TEMPERATURE EFFECT ON DIFFUSION COEFFICIENT IN DRYING WOOD

Ho-Yang Kang

Associate Professor
Department of Forest Products
Chung-Nam National University
Daejeon 305-764, Korea

and

C. Arthur Hart

Former Professor
Department of Wood and Paper Science
College of Forest Resources
North Carolina State University
Box 8005
Raleigh, NC 27695-8005

ABSTRACT

The effect of drying temperature on unsteady-state moisture diffusion was studied by drying small, nearly green, 25-mm-thick specimens of yellow-poplar (*Liriodendron tulipifera* L.) and red oak (*Quercus* sp.) at four temperatures (32.2, 43.3, 54.4, and 65.6°C) and at two successive equilibrium moisture contents (10 and 5% EMC). That the moisture diffusion through wood is an activated process was indicated by the fact that the plots of the logarithm of diffusion coefficient versus the reciprocal of absolute temperature were largely linear. However, the calculated activation energies (4195 cal/mol for yellow-poplar, 6166 cal/mol for red oak when dried to 10% EMC) differed greatly, were of low magnitude, and were possibly related to the specific gravity of the wood.

Keywords: Wood drying, drying temperature, moisture diffusion, activation energy, simulation.

INTRODUCTION

Fick's laws of diffusion (Crank 1975) have been used to describe the movement of moisture through wood in the hygroscopic range. The relationship between diffusion coefficient and temperature can be expressed by the Arrhenius equation (Barrer 1941; Stamm 1964; Choong 1965; Skaar and Babiak 1982):

$$D = D_o\exp(-E_b/(RT))$$

or

$$E_b = (A - \ln D)RT \qquad (1)$$

where:

D = diffusion coefficient (cm^2/sec)

R = gas constant (1.9872 cal/K mol)

T = absolute temperature (K)

D_o and A = constants ($A = \ln D_o$)

E_b = activation energy for moisture diffusion (cal/mol)

Some researchers have reported the relationship between moisture diffusion and temperature (Skaar 1958; Stamm 1959; Stamm and Nelson 1961; Choong 1965). The results have been variable, possibly due to differences in specimens' size, degree of control in drying conditions, and whether the moisture movement was in steady or unsteady state.

Most of the studies on the relationship between moisture diffusion and temperature were conducted before 1970. These results

have been widely used in the study of moisture diffusion in wood (Siau et al. 1986; Nelson 1991; Simpson 1993).

Bramhall (1979), in his sorption model, considered the activation energy for bound water diffusion to equal the sum of the heat of condensation and the differential heat of sorption. With his nonequlibrium thermodynamic model, Nelson (1991) reported that the heat of transfer for adsorbed water exceeds the activation energy for bound water diffusion. Hunter (1992) developed a model for the activation energy of diffusion, expressed in terms of enthalpy and entropy of sorption.

Yao (1966) surveyed free vapor, bound water, and their combined diffusion coefficients at five temperature levels for several softwoods from the studies of other researchers, and calculated their individual activation energies with Eq. (1). Comparing these values, he concluded that the activation energies for the combined diffusion are much closer to the values for the bound water diffusion (8200 cal/mol) than to the value for the free vapor diffusion (11440 cal/mol). He also indicated that it was unreasonable that the activation energies for the combined diffusion were lower than both those for the bound water diffusion and those for free vapor diffusion, and attributed this to the fact that the diffusion coefficient data had been collected from different species.

The activation energies for the combined diffusion should be between those for the bound water diffusion and those for the free vapor diffusion. It is possibly wrong that the activation energy for the free vapor diffusion is 11440 cal/mol. According to the kinetic theory of gases, the diffusion coefficient of a gas is positively proportional to the 1.5 power of temperature (refer to pp. 869–884 in Atkins 1982), which supports the concept that free vapor diffusion is not an activated process. Tarkow and Stamm (1960) measured the gas diffusion coefficient of carbon dioxide with radially sliced Sitka spruce heartwood veneers and concluded that the gas diffusion is not an activated one because the temperature coefficient is very small. Thus it is possibly concluded that the activation energies for the combined diffusion are proportional to the ratios of the bound and vapor diffusion, which relate to wood density.

Two solutions of Fick's unsteady-state diffusion equation are used herein to compute the diffusion coefficients: the infinite slab equation (Prager and Long 1951; Crank 1975) and a form of the interval diffusion equation employed by McNamara and Hart (1971). Due to their solution assumptions, the former and latter equations are valid respectively for the first half (hereafter period I) and the second half (hereafter period II) of desorption. Diffusion coefficients in both equations are assumed to be independent of moisture content. These equations are, respectively:

$$D = [\pi a^2/(4t)]E^2 \qquad (2)$$

$$D = -(2a/\pi)^2[1/(M_x - M_e)] \times (dM_x/dt) \qquad (3)$$

where:

D = diffusion coefficient (cm^2/sec)

π = 3.1415 ...

a = half-thickness of board (cm)

t = time (seconds)

E = fractional change in average moisture content at time t

$= (M_i - M_x)/(M_i - M_e)$

M_i = uniform initial moisture content (%)

M_x = average moisture content (%) at time t

M_e = equilibrium moisture content (%)

To calculate the diffusion coefficients for periods I and II, we used drying data obtained when $E \leq 0.5$ and $E > 0.5$, respectively. From Eq. (2), it may be seen that a plot of E^2 versus t is linear with a slope of $4 D/(\pi a^2)$ so D may be calculated from the slope of a linear re-

gression fitted to the experimental data. Equation (3) is simply the first term of an infinite series, but for period II, the error from using only one term is negligible.

It has been previously found that a lag of diffusion rates may occur at the start and at the end of drying (Comstock 1963; Biggerstaff 1965; McNamara and Hart 1971). To eliminate the effect of this lag upon the calculated diffusion coefficient for period II, Hart (1988) suggests that the slope of a regression for only the linear portion of the plot be substituted for the Fickian slope in Eq. (3). This substitution results in Eq. (4), which was used to calculate diffusion coefficients for period II in this study.

$$D = -(2 a / \pi)^2 b \qquad (4)$$

where:

b = slope of drying rate versus average moisture content

The objective of this paper was to determine temperature effect on moisture diffusion in drying wood using the Arrhenius equation. Of particular interest was to compare the activation energies obtained from the species of different densities.

EXPERIMENTAL PROCEDURE

This research was conducted with 25-mm-thick specimens by drying them in an environmental chamber with controlled temperature, humidity, and air velocity. The diffusion coefficients were calculated from the drying rate data using Eqs. (2) and (4), while the activation energy calculations were based upon Eq. (1).

The two hardwood species selected for this study were sapwood of yellow-poplar (*Liriodendron tulipifera* L.) and heartwood of red oak (*Quercus* sp.). The drying rate data were collected primarily at four temperatures (32.2, 43.3, 54.4, and 65.6°C) and two successive equilibrium moisture content levels (10 and 5%). The air velocity was about 2 m/s. Temperature settings were based upon the tables

of Rasmussen (1961). Two deviations were necessary in the final study plan. The original lower EMC was to be 3% rather than 5%, but after drying the two yellow-poplar runs at 3% at 65.6°C and at 54.4°C, it was found that the conditioning chamber could not maintain this low value at 43.3°C and 32.2°C. Thus an EMC of 5% was adopted for all subsequent runs. The second deviation occurred with red oak at 5% EMC which was run at 37.8°C instead of 32.2°C because of a cooling equipment failure.

There was a total of sixteen drying runs, consisting of four temperatures times two EMC levels times two species. Each drying run consisted of 12 specimens end-matched to those in other runs of the same species. All specimens were flatsawn and planed and sawn to nominal dimensions of 140 × 100 × 25 mm in length, width, and thickness. Three coats of neoprene were applied to all ends and edges of the specimens.

The yellow-poplar specimens were obtained from partially air-dried boards with moisture contents ranging from 31 to 40%, except that one set of four matching specimens was at 61%. They were kept in sealed polyvinyl bags at room temperature for more than 20 days to reduce moisture gradients in the specimens, but less than a month to limit the fungal growths that can occur in wood containing free water.

The red oak specimens were made from green boards with initial moisture contents exceeding 60%. To avoid drying defects that may occur early when drying a refractory species of high moisture content, the specimens were predried in the mild condition of 26.7°C dry bulb and 80% relative humidity until the average moisture content of the specimens approached about 40%. In a preliminary experiment, such predried specimens did not show surface checks or honeycomb at the severest drying condition employed in this experiment. Until used in the drying runs, these predried specimens were kept in polyvinyl bags at 4°C. This cold storage was intended to preserve the moisture gradients and thus prevent checking

in the subsequent drying by keeping the surfaces relatively dry.

Although the above techniques were employed so as to obtain specimens that would have initial moisture contents in the vicinity of fiber saturation, and thus be amenable to drying at elevated temperature without degrade, it was recognized that the initial moisture contents would not be uniform. Thus Eq. (2) may not be strictly applicable in the drying run to 10% EMC since its derivation assumes a uniform initial moisture content. However, analysis with a drying simulation showed that the error from this source was only about a two percent reduction for the period I diffusion coefficients, while the period II values were unaffected.

The specimens were preheated in plastic bags before the start of drying. For weighing, each specimen was withdrawn from the drying chamber through an access port and was prevented from cooling by keeping it in a polystyrene insulating box having 25-mm-thick sides. It was weighed within a minute to an accuracy of one hundredth of a gram. After drying at 10% EMC, the specimens were stored at temperature in polyvinyl bags for more than a month and then dried in the 5% EMC conditions.

RESULTS AND DISCUSSION

Diffusion coefficients

Table 1 shows the diffusion coefficient averages and standard deviations for each set of 12 specimens employed in this study. The coefficients were calculated for both periods I and II from the respective slopes of the linear regressions fitted to the data. Despite the fact that the initial moisture contents may not have been uniform and reached levels indicating the presence of some lumen water, the comparisons between periods I and II for both species are about the same in drying to the 10% EMC as in drying from 10% to the 5% EMC. Since the lower EMC step does not involve the presence of lumen water and nonuniform initial moisture gradients, the presence of these fac-

TABLE 1. *Initial moisture contents, diffusion coefficient averages (AV) (each for 12 observations), and standard deviations (SD) for both periods I and II in all 16 drying runs.*

| | | Diffusion coefficient ($cm^2/sec \times 10^5$) | | | | |
| | | Period I | | Period II | | Ratio |
RUN	Initial MC	AV	SD	AV	SD	II/I
YP10-32.2	37.2	0.517	0.135	0.585	0.030	1.1
YP10-43.3	35.1	0.605	0.086	0.742	0.074	1.2
YP10-54.4	35.3	0.869	0.093	1.001	0.065	1.2
YP10-65.6	32.8	0.899	0.097	1.128	0.097	1.3
YP5-32.3	12.1	0.239	0.036	0.227	0.034	0.9
YP5-43.3	11.5	0.409	0.033	0.395	0.023	1.0
YP3-54.4	10.4	0.560	0.056	0.658	0.055	1.2
YP3-65.6	10.8	0.994	0.166	0.829	0.093	0.8
RO10-32.2	42.3	0.077	0.008	0.085	0.013	1.1
RO10-43.3	43.9	0.108	0.011	0.117	0.019	1.1
RO10-54.4	42.5	0.153	0.012	0.168	0.023	1.1
RO10-65.6	43.6	0.218	0.017	0.232	0.054	1.1
RO5-37.8	9.8	0.056	0.013	0.076	0.019	1.4
RO5-43.3	9.8	0.110	0.023	0.093	0.008	0.8
RO5-54.4	10.2	0.237	0.033	0.177	0.017	0.7
RO5-65.6	9.9	0.350	0.038	0.333	0.038	1.0

tors in the high EMC run did not appear to seriously affect the results.

Activation energy

Equation (1) was used to calculate activation energies for the diffusion coefficients from both period I and II for each matched set of four specimens. The results are listed in Table 2. For the yellow-poplar in the second drying step, the fact that the EMC was 3% for the two higher temperatures but 5% for the two lower ones was disregarded. The Fig. 1 Arrhenius plot for the period II data from Table 2 does give a slight indication of less linearity in the YP3/5 data than in the other plots. Also shown in Table 2 are the average specific gravities (oven-dry weight/green volume basis).

The Arrhenius plots of the same species in Fig. 1 do not seem to converge as temperature increases infinitely, which is against Eq. (1). This discrepancy may be attributed to the differences of initial moisture contents between two steps since the activation energy required

TABLE 2. *Average of twelve activation energies (E$_b$) (cal/mol), the standard deviation, and the average correlation coefficient (R^2), along with the specific gravity (SG) (OD wt./green volume) for each run of 48 specimens.*

RUN	SG	Period I			Period II		
		Eb	SD	R2	Eb	SD	R2
YP10	0.442	3,857	1,158	0.879	4,195	396	0.960
YP3/5	0.442	8,459	968	0.979	8,182	839	0.970
RO10	0.550	6,431	397	0.996	6,166	830	0.980
RO5	0.550	13,708	1,280	0.954	11,543	1,541	0.979

for water molecules to diffuse varies with moisture content. However the variation of D_o in Eq. (1) does not influence the linearity between the logarithm of diffusion coefficient and the reciprocal of absolute temperature for all species.

Since each activation energy in Table 2 is the average of 12 values, the standard error for each average is the listed standard deviation divided by the square root of 12. It is worth noting that whether the comparison is made in period I or II, the activation energy for the high EMC run is considerably less than that for the low EMC run, for both yellow-poplar and red oak. And for comparisons within any given classification (high or low EMC, period I or II), the yellow-poplar is consis-

FIG. 1. The degree of linearity is shown by these plots of the natural logarithm of the diffusion coefficient (LN D) versus 1000/absolute temperature (1000/T) for the period II average values in Table 1.

tently lower in activation energy than the red oak.

Since a higher activation energy indicates a greater effect of increasing temperature in increasing the diffusion rates, and since the yellow-poplar is lower in both specific gravity and activation energy than the red oak, then it may be proposed that increasing temperature increases diffusion coefficient rates more in high density wood than in low density wood.

Table 3 presents previously collected but unpublished data for several runs of yellow-poplar. These data were collected with the same equipment and in the same manner as described herein, except that the specimens were freshly cut green at the start of drying. Thus only the period II calculations were made. These Table 3 data, along with the period II activation energies for the 10% EMC runs from Table 2, are plotted individually against their respective specific gravities in Fig. 2. Also shown are the 95% confidence intervals both for the individual averages and for a regression fitted to all of the data.

Although variable, these collective data in Fig. 2 do indicate the possibility that activation energy increases with increasing specific gravity. However, the specimens are of two species and varied in grain as well as in specific gravity. The data also indicate that the different populations of yellow-poplar may give quite different activation energies. Without these older data, it would be easy to underestimate the high degree of variability that exists.

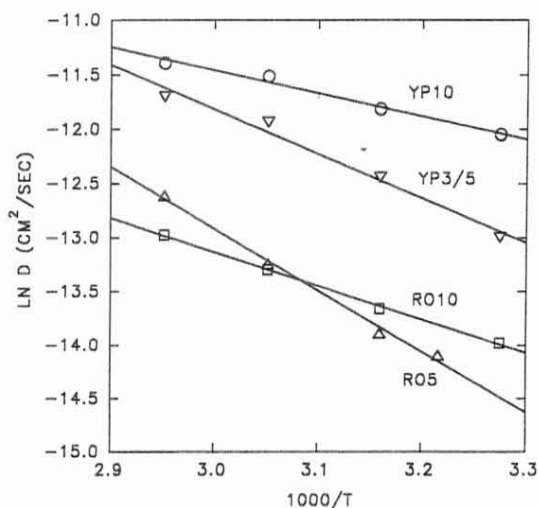One of the assumptions in the models of

TABLE 3. *Data from four previous drying studies of yellow-poplar using freshly cut green specimens, end-matched by pairs within each run, at two temperatures using the same drying procedures as the current study.*

RUN	A	B1	B2*	C	D
Thickness (inches)	1.50	1.14	1.14	1.13	1.13
SG	0.536	0.449	0.437	0.45	0.511
Grain	Bast	Flat	Flat	Qtr	Qtr
Sap/Heart	Both	Sap	Sap	Hrt	Sap
No. of pairs	7	3	2	4	4
Dry bulb (°C)	37.8	26.7	26.7	26.7	26.7
Nominal EMC	11.8	12.3	12.3	10.9	10.9
Diff. Coeff ($\times 10^5$)					
(cm²/sec)	0.302	0.397	0.441	0.250	0.175
Std. Dev. ($\times 10^5$)	0.017	0.033	0.006	0.011	0.020
Std. Err. ($\times 10^5$)	0.007	0.019	0.004	0.005	0.01
Dry bulb (°C)	60.0	48.9	48.9	48.9	48.9
Nominal EMC	11.9	11.5	11.5	12.1	12.1
Diff. Coeff ($\times 10^5$)					
(cm²/sec)	0.599	0.535	0.625	0.472	0.355
Std. Dev. ($\times 10^5$)	0.048	0.029	0.019	0.054	0.022
Std. Err. ($\times 10^5$)	0.018	0.017	0.013	0.027	0.011
Act. Eng. (cal/mol)	6,318	2,578	3,003	5,515	6,168
Std. Dev.	685	1,183	378	992	764
Std. Err.	259	683	267	496	382

* Each sample in B2 had a temperature probe hole which may have affected diffusivity and possibly the activation energy.
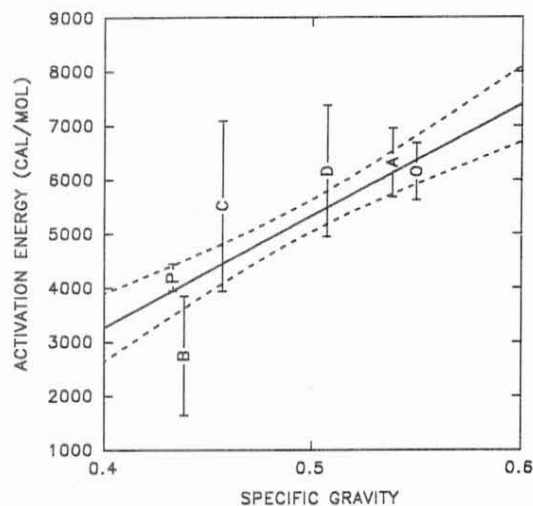

FIG. 2. Activation energy versus specific gravity for the period II YP10 (P) and RO10 (O) averages from Table 2 plus the data from Table 3 runs A, B, C, and D, with 95% confidence intervals on all values and on the regression fitted to all of the data.

Fickian diffusion used herein is that surface moisture content is at equilibrium moisture content so surface transfer is not a factor. But in actual drying, surface transfer is always a factor (Chen et al. 1995), and more so with faster drying species and with higher temperatures. To examine this effect, very wet yellow-poplar specimens were dried in the apparatus used in this study, and surface transfer rates for the constant drying rate periods were obtained. An average transfer coefficient, herein termed QRATE, of 0.003305 g/cm² hr °C with a standard deviation of only 0.000119, was obtained from eleven different specimens.

This average QRATE, which is applicable to any specimen regardless of species, was then used in drying simulations for yellow-poplar and red oak with runs at 32.2°C and at 65.6°C and with transfer coefficients of either QRATE or 10×QRATE. The resulting moisture content versus time data were analyzed for diffusion coefficient in the same

manner as the experimental data, and the results were compared to the input coefficient. The only appreciable effect was with the yellow-poplar, which exhibited a nearly 10% reduction in diffusion coefficient for period I and 7% for period II for the 65.6°C run. But the reduction at 32.2°C was nearly as great, so the activation energy was reduced by only 2.6% when compared to the 10×QRATE value. Thus surface transfer limitations did not appreciably affect the activation energies.

CONCLUSIONS

This drying study of the effect of four levels of temperature (from 32.2 to 65.6°C) and two successive levels of equilibrium moisture content (10% and either 3 or 5%) on the diffusion coefficients and activation energies of yellow-poplar and red oak, plus added prior data on yellow-poplar, has resulted in the following:

1. Good linear relationships between the logarithm of diffusion coefficient and the reciprocal of absolute temperature for all drying runs were obtained, thus confirming that moisture diffusion through wood is an activated process.
2. Within a species the activation energies obtained from the 10% EMC step were always lower than those obtained from the 5 or 3% EMC step. In other words, increasing temperature increased drying rates more at low moisture contents than at high moisture contents.
3. In the step to 10% EMC, the average activation energy for red oak was about 60% of the value for water, while the yellow-poplar was only about 41%.
4. Although the relationship was highly variable, the activation energy did increase with increasing specific gravity both within one species (yellow-poplar) and between two species.
5. For the runs approaching 10%, a drying simulation program indicated that the lim-

itations imposed by the surface transfer rate reduced the estimate of the activation energy based upon Fickian diffusion only by about 2.6% for the yellow-poplar and 1.1% for the red oak.

REFERENCES

ATKINS, P. W. 1982. Physical chemistry, 2nd ed. The University Press, Cambridge, England. 1095 pp.

BARRER, R. M. 1941. Diffusion in and through solid. The University Press, Cambridge, England. 464 pp.

BIGGERSTAFF, T. 1965. Drying diffusion coefficients in wood: As affected by temperature. Forest Prod. J. 15: 127–134.

BRAMHALL, G. 1979. Sorption diffusion in wood. Wood Science 12:3–13.

CHEN, Y., E. T. CHOONG, AND D. M. WETZEL. 1995. Evaluation of diffusion coefficient and surface emission coefficient by an optimization technique. Wood Fiber Sci. 27(2):178–182.

CHOONG, E. T. 1965. Diffusion coefficients of softwoods by steady state and theoretical methods. Forest Prod. J. 15(1):21–27.

COMSTOCK, G. L. 1963. Moisture diffusion coefficients in wood as calculated from adsorption, desorption, and steady state data. Forest Prod. J. 13:97–103.

CRANK, J. 1975. The mathematics of diffusion, 2nd ed. Oxford University Press, Oxford, England. 414 pp.

HART, C. A. 1988. A user's manual for a family of simulation of moisture sorption in wood. Dept. of Wood and Paper Science, North Carolina State University, Raleigh, NC. 44 pp.

HUNTER, A. J. 1992. On the activation energy of diffusion of water in wood. Wood Sci. Technol. 26:73–82.

McNAMARA, W. S., AND C. A. HART. 1971. An analysis of interval and average diffusion coefficients for unsteady-state movement of moisture in wood. Wood Science 4(1):37–45.

NELSON, R. M., JR. 1991. Heats of transfer and activation energy for bound water diffusion in wood. Wood Sci. Technol. 25:193–202.

PRAGER, S., AND E. S. LONG. 1951. Diffusion of hydrocarbons in polyisobutylene. J. Am. Chem. Soc. 73:4072–4075.

RASMUSSEN, E. F. 1961. Dry kiln-operator's manual. Forest Products Lab, Forest Service, USDA. 197 pp.

SIAU, J. F., F. BAO, AND S. AVRAMIDIS. 1986. Experiments in nonisothermal diffusion of moisture in wood. Wood Fiber Sci. 18(1):84–89.

SIMPSON, W. T. 1993. Determination and use of moisture diffusion coefficient to characterize drying of northern red oak. Wood Sci. Technol. 27:409–420.

SKAAR, C. 1958. Moisture movement in beech below the fiber saturation point. Forest Prod. J. 8:352–357.

————, AND M. BABIAK. 1982. A model for bound-water transport in wood. Wood Sci. Technol. 16:123–138.

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. The Ronald Press Company, New York, NY. 549 pp.

————, AND R. M. NELSON, JR. 1961. Comparison between measured and theoretical diffusion coefficients for southern pine. Forest Prod. J. 11:536–543.

TARKOW, H., AND A. J. STAMM. 1960. Diffusion through air-filled capillaries of softwoods: I. Carbon dioxide. Forest Prod. J. 10(5):247–250.

YAO, J. 1966. A new approach to the study of drying diffusion coefficients of wood. Forest Prod. J. 16(6):61–69.