

EXPERIMENTS ON STEADY-STATE NONISOTHERMAL MOISTURE MOVEMENT IN WOOD

Perry N. Peralta

Assistant Professor
Department of Forest Resources
Clemson University
Clemson, SC 29634

and

Christen Skaar

Professor Emeritus
Department of Wood Science and Forest Products
Virginia Polytechnic Institute and State University
Blacksburg, VA 24061

(Received September 1992)

ABSTRACT

The study was conducted to measure experimentally the steady-state uniaxial (tangential direction) moisture content and temperature profiles in moisture-sealed wood samples whose opposite faces were subjected to constant but different temperatures, and to compare these profiles with those predicted by several theoretical models. The experimental variables considered were wood species, initial moisture content, and temperature range.

Opposite faces of the moisture-sealed assembly were exposed continuously for approximately five weeks to different but constant temperatures until the original uniform moisture content redistributed itself. At the steady state, a moisture content gradient opposite to the temperature gradient was established. The temperature gradient was constant in all cases, with the moisture content profile increasing almost exponentially with decreasing temperature. The absolute value of the ratio of the moisture content gradient to the temperature gradient $(dM/dT)_s$ was found to increase with wood moisture content and was observed to be higher at the higher temperature range. There was only a small difference in the $-(dM/dT)_s$ between the two species studied.

The ratio $-(dM/dT)_s$ was analyzed in terms of five different theoretical models, two of which are based on nonequilibrium thermodynamics (NET) and three on classical thermodynamics. The two NET models (basic NET and Nelson models) provided the best agreement with the experimental values. The Siau model gave the next best prediction, followed by the Stanish model, and lastly by the Skaar-Siau model.

Keywords: Nonequilibrium thermodynamics, nonisothermal, thermal diffusion, moisture transport, Soré effect.

INTRODUCTION

The mechanism of moisture movement through wood has been extensively studied because of its fundamental importance in understanding the behavior of wood during processing and when it is in service. Despite the wealth of experimental and theoretical research devoted to it, moisture movement in

wood is neither well-characterized nor fully understood. Although wood in practice is rarely maintained in an isothermal state, most investigations on moisture movement have been performed under constant-temperature conditions. Furthermore, moisture transport in wood has often been treated independently of heat transfer, and vice versa, when in fact such

exclusivity does not occur. Studies have shown that couplings exist between the flow of heat and the flow of mass (Katchalsky and Curran 1965). One such heat-mass transport coupling phenomenon is known as the thermal-diffusion or Soret effect wherein mass is transported through a medium in the direction of decreasing temperature even in the absence of a concentration gradient. Studies have demonstrated that the Soret effect also occurs in wood; that water can move through wood against the moisture gradient if a reverse temperature gradient of sufficient magnitude is maintained in the material (Siau and Babiak 1983; Siau and Jin 1985; Siau et al. 1986; Avramidis et al. 1987; Avramidis and Siau 1987).

Over the years, several theoretical solutions to the problem of nonisothermal moisture movement in wood have been forwarded. Some of these are based on the principles of nonequilibrium thermodynamics (NET), while others are mechanistic in nature. The validity of these theoretical models can be verified only through careful experimental measurements. Only three sets of data on nonisothermal moisture diffusion are presently available. The oldest of these was obtained by Voigt et al. (1940), the second was reported by Choong (1963), and the most recent one was obtained by Siau and coworkers at the State University of New York (Siau and Babiak 1983; Siau and Jin 1985; Siau et al. 1986; Avramidis et al. 1987; Avramidis and Siau 1987). All these studies were carried out on solid wood samples. The experiments required long time periods to achieve moisture equilibrium such that very few samples were analyzed and insufficient data were generated to thoroughly test the various theories of nonisothermal diffusion.

This paper presents the results of a study conducted to measure experimentally the uniaxial temperature and moisture content profiles at steady-state conditions in wood samples whose opposite faces were maintained at different but constant temperatures. An experimental procedure was devised to generate a large database, which allowed a comparative evaluation of the applicability of several the-

oretical models proposed to quantify the phenomenon of nonisothermal moisture diffusion in wood.

THEORETICAL BACKGROUND

Isothermal moisture transport

Most analyses of moisture transport in wood have used Fick's law for quantifying the process. The steady-state form of this law expresses the rate of water diffusion as a product of a diffusion coefficient and a driving force. However, the identification of the proper driving force has been a source of controversy for years. Many investigators assumed that the potential that causes moisture movement is the concentration gradient, expressed either as mass of moisture per unit volume or as mass of moisture per unit mass of dry wood (Skaar 1957; Stamm 1959; Choong 1963; Comstock 1962). This approach was successfully applied to many moisture transport experiments; however, the diffusion coefficients obtained were strong functions of moisture content, temperature, and wood properties. Other researchers suggested that a gradient of a more fundamental potential than concentration is involved and proposed such driving forces as gradient in vapor pressure (Bramhall 1976, 1979), spreading pressure (Babbitt 1950; Skaar and Babiak 1982; Nelson 1986a), chemical potential (Kawai 1980), and concentration of activated moisture molecules (Skaar and Siau 1981).

The use of Fick's law to quantify the movement of moisture in wood was even extended to nonisothermal conditions. Bramhall (1976, 1979), in trying to identify the proper driving force for moisture movement in wood, attempted to explain the experimental results on nonisothermal diffusion obtained by Voigt et al. (1940) and Choong (1963) using the steady-state form of Fick's law but with vapor pressure gradient as the driving force. This approach resulted in a considerable controversy, which precipitated a lively exchange of ideas in the wood science literature and led to a renewed interest in the subject of nonisothermal moisture movement in wood (Stanish 1986).

Nonisothermal moisture transport

Siau and coworkers at the State University of New York (Siau and Babiak 1983; Siau and Jin 1985; Siau et al. 1986; Avramidis et al. 1987; Avramidis and Siau 1987) performed a series of experiments designed mainly to test Bramhall's hypothesis. These investigations confirmed the fact that Fick's law does not apply under nonisothermal conditions, and that neither moisture content nor partial pressure gradient alone could explain the observed results. However, when a combination of moisture content and temperature gradients was considered, a relatively good agreement was obtained between the experimental and theoretical fluxes.

The mathematical treatment of the coupling of mass and heat transfer can generally be categorized into the NET approach, or the mechanistic or classical approach. In the former, attempts are made to relate the entropy production in the system to the heat and mass transfer rates so that relevant driving forces and fluxes can be identified and related through a number of phenomenological coefficients. In the second approach, a physical model for the system is theorized, and macroscopic descriptions of mass and heat movements are derived. The mathematical models for nonisothermal moisture movement in wood proposed by Siau (1980), Skaar and Kuroda (1984), and Nelson (1986b) fall under the first category; while those forwarded by Skaar and Siau (1981), Siau (1983, 1984), and Stanish (1986) can be grouped under the second category.

The following discussion presents the theoretical models of thermal diffusion and outlines how these models can be manipulated to convert the equation variables into terms that can both be calculated independently and be measured experimentally, thereby providing a method for verification of the models.

One of the theoretical equations proposed to describe quantitatively the flow of moisture in wood under nonisothermal conditions is based on the NET approach, which for uniaxial flow in the x direction is given by (Skaar and Kuroda 1984):

$$J_w = -L_{ww} \frac{d\mu_{wc}}{dx} - L_{wq} \frac{d(\ln T)}{dx} \quad (1)$$

where J_w is the moisture flux; L_{ww} the phenomenological coefficient related to the diffusion coefficient; μ_{wc} the concentration-dependent component of the specific chemical potential of water; L_{wq} the coupling coefficient associated with the flow of water due to a thermal gradient; and T the absolute temperature. In terms of the heat of transfer Q^* , and moisture conductivity K_M , the above equation may be rewritten in the following form (Peralta 1990):

$$J_w = -K_M \left[\frac{dM}{dx} + \frac{Q^*H}{RT \left(\frac{\partial H}{\partial M} \right)} \frac{d(\ln T)}{dx} \right] \quad (2)$$

where M is the moisture content based on the oven-dry weight of the wood; H the relative humidity; and R the gas constant.

A modification of the NET model (Eq. 1) was proposed by Nelson (1986b) and is written as follows:

$$J_w = -\frac{\rho_c n m D B_n \Delta\mu}{RT} \times \left[\frac{-(\Delta H_o + \Delta H_s - C_p^v T) dT}{B_n \Delta\mu T} \frac{dT}{dx} + \frac{dm}{dx} \right] \quad (3)$$

where ρ_c is the density of the cell wall at the fractional moisture content m ; D the diffusion coefficient under isothermal conditions; n the dimensionless exponent relating the spreading pressure to vapor pressure; B_n the slope of the equation ($\ln \Delta\mu = A - B_n m$) relating the natural logarithm of the change in the molar free energy of adsorbed water $\Delta\mu$ with fractional moisture content m ; ΔH_o the molar heat of vaporization of liquid water; ΔH_s the differential molar heat of sorption; and C_p^v the heat capacity of water vapor at constant pressure.

An equation based upon the gradient of ac-

tivated water molecules was proposed by Skaar and Siau (1981). By assuming that the concentration of activated molecules in the cell wall follows a Boltzmann distribution, the following expression for moisture flux is obtained:

$$J_w = -K_b \left[\frac{dM}{dx} + \left(\frac{M}{RT + 70M} \right) \times \left(\frac{9,200 - 70M}{T} \right) \frac{dT}{dx} \right] \quad (4)$$

where K_b is the bound water conductivity coefficient.

Siau (1984) later proposed another equation by defining moisture flux in terms of the water potential gradient. After introducing some simplifying assumptions, the equation takes the form:

$$J_w = -K_b \left[\frac{dM}{dx} + \frac{H}{RT} \frac{\partial M}{\partial H} \times \left(\frac{\partial \mu_1^0}{\partial T} + \frac{\Delta H_o + \Delta H_s + E_s}{T} + R \ln \left(\frac{H p_o}{7,600} \right) \right) \frac{dT}{dx} \right] \quad (5)$$

where $\partial \mu_1^0$ is the chemical potential of pure water at atmospheric pressure; E_s the activation energy for bound water diffusion; and p_o the saturated water vapor pressure.

After reviewing the different equations used to characterize moisture transport through wood, Stanish (1986) developed a mathematical expression for the net migration rate of water in the bound and vapor phases by assuming that the diffusion of bound water is driven by the gradient in the chemical potential of the bound water molecules, while water vapor diffusion is driven by the gradient in the mole fraction of water in the gas phase. Thus the total flux of moisture through wood was defined as $J_w = n_b + n_v$, where n_b and n_v are the flux of bound water through the cell wall and the flux of water vapor through the gas phase, respectively. Expressions for n_b and n_v are given by:

$$n_b = -K_\mu \frac{(1 - \epsilon)}{m_v} \left[- \left(187 + c_p \ln \frac{T}{298.15} - R \ln \frac{p}{101,325} \right) \frac{dT}{dx} + \frac{RT}{p} \frac{dp}{dx} \right] \quad (6)$$

$$n_v = -1.21 \times 10^{-4} \left[\frac{m_v \alpha T^{0.75}}{R \left(1 - \frac{p}{p_t} \right)} \frac{d \left(\frac{p}{p_t} \right)}{dx} \right] \quad (7)$$

where K_μ is the bound water diffusion coefficient with chemical potential as the driving force; $(1 - \epsilon)$ the fractional volume occupied by the cell wall; m_v the molecular weight of water vapor; $187 \text{ J mol}^{-1} \text{ K}^{-1}$ the average of the statistical and third law entropies of water vapor at 298.15 K and one atmosphere pressure; c_p the heat capacity; p the water vapor pressure; α the attenuation factor; and p/p_t the mole fraction of water vapor in air.

Now consider a rectangular wood sample initially at a uniform temperature T_0 and moisture content M_0 , and sealed so that it can not exchange moisture with the environment (Fig. 1). If the two opposite faces are suddenly exposed to two different but constant temperatures, a temperature profile T_∞ will develop in a relatively short time. The initial uniform moisture profile will also commence to change to some intermediate profile M_1 due to thermal diffusion. This moisture distribution will continue to change as it approaches a steady-state condition. Under steady-state conditions, both temperature T_∞ and moisture content M_∞ profiles will remain invariant with time, and there will be no further net moisture flux since the flow of moisture due to the thermal gradient is opposed by the flow of moisture due to the moisture content gradient.

The equations for nonisothermal moisture movement presented above may be used to estimate the relationship between temperature and moisture content profiles in wood under

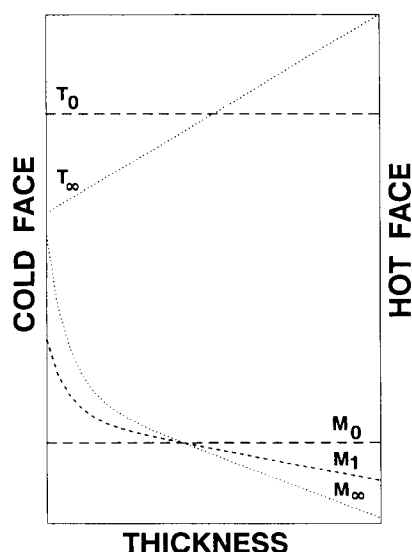


FIG. 1. Hypothetical temperature and moisture content profiles in a sealed wood sample sandwiched between hot and cold plates.

the steady-state condition with zero net moisture flux. Equation (2), for instance, can be shown to reduce to the following form at $J_w = 0$:

$$\left(\frac{dM}{dT}\right)_s = -\frac{HQ^*}{RT^2\left(\frac{\partial H}{\partial M}\right)_T} \quad (8)$$

Similarly, the equations of Nelson (1986b), Skaar and Siau (1981), and Siau (1984) reduce to the following forms, respectively, at $J_w = 0$:

$$\left(\frac{dM}{dT}\right)_s = \frac{\Delta H_o + \Delta H_s - C_p v T}{B_n \Delta \mu T} \quad (9)$$

$$\left(\frac{dM}{dT}\right)_s = -\frac{9,200 - 70M}{\frac{RT^2}{M} + 70T} \quad (10)$$

$$\begin{aligned} \left(\frac{dM}{dT}\right)_s = & -H \left(T \frac{d\mu_1^o}{dT} + \Delta H_s + \Delta H_o + E_s + \right. \\ & \left. + RT \ln \frac{Hp_o}{7,600} \right) \div \\ & \div RT^2 \left(\frac{\partial H}{\partial M} \right)_T \end{aligned} \quad (11)$$

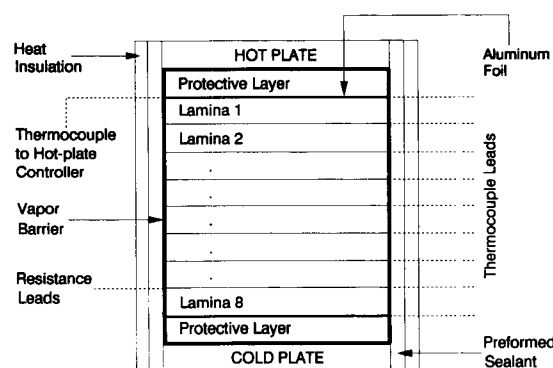


FIG. 2. Diagram of a specimen assembly in the nonisothermal experiment.

At steady-state conditions, the ratio of the moisture content gradient and the temperature gradient for the bound water diffusion equation of Stanish (1986) is given by:

$$\left(\frac{dM}{dT}\right)_s = -\frac{HTs_v}{RT^2\left(\frac{\partial H}{\partial M}\right)_T} \quad (12)$$

where s_v is the molar entropy of water vapor.

The different variables in Eqs. (8) to (12) can be calculated independently and, therefore, allow a direct comparison between the theoretical and experimental values of $(dM/dT)_s$. The experimental $(dM/dT)_s$ can be obtained by taking the ratio of the slopes of the moisture content and temperature profiles after fitting the appropriate regression equations through the data points.

EXPERIMENTAL PROCEDURE

Quarter-sawn wood laminae with dimensions of 2 (t) $\times$ 100 (r) $\times$ 100 (l) mm were conditioned to the desired initial moisture content (MC). Once the equilibrium moisture content was attained, eight end-matched laminae were combined to form a laminated (but not glued) assembly with a thickness of 16 mm in the tangential direction. During the process of assembling the specimen, a 30-gage copper-constantan thermocouple was inserted between each layer of wood to allow monitoring of the temperature profile when the specimen

was later pressed between the hot and cold plates (Fig. 2). With the thermocouples in place, the assembly clamped, and the protective layers positioned on the outer wide faces, the edges were glued with an adhesive. The protective layers were 2-mm-thick wood wafers bonded with aluminum foil on the face in contact with the wood assembly, and were added so that the outermost laminae of the sample were not coated with the vapor barrier. After gluing, the assembly was coated on all surfaces with six layers of a vapor barrier, then bonded with one layer of aluminum foil, and finally covered with six more layers of the vapor barrier. Once the last coating had dried, the sample was clamped between temperature-controlled plates wherein opposing radial faces of the specimen were subjected to different but constant temperatures. At this time, a preformed sealant was wrapped around the whole setup to further prevent moisture loss. To minimize the effects of environmental temperature, the setup was covered with a heat insulator.

The wood assembly was left between the platens until steady state was attained (about 4 to 5 weeks). To determine whether this condition had been reached, the MC of the veneer closest to the cold plate was monitored using electrical resistance electrodes consisting of two thin parallel strips of silver paint applied on one surface of the last lamina before the sample was assembled. These electrodes were connected to electrical terminals leading to the measuring instrument. Since it was difficult to determine accurately the MC based on resistance measurements due to the effects of temperature, electrode geometry, and species, the main function of the electrodes was just to determine moisture content constancy to indicate that the stationary-state condition had been attained. Gravimetric determination after disassembly was used to obtain the actual MC of the laminae.

Once successive electrical resistance measurements were constant, the samples were given an extra week in the setup to be certain that the steady-state condition had indeed been attained. After the final temperature readings

at the different thermocouple locations had been taken, the sample was removed from the platens. The edges of the material were then sawn to remove the glue and the seal and to separate the different layers. Each lamina was immediately weighed and its thickness measured, after which it was placed in an oven set at 103 ± 2 C for at least 24 h to obtain the oven-dry weight. From the oven-dry weight and the weight measured immediately after disassembly, the MC of each lamina was calculated; hence the moisture profile across the thickness was determined. The temperature profile was obtained from the thermocouple readings at the different layers just prior to disassembly.

The experimental variables considered were wood species (yellow poplar and hard maple), initial moisture content (9%, 12%, and 15%), and temperature range (15 to 35 C, and 25 to 45 C). Each condition was replicated 3 or 4 times for a total number of 42 different tests. The study was performed as a three-factor factorial experiment in a completely randomized design.

The procedure described above differs from that used by Voigt et al. (1940) and by Choong (1963), both of whom used solid wood blocks. The use of an assembly of laminae has some advantages over that of a solid block of wood. First, the moisture distribution upon completion of an experiment can be measured more quickly and accurately since the individual lamina can be removed and isolated rapidly, compared with the sectioning procedures required for a solid wood sample. Second, a given test sample assembly consisting of a number of end-matched laminae, all from similar growth increments, will generally be more homogeneous than a single block containing wood from a large number of growth increments. Third, temperature and resistance probes can be located easily in the test samples so that *in situ* temperature and MC values are determined conveniently. The primary disadvantage of the laminate assembly is the presence of discontinuities in the wood at the interfaces between laminae. This can be argued to cause

moisture movement between laminae to be faster than through the wood itself, since vapor transport is more rapid in air than through wood. There may also be a greater effect on heat transport, since it is swifter through wood than through still air. However, wood discontinuities at the laminae interfaces and their subsequent effect on moisture and heat transport are not considered serious problems since they were easily minimized by the application of sufficient pressure on the laminate to assure good contact between adjacent layers.

In addition to the above experiments, moisture sorption studies were also performed since isotherm data were required in the evaluation of the theoretical models for nonisothermal moisture transport in wood. Yellow poplar and hard maple specimens with cross-sectional area of 2,000 mm² and thickness of 6 mm in the longitudinal direction were used in the sorption study. Sample moisture equilibrations were performed in an insulated chamber supplied by a conditioned air generator. The sorption study was done at a dry bulb temperature of 30 °C at six successive levels of relative humidity (28%, 41%, 62%, 66%, 77%, and 84%) for the adsorption phase, and five levels (82%, 68%, 62%, 40%, and 34%) for the desorption phase.

RESULTS AND DISCUSSION

Curve-fitting of data

Both the temperature and moisture content profiles (T vs. x , and M vs. x , where x is the distance from the cold face) were plotted for each test. The temperature vs. distance data were fitted with a model of the form ($T = A_T + B_T x$), while the moisture content vs. distance data were fitted with an equation of the form [$M = A_M + B_M x + C_M \exp(-D_M x)$] where A_T , B_T , A_M , B_M , C_M , and D_M are constants. A strong linear relationship was obtained between temperature and distance from the cold face with a square sample correlation coefficient of at least 0.995 in all linear regression runs. A maximum absolute residual of only 0.96 K was obtained, indicating the appropri-

ateness of the linear model in predicting the temperature at different locations along the thickness of the material. The nonlinear MC model also gave a good description of the variation of moisture content with distance from the cold face. This was reflected in the values of the predicted moisture content, which were close to the actual values, the maximum absolute residual being only 0.45% MC. The moisture content points at the second layer from the hot face ($x \approx 1.3$ cm from the cold plate) were omitted in the analysis because the samples in this lamina had a different sorption history than the others in that they had once been oven-dried. Representative curves of temperature and MC variations across the thickness of the material are presented in Fig. 3. The temperature and MC profiles for all 42 samples were essentially similar to those shown in Fig. 3.

Experimental $(dM/dT)_s$ values

The observed development of a moisture gradient opposite to the imposed temperature gradient indicates the occurrence of thermal diffusion. The magnitude of this phenomenon is given here in terms of the relationship $(dM/dT)_s$, which is obtained directly by taking the ratio of the derivatives dM/dx and dT/dx of the moisture content and temperature regression equations. The ratio is interpreted as the moisture content gradient, which causes a flux of moisture equal and opposite to that due to an applied unit temperature gradient. Figure 4 shows the plots of $-(dM/dT)_s$ against distance from the cold face, for each of the samples shown in Fig. 3. The $-(dM/dT)_s$ ratio remained more or less constant near the hot face, and then increased exponentially as the cold face was approached. This may be due mainly to the variation in the moisture content across the thickness of the material—the layers near the cold face being at higher MCs than the sections near the hot face. The curves indicate that it is much easier to effect moisture migration under a thermal gradient when the moisture content is high than when the moisture content is low. From a theoretical point

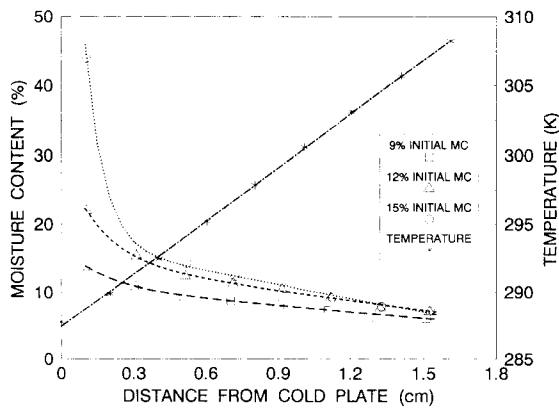


FIG. 3. Steady-state temperature and moisture content profiles in yellow poplar samples with different initial moisture contents (9%, 12%, and 15% MC) subjected to 15 C and 35 C on opposite faces.

of view, the ease of moisture flow should increase with increase in moisture content. At low MCs, water molecules are believed to be tightly bound to localized sorption sites in the wood, whereas at higher moisture contents a greater fraction of them are bound less tightly and therefore are more mobile (Stamm 1964). The temperature variation across the thickness of the material should also affect the magnitude of $-(dM/dT)_s$ at different locations in the sample. Studies on moisture diffusion in wood show that the diffusion coefficient is higher at higher temperatures, meaning that moisture movement is faster if the wood is at an elevated temperature. If this factor were the only one operating, then $-(dM/dT)_s$ would have increased with distance from the cold face, not the other way around as observed here. The inference that can be made from this is that $-(dM/dT)_s$ is affected more by moisture content variation than by temperature variation in the material.

The moisture content and temperature dependence of $-(dM/dT)_s$ may also be gleaned from the effects of the different experimental variables on the magnitude of this ratio. Mean comparisons revealed that $-(dM/dT)_s$ increased with increase in the initial moisture content, as expected. At a given location, the moisture content was high for the samples with high initial moisture content and, thus, as explained above, a unit temperature gradient was

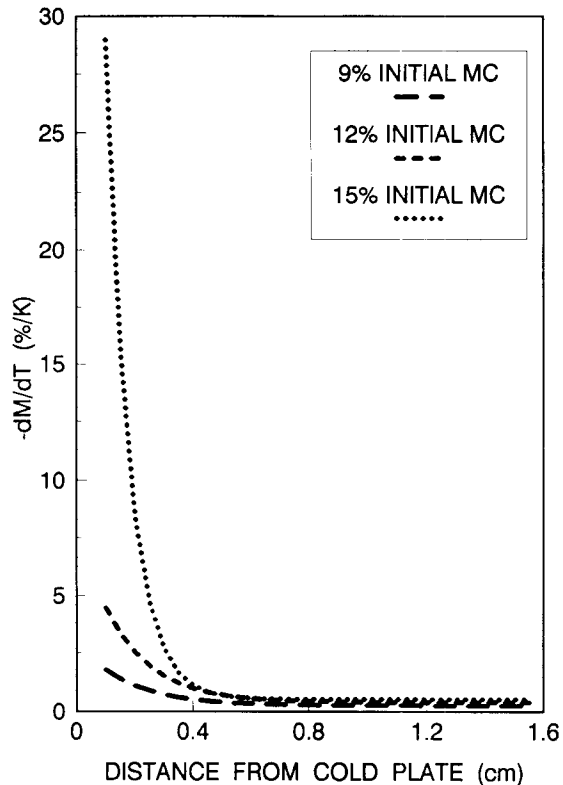


FIG. 4. $-(dM/dT)_s$ at different locations along the thickness of nonisothermal steady-state samples. The curves are those of yellow poplar samples of different initial moisture contents (9%, 12%, and 15% MC) subjected to 15 C and 35 C on opposite faces.

able to cause greater moisture flow in these samples.

The $-(dM/dT)_s$ ratio was higher in samples subjected to the 25 to 45 C temperature range than in the materials exposed to the 15 to 35 C temperature range at any given moisture content. Thus, to offset the moisture flow caused by a given temperature gradient, a higher moisture content gradient must be imposed on a material that is at a higher temperature. The reason for this may be that in wood at a higher temperature, a greater fraction of the water molecules have enough energy to overcome the potential energy barrier that keeps them bound to a particular sorption site (Choong 1965). Since the rate of movement is directly proportional to the number of molecules with energy in excess of the bonding energy, then a smaller temperature gradient must

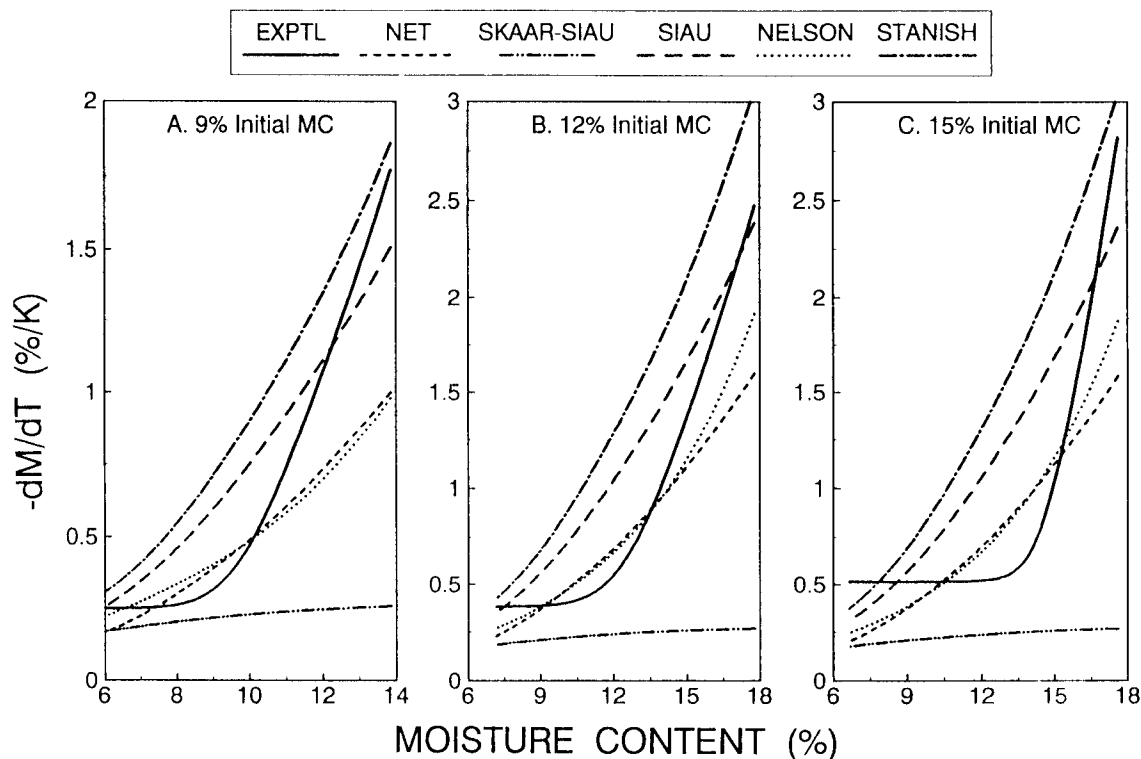


FIG. 5. Experimental and theoretical $-(dM/dT)$ plotted against moisture content at different locations along the thickness of nonisothermal steady-state samples. The curves are those of yellow poplar samples of different initial moisture contents (A: 9%, B: 12%, and C: 15% MC) subjected to 15 C and 35 C on opposite faces.

be applied to the sample that is at a higher temperature to obtain the same flux as the sample that is at a lower temperature.

The average $-(dM/dT)_s$ was slightly higher in hard maple than in yellow poplar at corresponding conditions. The difference was so small that it may have been due to experimental and curve-fitting errors.

Evaluation of the theoretical models

To test the various models proposed to explain the nonisothermal moisture transport in wood, information on the relative and/or absolute vapor pressures in the wood samples must be estimated. The data generated in the sorption experiments were for wood samples undergoing either desorption from the wet condition or adsorption from the fully dry condition, all at 30 C (Peralta 1990). However, the wood laminae used in the nonisothermal tests were subjected to different moisture and

temperature histories depending on their initial moisture contents and their locations in a given assembly. For instance, the laminae near the cold plate attained a lower temperature than the initial condition of 30 C, and were subjected to moisture adsorption, the reverse being true for the laminae near the hot plate. It was therefore necessary to adjust the sorption isotherms obtained experimentally to account for both sorption hysteresis and temperature effects in the nonisothermal experiments.

Hysteresis effects were estimated by constructing a composite sorption isotherm intermediate between the complete adsorption and desorption curves. For each assembly, the lowest moisture content (at or near the hot-plate face) was presumed to lie on the complete desorption curve, and the highest moisture content below 30% (at the cold-plate face) on the adsorption curve. Seven additional points,

corresponding to the intermediate moisture contents along the assembly thickness, were interpolated between the two extreme sorption curves in proportion to their locations in the assembly. Finally, the Hailwood-Horrobin sorption model was fitted to the nine data points to obtain an equation for the composite sorption curve. After adjusting the sorption isotherm for hysteresis, correction for temperature effects was performed using the differential heat of sorption defined by the Clausius-Clapeyron equation (Skaar 1988).

To determine the applicability of the five theoretical models in describing nonisothermal moisture movement in wood, the $-(dM/dT)_s$ values given by Eqs. (8) to (12) were obtained for each experimental unit and then compared with the experimental values. This was done by calculating, through numerical integration, the area bounded by the graphs of the experimental and theoretical $-(dM/dT)_s$; and by performing an analysis of the absolute residuals at the locations in the samples where the temperatures and moisture contents were measured.

The $-(dM/dT)_s$ values plotted against the final moisture content are shown in Fig. 5, while the results of the area calculations and residual analyses are presented in Table 1. In performing the numerical integrations and residual analyses, comparisons were restricted to data that fell within the range of moisture contents obtained in the sorption studies (~6 to 16% MC). This was done to minimize error associated with extrapolation of the sorption isotherms beyond the experimental relative humidity (RH) range. In interpreting the results of the model comparisons, less emphasis should be placed on the samples with an initial moisture content of 15% since for these samples, the laminae near the cold surface had moisture contents exceeding the fiber saturation point. Considering that the models deal only with moisture movement in the hygroscopic range, the presence of free water in the 15% EMC samples unduly complicates the analysis due to the contribution by other driving forces to the movement of water in wood.

Of the five theoretical models under consid-

TABLE 1. Area calculations and absolute residual analyses of $-(dM/dT)_s$ for nonisothermal steady-state samples of different initial moisture contents.

Initial MC	Model	Area (% cm K ⁻¹)	Absolute residual (% K ⁻¹) ^a	
			Mean	Std. dev.
9%	NET	0.132	0.123	0.205
	Nelson	0.144	0.133	0.211
	Skaar-Siau	0.314	0.280	0.418
	Siau	0.238	0.176	0.100
	Stanish	0.382	0.266	0.129
12%	NET	0.167	0.162	0.219
	Nelson	0.133	0.123	0.142
	Skaar-Siau	0.527	0.483	0.579
	Siau	0.358	0.273	0.174
	Stanish	0.633	0.492	0.253
15%	NET	0.230	0.234	0.223
	Nelson	0.204	0.204	0.169
	Skaar-Siau	0.494	0.495	0.511
	Siau	0.438	0.371	0.262
	Stanish	0.682	0.573	0.391

^a Absolute residual = ABS[(expt. dM/dT) - (theor. dM/dT)].

eration, the two NET models (basic NET model and Nelson model) gave the best fit to the experimental data; the Siau model followed closely. The Skaar-Siau activated molecule model underpredicted $-(dM/dT)_s$ in all the experimental runs; while the bound-water-flow component of the Stanish model overpredicted the ratio in most cases. The total divergence, as given by the area calculations, was in general lowest for the Nelson model. It was followed, in the order of increasing deviation, by the basic NET model, the Siau model, the Skaar-Siau model, and the Stanish model. The mean absolute residuals also yielded the same results. Interestingly, in the samples with an initial moisture content of 9%, the standard deviation of the absolute residual was low for both the Siau and the Stanish models. This indicates that the difference between the theoretical and experimental $-(dM/dT)_s$ values was more or less uniform for these two models. On the other hand, despite the low mean absolute residuals for the Nelson and basic NET equations, there are certain points in the graph where the calculated $-dM/dT$ deviated considerably from the experimental values. This is especially true near the cold plate where the moisture contents were high.

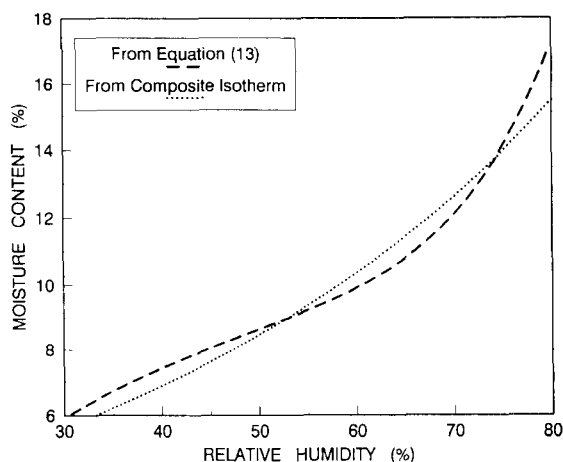


FIG. 6. Calculated relative humidity values corresponding to the different moisture contents at various locations in the yellow poplar sample with an initial moisture content of 9%.

Inaccuracies with the estimation of the effective relative humidities at the different locations in the test specimen may be partly responsible for the deviation of the theoretical values from the experimental results. Since it was not possible to measure the actual relative humidities in the sample, these values had to be inferred from the sorption isotherm data. The magnitude of the error associated with this approach may be gauged by back-calculating the effective RH using the theoretical equations and the experimental $(dM/dT)_s$. Thus, in the case of the basic NET equation, if it is assumed that the expression $Q^* = (9,200 - 70M)$ cal mol⁻¹ is valid, the theoretical RH profile in the material may be arrived at by manipulating Eq. (8) to yield:

$$H_2 = \exp \left[\ln H_1 - \frac{Q^*(M_2 - M_1)}{RT^2 \left(\frac{dM}{dT} \right)_s} \right] \quad (13)$$

In other words, for the experimental $-(dM/dT)_s$ curve to coincide exactly with that obtained using the NET model, Eq. (13) should give values equal to the actual RH profile in the sample. The results of such calculations, together with the curve obtained from the sorption isotherm, are presented in Fig. 6 for

the yellow poplar sample with an initial moisture content of 9%. A substantial difference exists between the two curves, indicating that a large error in the predicted $-(dM/dT)_s$ will result if an erroneous value of the effective RH is used in the calculations.

The difference in the $-(dM/dT)_s$ values computed from basic NET and Nelson models may be due to the assumption made in using Eq. (8) that the heat of transfer Q^* is equal to the activation energy E_s . Nelson (1986b) contended that the heat of transfer is greater than the activation energy. Based on the observation that the entropy of water vapor s_v at the steady state was more or less constant throughout the thickness of the samples in Choong's experiments (Choong 1963), Nelson took the temperature and moisture content dependence of s_v and came up with an equation for the heat transfer: $Q^* = \Delta H_o + \Delta H_s - C_p v T$. He then calculated Q^* using Choong's data and found that it exceeded the activation energy by a factor of as much as 1.33. Nelson could not explain this distinction between Q^* and E_s but hinted that it may be related to the diffusing molecules having a mean energy in excess of the minimum required for participation in diffusion. He reasoned that more energy is carried by the diffusing molecules than is required for activation of the diffusion process.

To investigate whether there is a difference in the values of E_s and of Q^* from the Nelson model, these quantities were calculated for each experimental unit in this study. The heat of transfer was also approximated from (Ts_v) of the Stanish model, and from the expression $[T(d\mu_1^o/dT) + \Delta H_s + \Delta H_o + E_s + RT \ln(Hp_o/7,600)]$ of the Siau model.

The heat of transfer from the Nelson model exceeded the activation energy at all levels of moisture content. When the ratio of these two quantities (Q^*/E_s) was taken, the resulting quotient ranged from 1.07 to 1.23, comparable to what Nelson (1986b) obtained from Choong's data. The calculated values of E_s and Q^* increased steadily with increase in distance from the cold face, that is, with decrease in wood moisture content. The magnitude varied from 7,900 to 8,800 cal mol⁻¹ for E_s , and from 8,500

to 9,900 cal mol⁻¹ for Q* computed from the Nelson model. The Siau and Stanish models yielded Q* values ranging from 11,700 to 13,600 cal mol⁻¹; and from 15,200 to 16,500 cal mol⁻¹, respectively.

SUMMARY AND CONCLUSIONS

The study confirms the results of other researchers who also showed that water can move through wood under the influence of a temperature gradient, even if such flow is opposite to the moisture content gradient. The value of the moisture content gradient that causes a flow of moisture equal and opposite to that of an applied unit temperature gradient was shown to be positively related to moisture content and temperature, an observation that is analogous to the relative effects of moisture content and temperature on the moisture diffusion coefficient of wood. Comparisons of the experimental $-(dM/dT)_s$ values with those computed using five theoretical models showed that the two NET models (basic NET and Nelson models) best described nonisothermal moisture flow in wood.

ACKNOWLEDGMENT

This paper is based on a study supported by the Cooperative State Research Service, under USDA Competitive Grants Project No. 87-FSTY-9-0260-A.

REFERENCES

- AVRAMIDIS, S., AND J. F. SIAU. 1987. Experiments in non-isothermal diffusion of moisture in wood. Part III. *Wood Sci. Technol.* 21:329-334.
- , N. KURODA, AND J. F. SIAU. 1987. Experiments in nonisothermal diffusion of moisture in wood. Part II. *Wood Fiber Sci.* 19(4):407-413.
- BABBITT, J. D. 1950. On the differential equations of diffusion. *Canadian J. Res.* 28A:449-474.
- BRAMHALL, G. 1976. Fick's laws of bound water diffusion. *Wood Sci.* 8(3):153-161.
- . 1979. Sorption diffusion in wood. *Wood Sci.* 12(1):3-13.
- CHOONG, E.T. 1963. Movement of moisture through a softwood in the hygroscopic range. *Forest Prod. J.* 13(11): 489-498.
- . 1965. Diffusion coefficients of softwoods by steady state and theoretical methods. *Forest Prod. J.* 15(1):21-27.
- COMSTOCK, G. L. 1962. Moisture diffusion coefficients in wood as calculated from adsorption, desorption, and steady state data. M.S. thesis, North Carolina State College, Raleigh, NC.
- KATCHALSKY, A., AND P. F. CURRAN. 1965. Nonequilibrium thermodynamics in biophysics. Harvard University Press, Cambridge, MA. 248 pp.
- KAWAI, S. 1980. Moisture movement and drying stresses in wood. Doctor of Agriculture dissertation, Kyoto University.
- NELSON, R. M. 1986a. Diffusion of bound water in wood. Part 2: A model for isothermal diffusion. *Wood Sci. Technol.* 20:235-251.
- . 1986b. Diffusion of bound water in wood. Part 3: A model for nonisothermal diffusion. *Wood Sci. Technol.* 20:309-328.
- PERALTA, P. N. 1990. Nonisothermal moisture transport in wood. Ph.D. dissertation, Virginia Polytechnic Institute and State University, Blacksburg, VA.
- SIAU, J. F. 1980. Nonisothermal moisture movement in wood. *Wood Sci.* 13(1):11-13.
- . 1983. Chemical potential as a driving force for nonisothermal moisture movement in wood. *Wood Sci. Technol.* 17:101-105.
- . 1984. Letter to the editor. *Wood Fiber Sci.* 16(4): 628-629.
- , AND M. BABIAK. 1983. Experiments on nonisothermal moisture movement in wood. *Wood Fiber Sci.* 15(1):40-46.
- , AND Z. JIN. 1985. Nonisothermal moisture diffusion experiments analyzed by four alternative equations. *Wood Sci. Technol.* 19:151-157.
- , F. BAO, AND S. AVRAMIDIS. 1986. Experiments in nonisothermal diffusion of moisture in wood. *Wood Fiber Sci.* 18(1):84-89.
- SKAAR, C. 1957. The moisture diffusion coefficient for beech. Ph.D. dissertation, Yale University, New Haven, CT.
- . 1988. *Wood-water relations*. Springer-Verlag, Berlin, Germany. 283 pp.
- , AND M. BABIAK. 1982. A model for bound-water transport in wood. *Wood Sci. Technol.* 16:123-138.
- , AND N. KURODA. 1984. Application of irreversible thermodynamics to moisture transport phenomena in wood. *Proc. N. American Wood Drying Symposium*. Miss. Forest Prod. Utiliz. Lab., Mississippi State, MS.
- , AND J. F. SIAU. 1981. Thermal diffusion of bound water in wood. *Wood Sci. Technol.* 15:105-112.
- STAMM, A. J. 1959. Bound water diffusion into wood in the fiber direction. *Forest Prod. J.* 9(1):27-31.
- . 1964. *Wood and cellulose science*. Ronald Press, New York, NY. 549 pp.
- STANISH, M. A. 1986. The roles of bound water chemical potential and gas phase diffusion in moisture transport through wood. *Wood Sci. Technol.* 20:53-70.
- VOIGT, H., O. KRISCHER, AND H. SCHAUSS. 1940. Die Feuchtigkeitsbewegung bei der Verdunstungstrocknung von Holz. *Holz Roh-Werkst.* 3:305-321.