

MODELING WOOD MOISTURE SORPTION HYSTERESIS USING THE INDEPENDENT-DOMAIN THEORY

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ABSTRACT

The mathematical modeling of wood moisture sorption hysteresis provides a means of correlating and interpolating experimental sorption data, which are often limited and are time-consuming to generate. The model may be incorporated in numerical treatments of wood-moisture relations such as wood drying or may provide better insights as to how water is held in wood. This paper introduces the application of the theory of independent domains to sorption hysteresis in yellow poplar. From the experimental sorption boundary curves and a family of primary desorption scanning curves, a grid of values is generated and then used to mathematically obtain several primary adsorption scanning curves, and secondary and tertiary scanning curves. The implication of the theory's assumptions to current understanding of wood-water interaction is briefly discussed.

Keywords: Modeling, independent-domain theory, sorption, adsorption, desorption, isotherm, hysteresis.

INTRODUCTION

The relationship between a dependent variable y and an independent variable x of a system is said to be reversible if when the direction of change in x is reversed, the variable y traces back the same set of values as those in the former process. Many physical properties, however, are known to exhibit hysteresis or irreversibility such that even at very gradual changes in x , the curve relating the two variables for increasing x does not coincide with that for decreasing x (Fig. 1). For such systems, it is generally found that as x oscillates between a lower and an upper limit, the curves relating y and x form a closed loop (Everett 1967). The curves corresponding to the maximum range of x values over which hysteresis occurs are called the ascending boundary curve (OCA) and descending boundary curve (ABO) for increasing and decreasing values of x , respectively. When the direction of change along the ascending boundary curve is reversed before the full limit of the loop is attained, the resultant path is called a primary descending

scanning curve (CEO). A primary ascending scanning curve (BDA) is similarly traced from the descending boundary curve. A secondary ascending scanning curve (EG) and a secondary descending scanning curve (DF) originate, respectively, from the primary descending and primary ascending scanning curves.

In a recent publication, results of a study on the phenomenon of hysteresis during moisture sorption by wood were reported (Peralta 1995). The ascending (adsorption) and descending (desorption) boundary curves, along with four primary desorption scanning curves, were established for yellow poplar at 30 C. The bulk of the experimental work was done using a vacuum system, making it possible to obtain the data in about a year instead of the five to six years expected if the conventional desiccator method were used. Still, the time requirement to complete the information on wood sorption hysteresis is substantial. A minimum of three more years of experimental work will be needed to study three or four primary adsorption scanning curves and to establish the secondary scanning curves for a given spe-

cies at a given temperature. However, by applying an appropriate mathematical model to the existing data, it may be possible to obtain useful information with more limited data. The model may be used in correlating and interpolating data or may be incorporated in numerical treatments of wood-moisture relations (e.g. wood drying models). More importantly, it may describe the mechanism of sorption and thus advance our understanding of the interaction of wood with water.

Though wood moisture sorption hysteresis has been the subject of numerous investigations and various theories have been forwarded to explain the phenomenon (Skaar 1979), no quantitative treatment of the subject has ever been performed. One model that holds promise is that based on the concept of independent domains. This paper attempts to apply the theory to the sorption hysteresis data obtained in the previous work. From the boundary and primary desorption scanning curves, a grid of values indicating the amount of water lost or gained over a small relative humidity (RH) range is constructed and used to predict the primary ascending scanning, and secondary and tertiary scanning curves for yellow poplar at 30 C.

THEORETICAL CONSIDERATION

A brief sketch of the independent-domain theory is given below. More detailed description of the theory can be obtained from the references cited.

The concept of independent domains was developed by Everett and his coworkers (Everett and Whitton 1952; Everett and Smith 1954; Everett 1954; Everett 1955) and by Enderby (1955). A synthesis of the previous works, together with the theory's application to adsorption hysteresis, is given by Everett (1967). In the model, a system exhibiting hysteresis is divided into small elements called domains, each of which exists in one of two states. The conversion from one state to the other is brought about by increasing or decreasing an external independent variable x . If x_{12} and x_{21} denote, respectively, the value of x when a

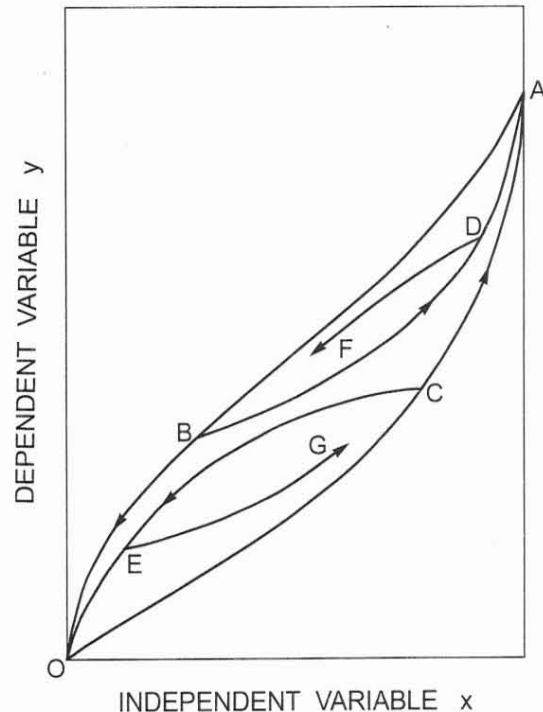


FIG. 1. Schematic representation of the relationship between a dependent variable y and an independent variable x for a system exhibiting hysteresis. The different letters define various curves as follows: OCA—ascending boundary; ABO—descending boundary; CEO—primary descending scanning; BDA—primary ascending scanning; EG—secondary ascending scanning; DF—secondary descending scanning.

particular domain converts from state 1 to state 2 and from state 2 to state 1, then $x_{12} \geq x_{21}$ if the domain as a whole behaves irreversibly in the cycle. It is further assumed that the values of x_{12}^a and x_{21}^a (where $a = 1, 2, 3, \dots$ indicates the number of the domain) are not influenced by the neighboring domains.

For wood moisture sorption, the relative humidity during adsorption (H_{12}) and the relative humidity during desorption (H_{21}) can be substituted for x_{12} and x_{21} , respectively. Hence sorption hysteresis may be represented diagrammatically using the rectangular coordinate system shown in Fig. 2. Since $H_{12} \geq H_{21}$, all representative points must lie in the triangle OAB on the H_{12} - H_{21} plane. Elements lying on line OB behave reversibly. Erected over the triangle OAB is a distribution function $w(H_{12},$

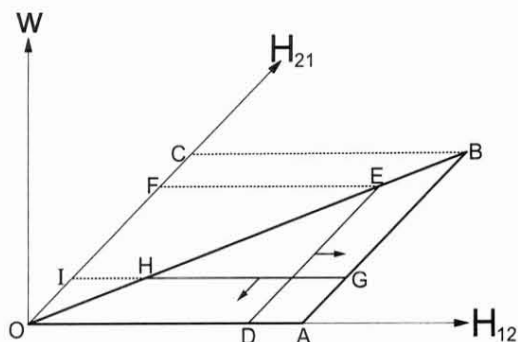


FIG. 2. Coordinate system showing the moisture distribution function (w) in relation to the values of the relative humidity (H) when a particular domain converts from state 1 to state 2 (H_{12}) and from state 2 to state 1 (H_{21}).

H_{21}), such that $w(H_{12}, H_{21})dH_{12}dH_{21}$ represents the amount of water in domains having transition points in the rectangle $dH_{12}dH_{21}$ near (H_{12}, H_{21}) . Hence, moisture gain can be characterized by the movement away from point O of a plane parallel to the w - H_{21} plane; while moisture loss may be characterized by the movement towards point O of a plane parallel to the w - H_{12} plane. For instance, when $H_{12} = D$ is reached during adsorption from the oven-dry condition, all domains for which $H_{12} < D$ would contain water and the amount adsorbed will be given by

$$M = \int_0^D \int_0^{g(H_{12})} w(H_{12}, H_{21}) dH_{21} dH_{12}$$

where $H_{21} = g(H_{12})$ is the function describing the diagonal OHE. The integral gives the volume of the solid figure bounded by the surface formed by $w(H_{12}, H_{21})$ and the base plane over the triangle ODE. If the sample is allowed to further adsorb moisture by exposing it to an RH of 100% (i.e., $H_{12} = A$ in Fig. 2), the plane parallel to the w - H_{21} plane will move from $H_{12} = D$ to $H_{12} = A$. The total amount of water in the material will be given by the integral of w over the triangle OAB. During subsequent desorption when the material is exposed to a relative humidity $H_{21} = I$, the plane parallel to the w - H_{12} plane will move down from H_{21}

$= C$ to $H_{21} = I$, and the amount of water in the material will be given by the integral of w over the trapezoid OAGH.

The concept is further demonstrated in Fig. 3, where only the H_{12} - H_{21} plane is presented, with the w -axis assumed to be coming out of the plane of the paper. The shaded region identifies the domains in state 2, i.e., those domains containing water. Figure 3a shows part of the ascending boundary curve (upper diagram) and its corresponding domain complexion (lower diagram). If the vertical line moved all the way to the right, the complete ascending boundary curve will be established and the triangle will be fully shaded. Once the upper limit of H_{12} is reached and the direction of change is reversed, the descending boundary curve may be obtained as shown in Fig. 3b. The domain complexion shows a horizontal line moving from top to bottom of the triangle, with the area it swept representing the domains that are emptied of water. Figures 3c and 3d show, respectively, the primary descending scanning curve and the primary ascending scanning curve together with their corresponding domain complexions.

METHODOLOGY AND RESULTS

Using the hypothetical adsorption boundary curve (OBCA) and primary scanning desorption curves (CEO and BDO) in Fig. 4, the general approach taken to build a grid of domain values is briefly outlined as follows. Curve BDO shows how M_B , the amount of water (expressed as a percentage of the oven-dry weight of the wood) adsorbed by the material when the relative humidity is increased from 0 to H_B , is distributed during subsequent desorption. Curve CEO provides the same information for M_C , the water adsorbed when the relative humidity is increased from 0 to H_C . $M_C - M_B$, the amount of water adsorbed due to the rise in relative humidity from H_B to H_C , is distributed among the different domains shown on the grid in Fig. 4 in such a way that $M_C - M_B = \sum_{i=1}^n M_i$. Each M_i is the difference between the amount of water desorbed over a given RH range fol-

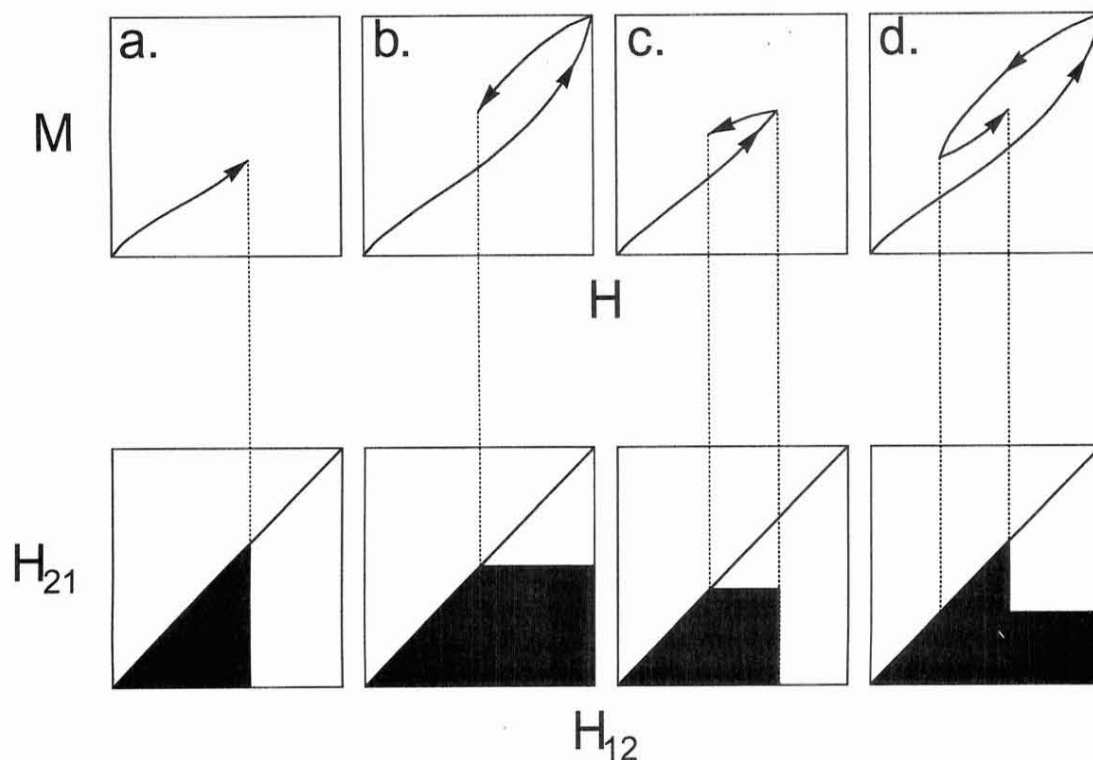


FIG. 3. Boundary and scanning curves (upper diagram) and their corresponding domain complexions (lower diagram): a. ascending boundary curve; b. descending boundary curve; c. primary descending scanning curve; d. primary ascending scanning curve.

lowing curve CEO and that over the same RH range following curve BDO. Hence, given a family of primary desorption scanning curves, it is possible to build a grid of domain values with H_{12} (the adsorption relative humidity) on the x-axis and H_{21} (the desorption relative humidity) on the y-axis.

Using the sorption hysteresis data (Table 1) from an earlier study (Peralta 1995), the distribution of moisture content (MC) among the various domains was constructed for yellow poplar at 30 C. The boundary curves are extended to 100% RH by extrapolating the adsorption and desorption boundary Hailwood-Horrobin equations, and taking the average (30.13% MC) of the extrapolated values as the upper closure point of the hysteresis loop. The assumption that the boundary curves form a close loop at the extreme values of relative humidity is made for modeling purposes only

and does not necessarily reflect the actual physical phenomenon.

The coordinates of the grid in Fig. 5 correspond to the reversal points (32%, 53%, 75%, and 92% RH) of the established primary desorption scanning curves, together with 11% RH and the two closure points of the sorption isotherms (0 and 100% RH). To illustrate how the grid cell values were obtained, consider the two primary desorption scanning curves with reversal points at 53% and 75% RH. On the adsorption boundary curve, when H_{12} is increased from 53% to 75%, the MC increases by $12.44\% - 8.27\% = 4.17\%$. This amount of water is distributed among the different domains in the H_{12} range of 53% to 75% in such a way that during subsequent desorption, the sum of the amount of water lost from these domains is equal to 4.17%. The domain values are obtained as the difference in the MC loss

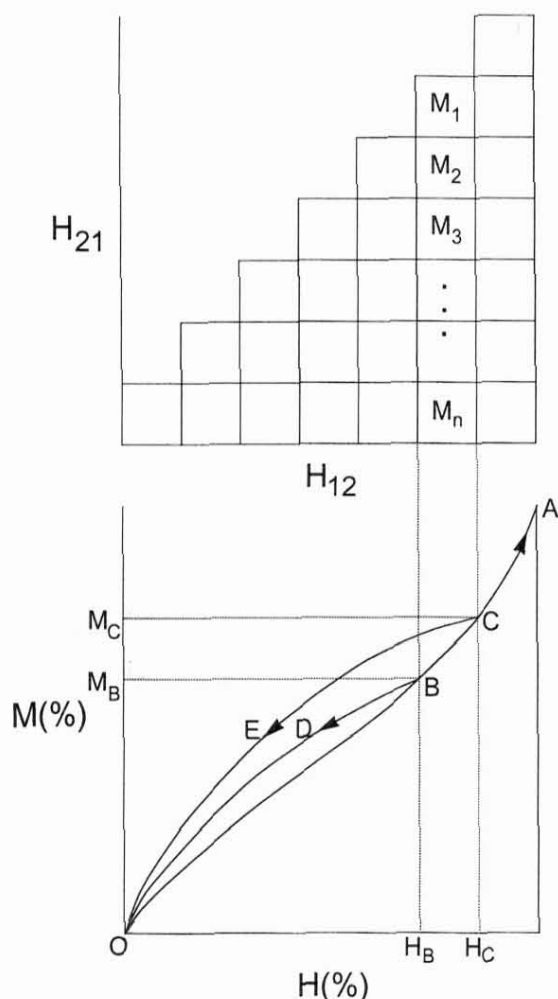


FIG. 4. Diagrammatic representation of the general approach taken to build a grid of moisture distribution values (upper diagram) from hypothetical boundary and scanning curves (lower diagram).

between the two desorption scanning curves over the H_{21} intervals 75 to 53, 53 to 32, 32 to 11, and 11 to 0: when the relative humidity is reduced from $H_{21} = 75\%$ to $H_{21} = 53\%$, the moisture loss along the 75% RH scanning curve is $12.44\% - 9.73\% = 2.71\%$; that for the 53% RH scanning curve is 0; the difference, $2.71 - 0 = 2.71\%$, is the entry for the cell at the H_{21} range of 75% to 53%. When humidity is further reduced from $H_{21} = 53\%$ to $H_{21} = 32\%$, the moisture losses are $9.73 - 6.50 = 3.23\%$ and $8.27 - 6.17 = 2.10\%$ for the 75% RH scanning curve and the 53% RH scanning curve, respectively. The difference $3.23 - 2.10 = 1.13\%$

TABLE 1. Average moisture contents of yellow poplar samples at the different relative humidities and sorption histories.

Relative humidity (%)	Moisture content (%)					
	Adsorption boundary	Desorption boundary	Desorption scanning ^a			
			92	75	53	32
11	2.61	3.19	3.16	3.11	3.06	2.98
32	5.39	6.67	6.62	6.50	6.17	5.39
53	8.27	10.19	10.11	9.73	8.27	—
75	12.44	14.81	14.46	12.44	—	—
92	20.91	23.69	20.91	—	—	—
100	30.13 ^b	30.13 ^b	—	—	—	—

^a Desorption scanning 92, 75, 53, and 32 refer to the desorption scanning curves whose reversal points correspond to relative humidities of 92, 75, 53, and 32%, respectively.

^b Average of the extrapolated adsorption and desorption boundary moisture contents.

is the entry for the cell at the H_{21} range of 53% to 32%. This process is repeated for the rest of the H_{21} intervals and for the other pairs of scanning curves, resulting in the values given in Fig. 5.

DISCUSSION

The grid in Fig. 5 may be used to obtain several primary adsorption scanning curves. If the wood is allowed to lose moisture by exposing it to 11% RH after equilibrating at 100% RH ($EMC = 30.13\%$), the MC will be reduced by a quantity equal to the sum of the values of the cells bounded by triangle ABC ($\Sigma_{ABC} = 26.94$) to yield an MC of 3.19%. If the direction of sorption is reversed at this point by exposing the wood to 32% RH, the wood will adsorb 2.41% moisture, to give an equilibrium moisture content of 5.60%. Sequential equilibrations at relative humidities of 53, 75, 92, and 100% will result in moisture gain differentials of 2.80, 4.12, 8.42, and 9.19%, yielding equilibrium moisture contents of 8.40, 12.52, 20.94, and 30.13%, respectively. Figure 6 presents, in addition to the boundary curves, the predicted primary adsorption scanning curves with reversal points of 11, 32, 53, and 75% RH. Secondary and tertiary scanning curves may also be created as in the spiral pattern in Fig. 7, which is obtained by subjecting the wood to successively narrower RH ranges of 0 to 75%, 75 to 11%, 11 to 53%, and 53 to 32%.

Mathematical modeling using the independent-domain theory could prove to be a pow-

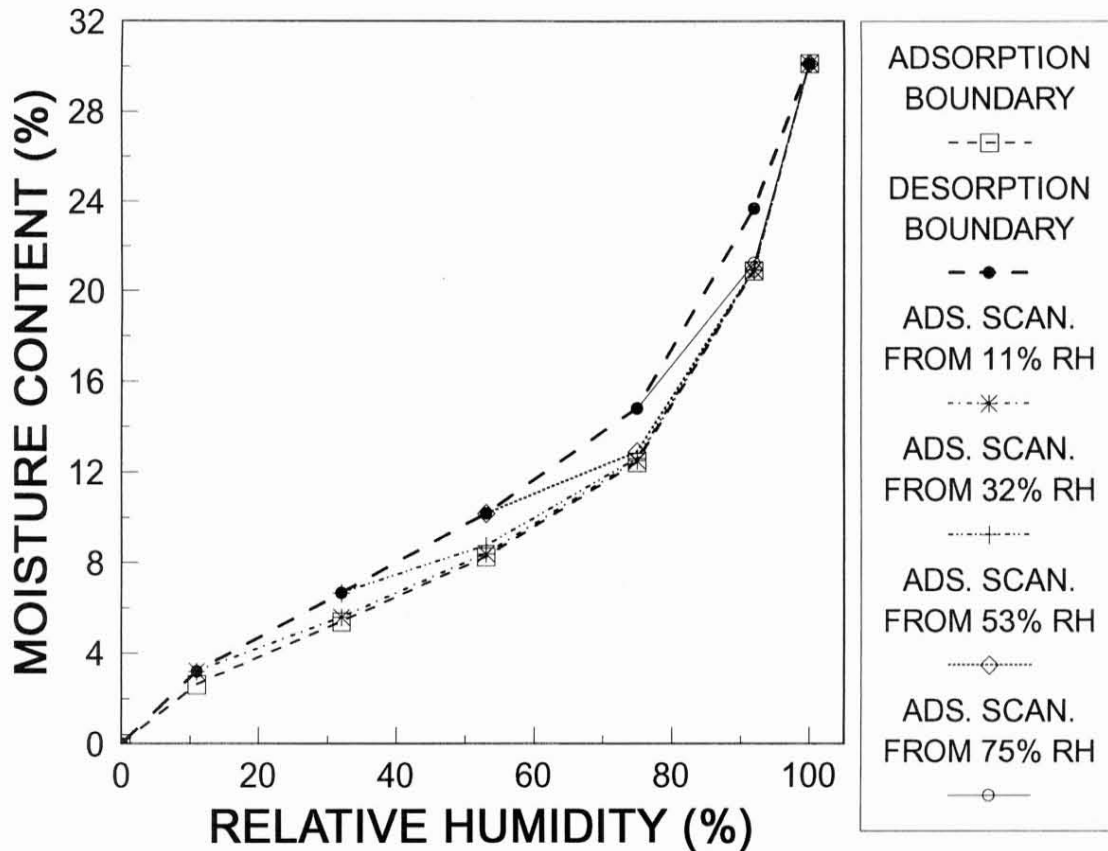


FIG. 5. Grid of values showing the distribution of moisture among the various domains specified by the appropriate range of adsorption relative humidity (H_{12}) and desorption relative humidity (H_{21}) for the yellow poplar sorption hysteresis data.

erful tool in analyzing wood moisture sorption behavior. It could easily be implemented numerically using a simple computer algorithm. Its validity, however, remains to be verified against experimental data, particularly in relation to the theory's assumptions. For the model to work, it is premised that the domains should have a distribution of characteristics; otherwise, the system will exhibit nonreproducible metastability. In the case of moisture sorption by wood, this may be interpreted to mean that the different sorption sites should have different degrees of accessibility by the water molecules. Those which are readily available for sorption will change state at lower relative humidities, with the less accessible sites being affected only at higher humidities. An alternate interpretation involves the capillary-condensation view of moisture sorption: at a

given relative vapor pressure, those microcapillaries in wood with radius less than the critical value given by the Kelvin equation would be filled with water. Since wood has a wide pore-size distribution, the requirement of non-identical domain properties is easily met, with moisture condensation occurring over a wide range of relative humidities.

Postulates that are more difficult to reconcile with widely accepted views of wood sorption behavior are those pertaining to the existence of each domain in either one of two states and to the independence among domains. The former implies that the wood sorption sites should be either unhydrated (state 1) or hydrated (state 2), with no distinction made between monolayer and multilayer water sorption. In terms of the capillary-condensation view of moisture sorption, the theory implies that capillary fill-

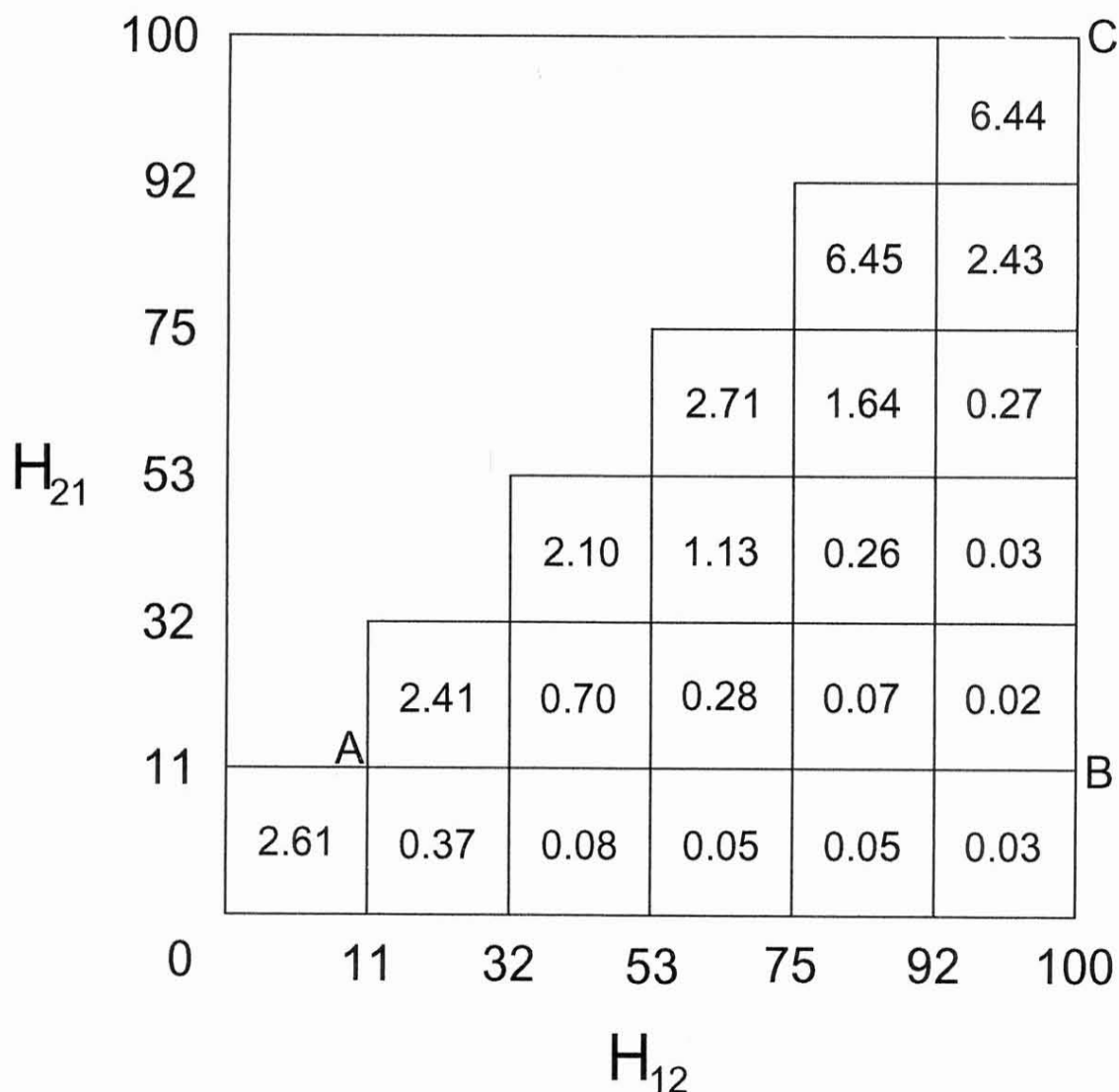


FIG. 6. Primary adsorption scanning curves calculated from the moisture distribution diagram of Fig. 5.

ing (and on desorption, emptying) should occur in jump transitions. It is, however, difficult to visualize the wood capillaries as not having geometries that favor partially full or partially empty states. The assumption of independence among domains is even more difficult to satisfy since it requires that the wood sorption sites should not in any way interact with one another. When wood is dry, the microfibrils are close to each other that adjacent sorption sites can easily form cross-linkages. On hydration, the water molecules attached to the sorption

sites may hydrogen-bond with one another or with adjacent sorption sites, forming bridges between or among sites, thereby allowing indirect interaction among the sites. Likewise, capillaries and pores in wood form an interconnected network such that the filling or emptying of one capillary affects its neighboring capillaries.

SUMMARY AND CONCLUSIONS

The independent-domain theory was applied in modeling the sorption hysteresis data

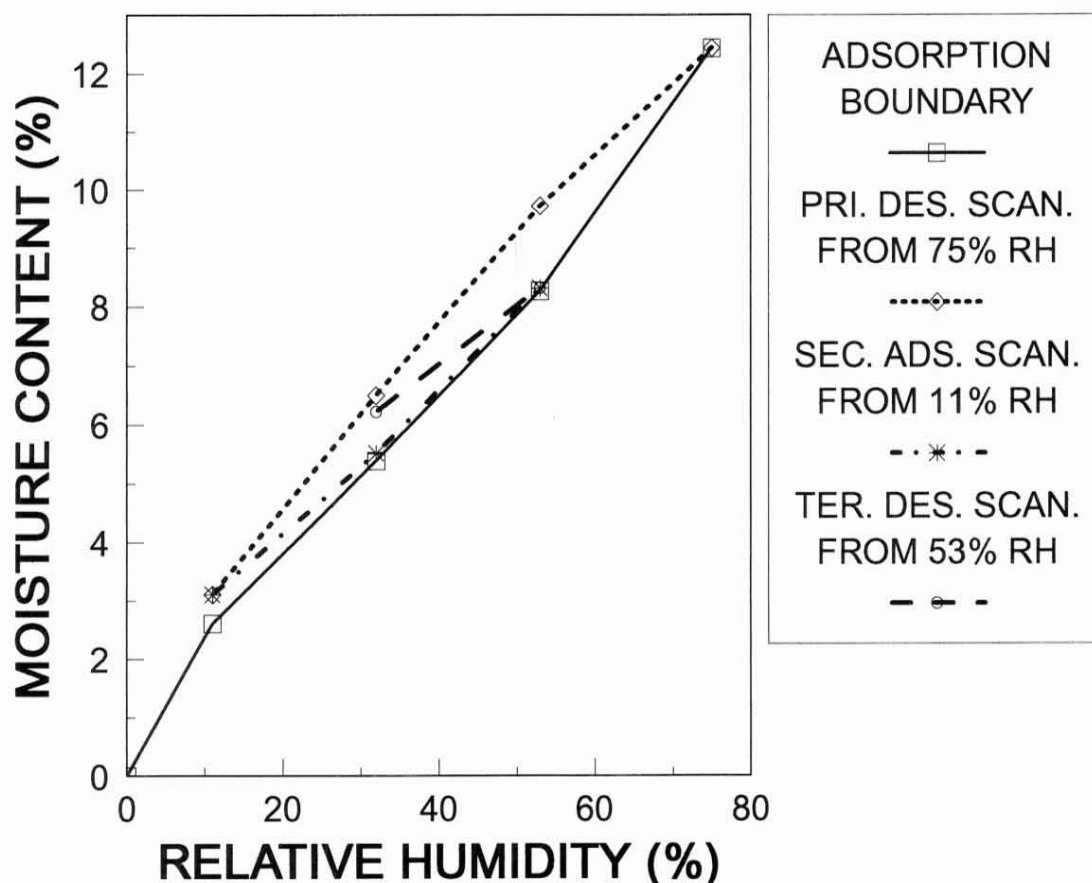


FIG. 7. Primary, secondary, and tertiary scanning curves forming a spiral path when wood is subjected to successively narrower relative humidity ranges.

for yellow poplar at 30 C. A grid, constructed from the experimental boundary and primary desorption data, was used to predict the primary adsorption, secondary adsorption, and tertiary desorption scanning curves. Work currently being undertaken in this laboratory in the way of model verification involves establishing actual primary adsorption scanning curves to determine how closely they are approached by the predicted values of Fig. 6.

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