MOISTURE SORPTION HYSTERESIS AND THE INDEPENDENT-DOMAIN THEORY: THE MOISTURE DISTRIBUTION FUNCTION

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ABSTRACT

To model the phenomenon of moisture sorption hysteresis using the independent domain theory, the moisture distribution among the domains must be established. This paper describes a procedure for obtaining such moisture distribution diagram from which may be calculated the moisture content of wood subjected to a series of relative humidity (RH) changes. The procedure is a refinement of the method described by the author in an earlier paper and is more consistent with the concept of independent domains. An alternative approach using numerical methods is also described.

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

INTRODUCTION

In a recent publication (Peralta 1995a), the phenomenon of hysteresis during moisture sorption by yellow-poplar wood samples at 30°C was reported. In a follow-up paper (Peralta 1995b), the sorption data were modeled by applying the concept of independent domains (Everett 1967). A grid of values indicating the amount of water lost or gained over a small relative humidity range was constructed from the experimentally generated boundary isotherms and primary desorption scanning curves. The grid was then employed to predict the primary adsorption, secondary adsorption, and tertiary desorption scanning curves. In this paper, a procedure for establishing the moisture distribution diagram is presented. It is a refinement of the earlier grid method and is more in agreement with the concept of independent domains.

THEORETICAL CONSIDERATION AND METHODOLOGY

According to the independent-domain theory, a system exhibiting sorption hysteresis is divided into minute elements called domains, each of which is defined in terms of the relative humidity range H_{12} to $H_{12} + \Delta H_{12}$ at which the element converts from state 1 (completely devoid of water) to state 2 (completely filled with water), and the relative humidity range $H_{21} + \Delta H_{21}$ to H_{21} at which the element reverts from state 2 to state 1. Hence, sorption hysteresis may be represented diagrammatically by a moisture distribution plot as in Fig. 1. Since $H_{12} \geq H_{21}$ at any given moisture content (MC), all representative points must lie in the triangle OAB on the H_{12}-H_{21} plane (see Fig. 1). The amount of water in the various domains may be indicated by plotting a third variable $w(H_{12}, H_{21})$ in the direction perpendicular to the H_{12}-H_{21} plane, thereby producing a surface in a three-dimensional Cartesian coordinate system. Such a surface is shown in Fig. 1 by the contour plots $w_1, w_2, \ldots, w_n$. Thus, the amount of water M (expressed as a percentage of the oven-dry weight of the wood) in the domain having a transition in the quadrilateral $\Delta H_{12}\, \Delta H_{21}$ is given by $w(H_{12}, H_{21})\, \Delta H_{12}\, \Delta H_{21}$, i.e., the volume of the prism having a base $\Delta H_{12}\, \Delta H_{21}$ and altitude $w(H_{12}, H_{21})$.

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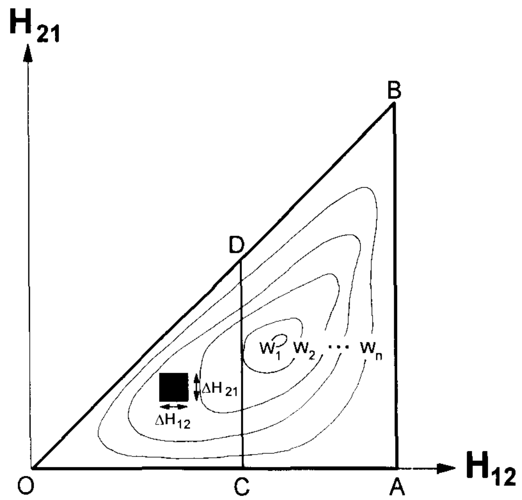

FIG. 1. Diagram showing the moisture distribution function (w) contour plots in relation to the values of the relative humidity when a particular domain converts from state 1 to state 2 (H_{12}) and from state 2 to state 1 (H_{21}).

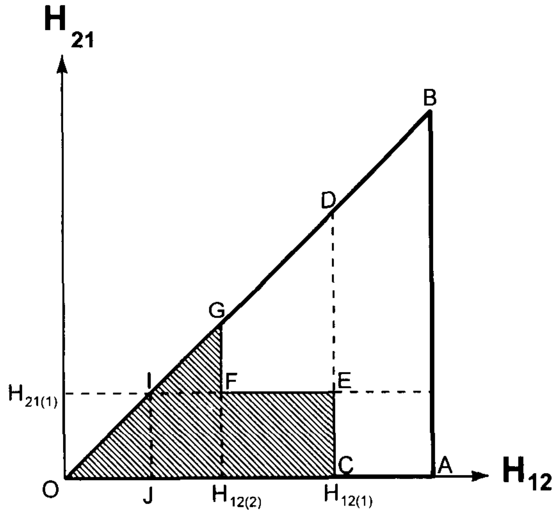

FIG. 2. State of domains for a piece of wood subjected to the following sorption series: adsorption from $H = 0$ to $H = H_{12(1)} \rightarrow$ desorption from $H = H_{12(1)}$ to $H = H_{21(1)} \rightarrow$ adsorption from $H = H_{21(1)}$ to $H = H_{12(2)}$. The shaded region shows the domains that contain water.

Moisture adsorption may be characterized by the movement away from point O of a plane parallel to the w-H_{21} plane, with the area it sweeps representing the domains that are filled with water. On the other hand, desorption may be characterized by the movement towards point O of a plane parallel to the w-H_{12} plane, with the area it sweeps representing the domains that are emptied of water. For instance, when $H_{12} = C$ is reached during adsorption from the oven-dry condition, all domains for which $H_{12} \leq C$ would contain water and the amount of adsorbed water M is given by

$$M = \int_0^C \int_0^{g(H_{12})} w(H_{12}, H_{21})\, dH_{21}\, dH_{12} \quad (1)$$

where $H_{21} = g(H_{12})$ is the function describing the diagonal OB. In general, the amount of water M in the material after a series of adsorption and desorption steps may be expressed as the sums and differences of the double integrals of w over triangles whose hypotenuses lie on the line OB. Take the case where wood is subjected to the following sorption series:

adsorption from $H = 0$ to $H = H_{12(1)}$
$\rightarrow$ desorption from $H = H_{12(1)}$ to $H = H_{21(1)}$
$\rightarrow$ adsorption from $H = H_{21(1)}$ to $H = H_{12(2)}$

The state of the domains at the end of the process is shown in Fig. 2 (note: the w axis is projecting out of the plane of the paper). The shaded region indicates the domains that contain water. Thus, the moisture content of the wood at the end of the process is given by:

M = integrals of w over ΔOCD −
− integrals of w over ΔIED +
+ integrals of w over ΔIFG

or

$$M = \int_0^{H_{12(1)}} \int_0^{g(H_{12})} w\, dH_{21}\, dH_{12} - \int_J^{H_{12(1)}} \int_{H_{21(1)}}^{g(H_{12})} w\, dH_{21}\, dH_{12} + \int_J^{H_{12(2)}} \int_{H_{21(1)}}^{g(H_{12})} w\, dH_{21}\, dH_{12} \quad (2)$$

It is apparent from the above discussion that if the moisture distribution function w is known, the moisture content M can be obtained after any given sequence of relative humidity changes.

In an earlier paper (Peralta 1995b), a grid of values was constructed to describe moisture sorption hysteresis in yellow-poplar at 30°C. Strictly speaking, the reported grid cell values are those of M over a given H interval and not those of the moisture distribution function w. Described below is a procedure for determining w and for constructing the moisture distribution diagram that is more in conformance with the theory of independent domains.

From Eqs. 1 and 2, it is apparent that the function w is given by the expression

$$w = \frac{\partial}{\partial H_{12}}\left(\frac{\partial M}{\partial H_{21}}\right) \quad (3)$$

Hence, it is possible to compute for w if a family of primary scanning curves as in Fig. 3a is available. In the diagram, the reversal relative humidities for the various primary desorption scanning curves are denoted by $H_{12(1)}$, $H_{12(2)}, \ldots, H_{12(n)}$. At a given relative humidity, say $H_{21(\beta)}$, the slope dM/dH of each scanning curve can be calculated and then plotted against the corresponding reversal relative humidity H_{12} to obtain a curve similar to Fig. 3b. The slope of the dM/dH vs. H_{12} curve at a given H_{12} value, say $H_{12(\alpha)}$, yields $w(H_{12(\alpha)}, H_{21(\beta)})$. By repeating the procedure for various values of H_{21}, a family of dM/dH vs. H_{12} curves can be obtained, from whose slopes the value of $w(H_{12}, H_{21})$ can be calculated for any pair of arbitrary H_{12} and H_{21}. The values of w may then be plotted against H_{12} and H_{21} to yield a moisture distribution diagram that can be used to calculate for M by integration.

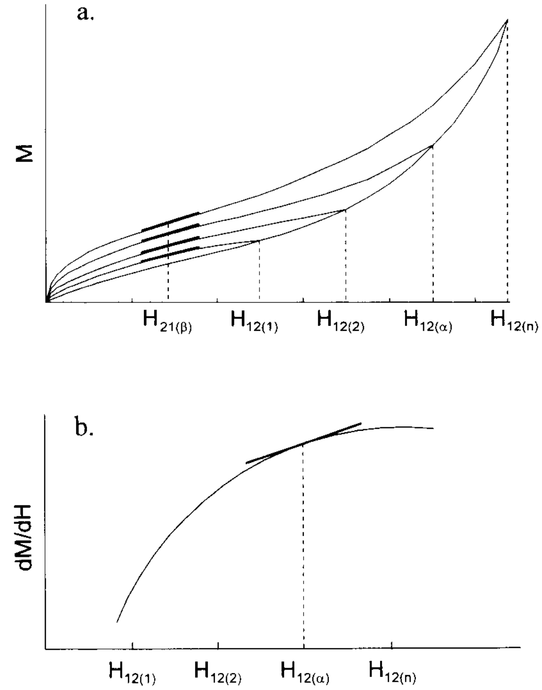

FIG. 3. Schematic representation of the general approach taken to obtain the moisture distribution function from the slopes of a family of desorption scanning curves (a), and the slopes of dM/dH vs. H_{12} curves (b), with $H_{21(\beta)}$ as a parameter.

RESULTS AND DISCUSSION

The above procedure for constructing a moisture distribution diagram was applied to the sorption data for yellow-poplar at 30°C (Peralta 1995a, b). Using the data in Table 1 of Peralta (1995b), the slopes of the secant lines ($\Delta M/\Delta H$) for the curves with reversal RH points (H_{12}) at 32, 53, 75, 92, and 100% were calculated over the relative humidity range (H_{21}) of 11 to 32%. Thus,

at $H_{12} = 32\%$,

$$\Delta M/\Delta H = (5.39 - 2.98)/(32 - 11) = = 2.41/21$$

at $H_{12} = 53\%$,

$$\Delta M/\Delta H = (6.17 - 3.06)/(32 - 11) = = 3.11/21$$

at $H_{12} = 75\%$,

$$\Delta M/\Delta H = (6.50 - 3.11)/(32 - 11) = = 3.39/21$$

at $H_{12} = 92\%$,

$$\Delta M/\Delta H = (6.62 - 3.16)/(32 - 11) =$$
$$= 3.46/21$$

at $H_{12} = 100\%$,

$$\Delta M/\Delta H = (6.67 - 3.19)/(32 - 11) =$$
$$= 3.48/21$$

The $\Delta M/\Delta H$ values obtained above were then plotted against H_{12} as in Fig. 3a. Since the moisture distribution function over the relative humidity range of 11 to 32% is of interest, the curve has to be extrapolated to $H_{12} = 11\%$. It is assumed here that the $\Delta M/\Delta H$ corresponding to this relative humidity is zero. Hence, the slopes of the secant lines $[\Delta(\Delta M/\Delta H)/\Delta H]$ for the above curves over the H_{12} ranges of 11 to 32, 32 to 53, 53 to 75, 75 to 92, and 92 to 100% were calculated as follows:

At $H_{12} = 11$ to 32%,

$$\Delta(\Delta M/\Delta H)/\Delta H = (2.41/21 - 0)/(32 - 11) =$$
$$= 2.41/(21)(21)$$

At $H_{12} = 32$ to 53%,

$$\Delta(\Delta M/\Delta H)/\Delta H$$
$$= (3.11/21 - 2.41/21)/(53 - 32) =$$
$$= 0.7/(21)(21)$$

At $H_{12} = 53$ to 75%,

$$\Delta(\Delta M/\Delta H)/\Delta H =$$
$$= (3.39/21 - 3.11/21)/(75 - 53) =$$
$$= 0.28/(21)(22)$$

At $H_{12} = 75$ to 92%,

$$\Delta(\Delta M/\Delta H)/\Delta H =$$
$$= (3.46/21 - 3.39/21)/(92 - 75) =$$
$$= 0.07/(21)(17)$$

At $H_{12} = 92$ to 100%,

$$\Delta(\Delta M/\Delta H)/\Delta H =$$
$$= (3.48/21 - 3.46/21)/(100 - 92) =$$
$$= 0.02/(21)(8)$$

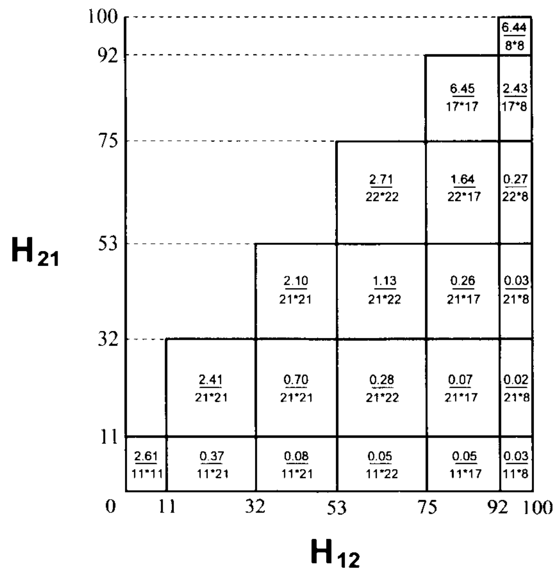

FIG. 4. Moisture distribution diagram for yellow-poplar at 30°C obtained using the slopes of secant lines approach. The moisture distribution function (w) is assumed to come out of the plane of the paper, and its magnitude is denoted by the numbers written in the different cells.

The $\Delta(\Delta M/\Delta H)/\Delta H$ values obtained above are the w's for the H_{21} range of 11 to 32%. Similar calculations may be performed for the H_{21} ranges of 0 to 11, 32 to 53, 53 to 75, 75 to 92, and 92 to 100% to yield the moisture distribution diagram in Fig. 4. This diagram, which is an improved version of the grid diagram reported in Fig. 6 of Peralta (1995b), has cell value denominators that reflect the H_{12} and H_{21} ranges over which a particular domain converts from one state to the other. The importance of the H_{12} and H_{21} values in the calculation of moisture content is depicted in the way Fig. 4 is presented, that is, the spacings of the grid are all drawn to scale. This was not included in the previous paper where the moisture content values of the different domains were reflected in the relative heights of the prisms (projecting out of the plane of the paper), with the H_{12} and H_{21} values playing no role in the calculations. In other words, the grid values reported in the previous paper are already those of M, while the grid values in

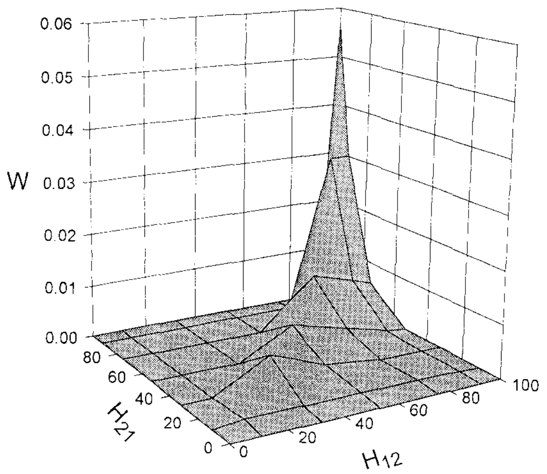

FIG. 5. Surface plot showing the moisture distribution function (w) obtained using the slopes of tangent lines approach.

Fig. 4 are those of w. The moisture content of a particular domain in Fig. 4 can be obtained from the domain's volume, i.e., from that domain's base area $\Delta H_{12}\Delta H_{21}$ and its corresponding altitude w.

An alternative approach to establishing the moisture distribution function involves the use of a numerical method to calculate the slopes of tangent lines. This is best implemented using a cubic spline algorithm which assigns first derivatives at the knots of a set of interpolation values. The procedure is first performed on the scanning curves to yield the dM/dH values at the different H_{21} levels. A series of cubic splines is then performed on the dM/dH vs. H_{21} data to yield the second derivative values [d(dM/dH)/dH] from which the moisture distribution function w can be obtained. The function w may be presented in the form of a surface plot (as in Fig. 5), which when integrated numerically gives the moisture content of the wood subjected to a series of relative humidity changes. This approach is harder to implement due to the complexity of performing the numerical integrations. Simplifying assumptions also have to be made during the calculation of the values of d(dM/dH)/dH at $(H_{12}, H_{21}) = (100, 100)$, and at $H_{21} = 0$ for all values of H_{12}. The former is related to singularity problem encountered in generating the surface plot at the high end of the relative humidity range. The latter is needed to force the moisture distribution function to go to zero at $H_{21} = 0$, thereby making the model agree with the physical observation that the wood moisture content goes to zero under zero relative humidity.

SUMMARY

A method for establishing the moisture distribution diagram for a piece of wood exhibiting sorption hysteresis is developed. The method is a refinement of a previously reported procedure and is implemented using slopes of secant lines. An alternative approach using slopes of tangent lines calculated numerically via cubic spline algorithm is also briefly described. The former is the preferred technique both for simplicity and accuracy. In fact, the latter tends to underestimate the moisture content of wood.

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