity. The pre-

dicted and experimentally generated moisture contents at different relative humidities for the primary desorption scanning curves are presented in Table 1 and Fig. 3.

DISCUSSION AND CONCLUSIONS

Figure 3 shows that the predicted primary scanning curves all fall within the hysteresis loop. This indicates that the capillary-radii model is in consonance with Urquhart's view of sorption hysteresis, that is, the boundary isotherms define the limiting equilibrium values and thus may be viewed not as equilibrium loci but as borders that outline the hysteresis area (Urquhart 1960). This property of the model is attributed to the fact that the term $[M_d(H_{21x}) - M_a(H_{12x})]$ is multiplied by $[M_a(H_{121}) - M_d(H_{12x})]/[M_u - M_a(H_{12x})]$, a factor greater than zero but less than one.

A comparison of predicted primary scanning desorption curves and actual experimental data for yellow-poplar reveals that the capillary-radii model consistently underestimates the primary desorption scanning moisture contents, with prediction errors ranging from -0.01 to -1.31% moisture content. Compared to the earlier model based on direct-approach similarity hypothesis (Peralta and Bangi 1998), predictions from the current model are less accurate. This may be due to the unsuitability of the Kelvin equation in interrelating moisture sorption and wood capillarity. The relationship between the parameter R and the water potential, ψ , is given by the Laplace equation

$$R = -\frac{2\sigma}{\psi D} \quad (18)$$

where σ and D refer to the surface tension and density of water, respectively. The water potential may be expressed in terms of the relative vapor pressure (p/p_o) as follows:

$$\psi = \frac{RT}{M_w} \ln\left(\frac{p}{p_o}\right) = \frac{RT}{M_w} \ln\left(\frac{H}{100}\right) \quad (19)$$

where R = universal gas constant, T = absolute temperature, and M_w = molecular weight

TABLE 1. Comparison of experimentally generated moisture contents of yellow-poplar during primary desorption with those predicted by Mualem's capillary-radii model.

Relative Humidity (%)	Moisture Content (%)											
	Scanning 92 ^a			Scanning 75 ^b			Scanning 53 ^c			Scanning 32 ^d		
	Model	Expt.	Error	Model	Expt.	Error	Model	Expt.	Error	Model	Expt.	Error
11	3.14	3.16	-0.03	2.96	3.11	-0.15	2.86	3.06	-0.20	2.80	2.98	-0.17
22	4.88	5.14	-0.26	4.57	5.00	-0.43	4.39	4.83	-0.44	4.29	4.62	-0.33
32	6.19	6.62	-0.44	5.76	6.50	-0.73	5.52	6.17	-0.65			
43	7.62	8.41	-0.79	7.07	8.19	-1.11	6.76	7.54	-0.78			
53	9.10	10.11	-1.01	8.42	9.73	-1.31						
63	10.91	11.84	-0.93	10.05	11.00	-0.94						
75	13.84	14.46	-0.62									
84	16.97	17.25	-0.28									

^a Scanning 92, Scanning 75, Scanning 53, and Scanning 32 refer to the primary desorption scanning curve whose reversal point corresponds to relative humidity of 92, 75, 53, and 32%, respectively.

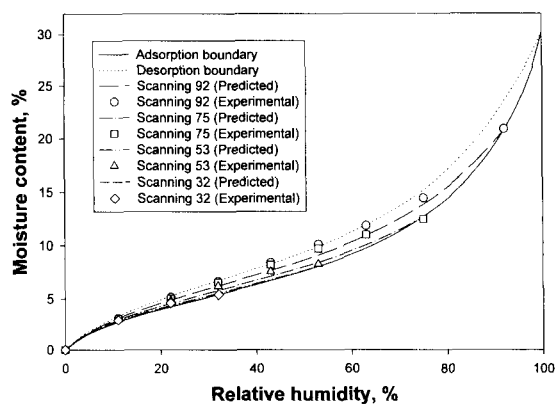


FIG. 3. Experimentally-generated data points for yellow-poplar and primary desorption scanning isotherms predicted by Mualem's capillary-radii model. Scanning 92, Scanning 75, Scanning 53, and Scanning 32 refer to the primary desorption scanning curves with reversal point at 92, 75, 53, and 32% relative humidity, respectively.

of water. Assuming a negligible osmotic water potential component, Eqs. (18) and (19) may be combined to yield the Kelvin equation, which relates the parameter R and relative humidity H ,

$$R = - \frac{2\sigma M_w}{DRT \ln\left(\frac{H}{100}\right)} \quad (20)$$

The applicability of the Kelvin equation at low relative humidities ($H < 90\%$) is questionable since the concept of surface tension loses its meaning when the radius R approaches the molecular dimensions of water. This restriction implies that Mualem's capillary-radii model could not be accurately used over most of the hygroscopic range, and most likely explains the large deviation of the predicted moisture content values from the actual experimental results. Nonetheless, the model is useful by virtue of the following properties: (1) the ability to generate scanning curves based solely on the moisture content–relative humidity relationship of the two boundary isotherms; and (2) the predicted scanning curves lie exclusively within the hysteresis region. It is anticipated to be of value in analyzing hys-

teresis data at relative humidities exceeding 90%. Such data are now just being gathered by researchers in Canada (Fortin 1979; Cloutier 1991) and the United States (Zhang 1997) in connection with studies on water potential in wood.

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