EFFECT OF PROCESS VARIABLES ON SUPERCRITICAL FLUID IMPREGNATION OF COMPOSITES WITH TEBUCONAZOLE

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ABSTRACT

This study examines the effects of pressure, temperature, and treatment time on supercritical fluid impregnation of such composites as plywood, particleboard, flakeboard, and medium-density fibe-board. Carbon dioxide with methanol as a cosolvent was used as the supercritical fluid, with tebucori-azole as the biocide. Biocide distribution, as measured by extraction and analysis, generally increased with pressure, temperature, and treatment time, although the retentions sometimes decreased at the highest pressure tested (4500 psig). In general, biocide retentions were far above those required for fungal protection, and the distribution was more uniform than that found with conventional pressure treatments. The results suggest that supercritical fluid impregnation represents a simple method for impregnating composites with biocides without the permanent damage typical of other treatment sys-tems.

Keywords: Composites, particleboard, plywood, waferboard, flakeboard, fiberboard, tebuconazole, pressure treatment, supercritical fluids, carbon dioxide.

INTRODUCTION

Impregnating wood-based composites with preservatives without inducing permanent deformation or other negative structural properties poses a major challenge for wood users (Deppe 1970; Hall et al. 1982). Yet the increasing use of wood-based composites where wetting may create conditions suitable for decay development will necessitate the development of effective but less damaging treat-ments. Treating flakes, particles, or veneers prior to lay-up has been proposed, but many chemicals negatively affect bonding and board properties (Laks et al. 1988; Vick 1990; Vick et al. 1990; Kreber et al. 1993). In addition, pressing conditions may encourage volatiliza-tion of biocides from the treated components, creating potential health and safety risks. Vapor phase treatments with trimethyl borate have been proposed for panel treatment (Murphy and Turner 1989). This process produces excellent penetration in dry panels, but the residual boron remains susceptible to leaching,

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TABLE 1. *Properties of exterior panels used for supercritical fluid (SCF) treatment.*

Board type	Components	Density (kg/m^3)	Thickness (mm)
Plywood (5 ply)	Douglas-fir face	470–500	15
Particleboard	Softwood shavings/sawdust	600–650	13
Flakeboard	Wafers from aspen (random orientation)	600–650	10
MDF	Softwood fibers (profiled facade)	800	13

making it unsuited for exposures where wetting is likely to occur.

Few of the current treatment practices appear suitable for protecting the diverse array of wood-based panel products; this lack creates an opportunity for researchers to rethink protection processes. One approach to improving composite treatment is to alter the treatment fluid to minimize potential disruption of the wood/resin matrix. Gases are likely to be the least destructive carriers; however, most gases lack the solvating properties necessary to deliver adequate chemical loadings into the wood. An alternative to gases is the use of supercritical fluids (SFCs), which have properties like those of gases in terms of diffusivity, but solvating capabilities that approach those of liquids (Hoyer 1985; Eckert et al. 1986; Krukonis 1988; Matson and Smith 1989). Preliminary trials with supercritical carbon dioxide suggest that this carrier with or without a cosolvent can effectively deliver various biocides into solid wood with little or no negative effect on the woods (Morrell et al. 1993; Smith et al. 1993). SCF would thus appear to be an ideal carrier for delivering biocides into composites, but there is little information on the conditions necessary for effective treatment. In this report, we describe trials to identify conditions suitable for using supercritical carbon dioxide with methanol to impregnate four panel types with tebuconazole. In a subsequent report, we will address the potential effects of SCF treatment on physical and mechanical properties of the various panel types (Acda et al. 1996).

MATERIALS AND METHODS
Panel type

Commercial plywood, particleboard, flakeboard, and medium-density fiberboard (MDF)

were used in this study (Table 1). Manufacturing conditions for these panels were not known. Because of limitations imposed by the size of the treatment vessel, panels were cut into defect-free strips (38 mm × 500 mm × panel thickness), and all four edges were sealed with two coatings of epoxy resin. Prior to treatment, all samples were conditioned to a constant moisture content in a chamber maintained at 65% RH and 21°C.

Biocide

Tebuconazole (Preventol® A8), a triazole fungicide (95% pure, pH = 4.5, from Bayer AG, Pittsburgh, PA), was chosen because it has a broad spectrum of activity against wood-decaying fungi, is leach-resistant, light- and heat-stable, and soluble in both solvent and water-borne formulations (Exner 1991).

Solvent and cosolvent

Carbon dioxide (CO_2) was used as solvent and methanol as cosolvent. Carbon dioxide is by far the most extensively used solvent in SCF processes because of its favorable transport properties, which include low viscosity, a high diffusion coefficient, and good thermal properties (Filippi 1982). The critical temperature (31.3°C) and pressure (1073 psig) were readily attainable with available equipment. Other fluids with critical parameters near those of CO_2 are often difficult to handle and to obtain in pure form and may be toxic or give rise to highly reactive or explosive mixtures. However, CO_2 does have limitations because its lack of polarity reduces its capacity for solvent-solute interactions that would enhance solubility of polar organic compounds. In order to overcome these potential limitations and
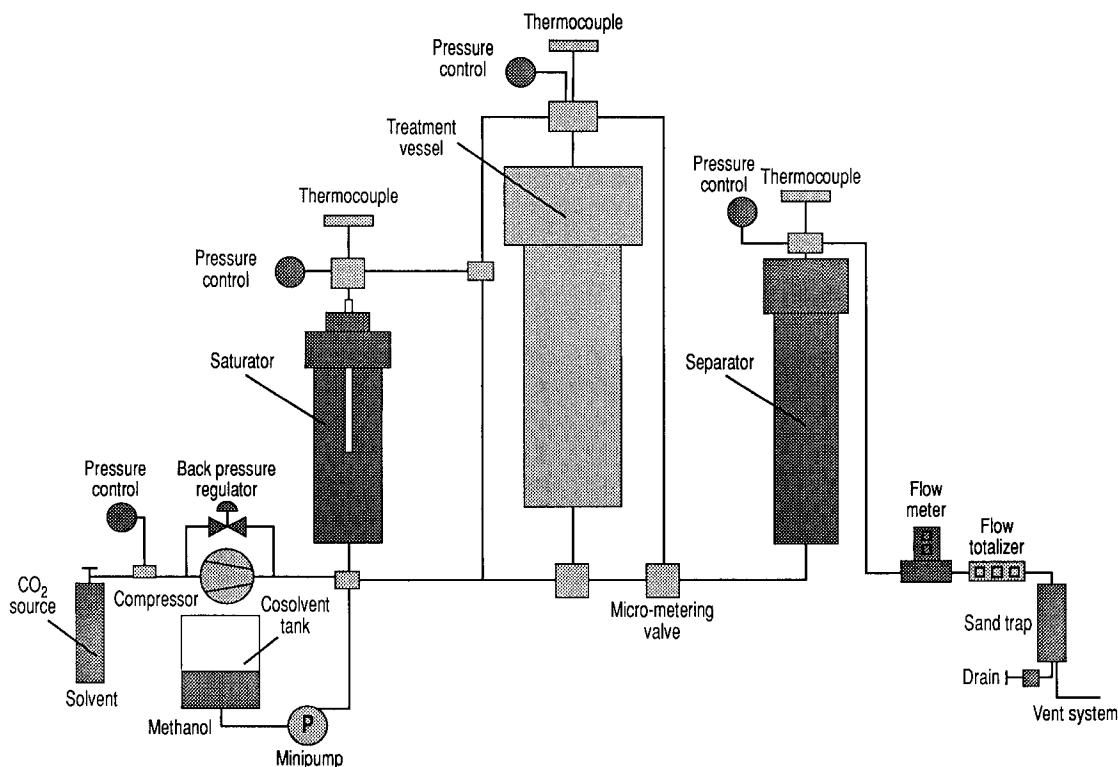
FIG. 1. Schematic of supercritical fluid impregnation device.

improve polarity, methanol was used as co-solvent. Previous studies showed excellent solubility of tebuconazole in this system (>2.0% weight fraction) (Junsophonsri 1994; Sahle Demessie 1994).

Supercritical fluid impregnation apparatus

Panels were treated by using an impregnation device (Fig. 1) in which a mixture of CO_2 (99.9 weight % purity) and methanol (3.5% mole fraction) was admitted into a preheated saturator (65-mm inner diameter (i.d.), 533-mm length) containing freshly mixed tebuconazole in methanol. Tebuconazole was packed on filter paper and glass wool to increase porosity and facilitate efficient solute-SCF contact. Methanol was metered through the saturator with a metering duplex pump (LDC Analytical, 0.48–9.7 ml/min flow rate) and compressed with a high-pressure compressor (Newport Scientific, 690 bars and 16

ml/min capacity) until the required experimental supercritical conditions were reached. Glass wool was placed at both the inlet and the outlet of the saturator to prevent biocide entrainment. A back pressure regulator was used to maintain the desired pressure. The saturator was opened into a preheated treatment vessel (120 mm inside diameter [i.d.] and 508 mm long) containing the wood samples. Pressure was then increased to the desired level while a 12 ml/min flow rate was maintained by using a micro-metering valve located after the treatment vessel. All tubing was heated to prevent sudden drops in temperature along the lines, which would cause premature biocide precipitation and clogging. Previous trials indicated that this flow rate resulted in a saturated mixture passing through the treatment vessel (Sahle Demessie 1994). Flow was reversed at 3-min intervals by using hand-operated valves to maintain an even distribution

of biocide along the length of the vessel. At the conclusion of the pressure period, the mixture was expanded at 5–10 psig/sec across a micro-metering valve. It flowed through a separator (38 i.d., 267 mm length), which retained the biocide while releasing the CO_2. A secondary separation was accomplished in a cold sand trap at atmospheric pressure. The sudden drop in pressure and temperature below the critical points during venting decreased solubility, resulting in biocide precipitation in the panels. The gas stream was monitored with a digital flow meter at atmospheric pressure. Pressure, temperature, and gas flow rate were continuously recorded on a National Instrument Data Acquisition program on a personal computer (National Instrument, Inc.).

Treatment conditions and experimental design

Biocide solubility in supercritical fluid is dependent on the biocide vapor pressure and solvent-cosolvent density. However, these variables are closely related to temperature and pressure during the process, and the effects of each variable on treatment are poorly understood (Sahle Demessie 1994). To better clarify these effects, the treatment apparatus was used to evaluate the effects of pressure (1,800, 3,600, 4,500 psig), temperature (45°, 60°, 75°C), and treatment time (5, 15, 30 min) on tebuconazole retention and distribution in each panel type. Each treatment used combinations of the above variables fitted in a completely randomized design on 9 replicates for each panel type (Neter et al. 1990). Untreated, unexposed samples for each type of panel were used as controls.

Chemical analyses

Tebuconazole retentions were determined by cutting 15-mm-thick sections from both ends and the middle of each sample (Fig. 2). Distribution of biocide from outer to inner zone was determined by slicing 2-mm sections from the face, middle, and inner parts of each of these sections to produce three samples for
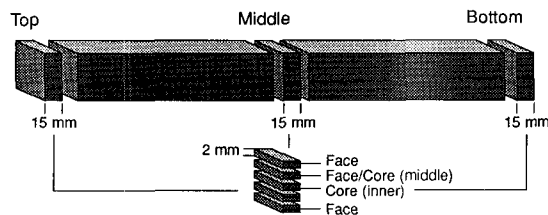

Fig. 2.   Sampling pattern for assessing biocide distribution and retention in SCF-treated composites.

analyses (face, mixed face/core, and core). The samples were ground to pass a 30-mesh screen, then extracted in methanol for 3 hours. The extract was filtered (45 μm) and analyzed on a Shimadzu high performance liquid chromatography (HPLC) according to procedures described in American Wood-Preservers' Association (AWPA) Standard A23-94 (1994). Separation was achieved by using a 100-mm × 4.6-mm i.d. column packed with 3-mm Hypersil ODS (C18) (Altech Associates) with an acetonitrile/water (95/5) mobile phase at a flow rate of 2.5 ml/min. Tebuconazole was detected with a UV detector at 280 mm and quantified by comparisons with standard solutions. The data were subjected to an Analysis of Variance, and retention means were examined by using Tukey's Highly Significant Difference Test at $\alpha = 0.05$.

RESULTS AND DISCUSSION

Effect of treatment pressure on biocide retention

Tebuconazole retentions increased significantly for all panels when pressure increased from 1,800 to 3,600 psig; the vessel was maintained at 60°C for 30 min (Table 2). Increasing pressure to 4500 psig, however, significantly decreased retention for all panels except plywood. All retentions exceeded the reported thresholds for tebuconazole toxicity against wood-degrading fungi of 0.13 kg/m^3 for unaged and 0.45 kg/m$_3$ for aged samples (Exner 1991).

The greater biocide uptake when pressure increased from 1,800 to 3,600 psig reflects the increasing tebuconazole solubility at higher

TABLE 2. *Effect of treatment pressure on tebuconazole retention in various panel types following impregnation with supercritical CO_2 at 60°C for 30 min.*

Pressure (psig)	Rep. (n)	Tebuconazole retention (kg/m^3)[a,b]			
		Plywood	Particleboard	Flakeboard	MDF
1,800	9	1.07 (0.39) A	1.04 (0.36) A	0.86 (0.31) A	2.72 (1.16) B
3,600	11	2.90 (0.72) B	6.74 (1.78) C	5.89 (1.48) C	4.51 (1.22) C
4,500	9	2.75 (3.04) AB	3.04 (1.43) B	2.12 (1.62) B	0.92 (0.68) A

[a] Value in parentheses represents one standard deviation.
[b] Values within a single column followed by the same letter do not differ significantly (Tukey's HSD, $\alpha = 0.05$).

CO_2 densities. Higher CO_2 density increases interactions between the biocide and the solvent, thereby enhancing solubility. The cause of the decreased retention at 4500 psig is unclear. Theoretically, biocide absorption should have increased or remained constant as solvent density rose with increasing pressure. Interactions between pressure and other treatment parameters may have caused this deviation. The limited number of observations, however, precludes further delineation of these effects.

Retentions obtained at 1800 psig were acceptable for biological performance, and hence this pressure level was used to explore the effects of other parameters on treatment.

Effect of treatment temperature on biocide retention

Increasing treatment temperature from 45° to 75°C in charges treated at 1,800 psig for 30 min resulted in significant decreases in retention for all panel types, although the effect on MDF was noted only at 75°C (Table 3). The highest biocide retentions were obtained at 45°C. Mean retentions at this temperature ranged from 0.066 to 2.62 kg/m^3 for the various panel types. Again, these levels were all

above the reported toxic thresholds for tebuconazole (Exner 1991).

The decreased retentions at higher temperatures may reflect the effect of retrograde vaporization, wherein the solvating power of CO_2 decreases because of increasing tebuconazole vapor pressure when temperature rises above the critical point (Marentis 1988). As a result, biocide solubility decreases as temperature rises, reducing the amount of chemical available for deposition.

Effect of treatment time on biocide retention

Treatment periods of 5 min resulted in mean retentions ranging from 0.13 to 1.3 kg/m^3, depending on panel type; panels were treated at 1800 psig and 60°C (Table 4). These levels were adequate to impart protection against wood-decaying fungi, although the lower retentions were at the edge of the threshold for fungal attack (Exner 1991). Increasing treatment time from 5 to 30 min increased tebuconazole retentions for all panel types, although retentions in plywood, particleboard, and MDF were lower at 15 min than at 5 or 30 min. The reasons for this difference are unknown. The rapid chemical absorption con-

TABLE 3. *Effect of treatment temperature on tebuconazole retention in various panel types following impregnation with supercritical CO_2 at 1,800 psig for 30 min.*

Temperature (C)	Rep. (n)	Tebuconazole retention (kg/m^3)[a,b]			
		Plywood	Particleboard	Flakeboard	MDF
45	9	1.73 (0.88) B	2.42 (0.72) C	2.62 (0.19) B	2.61 (0.16) B
60	9	1.07 (0.39) B	1.04 (0.36) B	0.86 (0.31) B	2.72 (1.16) B
75	9	0.19 (0.12) A	0.09 (0.06) A	0.07 (0.05) A	0.30 (0.27) A

[a] Value in parentheses represents one standard deviation.
[b] Values within a single column followed by the same letter do not differ significantly (Tukey's HSD, $\alpha = 0.05$).

TABLE 4. *Effect of treatment time on tebuconazole retention in various panel types following impregnation with supercritical CO_2 at 1,800 psig and 60°C.*

Time (min)	Rep. (n)	Tebuconazole retention (kg/m^3)[a,b]			
		Plywood	Particleboard	Flakeboard	MDF
5	9	0.48 (0.26) B	0.24 (0.18) A	0.13 (0.16) A	1.30 (0.16) B
15	9	0.07 (0.07) A	0.20 (0.17) A	0.22 (0.22) A	0.77 (0.72) A
30	9	1.08 (0.39) C	1.03 (0.36) B	0.86 (0.31) B	2.72 (0.16) C

[a] Value in parentheses represents one standard deviation.
[b] Values within a single column followed by the same letter do not differ significantly (Tukey's HSD, $\alpha = 0.05$).

firms earlier reports of extremely rapid penetration of materials by SCF when compared with conventional liquid solvents (Smith et al. 1993).

FIG. 3. Tebuconazole distribution at selected depths from the surface of panels treated with supercritical CO_2 at a) 1800, b) 3600, or c) 4500 psig and 60°C for 30 min.

Preservative distribution

Biocide penetration was complete in all panel types regardless of variations in pressure or temperature (Figs. 3–5). The excellent preservative distribution across all samples illustrated the ability of SCF to rapidly deliver biocide through a variety of panel types. Retention gradients from the outer to inner zones, with outer-to-inner zone ratios between 1.1 and 9.6, were generally far lower than would be found with conventional pressure impregnation (Mitchoff and Morrell 1991). These re-
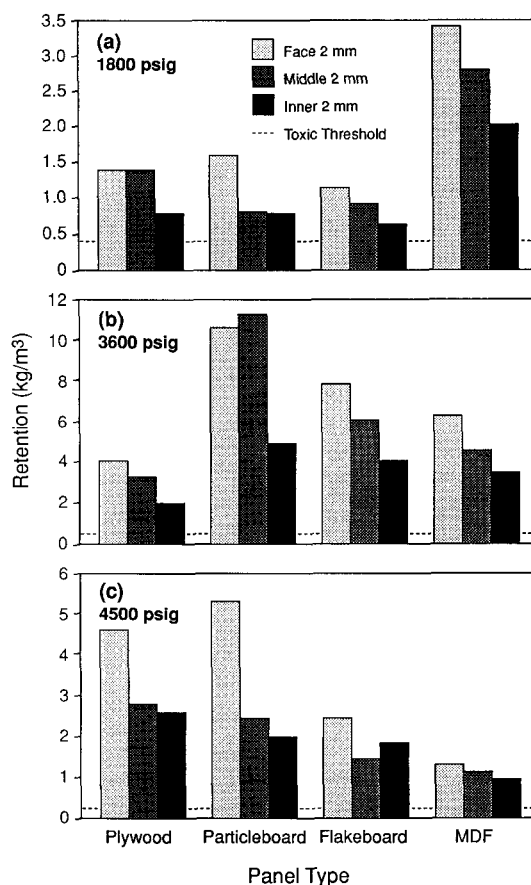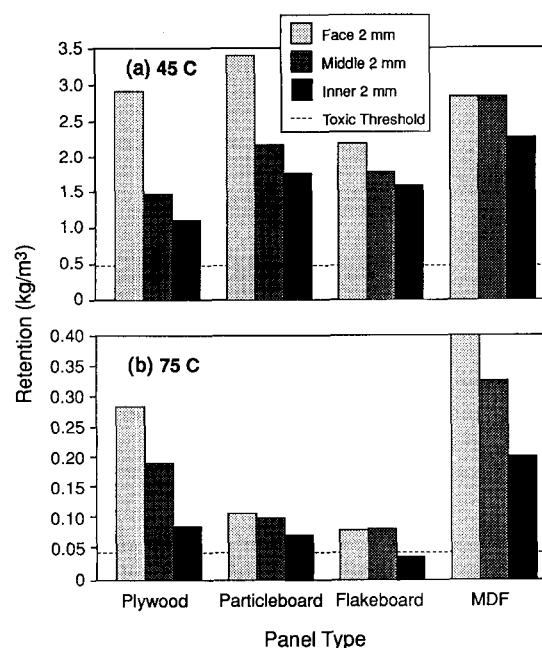

FIG. 4. Tebuconazole distribution at selected depths from the surface of panels treated with supercritical CO_2 at a) 45°C or b) 75°C for 30 min at 1800 psig.
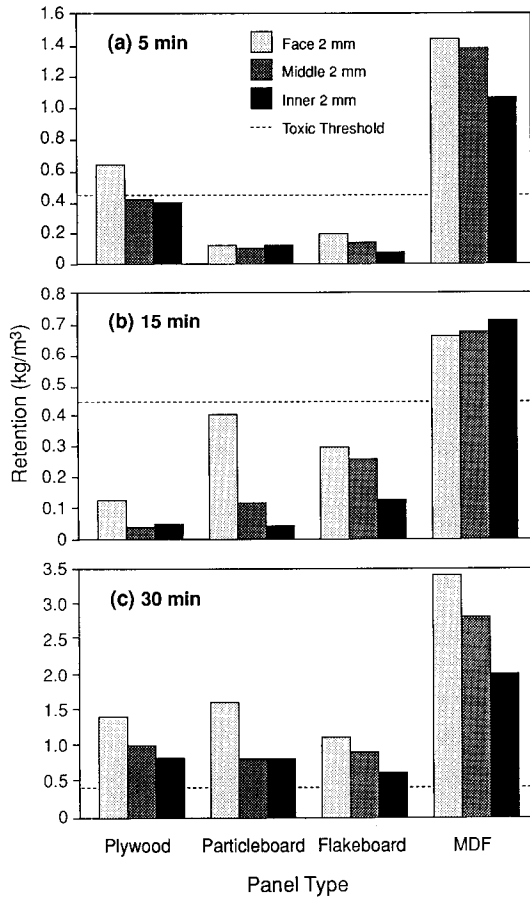
FIG. 5. Tebuconazole distribution at selected depths from the surface of panels treated with supercritical CO_2 at 1800 psig and 60°C for a) 5, b) 15, or c) 30 min.

FIG. 6. Tebuconazole distribution at selected points along the length of panels treated with supercritical CO_2 at a) 1800, b) 3600, or c) 4500 psig. Values above the bars represent retention ratios from the end to the middle of each panel sample.

sults suggest that as the solvent drops below the critical temperature or pressure, deposition is fairly rapid and uniform.

Analyses of biocide retentions at selected distances from the panels' surfaces showed that tebuconazole distribution was higher in MDF than in other panels under the same treatment conditions (Fig. 3–5). The uniform and fibrous structure of MDF may have assisted in penetration, whereas the different species composition in plywood or the disordered particle orientation in flakeboard may have inhibited uniform chemical penetration and absorption. Further studies will be required to clarify the influence of variables
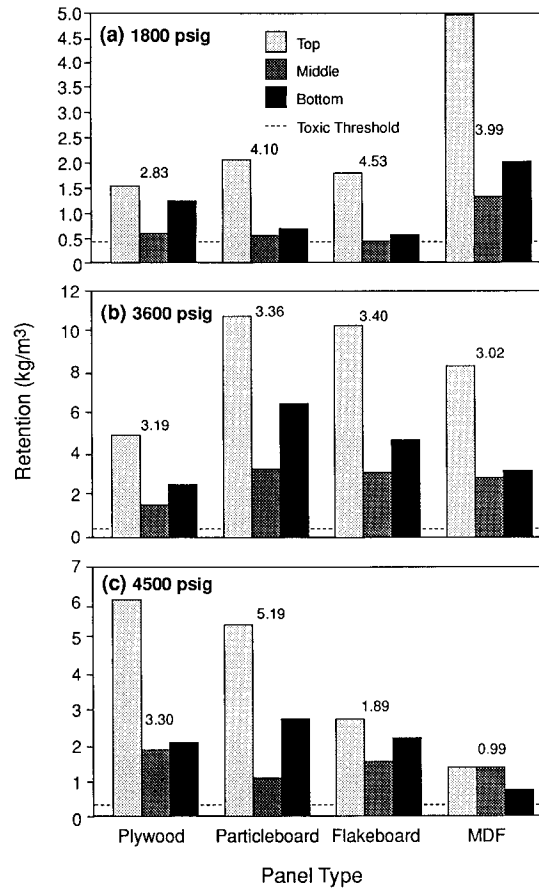
such as resin type, particle geometry, and additives such as wax on biocide distribution under supercritical conditions.

Although gradients from the face to the core were generally small, the top and bottom portions of all panels showed higher levels of chemical absorption than the middle portions. Ratios between preservative retentions in the ends and middle portions ranged from about 1.0 to 4.5 as pressure varied (Fig. 6). These ratios suggest that the rapid expansion during venting created an uneven biocide nucleation along the length of the panels. The top and bottom portions, being close to the transition

point between supercritical to subcritical conditions, received more chemical. This venting effect could have potential application in the treatment of materials (e.g., utility poles and cross-ties) wherein it is desirable to have higher levels of preservative in one or both ends.

CONCLUSIONS

Supercritical carbon dioxide with methanol was capable of solubilizing and delivering acceptable levels of tebuconazole into a variety of panel products. Process parameters such as pressure, temperature, and duration of treatment were closely related to tebuconazole retention. The process produced rapid biocide penetration at levels that were well above the reported toxic threshold for tebuconazole. In addition, the process resulted in relatively uniform treatments across the panels without the steep preservative gradients typical of conventional liquid treatment processes.

The use of supercritical fluids provides an attractive alternative to conventional liquid impregnation; however, further studies will be required to better determine the relationship between process variables and biocide deposition. Such information will be essential for the development of controllable treatment processes.

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