EFFECT OF PROCESS VARIATIONS DURING SUPERCRITICAL FLUID IMPREGNATION ON CYPROCONAZOLE RETENTION AND DISTRIBUTION IN PONDEROSA PINE SAPWOOD

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ABSTRACT

The effect of process variations under supercritical conditions on cyproconazole retention and distribution in ponderosa pine sapwood boards was assessed. While pressure and temperature appeared to affect biocide solubility to some extent, the overall results suggested that biocide movement into wood was influenced more by diffusion than bulk flow. Biocide distribution also varied along the specimen length and within the treatment vessel illustrating the importance of mixing and the need to ensure that adequate levels of biocide are available in the supercritical fluid. The role of fluid phase changes near the critical region on final biocide distribution in the wood is also discussed.

Keywords: Cyproconazole, ponderosa pine, supercritical fluids, wood treatment.

INTRODUCTION

Biocide impregnation of wood using conventional liquid preservative systems and pressure processes often produces treatability problems including shallow penetration, uneven biocide distribution in refractory species, and incompatibility with wood composites. One approach to overcoming these problems with liquid systems is to develop modified fluid processes.

Supercritical fluids (SCF) exhibit attractive features for wood impregnation including high diffusivities, low viscosities, and miscibilities with gases that allow them to move through semiporous materials in a manner similar to gases. SCFs can also solubilize various solutes at levels approaching those of liquid solvents (Brogle 1982; Krukonis 1988). A number of studies have evaluated the feasibility of using SCFs as alternative carriers to overcome treatability problems associated with traditional liquid carrier systems (Kayihan 1992; Morrell et al. 1993; Sahle-Demessie 1994; Acda 1995; Acda et al. 1997a, 1997b, 2001; Kim and Morrell 2000; Muin and Tsunoda 2001).

Although SCF treatment appears to be an important technological improvement, commer-

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cialization of this process has been limited because of the high capital costs as well as the lack of a fundamental understanding of the treatment process. As we move from metal-based, waterborne systems, however, SCF may play an increasingly important role because of the ability to solubilize a diverse array of organic biocides.

Several studies have investigated the relationship between process conditions such as pressure, temperature, or treatment time and biocide solubility (Sahle-Demessie 1994; Acda 1995; Acda et al. 2001). While higher retentions and more uniform biocide distributions in wood were found under higher-pressure conditions, biocide retentions decreased as treatment temperature rose (Sahle-Demessie 1994; Acda 1995). Increased fluid density at higher-pressure conditions enhances specific interactions between the solute and solvent molecules due to decreased intermolecular mean distances between molecules (Chrastill 1982). These higher interactions improve biocide solubility, resulting in better biocide treatability. Increasing treatment temperature, however, can decrease solute solubility as fluid density decreases, in a phenomenon termed retrograde vaporization (Marentis 1988).

Previous studies have circulated SC-CO_2 through a bed of biocide to the point where the fluid is saturated with biocide. It is difficult to observe the effects of pressure or temperature on SCF impregnation using this saturation method since solute solubility varies with pressure/temperature conditions as do the amounts of biocide that can be introduced into the system. While higher pressures increase retention and penetration in conventional liquid treatments (Hunt and Garrett 1967), the role of pressure in SCF treatment is less clearly understood because of the confounding effects of solubility.

Biocide solubility can change markedly with small changes in pressure, temperature, or amount of cosolvent, leading to errors and control problems between batches when the saturation method is employed. Kang (2002) fed a mixture of biocide and liquid cosolvent into the treatment vessel to control biocide level and then induced deposition by decreasing temperature. Biocide input was maintained below the saturation point to ensure that all biocide added into the system was dissolved in the SCF under the given conditions. This method produced more reproducible retentions between batches and reduced biocide consumption in comparison with the saturation method. There are, however, still a number of questions about how process conditions can be manipulated to ensure more uniform treatment.

In this report, we assessed the effects of pressure and temperature on cyproconazole retention and distribution in wood under subsaturated SCF conditions.

MATERIALS AND METHODS

Kiln-dried ponderosa pine sapwood (*Pinus ponderosa* Laws) lumber was cut into specimens (10 by 100 by 300 mm long) that were conditioned to a constant weight at 20°C and 65% RH. Samples were not end-sealed to reduce the risk of developing pressure gradients that might lead to mechanical failure during treatment and to minimize errors in mass balance due to solubilization of the seal. Twelve specimens were treated in each cycle, six in the upper and six in the lower halves of the treatment vessel, to assess the effect of position in the treating vessel on biocide distribution.

The biocide evaluated was cyproconazole (Evipole™), (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/m^3 depending on a target fungus and sample aging procedures (Janssen Pharmaceutica product information sheet, n.d.)

Samples were treated using a SCF impregnation device (Fig. 1). Standard grade carbon dioxide (99.9 weight %, Industrial Welding Supply) was admitted into a preheated 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

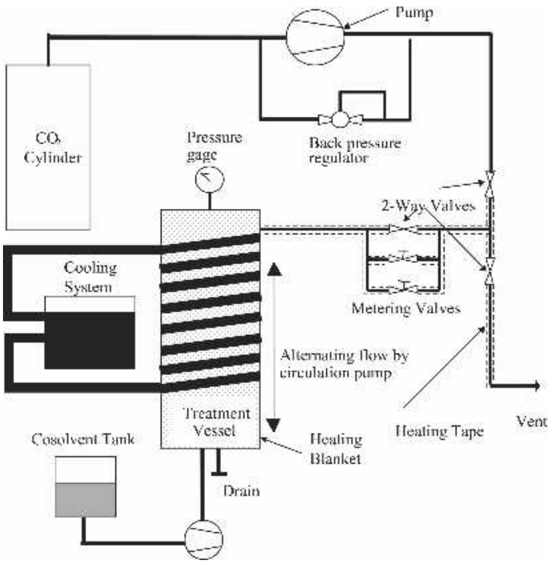


FIG. 1. Schematic of the supercritical fluid impregnation device.

fluid back into the compressor. After the desired pressure was achieved, a known amount of cyproconazole (20 g) mixed with 3.5 % mole fraction methanol (99.9 weight %, Fisher) was introduced into the treating vessel using a cosolvent pump (Milton Roy). Once pressure reached the target level, the fluid was circulated through the vessel at 2 kg/min for 1 h. Flow was reversed every 15 min to encourage even distribution of biocide along the length of the vessel. The treatment conditions were maintained for one hour.

We evaluated four temperature/pressure combinations (40°C/10.3 MPa, 40°C/20.6 MPa, 60°C/10.3 MPa, 60°C/20.6 MPa) to investigate the relationship between pressure/temperature and retention under subsaturated fluid conditions. Each combination was replicated in three batches, and each batch had 12 replicate wood samples. Samples were allocated into each treatment by specific gravity to distribute variability across the treatments and improve precision.

Temperature was reduced 0.4°C/min using a Brinkmann cooling circulator at the end of the treatment period. Pressure also decreased as temperature decreased. When both temperature and pressure decreased below the respective critical values (31.3°C and 7.4 MPa), the pressure was reduced at a rate of 0.414 MPa /min by venting the system.

Pressure, temperature, and fluid density changes were recorded from controller panels during the treatment process and were used to draw plots representing various process conditions and fluid phases.

After treatment, the samples were removed from the treating vessel, and the top, middle, and bottom 20 mm along the length of of each sample were removed and segmented into zones corresponding to zones 0–1.5 mm, 1.5–3 mm, and 3–5 mm from the surface. 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.

Biocide concentrations in the wood extracts and recovered cosolvent were determined by injecting 10 μL of extract into a Shimadzu high performance liquid chromatography-UV detector (HPLC-UV) using a modification of American Wood Preservers' Association Standard A 23 (AWPA 1996). Separation was achieved using an Altech Hypercil ODS (C18) column (4.6 mm ID by 10 m long). The elution solvent consisted of mobile phase A (55% acetonitrile/45% buffer) and B (95% acetonitrile/5% buffer). The buffer was 0.5% w/v ammonium carbonate. The elution mode was programmed for mobile phase A from 0 to 3.5 min, B from 3.5 to 5.0 min, and A from 5.0 to 8.0 min. Flow rate and detector wavelength were 1.5 mL/min and 230 nm, respectively.

The retention data from different treatments were subjected to an analysis of variance (ANOVA) for retention vs. process condition, and means were compared using Duncan's multiple range tests at $\alpha = 0.05$ ($n = 18$: 3 batches × 6 replicates). These data along with amount of recovered methanol were used to draw contour plots illustrating biocide distribution within individual wood samples and methanol loss in a treating vessel after 4 different pressure/temperature treatments.

RESULTS AND DISCUSSION

Metering of biocide-laden methanol into the supercritical carbon dioxide allowed us to work in unsaturated and therefore more controllable conditions. This limited the potential effects of solubility in most treatments except for the treatment at 60°C and 10.3 MPa, where the conditions approached the limits of solubility for the biocide employed.

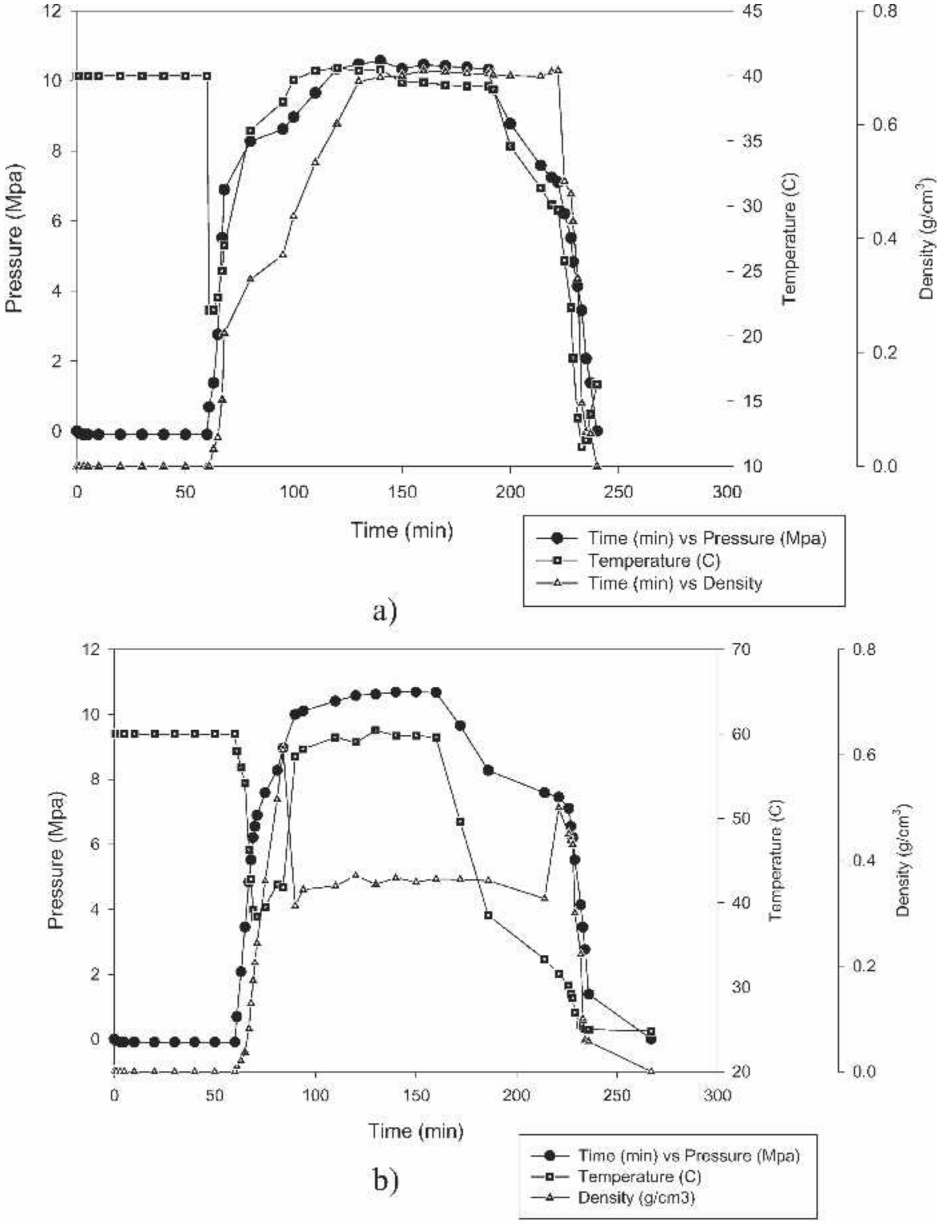
Altering process conditions (temperature and pressure) should have marked effects on fluid density, which should, in turn, affect biocide solubility (Fig. 2). For example, temperature quickly dropped as CO_2 expanded as it was introduced into the treatment vessel. Temperature then started to rise, after the initial pressure drop, as CO_2 was compressed in the heated treatment vessel. Rapid temperature fluctuations were observed as the pressure approached the supercritical region as a result of increased CO_2 conductivity (Vesovic et al. 1990). These fluctuations reflect energy released from condensation of gaseous carbon dioxide (latent heat), which increased the temperature. Temperature and pressure were relatively constant once the desired treatment conditions were reached for all four pressure/temperature combinations evaluated.

The effects of process conditions on fluid density were evident when pressure was increased from 10.34 to 20.68 MPa while holding temperature constant. This increase produced only a slight effect on density at 40°C (0.7 to 0.8), but density nearly doubled when temperature increased to 60°C (0.38 to 0.75) (Fig. 2). These changes reflect the opposing effects of pressure and temperature on density. Fluid density lagged behind pressure and temperature changes during cooling, and equilibrated during venting (Fig. 2). Phase changes were also evident during cooling. A liquid phase was observed through the vessel view cell after cooling below the critical temperature. The liquid stage density was very close to that of the SCF, and an increased density was noted at 10.34 MPa and 60°C (Fig. 2).

While it is unclear how the liquid or subcritical CO_2 affected biocide impregnation, solvent properties (density, solvating strength, viscosity etc.) should experience the most dramatic changes at near-critical conditions. Subcritical liquid CO_2 exists from −55°C to +31°C and from 0.51 MPa to 7.50 MPa (Brogle 1982). This liquid CO_2 can act like an ordinary liquid under constant pressure, but can be easily evaporated and reliquefied with slight temperature changes.

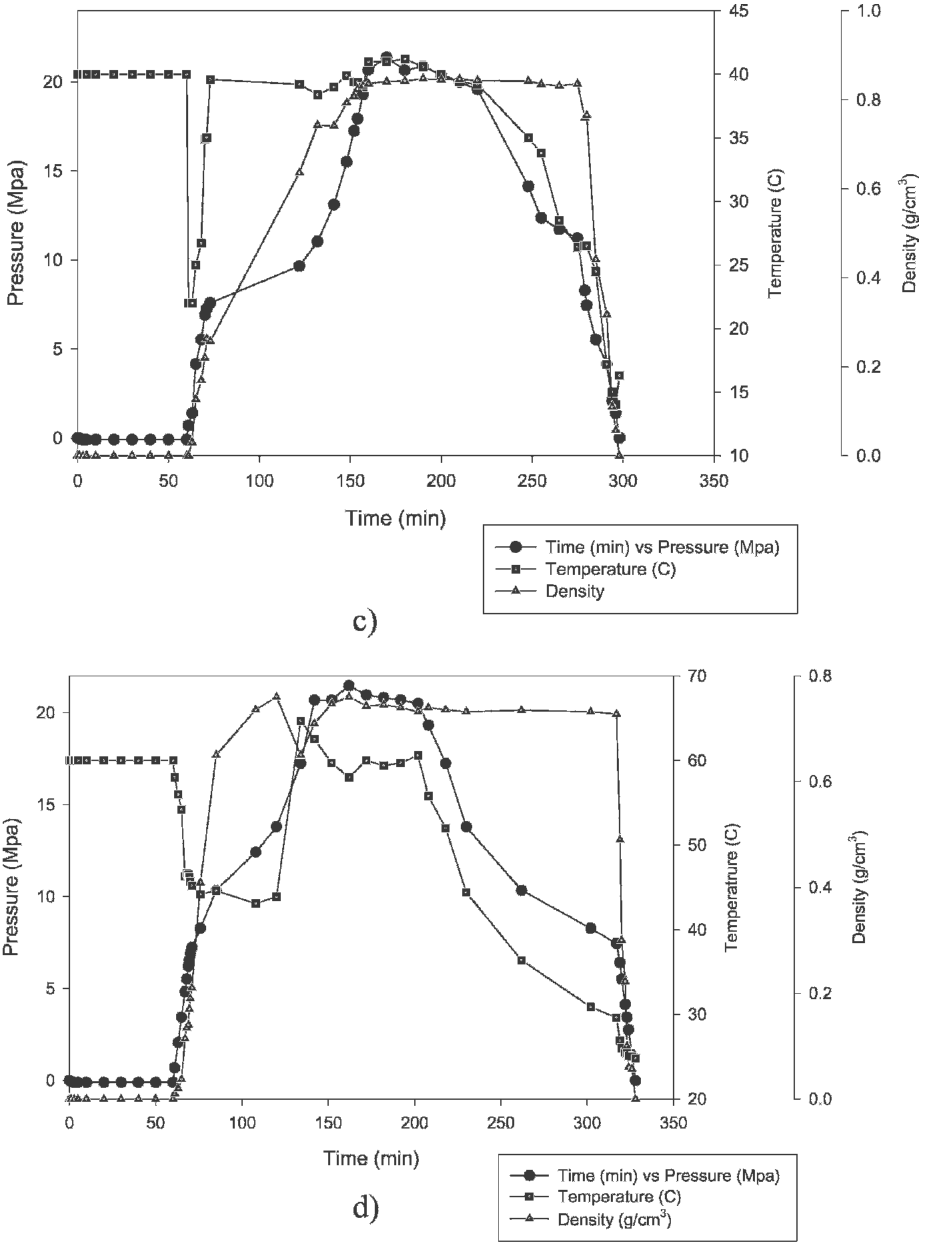
The presence of liquid carbon dioxide could affect biocide distribution in the wood. Liquid CO_2 is miscible with common liquid solvents including methanol (Francis 1954). However, cyproconazole solubility in liquid CO_2 would be very low in the treating vessel because liquid CO_2 is a very nonpolar solvent with a polarity much like hexane or pentane (Francis 1954). The addition of cosolvents can enhance the solvating power of liquid carbon dioxide, and a liquid CO_2/cosolvent mixture could redistribute biocide to the lower part of a treating vessel during the liquid phase, yielding higher retentions in samples located at the bottom of the treating vessel. Although ordinary nonpolar solvents exhibit increased solvating power with increased temperature, liquid CO_2 could behave similarly to a supercritical fluid, including a potential for retrograde vaporization at the end of treating cycle (Brogle 1982).

Cyproconazole retentions for ponderosa pine sapwood decreased significantly (70%) as the temperature increased from 40 to 60°C at 10.34 MPa, while temperature increases essentially had no effect on retention at 20.68 MPa (Table 1, Fig. 3). Decreased solute solubility likely reduced the amount of biocide deposited at the higher temperature. Acda (1995) also observed decreased tebuconazole retentions as treatment temperature rose from 45° to 75°C. Higher temperatures increase the solute vapor pressure, but decrease fluid density. Decreasing solvent density has a greater effect on solubility than increasing the solute vapor pressure just above the critical pressure (Johnston and Eckert 1981; Hoyer 1985; Marentis 1988). Solute vapor pressure effects, however, can dominate the solvent density effect at higher pressures, leading to higher solubility and higher retention. Thus, any effects should be accentuated near the critical region, while the temperature effect at the higher



V_1: Vacuuming period
P: Pressurization period
T: Treatment period
C: Cooling period
V_2: Venting period

FIG. 2. Temperature, pressure, and fluid density during supercritical CO_2 treatment of ponderosa pine sapwood samples with cyproconazole at different pressure/temperature combinations a) 10.3 MPa/40°C, b) 10.3 MPa/60°C, c) 20.6 MPa/40°C, d) 20.6 MPa/60°C.



c)

d)

V_1: Vacuuming period
P: Pressurization period
T: Treatment period
C: Cooling period
V_2: Venting period

FIG. 2. Continued.

TABLE 1. *ANOVA of the effect of treatment condition (pressure/temperature combination) on cyproconazole retention, and comparisons between retentions as shown by Duncan's multiple range test.*

Source	DF	Sum of square	Mean square	F-value	Pr > F
Model	3	1.1777	0.3926	74.51	<0.0001
Error	68	0.3583	0.0053		
Corrected total	71	1.5360			

Treatment	Replication (N)	Cyproconazole retention (kg/m^3)[a]
40°C/10.3 MPa	18	0.510 (0.074) A
40°C/20.6 MPa	18	0.378 (0.114) B
60°C/20.6 MPa	18	0.370 (0.035) B
60°C/10.3 MPa	18	0.153 (0.038) C

[a] Values in parentheses represent a standard deviation. Means in the same column followed by the same letter(s) do not differ significantly by Duncan's multiple range test ($\alpha = 0.05$).

pressure level were likely muted by the vapor pressure effect.

Although fluid density increases of 21.4% and 7.1% were observed at 40° and 60°C, respectively, at 20.68 MPa compared to the density at the lower pressure, there was no corresponding improvement in treatment results (Table 1 and Fig. 3). Enhanced solubility due to increased density should raise biocide input as evidenced by improved biocide treatability when using a saturated SCF (Sahle-Demessie 1994). In our study, increased solvating power with increased fluid density at the higher pressure had little effect under the subsaturated conditions because there was no additional biocide available to solubilize. However, higher temperatures at the higher pressure did tend to reduce biocide retention variation among individual samples, suggesting that biocide distribution in the SCF was more uniform under these conditions.

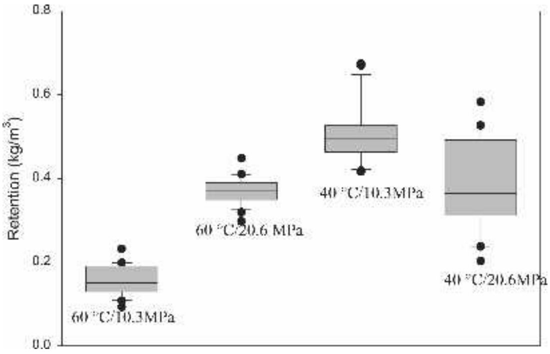


FIG. 3. Box and whiskers plot showing the effect of temperature and pressure combinations on cyproconazole retentions in ponderosa pine sapwood samples following supercritical CO_2 treatment. Box boundaries represent the 25 and 75th percentiles, the mid-line represents the median, error bars signify 2 standard deviations, the points represent outliers in the data.

It is not clear why retentions decreased at both higher density conditions compared to the 10.34 MPa and 40°C treatment. One possible explanation could be the effect of liquid CO_2 during the cooling. As the temperature dropped below the critical point in the 10.34 MPa and 40°C treatment, pressure also decreased below the critical point. However, pressure remained well above the critical point even after temperature decreased below the critical point in the 20.68 MPa treatment. These conditions would result in the presence of liquid CO_2, which is more sensitive to sudden phase changes during venting. The thermodynamic characteristics of liquid phases must be considered for future applications of SCF treatments.

While SCFs have the potential to fully penetrate into a variety of refractory wood–based materials, it is also important to control both the amounts and distribution of biocide delivered to various materials. Figure 4 illustrates biocide distribution in the wood specimens and the amount of recovered methanol in the treating vessel after 4 different pressure/temperature treatments. Biocide levels in the wood tended to be lower at 60°C and 10.34 MPa, suggesting that reduced solubility as a result of the higher tem-

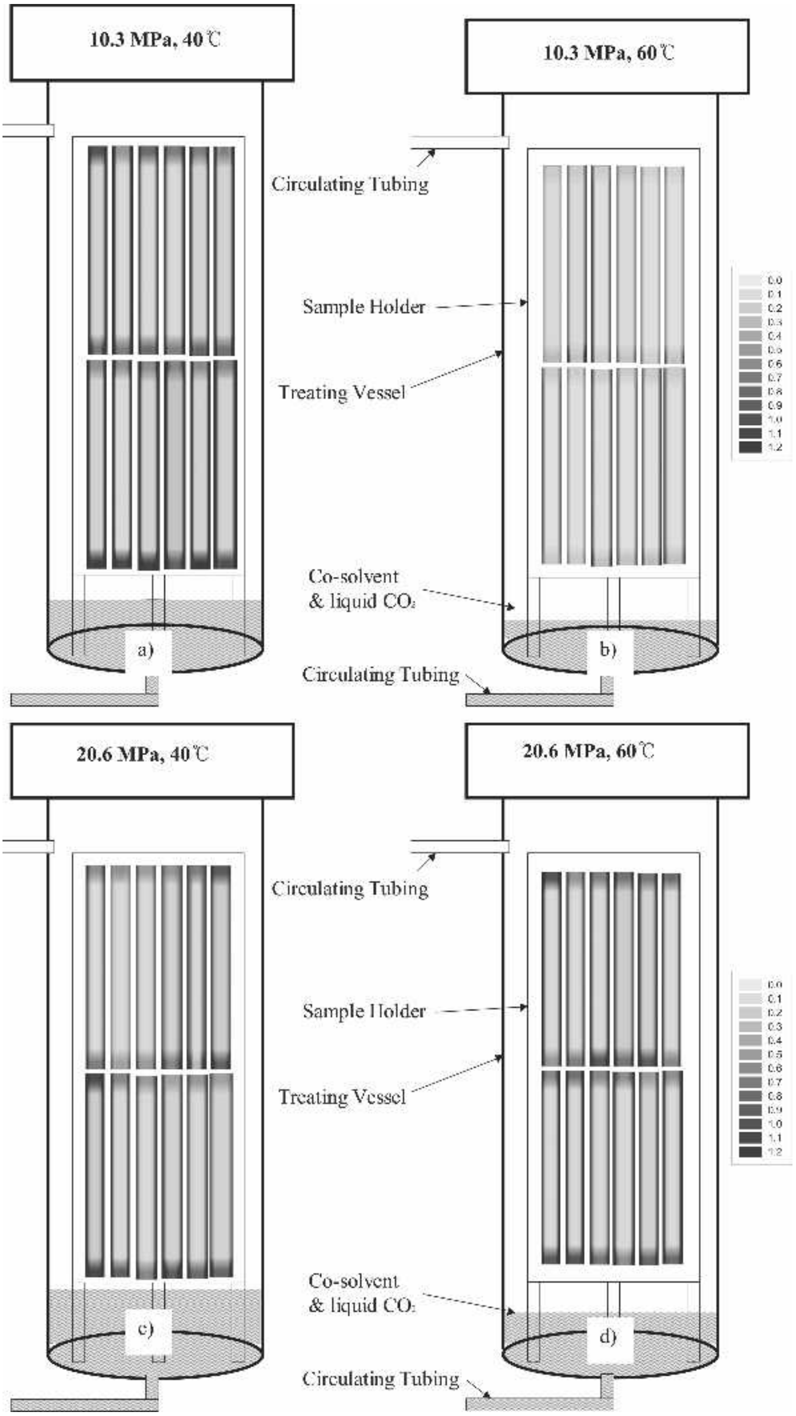


FIG. 4. Biocide distributions and the amount of recovered methanol in the treating vessel in ponderosa pine sapwood samples following supercritical CO_2 treatment using 4 different pressure/temperature combination treatments a) 10.3Mpa/40°C, b) 10.3Mpa/60°C, c) 20.6Mpa/40°C, d) 20.6Mpa/60°C. Gray scale in figure legend ranges from 0 to 1.2 kg/m^3. The amount of recovered methanol is shown by the hatching at the bottom of the vessel

perature lowered cyproconazole solubility and consequently, reduced the retention.

Selective biocide penetration into the ends of the unsealed samples was evident by the higher retentions in these zones in samples at all four pressure/temperature combinations. Relatively uniform treatments in the test cylinder were obtained among samples in the same upper or lower group (Fig. 4). Samples located lower in the treating vessel experienced higher overall biocide retentions, suggesting that the presence of liquid CO_2 and cosolvent at the bottom of the vessel might have affected retention in these samples at the end of treatment cycle. Retentions were also higher in sections cut from the upper ends of samples located at the top part of the vessel. We suspect that these samples were exposed more directly to biocide-laden SCF entering the treating vessel. Similar trends were also observed at bottom parts of samples located at the bottom of the vessel.

The amount of recovered methanol also varied with different pressure/temperature combinations (Fig. 4). Higher methanol losses (82.9% and 60.7%) were observed at 10.34 and 20.68 MPa, respectively, at 60°C, suggesting that methanol penetrated wood to a greater extent at higher temperatures. Since solute solubility is highly dependent on the small amount of cosolvent (Clifford 1998; Sahle-Demessie 1994; Brantley et al. 1999), decreased solute solubility due to cosolvent loss could lead to lower retentions at elevated temperatures.

Although higher pressure creates a larger driving force for bulk flow into wood, the depth of biocide penetration did not increase with pressure in our tests (Fig. 4). While the effects of pressure under SCF conditions are poorly understood, the minimal effects of process variations on subsequent biocide distribution suggest that diffusion might be the primary phenomena accounting for biocide penetration into the sample interior rather than mass flow. If bulk flow were the predominant mode of movement, then increasing pressure should produce a correspondingly large increase in the resulting biocide levels. This clearly did not occur under our test conditions. This premise that diffusion rather than bulk flow is the primary force for biocide movement would markedly alter approaches to using process variables to affect SCF impregnation of wood.

CONCLUSIONS

Although retrograde vaporization affected biocide solubility between 10.34 and 20.68 MPa and consequently biocide retention in the wood, temperature had only minimal effects on subsequent biocide retention and distribution. These results suggest that biocide movement into wood is dominated by diffusion rather than by bulk flow. This would alter approaches to using process manipulations to enhance SCF impregnation and merits further study.

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