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ORIGINAL

Cyproconazole impregnation into wood using sub- and supercritical carbon dioxide

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Abstract Supercritical fluid (SCF) impregnation is a promising preservative treatment method for wood. In order to commercialize the sub- and supercritical CO_2 biocide treatment, better understanding of the fluid phase and its effect on treatment results have to be demonstrated and developed. Preservative treatability under super- and subcritical fluid conditions was evaluated using radiata pine sapwood, and treating characteristics in relation to different fluid phases and treatability were discussed. Various treatment conditions resulted in varying biocide retentions and distributions. Higher pressure conditions enhanced biocide retentions resulting from increasing biocide input in the applied saturation method. Subcritical CO_2 condition produced higher biocide retentions and little retention gradients from face to core. Subcritical CO_2 treatment has a couple of benefits such as investment costs and energy consumption compared with supercritical CO_2.

Introduction

A liquid carrier system for wood preservation has been used over the last 160 years to protect wood from various biodegradation agents. Liquid carriers with high viscosity and low diffusivity limit their impregnation into many wood species, resulting in uneven biocide distribution and shallow penetration in refractory species.

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Since metal components for wood biocides have been limited or banned in many countries, the use of organic preservatives has increased. These organic preservatives permit the treated wood to be burned, pulped, or otherwise reused at the end of its service life. Many of these organic preservatives are not soluble in water, and the use of organic solvents is being discouraged due to adverse environmental effects of volatile organic emissions. Therefore, it is urgently needed to develop an environmentally sound preservative treatment for wood products.

Supercritical fluid treatment for biocide impregnation has been studied to overcome the problems of liquid carrier systems (Itou et al. 1984; Krukonis 1988; Kang 2002). The SCF treatment showed many beneficial properties including fast treatment, no post-drying requirement, and better treatability for wood materials. Wood treated with supercritical carbon dioxide is ready to be used immediately after impregnation because no post-drying is needed. The process is also capable of treating frozen lumber, and it causes no swelling of the lumber (Acda et al. 2001; Sahle-Demessie et al. 1995a, b; Tsunoda and Muin 2003).

Although SCF treatment is an effective and promising way to impregnate biocides into wood materials, the method has also raised concerns since the wood materials are exposed to high pressures. SCF treatment did not affect the mechanical properties of small spruce samples (Smith et al. 1993a, b). Unlike small samples, larger samples experienced significant reductions in modulus of rupture (MOR), modulus of elasticity (MOE), and work to maximum load (WML) (Kim et al. 1997). Treatment defects result from pressure gradients, not hydrostatic pressure on wood, resulting in collapse, loss of physical properties, and decreased mechanical strength. High pressure (300 and 600 bar) itself did not produce obvious effects on the compressive and tensile strength in spite of slight increases in cellulose crystallinity (Yashiro and Takahashi 1996). However, a supercritical ethanol/CO_2 mixture did not build up high-pressure gradient and the media system can apply pressure up to 175 bar without any treatment defect (Drescher et al. 2006).

A supercritical fluid shows physicochemical characteristics to those of liquid and gas including higher diffusion coefficients, low viscosities, and the absence of surface tension. These properties enhance mass transfer leading to deeper preservative penetration (Kang 2002).

The critical point of carbon dioxide exists at temperature and pressure conditions of $Tc = 31.04°C$, $Pc = 73.82$ bar. At lower (subcritical) temperatures and/or pressures, the CO_2 can show two different phases, a liquid and a gaseous state, as well as two-phase mixtures of these states (Pruess 2003).

The subcritical treatment has a couple of advantages over SCF such as investment costs (lower pressure) and energy consumption (heating the raw materials). Although SCF provides better mass-transfer than the subcritical one because of high diffusivity of SCF, subcritical treatment can produce relatively similar results, compared with supercritical fluid treatment in extraction abilities and chemical reaction rates for the production and decomposition (Ginneken et al. 2003; Sotelo et al. 2006; Ehara and Saka 2005). Ginneken et al. (2003) reported on the effect of subcritical (liquid) and supercritical CO_2 treatments on treatments and on the leaching behavior of a cementitious waste. Although liquid and supercritical carbonation of cement-immobilized slags affected the leaching of the different

contaminants investigated, the different CO_2 treatments did not influence the leaching behavior in this experiment. Supercritical CO_2 (as compared to liquid CO_2) provides the mass-transfer advantage of penetration into the micro-pores. This fast penetration of supercritical CO_2 due to the high diffusivity of supercritical CO_2 is one to two orders of magnitude higher than that of liquid CO_2, but the solubility of heavy organics may be lower, leading to changes in product selectivity. Sotelo et al. (2006) proved that the trans-alkylation rate was not accelerated by increasing pressure from subcritical to supercritical condition.

Although there are clear advantages of supercritical fluids over gases for enhancing heterogeneous alkylation catalysis, it is not clear whether supercritical fluids may perform better than liquid media. A comparative study on the decomposition of cellulose between supercritical and subcritical water treatments was made to elucidate the difference in their decomposition behaviors (Ehara and Saka 2005). The supercritical water treatment was found to be more suitable for obtaining high yields of hydrolyzed products. However, cellulose was more likely to fragment under supercritical water treatment, resulting in a decrease in the yield of hydrolyzed products. On the contrary, cellulose tended to more dehydration in the subcritical water treatment.

A better understanding of the fluid phase and its effect on treatment results would facilitate a more rational development of supercritical fluid (SCF) impregnation. In this project, the preservative treatability under super- and subcritical fluid conditions was evaluated using radiata pine sapwood.

Materials and methods

Air-dried radiata pine lumber was cut into specimens (30 by 30 by 150 mm long), and the specimens were conditioned at approximately 12% moisture content. Defect-free specimens were double-coated with epoxy resin on each end surface to limit longitudinal flow.

The biocide evaluated was cyproconazole (2RS, 3RS; 2RS, 3RS)-2-(4-chlorophenyl)-3-cycloprophenyl-1-(1H-1,2,4,triazole-1-yl) butan-2-ol, showing high solubility in lower molecular weight alcohols.

Samples were treated using a supercritical fluid impregnation device (Fig. 1). Standard grade carbon dioxide from a 20-kg gas cylinder (99.5 purity, Seoul Specialty Gas CO., LTD.) was passed through a high-pressure liquid pump (Chrom Tech prep pump) equipped with an external cooling jacket. The temperature of the cooling ethanol was maintained by a chiller (Daihan Scientific Wisecircu) at −20°C to ensure that only liquid CO_2 existed in the pump. The pump was capable of delivering a constant flow rate ranging from 0.1 to 99.9 ml/min. Pressure control was achieved using a back-pressure regulator (Tescom Model 26-1762-24-161) to direct excess fluid back. The reactor vessel was equipped with an external cooling jacket, and a chiller (Lab. companion RW-0525G, 0540G) was used to maintain the temperature of the vessels. The temperature of the vessels and the connecting line was monitored by thermocouple wires connected to a digital thermometer (Nova

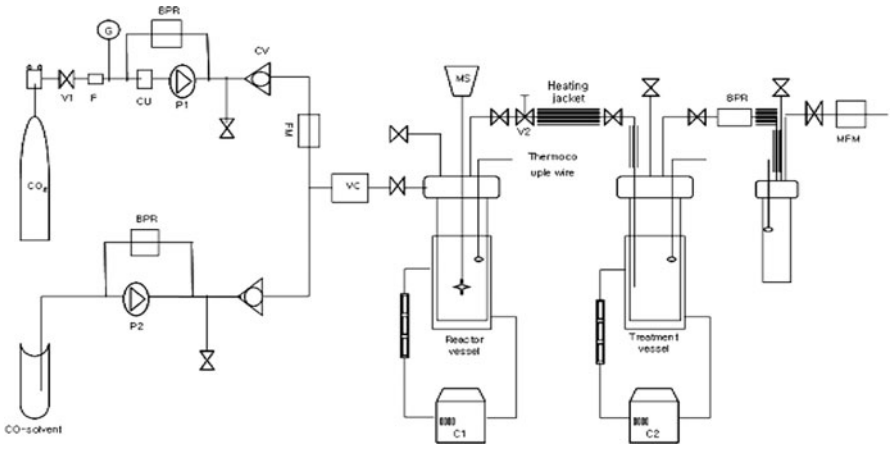

Fig. 1 Schematic of the supercritical fluid impregnation device. *V1*, valve; *V2*, micro-metering valve; *F*, line filter; *G*, gauge; *CU*, cooling unit; *P1*, *P2* pump; *BPR*, back pressure regulator; *CV*, check valve; *FM*, flow meter; *VC*, view cell; *C1*, *C2* chiller; *MFM*, mass flow meter; *MS*, magnetic stirrer

STS40). The glass wool was inserted into the reactor vessel to prevent entrainment of the biocide.

Several process variables were evaluated to produce sub- and supercritical fluid conditions and to investigate phase effects on biocide retentions and distributions. The reactor vessel served as a feed tank where the solvent and biocide were mixed and reached equilibrium conditions (25°C/70 bar, 25°C/100 bar, 40°C/100 bar and 40°C/200 bar) in solute dissolving stage. The solvent, sub- or supercritical CO_2, was fed to the reactor vessel through a back pressure regulator using the HPLC pump.

In the impregnation stage, the treatment vessel was loaded with wood samples and glass wool. When the operating conditions reached the target conditions, the treatment vessel was maintained under the test conditions for 30 min. At the end of the treatment process, the pressure was reduced using a-pressure regulator and micro-metering valves to control the flow rates.

After preservative treatment, the samples were removed from the treating vessel. The top, middle, and bottom 20 mm of each sample were obtained and segmented into outer faces (0–10 mm), intermediate zones (10–20 mm), and inner cores (20–30 mm). The segments from each location were ground using a wood mill to pass a 30 mesh screen. Wood dust (0.1–1 g) was weighed to a 20-ml screw cap tube. Methanol of 10.0 ml was added into the tube with a dispenser. The tube is capped with a Teflon line cap and sonicated for 3 h in an heated ultrasonic bath (Woori Science durasonic 2). All samples were filtered through a 0.45-μm PTFE membrane filter before HPLC analysis.

Biocide concentrations in the wood extracts were determined by injecting 10 μl of extract into a Shimadzu high-performance liquid chromatography-PDA detector (HPLC–PDA), using a modification of the American Wood Preserver's Associate Standard A 23 (AWPA 2005). Separation was achieved using a 150 × 4.6 mm (length × i.d.), 4.6 μm particle, ODS analytical column. The elution solvent

contained the mobile phases A (55% acetonitrile/45% buffer) and B (95% acetonitrile/5% buffer). The buffer was 0.5% w/v ammonium carbonate in water. The gradient was 100% A for 7 min and then changed to 100% B for 0.5 min and was held for 3 min, giving a total analysis time of 15 min. Flow rate and temperature of the HPLC column were 1.0 ml/min and 30°C. A volume of 1 μl was injected to the system using an auto sampler, and a diode array detector was set at 235 nm. A basic validation of standard solutions was performed by the ICH Q2B guideline on validation methodology (ICH Q2B Validation of Analytical Procedures, 1996) to calculate the limits of detection (LOD) and quantification (LOQ). Once the qualitative methodology was validated, it was applied to cyproconazole analysis in treated wood. The linearity of the standard curves was evaluated in the range from 10 to 200 (μg/ml) for each of the five points ($N = 3$), with a peak retention time of 3.588 min. LOD and LOQ were calculated as 0.005 and 0.003 μg/ml, respectively, and all analyzed values met the LOD and LOQ requirements.

Results and discussion

The rates of pressurization and their orders of magnitude varied with the treatment conditions (Fig. 2). At subcritical (25°C) conditions, the rate of pressurization was 14 bar/min to reach a target pressure of 70 bar (approximately 40% faster than that at a pressure of 100 bar) and was 10 bar/min for a target pressure of 100 bar. At supercritical (40°C) conditions, the rate of pressurization was 20 bar/min for a target pressure of 200 bar (approximately 70% faster than that at a pressure of 100 bar) and was 14 bar/min for a target pressure of 100 bar.

Compared with the rate of supercritical counterparts, the rate of pressurization for subcritical was extremely slow during the initial stage of the introduction of CO_2, and then, it sharply increased after the pressure reached its critical point. The higher temperature resulted in a higher rate of pressurization since vapor pressure of CO_2 increased (Kang 2002).

The temperature changes showed similar patterns to the pressure changes. Kang (2002) explained that energy released from condensation of CO_2 (latent heat) increased the temperature along the saturation line and vice versa. Fluid densities were obtained from IUPAC data, representing 0.7, 0.8, 0.68, and 0.85 (g/m^3) at 25°C/70 bar, 25°C/100 bar, 40°C/100 bar, and 40°C/200 bar, respectively (IUPAC 1976). While the density at 25°C/100 bar was approximately 14% higher than at 25°C/70 bar, that of 40°C/200 bar was about 25% higher than at 40°C/100 bar. These density changes revealed phase changes during sub- and supercritical fluid treatment. Carbon dioxide gases turned to liquid due to compression during pressurization, and liquid became a supercritical fluid at its critical point.

The sample weight increased as the liquid or supercritical CO_2 penetrates into the wood sample. The percent weight gains varied with treatment conditions and venting rates. After treatment with supercritical CO_2 at 40°C/100 bar and 40°C/200 bar (venting rate 30 bar/min), the average weight increase was 0.99 and 5.17% of the wood samples, while treatment with subcritical CO_2 at 25°C/70 bar and

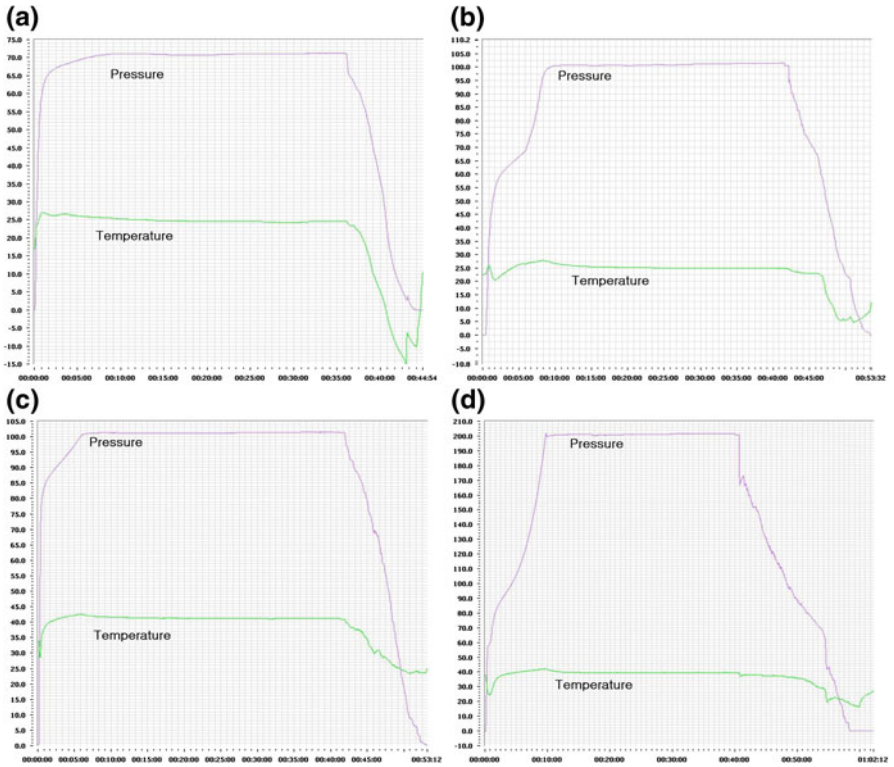

Fig. 2 Pressure and temperature changes during sub- and supercritical CO_2 treatment of wood samples with cyproconazole at 25°C/70 bar (**a**), 25°C/100 bar (**b**), 40°C/100 bar (**c**) and 40°C/200 bar (**d**)

25°C/100 bar resulted in average weight gains of 22.63 and 35.64% of the wood sample (Table 1; Fig. 3).

At subcritical condition, the rate of weight gain was higher than at supercritical condition, suggesting that more CO_2 entered the wood. Since the density of liquid CO_2 is higher than that of supercritical CO_2 in the same pressure condition, this means that more CO_2 molecules exist in the same amount of volume. In addition, denser CO_2 might extend the contact time with wood substances. When comparing 40°C/200 bar and 25°C/70 bar, the densities were 0.85 and 0.7, respectively. Although the fluid density was 0.82 times lower in the subcritical fluid condition, CO_2 uptake was 4.38 times bigger than supercritical fluid treatment. The lower CO_2

Table 1 Weight gains of the wood sample immediately after treatment using supercritical and subcritical carbon dioxide

40°C/100 bar weight gain (%)	40°C/200 bar weight gain (%)	25°C/70 bar weight gain (%)	25°C/100 bar weight gain (%)
0.99 (0.17)	5.17 (1.92)	22.63 (7.07)	35.64 (6.57)

Numbers in parentheses represent one standard deviation

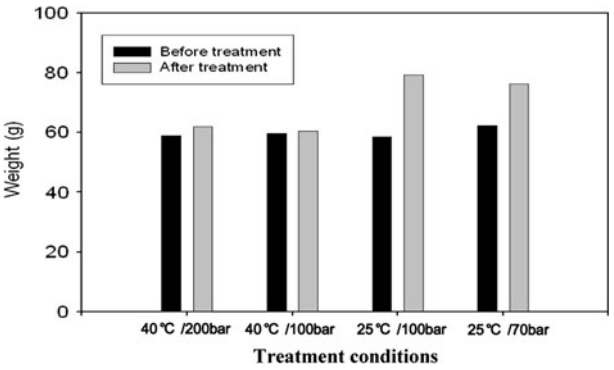

Fig. 3 Effect of sub- and supercritical CO_2 treatment on the weight gains of the treated wood samples

uptake for SCF might attribute to the higher temperature condition helping supercritical CO_2 quickly turning into CO_2 gas after treatment. In subcritical condition, on the other hand, liquid CO_2 remained in the wood after treatment because the lower temperature may hold CO_2 as liquid state longer.

All biocide retentions were well above the cyproconazole toxic threshold, 0.02–0.096 kg/m^3 (Janssen's product information sheet, n.d.). The higher retention had a larger standard deviation compared with the low retentions. Similar results were reported using the saturation method (Sahle-Demessie 1994; Acda 1995; Acda et al. 2001).

Cyproconazole retentions for radiata pine sapwood increased significantly as pressure increased from 70 to 100 bar at 25°C, 100 to 200 bar at 40°C (Fig. 4; Table 2). At 40°C supercritical fluid condition with a venting rate of 10 bar/min, a higher pressure condition (200 bar) produced 3.75 times higher biocide retention than lower pressure (100 bar). At subcritical (25°C) conditions the biocide retention showed a similar trend to the one of the supercritical fluid treatment (2.03 times difference). Higher pressure increased the biocide solubility, because of increased specific interactions between the solute and solvent molecules (Kang 2002), resulting in increasing biocide input. Chrastill (1982) reported that enhanced interactions resulted from increased fluid density and decreased intermolecular mean distances between molecules.

As the temperature becomes lower than the critical point but pressure exceeds the point, subcritical liquid is generated. Cyproconazole retentions increased significantly in the subcritical fluid condition at 25°C and 100 bar compared with its counterpart, supercritical fluid condition at 40°C and 100 bar (Fig. 4; Table 3). For example, at 100-bar conditions with a venting rate of 10 bar/min, the subcritical liquid treatment produced 5.3 times higher biocide retention than the supercritical condition (Table 3).

Higher liquid density increased the solvating power resulting from improved intermolecular interactions. The strengthened solvating power caused more concentrated biocide in the system. A 17% higher solute density (0.8 g/m^3) in the subcritical fluid condition at 25°C and 100 bar was observed than (0.68 g/m^3) in

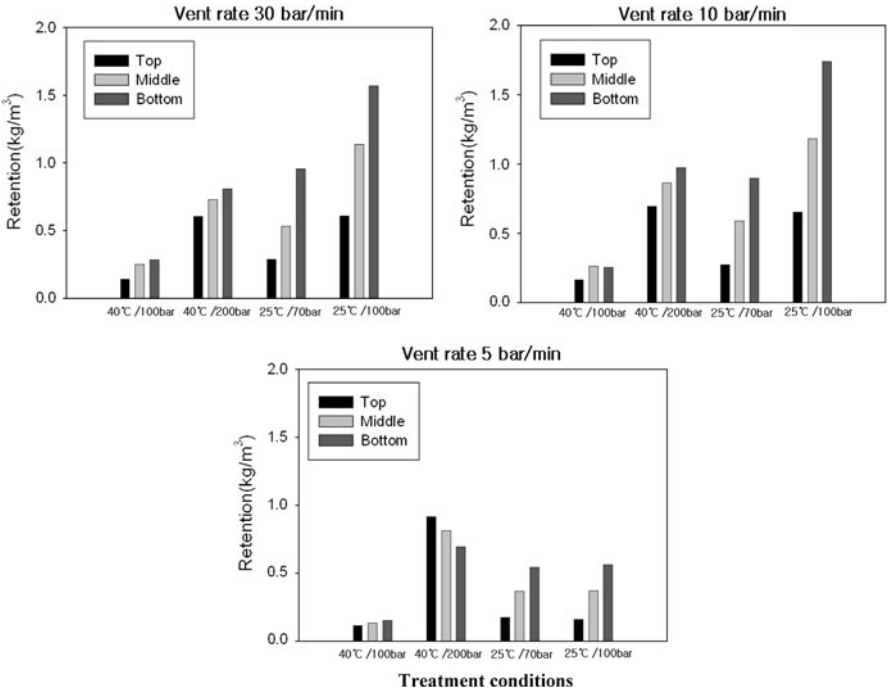

Fig. 4 Cyproconazole retentions in radiata pine samples following impregnation with subcritical and supercritical CO_2

Table 2 Cyproconazole retentions in radiata pine samples following impregnation with subcritical and supercritical CO_2

Treatment condition (°C/bar)	Vent rate (bar/min)	Biocide retention (kg/m^3)[a]			Average
		Top	Middle	Bottom	
Supercritical					
40/100	30	0.142 (0.034)	0.251 (0.059)	0.287 (0.056)	0.227
	10	0.162 (0.056)	0.261 (0.070)	0.252 (0.060)	0.225
	5	0.115 (0.031)	0.134 (0.035)	0.152 (0.029)	0.134
40/200	30	0.606 (0.298)	0.729 (0.160)	0.808 (0.161)	0.714
	10	0.695 (0.390)	0.863 (0.461)	0.974 (0.392)	0.844
	5	0.914 (0.178)	0.816 (0.245)	0.693 (0.199)	0.808
Subcritical					
25/70	30	0.288 (0.118)	0.534 (0.171)	0.956 (0.353)	0.593
	10	0.274 (0.038)	0.588 (0.105)	0.896 (0.155)	0.586
	5	0.173 (0.034)	0.365 (0.186)	0.545 (0.222)	0.361
25/100	30	0.609 (0.239)	1.136 (0.373)	1.571(0.443)	1.105
	10	0.654 (0.220)	1.184 (0.429)	1.74 (0.521)	1.193
	5	0.159 (0.041)	0.37 (0.115)	0.563 (0.175)	0.364

Numbers in parentheses represent one standard deviation

[a] Values represent means of retention measurements on 5 samples per location

Table 3 ANOVA for the effect of treatment conditions (pressure/temperature combination) on cyproconazole retentions and comparison between retentions as shown by Duncan's multiple range test

Venting rate	Treatment condition	Retention (kg/m^3)[a]	Source	DF	Sum of square	Mean square	F-value	Pr > F
5 bar/min	40°C/200 bar	0.741 A	Model	3	1.138	0.379	27.13	<0.0001
	25°C/100 bar	0.364 B	Error	18	0.251	0.013		
	25°C/70 bar	0.361 B	Corrected total	21	1.390			
	40°C/100 bar	0.133 C						
10 bar/min	25°C/100 bar	1.193 A	Model	3	3.914	1.304	20.42	<0.0001
	40°C/200 bar	0.844 B	Error	22	1.405	0.063		
	25°C/70 bar	0.586 B	Corrected total	25	5.320			
	40°C/100 bar	0.225 C						
30 bar/min	25°C/100 bar	1.105 A	Model	3	2.932	0.977	19.55	<0.0001
	40°C/200 bar	0.715 B	Error	22	1.099	0.049		
	25°C/70 bar	0.593 B	Corrected total	25	4.032			
	40°C/100 bar	0.227 C						

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

supercritical fluid condition at 40°C and 100 bar (IUPAC 1976). Sahle-Demessie (1994) suggested that enhanced solubility due to increased density should raise biocide input, and this was evidenced by improved biocide treatability when using the saturated method. The solubility of cyproconazole in subcritical carbon dioxide might be higher than that in supercritical carbon dioxide, resulting in higher retention in subcritical treatment.

Retention gradients were observed from top to bottom within individual samples (Table 2). While subcritical fluid treatment showed retention ratios of 3.27 and 2.66, little retention gradients of 1.55 and 1.47 for supercritical fluid were observed. The liquid system produced higher retention gradients from top to bottom in each wood sample. Hassan et al. (2001) and Kang (2002) also observed similar results. They explained that the top phase was the lightest and the bottom phase the heaviest liquid phase, resulting in different solvating power.

The rate of pressure release produced a variable effect on biocide retentions (Tables 2, 3). Fast venting rates generally produced high biocide retention except for 40°C/200 bar condition, because a large pressure difference (ΔP) was built between the inside and the outside the wood. The bigger ΔP resulted in more biocide precipitation in the wood samples, compared with a low venting rate producing smaller ΔP. It is not clear why the effect was not observed at 40°C/200-bar condition. One possible explanation could be the difficulty in controlling the venting rate because of a too high pressure at the initial venting stage.

Retention gradients were observed from surface to core within individual samples (Fig. 5). Liquid conditions produced even biocide distribution in the samples, showing no significant differences from surface to core in most treatment conditions except for 30 bar/min venting rate. SCF conditions, however, exhibited

distinctive retention ratios of 1.7, 2.7, and 2.2 for venting rates of 5, 10, and 30 bar/min, respectively, at 40°C/100 bar. Even more severe biocide gradients were observed at higher pressure SCF conditions (40°C/200 bar), where the retention gradient represented ratios of 3.7, 6.2, and 4.3 for venting rates of 5, 10, and 30 bar/min (Fig. 5; Tables 4, 5). One possible explanation for the different gradient between sub- and supercritical fluid could be the effect of biocide movement to the outside after treatment. While subcritical liquid conferred weight gains after treatment, the weight increase was not observed clearly in supercritical CO_2 treatments. The supercritical CO_2 in wood sample very quickly transited from a supercritical fluid to gas, leaving most biocides on the surface of the wood in the treating vessel. Increased weights of subcritically treated wood suggested that more CO_2 with biocides might enter the wood and remain in the wood even after treatment.

Carbon dioxide gas becomes liquid at 5.11 atm below −56.6°C (Brubacher 2006). After terminating the venting stage, the vessel pressure returned to atmosphere, but the pressure inside the wood would be higher than that of the atmosphere. As liquid CO_2 expands to gas, the temperature of wood drops dramatically. The temperature of the vessel decreased to −15 and 5°C, respectively, in 25°C/70 bar and 25°C/100-bar conditions (Fig. 2). The condition might lengthen the liquid stage of CO_2 inside the wood, and the liquid CO_2 transits very slowly from liquid to gas. More biocide deposition, therefore, could occur in the wood

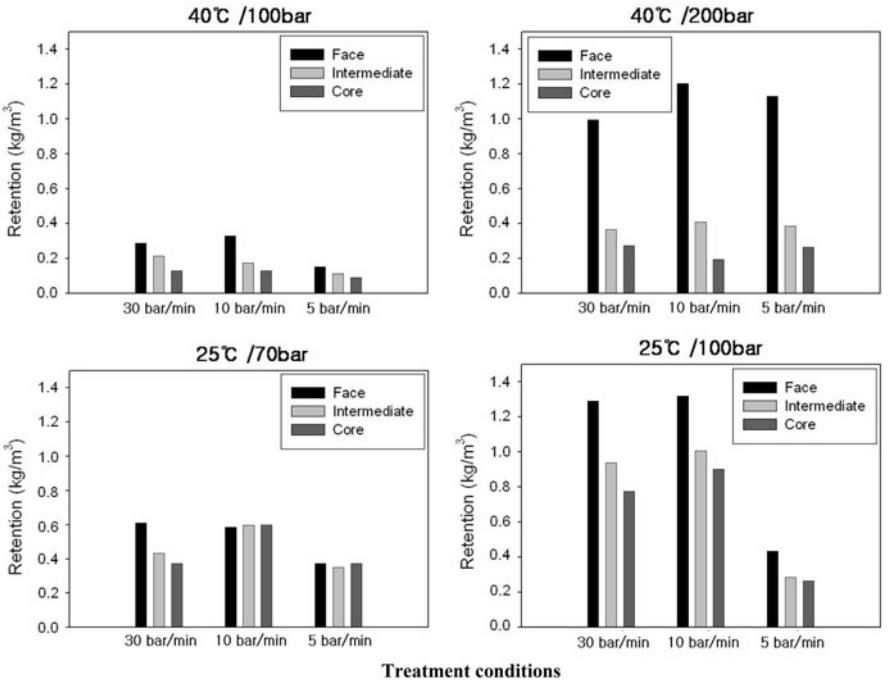

Fig. 5 Effect of pressure/temperature conditions on biocide retentions at selected distances from the surface in radiata pine samples treated with cyproconazole in subcritical and supercritical CO_2

Table 4 Cyproconazole retentions at selected distances from the surface in radiata pine samples treated with cyproconazole in subcritical and supercritical CO_2

Operating condition (°C/bar)	Vent rate (bar/min)	Retention (kg/m$^{3)}$		
		Face	Intermediate	Core
40/100	30	0.287 (0.063)	0.213 (0.063)	0.128 (0.052)
	10	0.327 (0.104)	0.172 (0.037)	0.129 (0.030)
	5	0.151 (0.053)	0.112 (0.025)	0.088 (0.009)
40/200	30	0.993 (0.219)	0.365 (0.180)	0.271 (0.165)
	10	1.203 (0.637)	0.408 (0.047)	0.193 (0.052))
	5	1.13 (0.294)	0.384 (0.136)	0.263 (0.116)
25/70	30	0.611(0.173)	0.432 (0.201)	0.373 (0.114)
	10	0.584 (0.130)	0.595 (0.081)	0.598 (0.141)
	5	0.374 (0.184)	0.349 (0.195)	0.374 (0.212)
25/100	30	1.29 (0.391)	0.939 (0.419)	0.773 (0.324)
	10	1.32 (0.481)	1.006 (0.405)	0.901 (0.473)
	5	0.433 (0.155)	0.284 (0.099)	0.264 (0.091)

Numbers in parentheses represent one standard deviation

[a] Values represent means of retention measurements on 5 samples per location

Table 5 ANOVA for the effect of deposition methods on cyproconazole distributions as shown by Duncan's multiple range test

	Retention (kg/m^3)[a]		Source	DF	Sum of square	Mean square	F-value	Pr > *F*
40°C/200 bar								
30 bar/min	Face	0.993 A	Model	2	1.848	0.924	19.11	<0.0001
	Intermediate	0.365 B	Error	15	0.725	0.048		
	Core	0.271 B	Corrected total	17	2.573			
10 bar/minr	Face	1.203 A	Model	2	2.830	1.415	8.94	0.0042
	Intermediate	0.408 B	Error	12	1.900	0.158		
	Core	0.193 B	Corrected total	14	4.731			
5 bar/minr	Face	1.130 A	Model	2	2.644	1.322	33.33	<0.0001
	Intermediate	0.384 B	Error	15	0.595	0.039		
	Core	0.263 B	Corrected total	17	3.239			
40°C/100 bar								
30 bar/min	Face	0.287 A	Model	2	0.088	0.044	12.16	0.0005
	Intermediate	0.213 B	Error	18	0.065	0.033		
	Core	0.128 C	Corrected total	20	0.154			
10 bar/min	Face	0.327 A	Model	2	0.176	0.088	20.16	<0.0001
	Intermediate	0.172 B	Error	21	0.092	0.004		
	Core	0.127 B	Corrected total	23	0.268			
5 bar/min	Face	0.151 A	Model	2	0.012	0.006	5.05	0.0211
	Intermediate	0.112 AB	Error	15	0.017	0.001		
	Core	0.088 B	Corrected total	17	0.030			

Table 5 continued

	Retention (kg/m^3)[a]		Source	DF	Sum of square	Mean square	F-value	Pr > F
25°C/100 bar								
30 bar/min	Face	1.290 A	Model	2	1.115	0.557	3.85	0.0377
	Intermediate	0.939 AB	Error	21	3.042	0.144		
	Core	0.773 B	Corrected total	23	4.157			
10 bar/min	Face	1.131 A	Model	2	0.760	0.380	1.84	0.1834
	Intermediate	1.005 A	Error	21	4.341	0.206		
	Core	0.900 A	Corrected total	23	5.102			
5 bar/min	Face	0.433 A	Model	2	0.085	0.042	3.02	0.0868
	Intermediate	0.284 A	Error	12	0.170	0.014		
	Core	0.263 A	Corrected total	14	0.255			
25°C/70 bar								
30 bar/min	Face	0.611 A	Model	2	0.153	0.076	2.76	0.1032
	Intermediate	0.431 A	Error	12	0.334	0.027		
	Core	0.373 A	Corrected total	14	0.488			
10 bar/min	Face	0.584 A	Model	2	0.0005	0.0002	0.02	0.9823
	Intermediate	0.595 A	Error	12	0.174	0.014		
	Core	0.597 A	Corrected total	14	0.175			
5 bar/min	Face	0.373 A	Model	2	0.0019	0.0009	0.02	0.9756
	Intermediate	0.349 A	Error	12	0.470	0.039		
	Core	0.374 A	Corrected total	14	0.472			

[a] Means in the same column followed by the same letter(s) do not differ significantly by Duncan's multiple range test ($a = 0.05$)

sample for liquid subcritical CO_2 treatment, producing significantly more uniform distributions. However, supercritical CO_2 treatment makes most biocides precipitate in the treating vessel as the venting period begins.

Increasing biocide gradient was observed with high-pressure release rate. As mentioned earlier, more biocide may migrate to the surface resulting from high ΔP during the higher venting rates (Kang 2002; Acda et al. 2001).

Conclusion

Different treatment conditions resulted in varying biocide retentions, distributions, and weight gains. Higher pressure conditions enhanced biocide retentions resulting from increasing biocide input in the applied saturation method. Subcritical fluid conditions produced higher cyproconazole retentions than supercritical fluid conditions. Higher liquid density increased solvating power producing improved biocide treatability. Subcritical fluid conditions also yielded higher retention gradients from top to bottom in each wood sample because dense liquid CO_2 moved to the vessel bottom.

The rate of pressure release resulted in a variable effect on biocide retentions. A fast venting rate generally produced high biocide retention because of the large pressure difference (ΔP), causing more biocide precipitation in the wood samples.

Even biocide distributions from surface to core in the samples were obtained in liquid conditions. After subcritical treatment, increased sample weight and decreased vessel temperature explained why the liquid CO_2 state was extended.

Subcritical CO_2 treatment produced higher retentions and more even distributions than supercritical fluid treatment. In addition, the subcritical fluid treatment has other advantages over supercritical CO_2 with economical points such as investment costs (lower pressure) and energy consumption (heating of the raw materials).

Supercritical fluid treatment has been investigated to improve the biocide treatability of refractory species, but the results were discouraging because of treating defects and limited biocide penetrations. As metal preservatives have been substituted by organic ones soluble in organic solvents causing adverse environmental effects, supercritical fluid treatment has recently received increasing interest to solve this problem.

Environmentally benign subcritical fluid treatment showed better biocide treatability but also economic advantages. Therefore, development of subcritical fluid impregnation as a potential wood preservative treatment application requires a better understanding of the liquid phase affecting the treatment process and biocide treatability.

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