Mokchae Konghak 33(5) : 50~56, 2005

Effect of Wood Material Type on Biocide Retention and Distribution Using Supercritical Fluid Impregnation[*1]

Sung-Mo Kang[*2†], Doo-Jin Jung[*2], Ja-Oon Koo[*2], and J. J. Morrell[*3]

ABSTRACT

The effect of wood material type on biocide retention and distribution during supercritical fluid impregnation was assessed using three different wood types including solid wood, plywood and oriented strand board (OSB). The result revealed that biocide treatability differed with structural composition and permeability of the various materials. Low treatability of plywood might be attributed to interferences of glue line limiting fluid movement. OSB samples showed higher biocide retentions, resulting from the presence of interconnecting gaps permitting more open flow.

Keywords : treatability, retention, distribution, supercritical fluid (SCF)

1. INTRODUCTION

Supercritical fluid (SCF) can carry biocides like liquid solvents, and also moves through semiporous materials like gases (Brogle, 1982; Krukonis, 1988). The treatment appears to be an ideal carrier for delivering biocide into wood materials, but inconsistent process data due to the difficulty of controlling the treating system have prevented from developing more controlled commercial treatments.

Previous studies have circulated SC-CO_2 through a bed of biocide to a point where the fluid is saturated with biocide; however, biocide solubility can change markedly with small changes in pressure/temperature or amount of cosolvent, leading to errors and control problems between batches (Acda, 1995; Sahle-Demessie, 1994). In order to get consistent data, Kang (2002) studied a new approach, SCF treatment with a mixture of biocide and liquid cosolvent using temperature reduction. This unsaturated method produced more reproducible retentions between batches and reduced biocide consumption in comparison with the saturation method along with several advantages including an absence of clogging in lines, methanol recycling, and the potential for recycling liquid CO_2.

A number of studies has evaluated SCF impregnation of various wood materials using saturated method (Acda 1995; Acda *et al.*, 1997a, 1997b; Muni *et al.*, 2001; Tsunoda and Muin, 2003). There is, however, not enough information about the relative treatability of various

---

[*1] Received on June 11, 2005; accepted on July 7, 2005.

[*2] Division Quality Control and Standardization Team, Korea Forest Research Institute, Seoul 130-712, Korea

[*3] Wood Science and Engineering, Oregon State University 119 Richardson Hall, Corvallis, OR 97331

[†] Corresponding author : Sung-Mo Kang (kangsm@foa.go.kr)

wood materials, and the effect of wood type on treatment results using this unsaturated method.

This report describes the effect of wood type on cyproconazole retention and distribution under sub-saturated fluid conditions, investigating material properties such as structural composition, permeability, mass or heat capacity and density, which can influence fluid flow.

2. MATERIALS and METHODS

Commercial plywood, OSB and ponderosa pine sapwood (*Pinus ponderosa Laws*) lumber were cut into 100 by 300 mm long specimens. The specimens were conditioned to constant weight at 20°C and 65% RH. The samples were not end-sealed in order to reduce the risk of developing pressure gradients that might lead to mechanical failure during treatment and to minimize error in mass balance due to solubilization of the seal. Twelve specimens were treated in each cycle.

The biocide evaluated was Cyproconazole (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/m^3 depending on a target fungus and sample aging procedures (Janssen's product information sheet, n.d.)

Samples were treated using a SCF impregnation device (Fig. 1). Standard grade carbon dioxide from a 23 kg gas cylinder (99.9 weight %, Industrial Welding Supply) was admitted into a pre-heated 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 pressure reached desired pressure (1500 psi), 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 (1500 psi), the fluid was circulated through the vessel at 2 kg/min for 1 hour. Flow was reversed every 15 minutes to encourage even distribution of biocide along the length of the vessel. The treatment conditions were maintained for one hour.

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 1073 psi), the pressure was reduced at a rate of 60 psi/min by venting the system.

After treatment, the samples were removed from the treating vessel and the top, middle, and bottom 20 mm of each sample was removed and segmented into zones corresponding to 0~1.5 mm, 1.5~3 mm and 3~5 mm zones. 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 hr 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 America Wood Preserver's Associate 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

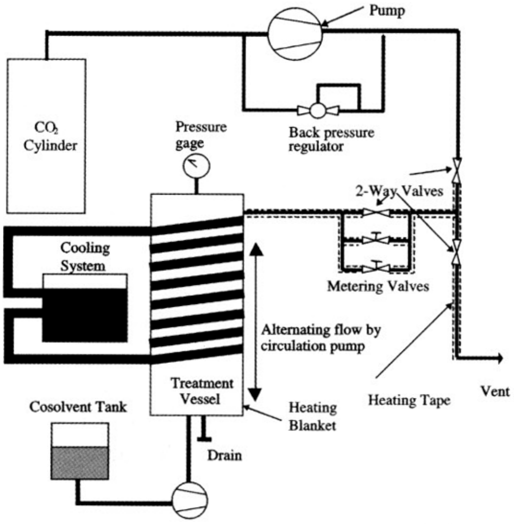

Fig. 1. Schematic of the supercritical fluid impregnation device.

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 detection wavelength were 1.5 mL/min and 230 nm, respectively.

The mean biocide retentions for the different wood types were subjected to an ANOVA, and compared using Duncan's multiple range tests (solid wood, plywood, OSB) at $\alpha = 0.05$ (n = 18:3 batches × 6 replicates).

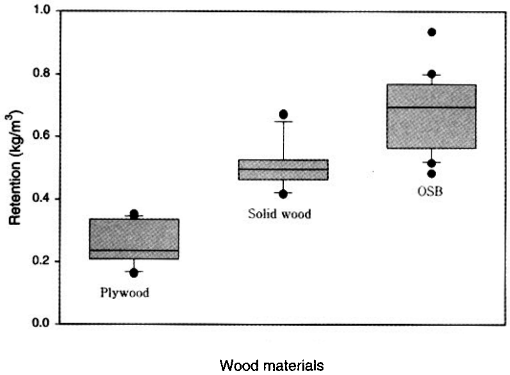

Fig. 2. Biocide retentions in plywood, OSB and solid wood following supercritical CO_2 impregnation at 1500 psi and 40°C.

3. RESULTS and DISCUSSION

OSB samples experienced higher retentions as well as more uniform biocide distribution than found in solid wood or plywood at a given biocide input (20 g), while retentions of plywood samples were lower than those found for ponderosa pine sapwood (Fig. 2 and Table 1). These results indicated that biocide treatability might reflect differences in structural composition, permeability and mass or heat capacity of the various materials.

Permeability differences could be an important factor in biocide retention and penetration in

Table 2. ANOVA and Duncan's multiple range tests examining the effects of wood material type on cyproconazole retention

Source	DF	Sum of square	Mean square	F-value	Pr > F
Model	2	1.6566	0.8283	100.36	< 0.0001
Error	51	0.4209	0.0083		
Corrected Total	53	2.0775			

Treatment	Replication (N)	Cyproconazole Retention (kg/m^3)[a]
OSB	18	0.679 (0.122) A
Solid wood	18	0.510 (0.074) B
Plywood	18	0.253 (0.066) C

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

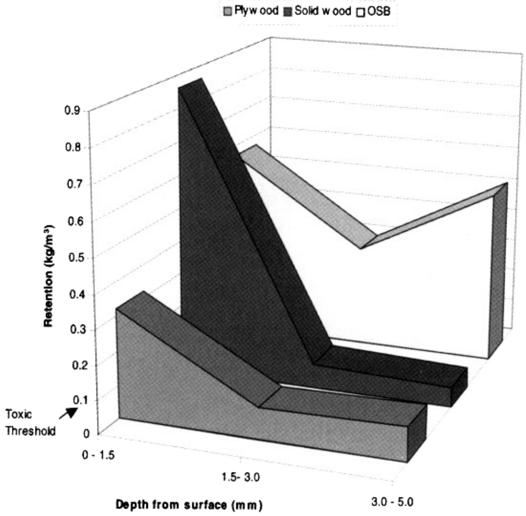

Fig. 3. Biocide retention in different wood materials following supercritical CO_2 treatment with cyproconazole at 1500 psi and 40°C.

wood materials. Wood-based composites are generally more permeable than solid wood of comparable specific gravities (Lehmann, 1972; Bolton and Humphrey, 1994). The permeabilities of composite panels are influenced by density, density distribution, particle geometry and size, and resin content (Futo, 1970; Denisov *et al.*, 1975; Haas *et al.*, 1998). While the permeabilities of ponderosa pine sapwood are 1.88×10^{-13} m^2 and 1.97×10^{-14} m^2 in the longitudinal and transverse directions, respectively (Schneider, 1999), permeabilities of OSB were calculated to be 2.64 and 1.66×10^{-10} m^2 in the longitudinal and transverse directions, respectively (Oberdorfer, 2001). The higher permeability of OSB results from the presence of interconnecting gaps that provide for more open flow around particles rather than through them (Haas *et al.*, 1998). These gaps help to explain the higher biocide retentions in OSB (Fig. 3).

Reductions in biocide retention and penetration in plywood might result from interference of glue lines as if glue line limits moisture or gas movement (Hoyle *et al.*, 1994; Zavala and Humphrey, 1994). Oberdorfer (2001) observed large pressure differentials in laminated veneer lumber during SCF treatment. The relative magnitude of the permeability reductions is influenced by glue viscosity, glue content, pressing condition and wood-glue interactions (Futo, 1970).

Plywood experienced lower surface retentions than are found in ponderosa pine because the outer plies were Douglas-fir heartwood (Fig. 3). Since permeabilities of Douglas-fir heartwood were 2.6 and 3.0 times less than those of ponderosa pine sapwood in the longitudinal and transverse directions, respectively, SC-CO_2 penetration was 25% slower in the Douglas-fir heartwood at 1500 psi (Schneider, 1999).

Material density had little effect on biocide retention and distribution in ponderosa pine sapwood samples. The average densities of OSB, solid wood and plywood were 0.56, 0.41 and 0.40 g/cm^3, respectively. Since OSB was much denser, the material should have less void space compared to solid wood and plywood. However, the OSB showed better biocide treatability (retention and penetration), because gaps between flakes had a greater effect on flow.

Thermal conductivity might influence biocide distribution. Since this property is closely related to material density (USDA, 1999), the potential for a thermal effect would be negligible because of the absence of a density effect. However, fluid phase is easily changeable with small change of temperature especially near the critical point, and this issue becomes more important at the end of treating cycle. Thermodynamic parameters should be investigated more sophisticatedly for the varying fluid phase when process parameters approach the critical point.

Retention gradients were observed from the surface to core within individual samples of solid wood and plywood, but the trends were similar (Fig. 3). While retention ratios had surface to core ratios in plywood and solid wood of 15.07 and 3.16, respectively, little reten-

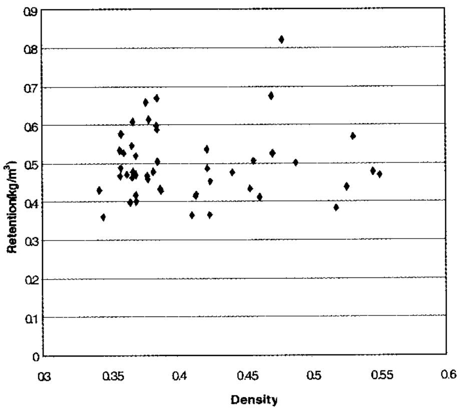

Fig. 4. Relationship between wood density and retention of cyproconazole in ponderosa pine sapwood treated with supercritical CO_2 at 1500 psi and 40°C.

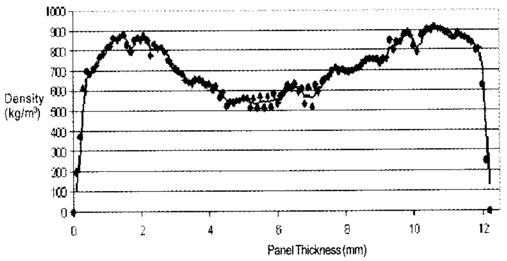

Fig. 5. Density profile of oriented strand board (OSB) (from Oberdorfer, 2001).

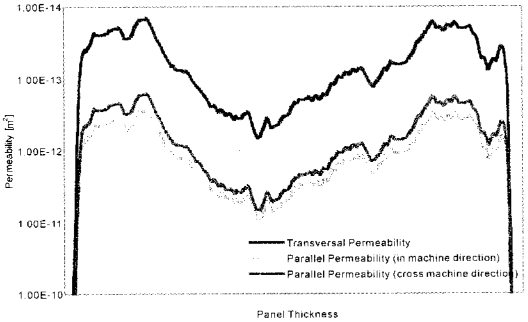

Fig. 6. Variation in permeability with panel thickness for OSB (from Oberdorfer, 2001).

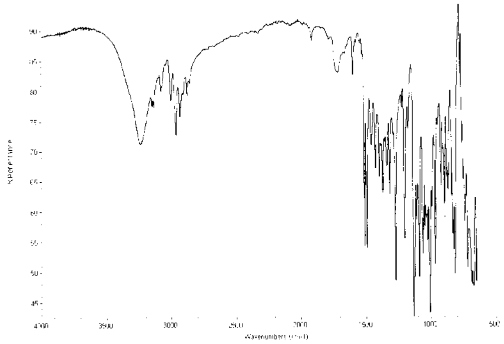

Fig. 7. FT-IR spectra for unknown material from recovered methanol after supercritical CO_2 treatment of OSB.

tion gradient (1.08) was observed in OSB samples (Fig. 3). Acda (1995) also observed retention ratios in plywood and OSB using the saturated biocide method. The smaller gradients in OSB probably reflect the presence of interconnecting gaps. The larger gradients in solid wood and plywood samples compared to OSB samples suggest that different flow mechanisms (mass flow vs. diffusion) might contribute to biocide impregnation on these different materials. OSB is 1000 to 10000 times more permeable than ponderosa pine sapwood, and the huge permeability difference might confer different flow mechanism to each material. This premise requires a set of experiment evaluating the potential contributions of mass flow and diffusion on biocide distribution during SCF impregnation process.

Despite the absence of density effects (Fig. 4), density profiles did appear to affect biocide distribution in the OSB samples (Fig. 5 and Fig. 6). Segmented zone from 2 mm from panel surface showing the highest density (Fig. 5) and the lowest permeability (Fig. 6) in the OSB panel, had the lowest retentions (Fig. 3). Decreased void volume at the segment of the panels would decrease the volume of biocide laden supercritical CO_2 present at the end of the process.

During SCF treatment for OSB, we also found that wax present in the panels was extracted. Fourier Transform Infrared Spectroscopy (FT-IR: Nexus^{TM} 470 spectrometer) revealed that only wax was extracted and no resin was present (Fig. 7). The removal of the wax was an unexpected side effect of the treatment. Supercritical CO_2 should be capable of solubilizing a variety of non-polar materials from wood including wax additives. This extraction could have major effects on composite performance under wetting conditions, and might also help explain prior studies showing strength effects in supercritical CO_2 treated OSB (Muin *et al.*, 2001). One approach to overcoming this problem would be to omit waxes during manufacture, then add them during SCF impregnation. This anomaly also clearly illustrates the importance of testing materials prior to scale-up of processes.

4. CONCLUSION

The experiments using different wood materials revealed that biocide treatability differed with structural composition and permeability of the various materials. The presence of interconnecting gaps provided for more open flow, resulting in higher biocide retentions in OSB. The thermal effect was not fully addressed in this study. Thermodynamic parameters, however, should be investigated more sophisticatedly for the varying fluid phase near the critical point.

REFERENCES

1. Acda, M. N. 1995. Supercritical fluid impregnation of wood based composites. Ph. D. dissertation, Oregon State University. Corvallis, OR, p. 160.
2. Acda, M. N., J. J. Morrell, and K. L. Levien. 1997a. Effects of supercritical fluid treatments on physical and mechanical properties of wood-based composites. Wood and Fiber Science 29(2): 121 ~ 130.
3. Acda, M. N., J. J. Morrell, and K. L. Levien. 1997b. Effects of process variables on supercritical fluid impregnation of composites with tebuconazole. Wood and Fiber Science 29(3): 282 ~ 290.
4. Acda, M. N., J. J. Morrell, and K. L. Levien. 2001. Supercritical fluid impregnation of selected wood species with tebuconazole. Wood Science and Technology. 35: 127 ~ 136.
5. Bolton, A. J. and P. E. Humphrey. 1994. The permeability of wood-based composite materials. Part 1. A review of the literature and some unpublished work. Holzforschung 48: (Suppl.) 95 ~ 100.
6. Brogle, H. (1982) CO_2 in solvent extraction. Chemistry and Industry (19): 385 ~ 390.
7. Denisov, O. B., P. P Anisov, and P. E. Zuban. 1975. Untersuchungen der Permeabilitaet von Spanvliesen. Holztechnologie 14(1): 43 ~ 46.
8. Futo, L. P. 1970. Pruefung der Luft-, Dampf- und Wasserdurchlaessigkeit von Holzwerkstoffen (Testing the air-, steam- and water permeability of wood based materials). Holz als Roh- und Werkstoff. 28(11): 423 ~ 429.
9. Haas, G. V., A. Steffen, and A. Fruehwald. 1998. Untersuchungen zur Permeabilitaet von Faser-, Span- und OSB-Matten fuer Gase. Holz als Roh- und Werkstoff 56: 386 ~ 392.
10. Hoyle, R. J. Jr., R. Y. Itani, and J. T. Anderson. 1994. The effect of moisture cycling on creep of small glued laminated beams. Wood Fiber Sci. 26(4): 556 ~ 562.
11. Janssen's product information sheet, n. d. Retrieved May 1, 2002. from http://www.janssenpharmaceutica.be/pmp/Pages/database/$Evipol/$leaflets/PIS%20Evipol%20technical.pdf.
12. Kang, S. 2002. Supercritical fluid impregnation with biocides of wood using temperature reduction. Ph.D. Dissertation, Oregon State Univ., Corvallis, OR. p. 126.
13. Krukonis, V. J. 1988. Processing with supercritical fluids: overview and applications. ACS Symposium Series. 366: 27 ~ 43. America Chemical Society, Washington D.C.
14. Lehmann, W. F. 1972. Moisture-stability relationship in wood-based composition boards. For. Prod. J. 22(7): 53 ~ 59.
15. Muin, M., A. Adachi, and K. Tsunoda. 2001. Applicability of supercritical carbon dioxide to the preservative treatment of wood-based composites. Int. Res. Group on Wood Pres. Doc. No.

IRG/WP/01-40199. Stockholm, Sweden. p. 5.

16. Oberdorfer, Georg. 2001. Development of internal pressure during supercritical fluid impregnation of wood composites and its effect on material properties. M.S. Dissertation, University of Agricultural Science, Vienna.
17. Sahle-Demessie, E. 1994. Deposition of chemicals in semi-porous solids using supercritical fluid carriers. Ph.D. dissertation, Oregon State University, Corvallis, OR, p. 301.
18. Schneider, P. F. 1999. Pressure measurement in wood as a method to understand pressure impregnation processes: Bethell, Rueping, Lowry, and supercritical carbon dioxide. Ph.D. Dissertation, Oregon State Univ., Corvallis, OR. p. 243.
19. Tsunoda and Muin. 2003. Preservative treatment of wood-based composites with mixture formulation of IPBC-silafluopen using supercritical carbon dioxide as a carrier gas. Int. Res. Group on Wood Pres. Doc. No. IRG/ WP/03-40251. Stockholm, Sweden. p. 8.
20. United Sates Department of Agriculture (USDA). 1999. Wood Handbook: Wood as an engineering material. USDA. Washington, D.C. p. 474.
21. Zavala, D. and P.E. Humphrey. 1996. Hot pressing veneer-based products: the interaction of physical process. Forest Prod. J. 46(1): 69～77.