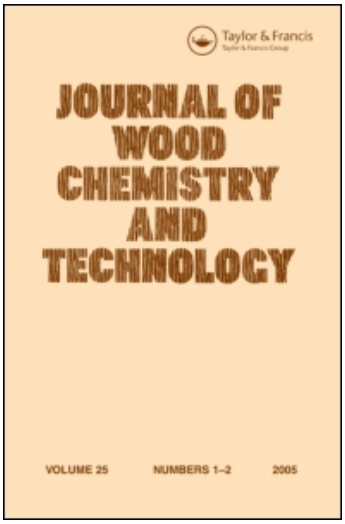

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Developing Diffusion Coefficients for SCF Impregnation of Douglas Fir Heartwood with Cyproconazole

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Abstract: The effects of the treating period and specimen length on supercritical fluid impregnation of cyproconazole were investigated for Douglas fir heartwood using cooling to induce biocide deposition. Retention levels at various treatment periods and locations were measured. These retention values were assumed to be equivalent to the concentration of biocide at the end of the treatment period. The concentration values versus distance from the surface were then fitted to an empirical expression as a function of time and distance. From the resultant concentration formulae, time-varying effective diffusion coefficients for the biocide at the depth locations of the data were determined using Egner's solution method for the Fickian diffusion equation in one direction. The diffusion coefficient values suggested that diffusion was probably the rate-limiting phenomena accounting for biocide penetration.

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Prolonged treatment appeared to increase the effective diffusion coefficients, probably by removing extractives in heartwood pits.

Keywords: Supercritical fluids, diffusion, cyproconazole, carbon dioxide, Douglas-fir

INTRODUCTION

The feasibility of using supercritical fluid (SCF) impregnation to protect wood from biodeterioration has been evaluated in a number of studies.[1–6] This process has the potential to overcome treatability problems associated with conventional liquid preservative systems such as shallow penetration, uneven biocide distribution in refractory species, and incompatibility with wood composites. SCF impregnation can produce deeper penetration and more uniform biocide distribution than conventional treatment in solid wood[7] and wood-based composites.[2,8,9] In spite of its potential as a new treatment method, commercialization of SCF impregnation has been limited because of expected high capital costs as well the lack of a fundamental understanding of this new treatment process.

Although SCF treatment produces excellent biocide penetration, the process can also result in large biocide gradients from the surface to the core of the wood.[3,7,8,10] The causes for these gradients are not obvious. Although SCF penetration is presumed to be rapid, the process of actual deposition of the biocide from the solution within the wood involves a number of process operation steps. In previous experiments, a vessel containing SC-CO_2, biocide, and co-solvent at a supercritical temperature was pressurized well above the critical pressure. This vessel was then opened to a second vessel containing wood at atmospheric pressure. This resulted in a rapid drop in total pressure and a subsequent loss of solubility. Pumps were then used to raise the pressure back above the critical pressure and biocide solubility was restored. Because of this temporary loss in solubility, however, the semi-porous wood may have been filled initially with SC-CO_2 that was nearly free of biocide. As a result, a process that many have described as a bulk flow of biocide-laden SC-CO_2 into wood may, in fact, depend on slower diffusion of biocide from higher concentrations near the surface toward the semi-porous wood interior.

Biocide may also move back from the interior toward the surface as pressure or temperature decreases at the end of the treatment cycle. For example, overly rapid venting can induce biocide movement at the end of the process reducing retention levels.[3] Kang[10] evaluated several approaches to reduce biocide gradients, including drawing a vacuum at the start of the process to remove initial air and using a variety of cooling rates prior to venting, but none of these variations yielded dramatic improvements. These results imply that other process factors affected biocide distribution.

Longer pressure periods, however, typically result in higher retentions and more even biocide distribution in solid wood.[6–8] These results suggest that biocide movement might be dominated by diffusion rather than bulk flow. Biocide gradients might reflect diffusion of biocide from high concentrations in the treatment fluid to lower levels in the wood that had not yet reached a steady state. There has been, however, little quantitative analysis of experimental data to support this premise.

Diffusion is an important mechanism for movement of biocides into wood during conventional treatments using boron.[11] A diffusion coefficient used to express the rate of a diffusion process is defined as the flux of the diffusing substance (mass/time per area) moving in a given direction divided by the spatial derivative of that concentration with respect to the direction of movement. Many methods for evaluating diffusion coefficients based on concentration measurements assume constant coefficients when specifying the solution of the differential mass balances. This assumption, however, does not hold for diffusion of chemicals through wood because the diffusion coefficient can vary with biocide concentration and properties of the wood, which may change during treatment. Egner's method can be used to obtain the diffusion coefficient graphically, numerically, or in some cases analytically.[12–14] Although this method is sensitive to experimental errors and the choice of fitting function, once the concentration as a function of distance and time is specified, it requires no assumptions on the functional form of the diffusion coefficient itself.[12]

This project investigated the effects of pressure period and flow path length in wood on biocide retention following supercritical fluid impregnation. The resulting data were further analyzed to assess the role of diffusion on biocide distribution by determining effective diffusion coefficients for cyproconazole in supercritical CO_2 using Egner's solution of the material balance with mass transfer due to diffusion.

MATERIALS AND METHODS

Air-dried Douglas fir (*Pseudotsuga menziesii* (Mirb.) Franco) heartwood lumber was cut into three different block sample sizes (20×20 mm, 40×40 mm, and 90×90 mm squares of 100 mm lengths—radial $\times$ tangential $\times$ longitudinal). Blocks were end-sealed with epoxy resin to limit end flow. Three blocks were treated for each size under a given set of conditions using cyproconazole as the biocide (Evipole TM), (2RS, 3RS; 2RS, 3RS)-2-(4-chlorophenyl)-3-cyclopropyl-1-(1H-1,2,4,triazole-1-yl)butan-2-ol. This chemical has high solubility in lower molecular weight alcohols. The toxic threshold for cyproconazole varies from 0.02 to 0.096 kg/m3, depending on target fungi and sample aging procedures.[15]

Samples were treated using a SCF impregnation device (Figure 1). Standard grade carbon dioxide from a 23 kg gas cylinder (99.9 weight %,

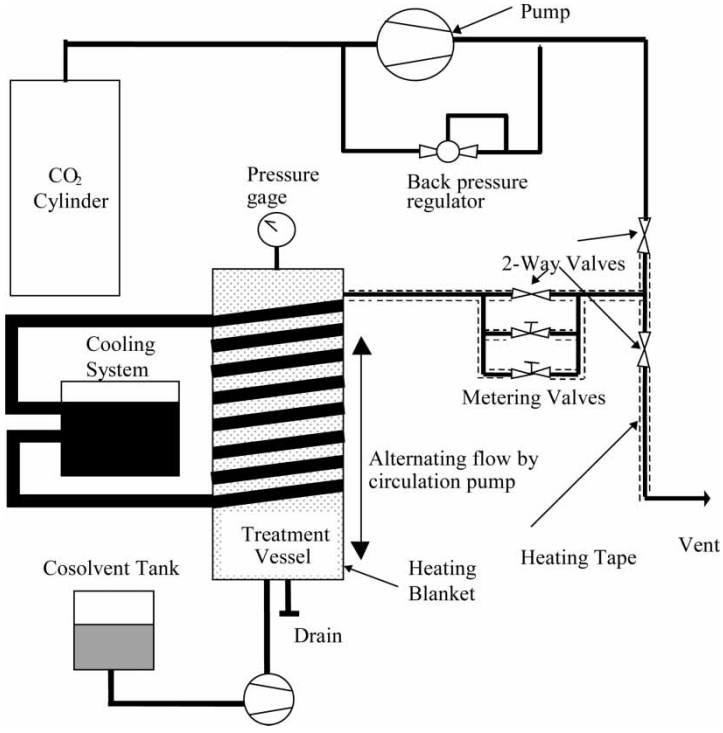

Figure 1. Schematic of the supercritical fluid impregnation device.

Industrial Welding Supply) was admitted into a pre-heated (40°C) treatment vessel (15.24 cm inside diameter, 127 cm inside length) using a single-stage diaphragm compressor (Fluiton Model A1-400). Pressure control was achieved using a back-pressure regulator (Tescom Model 26-1722-24) to direct excess fluid back into the compressor. After the pressure reached 10.3 MPa (1500 psi), a known amount of cyproconazole mixed with 3.5% mole fraction methanol (99.9 weight %, Fisher) was introduced into the treating vessel using a cosolvent pump (Milton Roy). Once the pressure reached the desired level (10.3 MPa), the fluid was circulated through the vessel at 2 kg/min. Flow was reversed every 15 min to encourage even distribution of biocide along the length of the vessel. The temperature was reduced at a rate of 0.4°C/min using a Brinkmann cooling circulator at the end of the treatment period (30, 180, 360, or 720 min). The pressure also decreased during this cooling, although no venting was done. When both the temperature and pressure decreased below the respective critical values (31.3°C and 7.4 MPa), the pressure was further reduced at a rate of 0.4 MPa/min by venting the system.

After treatment, a 20 mm thick wafer was cut from the middle of each block. These wafers were then segmented into zones corresponding to 0 to

Table 1. Biocide retentions at selected locations in Douglas fir heartwood blocks of different dimensions following supercritical CO_2 treatment with cyproconazole at 10.3 MPa and 40°C for 30, 180, 360, or 720 min

	Retentions (kg/m^3)[a]											
	90 mm square				40 mm square				20 mm square			
	Time (min)											
Depth from surface (mm)	30	180	360	720	30	180	360	720	30	180	360	720
0–5	0.33	0.32	0.40	0.66	0.21	0.21	0.21	0.31	0.22	0.21	0.18	0.24
5–10	0.10	0.09	0.12	0.15	0.06	0.06	0.10	0.16	0.07	0.05	0.07	0.09
10–15	0.08	0.09	0.09	0.10	0.04[b]	0.04[b]	0.07[b]	0.14[b]				
15–25	0.06	0.06	0.07	0.07								
25–35	0.04	0.05	0.06	0.07								
35–45	0.01	0.03	0.02	0.06								

[a]Values represent means of 9 samples.

[b]Retentions were evaluated at 10 to 20 mm from the surface instead of 10 to 15 in the 40 mm square sample.

5, 5–10, 10–15 (10–20 mm for the 40 mm sample), 15–25, 25–35, and 35–45 mm from the surface for each sample (smaller blocks lacked samples at deeper depths). As a result, the 20, 40, and 90 mm square samples produced 2, 3, and 6 assay zones, respectively.

Material from each location was ground in a Wiley mill to pass a 30-mesh screen. The ground wood was subjected to methanol extraction for 3 h at 65°C. Recovered cosolvent at the bottom of the treating vessel was also collected and the total volume of the liquid was measured. These measurements were used to determine how much biocide remained in the system and the data was used to calculate the quantity of biocide to be added for the next treatment cycle.

Biocide concentrations in the wood extracts and remaining liquid were determined by injecting 10 uL of extract into a Shimadzu high performance liquid chromatograph interfaced with a UV detector (HPLC-UV).[16] Separation was achieved using an Altech Hypercil ODS (C18) column (4.6 mm id by 10 m long). The elution solvents consisted of A (55% acetonitrile and 45% buffer) and B (95% acetonitrile and 5% buffer). The buffer was 0.5% w/v ammonium carbonate. The elution was programmed for phase A

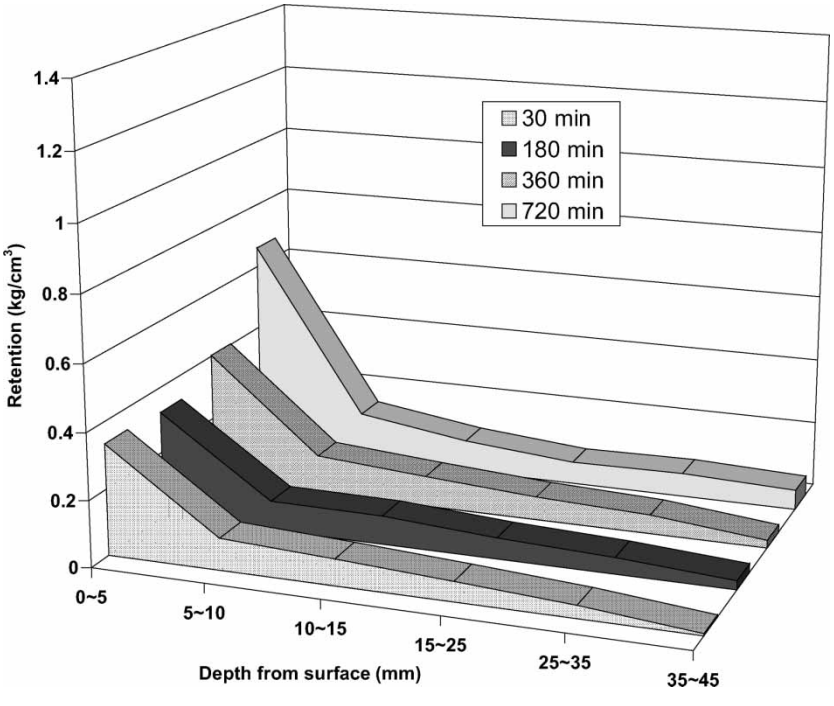

Figure 2. Biocide retention at selected distances from the surface in 90 mm square Douglas fir heartwood blocks following supercritical CO_2 treatment with cyproconazole at 10.3 MPa and 40°C for 30, 180, 360, or 720 min.

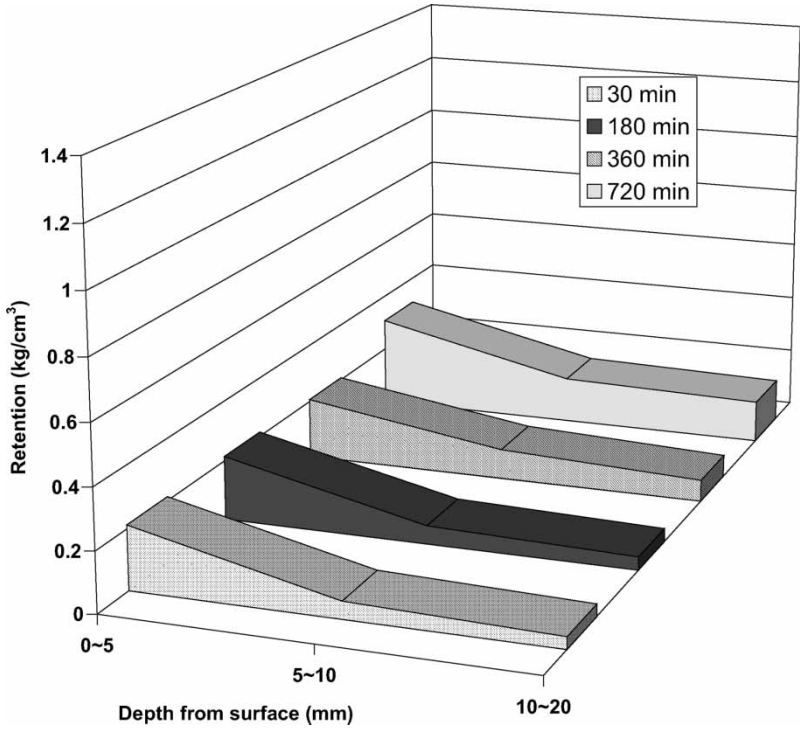

Figure 3. Biocide retention at selected distances from the surface in 40 mm square Douglas fir heartwood blocks following supercritical $C0_2$ treatment with cyproconazole at 10.3 MPa and 40°C for 30, 180, 360, or 720 min.

from 0 to 3.5 min, B from 3.5 to 5.0 min, and A from 5.0 to 8.0 min. the flow rate and wavelength were 1.5 mL/min and 230 nm, respectively.

The retention data were then used to calculate diffusion coefficients using Egner's solution using the following methods. Concentration-distance data were plotted and fit using exponential functions of distance used in previous studies of boron diffusion within wood.[11]

Slopes ($\partial C/\partial x$) and areas ($\int_0^x Cdx$) were calculated at various thickness values from the fitted exponential functions. Although this slope ($\partial C/\partial x$) was equivalent to the denominator in Egner's solution, the area ($\int_0^x Cdx$) at a given thickness was plotted against time and the derivative of the area versus time was used as the numerator in Egner's solution, $\partial \int_0^x Cdx/\partial t$.

$$D = \frac{\partial(\int_0^x Cdx)/\partial t}{\partial C/\partial x}$$

where $D =$ diffusion coefficient (cm^2/s), $C =$ the concentration of the

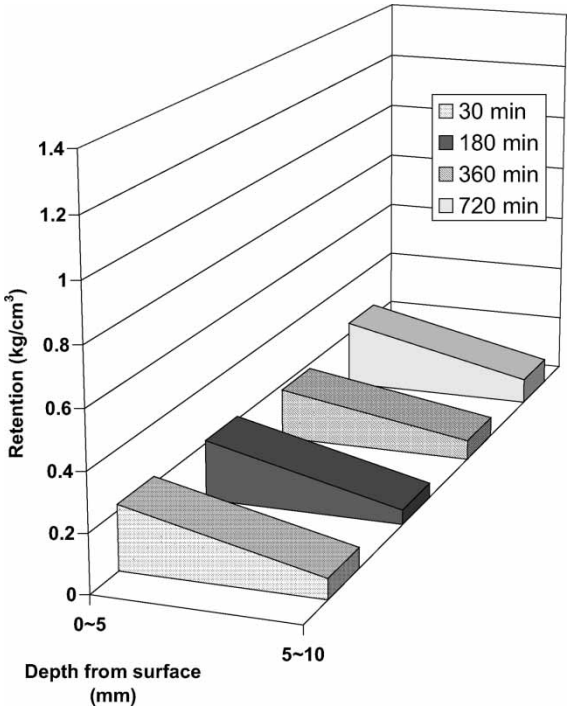

Figure 4. Biocide retention at selected distances (mm) from the surface in 20 mm square Douglas fir heartwood blocks following supercritical CO_2 treatment with cyproconazole at 10.3 MPa and 40°C for 30, 180, 360, or 720 min.

diffusing substance, x = the thickness of sample in the direction of diffusion (cm), and t = time.

RESULTS AND DISCUSSION

As expected, samples from the 90-mm square blocks exhibited steeper preservative retention gradients than those from the 40- or 20-mm square blocks (Table 1). Samples from the largest blocks also contained higher biocide concentrations at a given sample depth compared to the 40- and 20-mm square samples.

Although biocide retentions for a given assay zone increased with treatment time, the relative proportions of biocide retention among zones were not markedly different for the three sample dimensions (Table 1 and Figures 2–4). Prolonged treatment did not completely overcome the uneven biocide distribution from the surface to the core within individual samples. However, the results indicated slow biocide movement from surface to core. Interior zones in samples treated for longer times, especially the 12 h cycle,

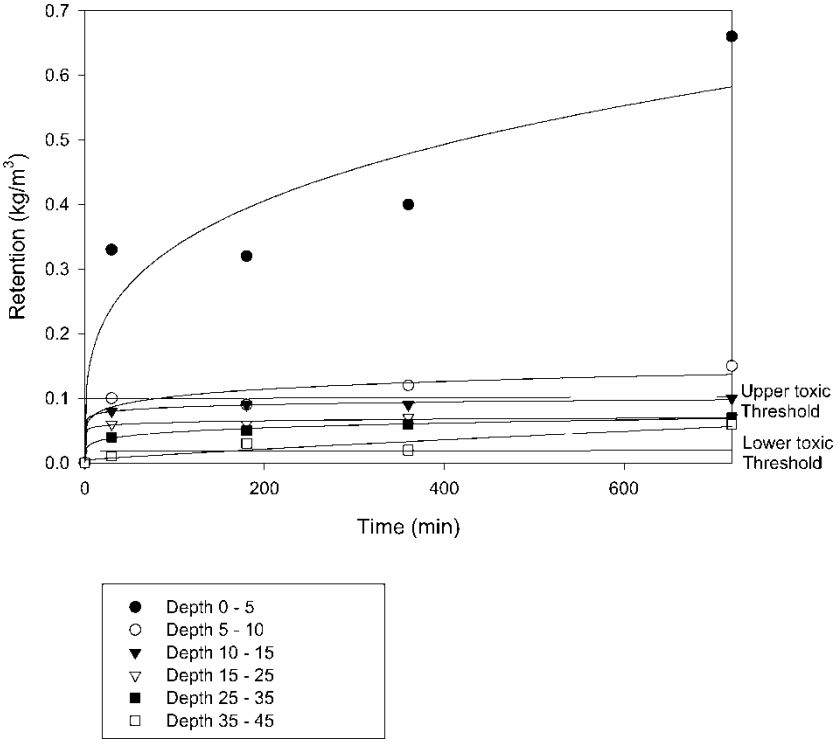

Figure 5. Cyproconazole retention variation with treatment time at selected distances from the surface in 90 mm square Douglas fir heartwood blocks following supercritical CO_2 treatment at 10.3 MPa and 40°C for 30, 180, 360, and 720 min.

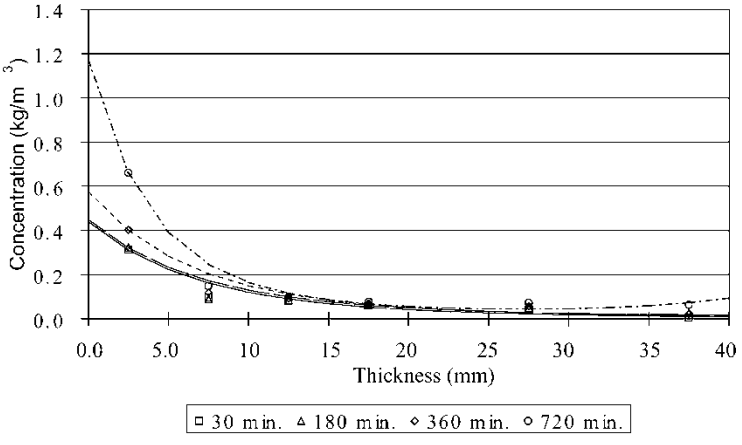

Figure 6. Concentration-distance curves for cyproconazole in Douglas-fir after 30, 180, 360, or 720 min of supercritical fluid treatment.

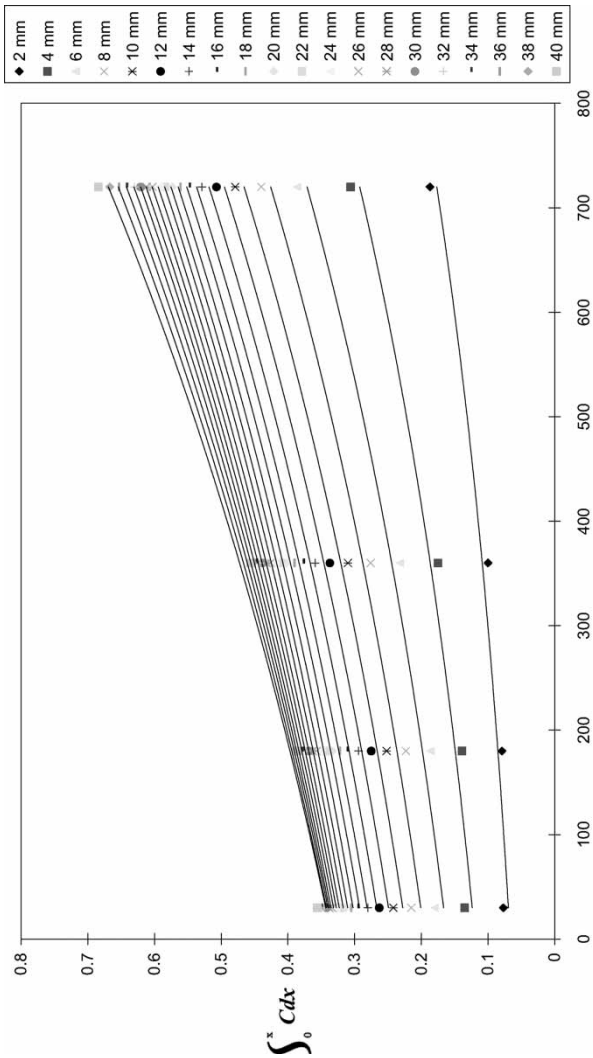

Figure 7. The integral of the concentration-distance curves vs. time from 0 to x at various distances from the wood surface during supercritical fluid impregnation with cyproconazole.

Table 2. Diffusion coefficients of cyproconazole during SCF treatment of Douglas fir heartwood at 10.3 MPa and 40°C

Distance from surface (mm)	Diffusion coefficients (10^{-8}cm^2/s) treatment time (min)			
	30 min	180 min	360 min	720 min
4	2.27	2.72	2.54	1.77
8	6.07	7.11	6.76	6.31
12	11.90	13.57	13.11	15.40
16	20.33	22.55	22.09	31.56
20	35.78	39.14	39.47	73.29
24	59.68	64.52	66.70	210.60
28	95.61	102.70	108.20	791.50
32	148.50	160.20	170.80	—
36	224.60	249.00	264.90	—
40	373.80	434.20	477.30	—

contained more biocide than interiors treated for shorter times (Figure 2). The effect of treatment time was less distinctive in smaller samples, but similar trends were observed (Figures 3 and 4).

Our results show that biocide movement occurs more slowly than would be expected if bulk flow were the predominant flow mechanism. If diffusion is the main impregnation mechanism in SCF treatment in larger specimens, then process variations such as higher pressures or cycling pressures may have only minimal effects on subsequent biocide distribution.

The slow rate of biocide movement in 90-mm square blocks is illustrated more clearly in Figure 5. Biocide retentions, with the exception of the inner core treated for only 30 min, were between the lower and upper toxic thresholds of cyproconazole. These data suggest that at least 24 h of pressure treatment would be required to achieve retentions at the upper threshold in the inner core of the samples.

One cause for the biocide gradients previously proposed is the movement of biocide to the surface as supercritical fluid returns to the liquid or gas state at the end of the treatment cycle.[3,8,10,17] Analysis of biocide concentrations at the ends of samples showed that these zones contained higher levels of chemical than the middle. These results suggest that some biocide redistribution occurs at the end of the treatment cycle.

Diffusion coefficients calculated using Egner's solution (Figures 6 and 7) for cyproconazole through Douglas fir heartwood were markedly lower than those determined in pure SC-CO_2, illustrating the effect of the semi-porous wood media on biocide movement.[18] Diffusion coefficients also tended to increase with treatment time (Table 2 and Figure 8) suggesting that permeability of the wood increased over time. Wood samples exposed to long SC-CO_2 treatment times may have experienced more extraction. SCF

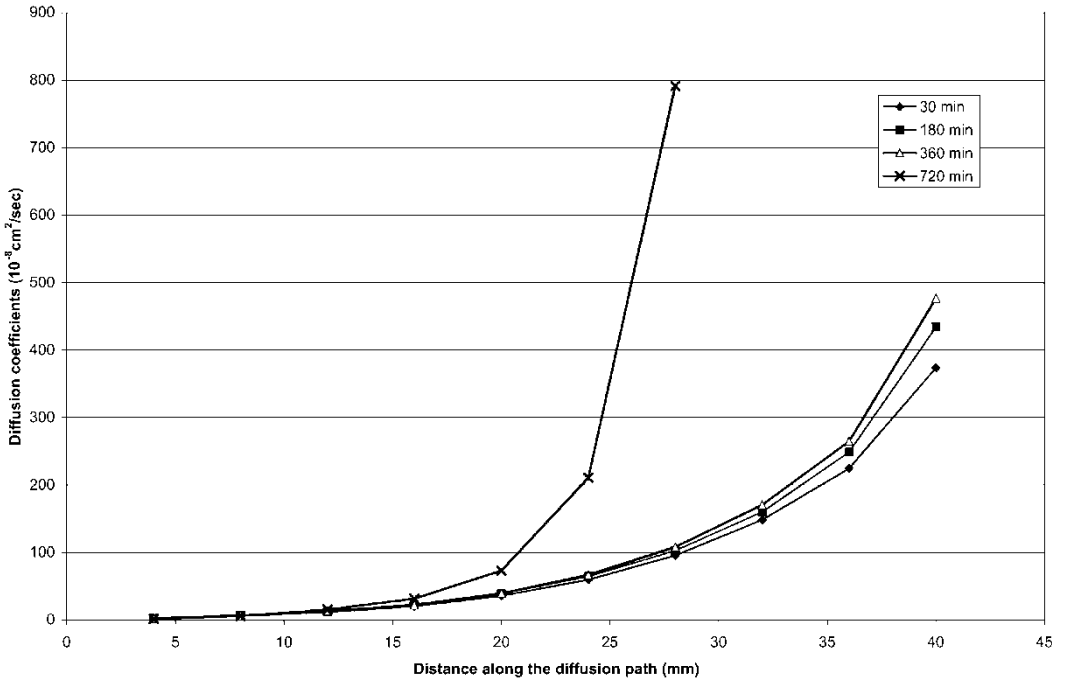

Figure 8. Effect of treatment time on the cyproconazole diffusion coefficients in the Douglas fir heartwood during SCF impregnation at 10.3 MPa and 40°C.

treatment is a dynamic process in which biocides can be deposited whereas wood components, notably extractives, can be solubilized. This extraction would be particularly important near the pits because the process could enhance permeability, resulting in increased diffusion. SCFs have been used to remove extractives, resin acids, and fatty acids from wood[19–23] and these processes appear to increase the permeability of the wood.[24]

Increased diffusion coefficients were also observed with distance from the surface (Table 2 and Figure 8). Higher diffusion coefficients were observed as the concentration gradients approached zero. The smaller slope, which is the denominator in Egner's equation, resulted in abnormally high diffusion coefficients suggesting that Egner's solution is not valid as the slopes of the concentration-distance curves approach zero. This anomaly prevented us from obtaining diffusion coefficients for the 3 deeper depths in the 720 min treatment and highlights the limitations of this approach for assessing diffusion.

CONCLUSIONS

The models indicate that diffusion, not rapid bulk flow, is the predominant mode for biocide movement into wood during SCF treatment. Prolonged treatment, however, appeared to enhance diffusion coefficients possibly as a result of solubilization of extractives that blocked flow through heartwood pits. The role of this solubilization on movement merits further study. The results also suggest that small process changes in temperature or pressure will have relatively little effect on treatment.

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