MEASURING DEPENDENCE OF DIFFUSION COEFFICIENT OF WOOD ON MOISTURE CONCENTRATION BY ADSORPTION EXPERIMENTS

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(Received 14 December 1973)

ABSTRACT

The dependence of the diffusion coefficient on moisture concentration of aspen wood at 110 F was determined by using an experimental method that requires a series of adsorption experiments and by applying a numerical method that includes using a finite difference technique to solve the diffusion equation with a diffusion coefficient that is dependent on concentration. The analysis showed that the diffusion coefficient increases with mosture content. Between 2.5 and 18.0% moisture content, the diffusion coefficient increases by a factor of 8.

Additional keywords: Populus sp., seasoning, prediction, finite difference technique.

INTRODUCTION

The ability to predict moisture content of wood while it is changing or, conversely, the time required for a certain moisture content change to occur is a perennial desire of many involved in wood utilization and processing. It is further desirable to use a prediction system that is as generalized as possible. The mathematics of diffusion offers a generalized system with potential as a prediction tool for moisture changes below the fiber saturation point.

Two important aspects of the mathematics of diffusion and their application to wood are the dependence of the diffusion coefficient on moisture concentration and the use of numerical solutions to the diffusion equation. The purpose of this paper is to describe and to apply a method to determine the dependence of the diffusion coefficient of wood on moisture concentration that, to the author's knowledge, has not been reported in the wood technology literature and to apply a finite difference technique of solving the diffusion equation with a diffusion coefficient that is dependent on concentration.

PREVIOUS WORK

Martley (1926) apparently was one of the first to observe a dependence of the diffusion coefficient of wood on moisture concentration. In steady-state diffusion he found that the diffusion coefficient increased parabolically with moisture content at the low-moisture-content surface of the steady-state wood membrane. Skaar (1958) used a numerical technique in which he calculated the dependence of the diffusion coefficient on moisture concentration from the moisture content gradient at two successive times during desorption. He found that the logarithm of the diffusion coefficient increased approximately linearly with moisture content. Stamm (1959, 1960) also found evidence that the diffusion coefficient of wood increases with moisture content. Using steady-state, adsorption, and desorption experiments, Comstock (1963) also found that the diffusion coefficient of wood increases with moisture content. Choong (1965) used a steady-state experimental method and a numerical technique to determine that the diffusion coefficient increased with moisture content. Martin and Moschler (1970) measured the moisture concentration dependence of the diffusion coefficient with a technique that uses concentration-distance curves. As Skaar (1958) had found, Martin and Moschler also found an approximately linear increase of the logarithm of the diffusion coefficient with moisture content.

Apparently little is in the literature on

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TABLE 1. *Salt solutions used to control relative humidity (RH) at 110 F and average equilibrium moisture content attained by specimens*

Salt	RH (%)	Equilibrium moisture content (%)
Potassium acetate	19	2.66
Potassium carbonate	41	5.06
Sodium nitrite	65	7.49
Sodium chloride	75	9.89
Potassium chloride	81	12.16
Potassium nitrate	87	13.65
Potassium dichromate	98	16.19
Distilled water	99+	17.90

applying numerical solutions to the diffusion equation for sorption in wood. These solutions become necessary when the diffusion coefficient depends on moisture concentration because formal mathematical solutions to the diffusion equation exist only if the diffusion coefficient is constant or has special other forms. Moschler and Martin (1968) used a finite difference technique in an attempt to describe wood drying. They took diffusion coefficients and their concentration dependence from the literature and used them in the finite difference analysis, but found that these did not accurately describe the experimental wood drying they conducted.

NUMERICAL METHOD OF SUCCESSIVE APPROXIMATIONS

There are a number of experimental and numerical methods of determining the moisture diffusion coefficient and its dependence on concentration. Crank (1956) outlined a number of different methods, and Skaar (1954) discussed some of the methods and their application to wood. The method used in this paper is one by Crank and Park (1949) (also see Crank 1956, p. 242). The method is attractive because it is relatively simple experimentally. Other methods usually require either the construction of a steady-state cell or a slicing technique to determine moisture content gradients, both of which introduce additional opportunities for experimental error. The method used here requires only a series of adsorption-time curves. A disadvantage is that it requires many numerical calculations and without a high-speed digital computer, the method becomes formidable.

The method is built around a series of approximations. A formal mathematical solution to the diffusion equation for a constant diffusion coefficient is used to make certain approximations to the concentration dependent system. The formal mathematical solution used is (Crank 1956)

$$D = \frac{0.1976\ell^2}{t_{0.5}} \qquad (1)$$

where

$t_{0.5}$ is time for one-half of the total adsorption to occur; ℓ, one-half of the thickness; and D, the diffusion coefficient that is constant over the entire adsorption range.

This solution is based on the boundary condition that both surfaces come to an immediate equilibrium with the surrounding atmosphere. Application of Eq. (1) to some adsorption interval in a system in which the diffusion coefficient depends on concentration yields some average value of the diffusion coefficient over that concentration range.

The integral diffusion coefficient in a concentration dependent system is defined as

$$\bar{D} = \frac{1}{C_o}\int_0^{C_o} D\,dC \qquad (2)$$

for the concentration range zero to C_o. The approximation involved is that the D value determined from Eq. (1) is a reasonable approximation to $\bar{D}$ and thus to $(1/C_o)\int_0^{C_o} D\,dC$. Differentiating Eq. (2) with respect to the upper limit of integration yields an approximation to D as a function of concentration.

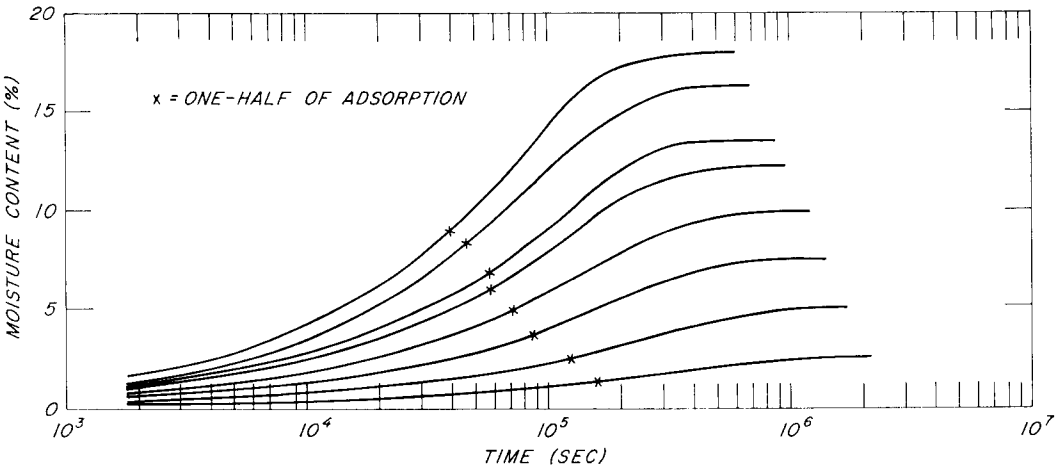

FIG. 1. Family of adsorption-time curves for aspen at 110 F between zero percent moisture content and final moisture content.

$$D(C) = \frac{d(\bar{D}C_o)}{dC_o} \tag{3}$$

Therefore, if the half times of adsorption from zero concentration to a number of different final concentrations C_o are known, the approximation to $\bar{D}$ can be calculated from Eq. (1). These values are then multiplied by the corresponding values of C_o, and differentiating $\bar{D}C_o$ with respect to C_o gives a first approximation to the value of D at the corresponding value of C_o.

The first approximation to D as a function of concentration may or may not be good enough. If it is not good enough, the approximations can be repeated any number of times. The first approximation to D can be used with a numerical solution to the diffusion equation, and a new series of adsorption-time curves can be calculated. From the half times of these calculated curves, a new set of $\bar{D}$ values are determined using Eq. (1), and further approximations are calculated in the same manner as the first. The approximations are carried out until the calculated values of $\bar{D}$ agree with the original experimental values of $\bar{D}$ as determined by Eq. (1).

FINITE DIFFERENCE TECHNIQUE

To carry out the series of approximations necessary to relate D to concentration, it is necessary to solve the diffusion equation numerically so that a concentration dependence of the diffusion coefficient can be incorporated. Crank (1956) has discussed a number of methods of numerically solving the diffusion equation, and the method used in this analysis is generally the same as one he discusses.

If the diffusion coefficient depends on concentration according to the general relationship

$$D_c = D_o f(C) \tag{4}$$

where

D_c is the diffusion coefficient at moisture concentration C and D_o, the diffusion coefficient at zero moisture content,

then the diffusion equation to be solved is Fick's second law,

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D_c \frac{\partial C}{\partial x}\right) \tag{5}$$

with the boundary conditions that the surface ($x = -\ell$, $x = +\ell$) comes to immediate equilibrium with the surrounding atmosphere, and that the initial concentration is uniform at time $t = 0$. Nondimensional variables are convenient to use and are defined as follows:

$$c = \frac{C}{C_m} \tag{6}$$

TABLE 2. *Value of upper adsorption limit* C_o, *half-time of adsorption* $t_{0.5}$, *integral diffusion coefficient* $\bar{D}$, *and product* $\bar{D}C_o$ *necessary to determine concentration dependence of diffusion coefficient*

C_o (percent moisture content)	$t_{0.5}$ (sec x 10^{-5})	$\bar{D}$ ($cm^2\ sec^{-1}$ x 10^6)	$\bar{D}C_o$ ($cm^2\ sec^{-1}$ % x 10^6)
2.66	1.59	0.436	1.16
5.06	1.16	0.605	3.06
7.49	0.857	0.824	6.16
9.89	0.703	1.00	9.91
12.16	0.574	1.23	15.0
13.65	0.570	1.26	17.3
16.19	0.458	1.58	25.4
17.90	0.390	1.85	33.0

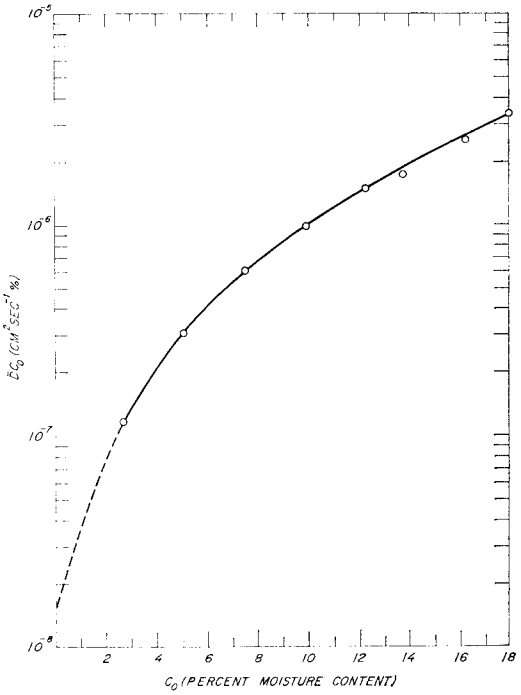

FIG. 2. Relationship between product $\bar{D}C_o$ and C_o.

where

C_m is maximum final concentration; $X = x/\ell$; $T = (D_o t)/\ell^2$; and $D = D_c/D_o$.

The diffusion equation now becomes

$$\frac{\partial c}{\partial T} = \frac{\partial}{\partial X}\left(D\frac{\partial c}{\partial X}\right) \tag{7}$$

with boundary conditions corresponding to the equation in dimensional variables. Crank (1956) introduces the variable s as a means of dealing with the concentration dependence of the diffusion coefficient. He defines s as

$$s = \frac{\int_0^c Ddc}{\int_0^1 Ddc} \tag{8}$$

and the equation to be solved becomes

$$\frac{\partial s}{\partial T} = D\frac{\partial^2 s}{\partial X^2} \tag{9}$$

with the boundary conditions

$s = 1,\ X = \pm 1,\ T > 0$
$s = 0,\ -1 < X < 1,\ T = 0.$

If D is known as a function of c, Eq. (8) can be solved and it is possible to proceed with a numerical solution to Eq. (9).

The finite difference method attributed to Schmidt as discussed in Crank (1956) was used to approximate the solution to Eq. (9). The left side of Eq. (9) can be approximated by

$$\left(\frac{\partial s}{\partial T}\right)_m \simeq \frac{s_m' - s_m}{\Delta T} \tag{10}$$

and the right side by

$$\left(D\frac{\partial^2 s}{\partial X^2}\right)_m \simeq D\left(\frac{s_{m+1} - 2s_m + s_{m-1}}{(\Delta X)^2}\right) \tag{11}$$

where s_m' and s_m are the values of s at the points $X = m(\Delta X)$ at $T = (n+1)\Delta T$ and $T = n(\Delta T)$, respectively, and s_{m+1} and s_{m-1} are the values of s at $X = (m+1)(\Delta X)$ and $X = (m-1)(\Delta X)$ at $T = n(\Delta T)$.

Combining Eq. (10) and (11), the numerical solution to Eq. (9) is

TABLE 3. *Successive approximations for determining moisture concentration dependence of diffusion coefficient of aspen wood at 110 F*

C_o (%)	$\frac{C_o}{C_m}$	$\overline{D}$ experimental ($cm^2\ sec^{-1} \times 10^6$)	$\frac{1}{C_o}\int_o^{C_o} D dC$ ($cm^2\ sec^{-1} \times 10^6$)	D_c ($cm^2\ sec^{-1} \times 10^6$)	$D = \frac{D_c}{D_o}$	$\overline{D}$ calc. ($cm^2\ sec^{-1} \times 10^6$)
				First approximation		
0	0			0.172[a]	1	
2.66	0.148	0.436	0.436	0.540	3.13	0.097
5.06	0.283	0.605	0.605	1.04	6.03	0.166
7.49	0.418	0.824	0.824	1.50	8.68	0.239
9.89	0.553	1.00	1.00	1.78	10.33	0.301
12.16	0.679	1.23	1.23	2.05	11.9	0.350
13.65	0.762	1.26	1.26	2.38	13.8	0.383
16.19	0.905	1.58	1.58	3.70	21.5	0.469
17.9	1.000	1.85	1.85	5.73	33.3	0.575
				Second approximation		
0	0			0.577[a]	1	
2.66	0.148		1.44	1.77	3.06	0.318
5.06	0.283		1.96	2.71	4.70	0.535
7.49	0.418		2.64	4.70	8.15	0.763
9.89	0.553		3.20	5.63	9.77	0.957
12.16	0.679		3.91	6.52	11.3	1.11
13.65	0.762		4.01	7.59	13.2	1.22
16.19	0.905		5.02	12.0	20.7	1.50
17.9	1.000		5.89	18.8	32.5	1.83
				Fifth approximation		
0	0			0.820[a]	1	
2.66	0.148		1.97	2.00	2.44	0.386
5.06	0.283		2.33	3.44	4.19	0.591
7.49	0.418		2.92	4.83	5.89	0.807
9.89	0.553		3.48	5.95	7.26	1.01
12.16	0.679		4.21	7.01	8.55	1.18
13.65	0.762		4.31	8.11	9.89	1.30
16.19	0.905		5.32	11.7	14.2	1.57
17.9	1.000		6.05	16.6	20.2	1.85
				Eighth approximation		
0	0			0.895[a]	1	
2.66	0.148		2.14	2.09	2.33	0.406
5.06	0.283		2.45	3.47	3.87	0.607
7.49	0.418		2.99	4.80	5.36	0.817
9.89	0.553		3.52	5.90	6.59	1.01
12.16	0.679		4.24	7.01	7.83	1.18
13.65	0.762		4.34	8.09	9.03	1.30
16.19	0.905		5.35	11.6	13.0	1.57
17.9	1.000		6.08	16.3	18.2	1.86

[a]Extrapolated values.

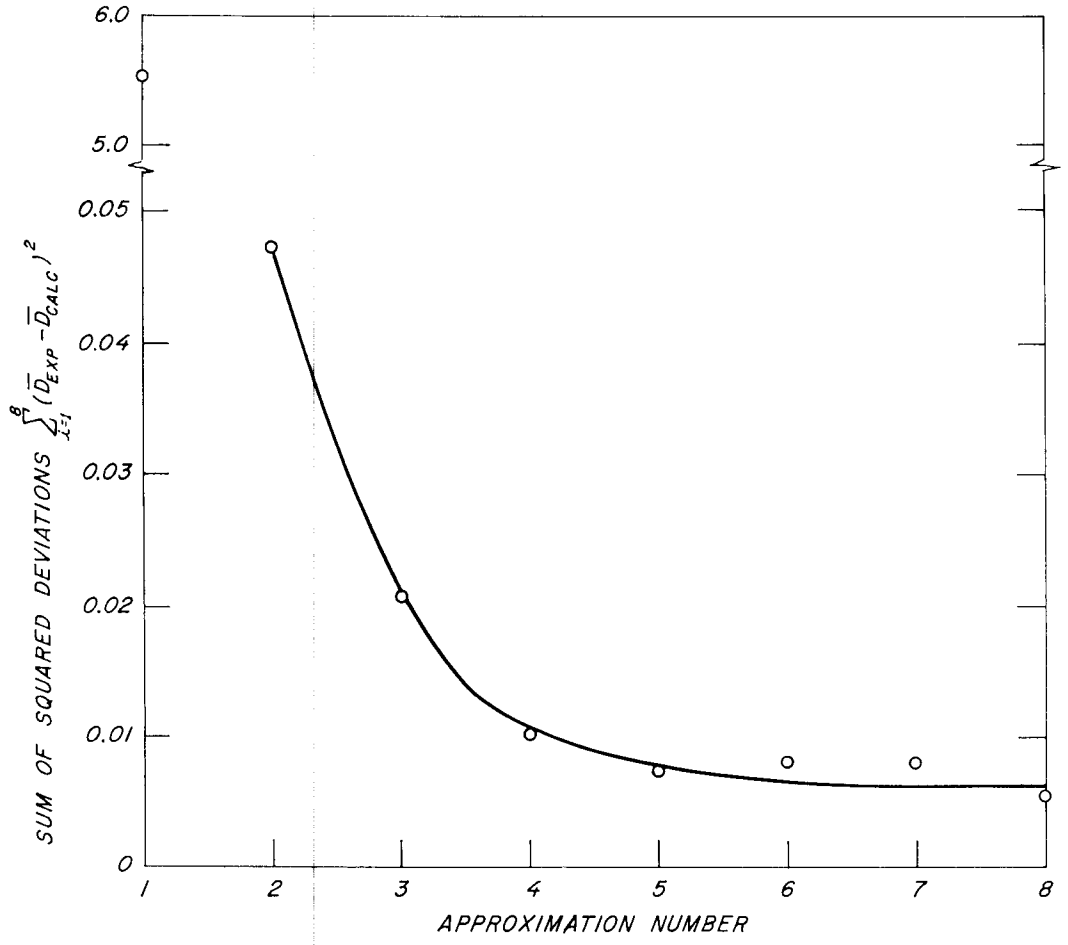

FIG. 3. Sum of squared deviations of calculated $\bar{D}$ from original experimental $\bar{D}$ as function of approximation number.

$$s'_m = s_m + D\frac{\Delta T}{(\Delta X)^2}\left(s_{m+1} - 2s_m + s_{m-1}\right) \qquad (12)$$

The s_m' values are converted back to c values with Eq. (8).

EXPERIMENTAL PROCEDURE

The experimental procedure consisted of measuring the moisture adsorption between zero percent moisture content and a series of eight higher moisture contents. The wood, aspen (*Populus* sp.), was kiln-dried to 12% moisture content. The specimens were 3 by 5¾ inches by ½ inch thick. Adsorption occurred into the ½-inch thickness plane (radial direction), and the edges of the specimens were coated with three coats of a heavily pigmented aluminum paint. Three replicates were included in each adsorption experiment. Each specimen was oven-dried at 220 F for 24 hr before adsorption was started. The specimens were then wrapped in aluminum foil and cooled to the adsorption temperature (110 F) for 20 min in a desiccator over phosphorous pentoxide. Thermocouples placed in the center of similar specimens showed that the temperature of the wood was within 1° of 110 F after 15 to 17 min of cooling.

The adsorption experiments were conducted in small cabinets in which the relative humidity was controlled by saturated

salt solutions; the temperature was thermostatically controlled at 110 F. A fan provided air velocity at approximately 200 ft/min through the rack that held the specimens. The salts used, the approximate relative humidity, and the average equilibrium moisture content of the three specimens in each group are shown in Table 1. The maximum final concentration C_m was 17.9% moisture content.

RESULTS AND DISCUSSION

The eight adsorption-time curves are shown in Fig. 1; the time for one-half of adsorption to occur is marked on each curve. Table 2 lists the time for one-half of sorption to occur, the integral diffusion coefficient $\bar{D}$ as calculated from Eq. (1), and the product $\bar{D}C_o$. All data in Table 2 and in Fig. 1 are the averages of the three replicates; all of the subsequent numerical analysis is based on these averages.

As discussed, the first approximation to D as a function of concentration is obtained by differentiating $\bar{D}C_o$ with respect to C_o (Eq. (3)). $\bar{D}C_o$ is plotted as a function of C_o in Fig. 2, and the relationship can be well represented by the following equation:

$$\bar{D}C_o = \exp\left(a + bC_o + dC_o^2 + fC_o^3\right) \qquad (13)$$

where a, b, d, and f are constants.

Differentiating with respect to C_o, the first approximation to the diffusion coefficient is

$$D_c = (b + 2dC + 3fC^2)\exp(a + bC + dC^2 + fC^3) \qquad (14)$$

or, in terms of reduced variables

$$D = \frac{D_c}{D_o} = \frac{D_c}{b\exp(a)} \qquad (15)$$

$$= \left(1 + \frac{2d}{b}C_m c + \frac{3f}{b}C_m^2 c^2\right)\exp\left(bC_m c + dC_m^2 c^2 + fC_m^3 c^3\right).$$

Equations (13), (14), and (15) were used throughout the series of approximations since the general shape of the curve remained the same. The values of the constants a, b, d, and f change with each approximation.

The finite difference technique is basically the repetition of three calculations. The diffusion coefficient is calculated; it is substituted into the finite difference formula (Eq. (12)); and finally the s value is converted to a c value. The correct D value is calculated from Eq. (8) and (15). Substituting Eq. (15) in Eq. (8) and integrating yields:

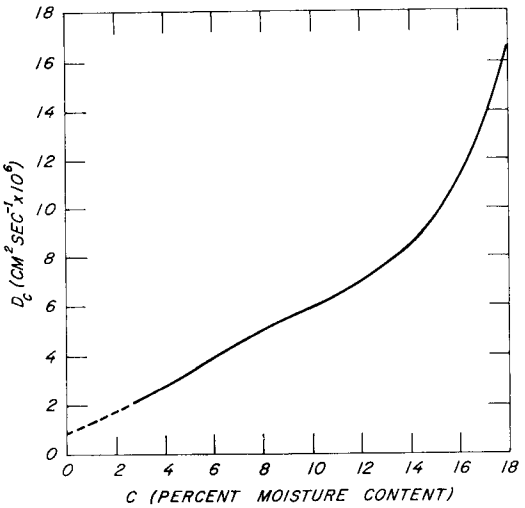

FIG. 4. Moisture concentration dependence of diffusion coefficient of aspen wood at 110 F.

$$s = \frac{\exp(bc + dc^2 + fc^3) - 1}{\mu} \qquad (16)$$

where μ is $\exp(b + d + f) - 1$.

Equation (16) can be manipulated so that D can be substituted and then solved for D as follows:

$$D = 1 + \frac{2d}{b}c + \frac{3f}{b}c^2\,(s\mu + 1) \qquad (17)$$

To convert the s values to c values, Eq. (16) is solved for c, i.e.,

$$fc^3 + dc^2 + bc - \ln(s\mu + 1) = 0 \qquad (18)$$

With the range of c values used here, Eq. (18) has only one real root and can be solved for c with the formulas of the algebra of cubic equations. Equations (17), (12), and the solution of (18) are therefore the three basic formulas that are applied again and again for each point and time.

The choice of $\Delta T/(\Delta X)^2$ in Eq. (12) is

important. Ideally it is desirable to take these time and distance increments as small as possible to make the approximate numerical solution as accurate as possible. Conversely, for practical reasons, it is desirable to use large increments so that the number of calculations is minimized. In addition to becoming less accurate as the size of the increments is increased, the solution sometimes becomes unstable, i.e., solutions at successive times oscillate. Oscillations were observed for $\Delta T/(\Delta X)^2$ as low as 0.04. In this analysis the increments chosen were $\Delta T = 0.00005$ and $\Delta X = 0.05$, or $\Delta T/(\Delta X)^2 = 0.02$. These were small enough to avoid oscillations and hopefully small enough to give a good approximation to the solution. In real time and space the solutions were calculated at space increments of 0.03 cm through the thickness of the wood at about every 2 min throughout the adsorption process.

The analysis was carried through eight approximations until the calculated $\bar{D}$ agreed closely with the original experimental $\bar{D}$. The first, second, fifth, and eighth approximations are summarized in Table 3. It is apparent from Table 3 that the second approximation accomplishes most of the adjustment. The sum of the squared deviations of the calculated $\bar{D}$ from the original experimental $\bar{D}$ is plotted as a function of the approximation number in Fig. 3, and it is apparent that little improvement occurs after the fifth approximation.

$\bar{D}$, of the eighth approximation is plotted as a function of C in Fig. 4, and it shows that the diffusion coefficient increases rapidly with moisture content in the high range of moisture contents. At about 14% moisture content, it begins to increase very rapidly with moisture content.

The values of the constants a, b, d, and f of Eqs. (14) and (15) for the eighth approximation are: $a = -13.198$, $b = 0.4827$, $d = -0.02417$, and $f = 0.0005546$.

When these values of the constants are used in the finite difference analysis to try to reproduce the experimental sorption-time curves, the calculated curves never differ from the experimental curves by more than 0.5% moisture content. At the beginning and the end of each sorption range, the calculated curves give a slightly higher moisture content than do the experimental curves at a given time.

SUMMARY

The purpose of this study was to determine the dependence of the diffusion coefficient of aspen wood on moisture concentration, to assess the feasibility of applying a particular experimental and numerical technique to accomplish this, and to test the use of a particular finite difference technique to solve the diffusion equation with a diffusion coefficient that is concentration-dependent. Experimentally, the method requires only a series of simple adsorption experiments. The numerical technique consists of a series of approximations that are repeated until certain experimental and calculated values agree. The finite difference technique is a part of each approximation.

The results showed that the moisture diffusion coefficient of aspen wood at 110 F increases with moisture content. The diffusion coefficient increases by a factor of approximately 8 between 2.5 and 18% moisture content. The numerical method of approximations and the finite difference technique worked well; no difficulties were encountered. At the end of the analysis the experimental sorption-time curves could be reproduced very closely by the mathematics involved. The greatest disadvantage of the technique was the large number of successive approximations, which means that a high-speed computer is necessary to apply the method.

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