IMPREGNATION OF WOOD-BASED COMPOSITES USING SUPERCRITICAL FLUIDS: A PRELIMINARY REPORT

Menandro Acda[1], Jeffrey J. Morrell[2] and Keith L. Levien[3],
Oregon State University
Corvallis, Oregon

Summary

The potential for using supercritical carbon dioxide to impregnate composites with preservatives was investigated using tebuconazole as the biocide and plywood or particleboard. Treatment pressure, temperature and impregnation time were varied to determine the effects of these parameters on biocide retention, then the treated panels were subjected to various tests for dimensional changes, water sorption, and mechanical properties. Treatment for 30 minutes at 1800 psi and 60°C produced retentions well above those required for fungal protection. None of the treatment conditions involved induced significant changes in mechanical properties, nor did exposure to these conditions alter the thickness of the panels. The results indicate that preservative impregnation using supercritical fluids such as carbon dioxide can produce well treated panels with no negative effects on board properties.

1. Introduction

Demand for wood-based structural panels is expected to continue growing as these materials see increased use in structural applications. In many instances, these applications occur where conditions are conducive for decay development. The problems associated with these uses have stimulated research to protect wood-based composites against the deleterious effects of moisture, wood-boring insects and decay organisms (Gertjejansen et al., 1989; Hall and Gertjejansen, 1982; Smith et al.,1993a,b).

In theory, wood-based composites should provide improved resistence to fungal deterioration due to their higher pH and the presence of residual non-condensed phenols (Schmidt, 1984; Deppe, 1970). However, in exterior applications, leaching offsets these advantages whenever construction practices and coatings do not provide reliable, permanent protection against moisture absorption. Thus, supplemental protection of these materials by preservative treatment is usually necessary to maximize performance.

Preservative treatment of wood-based composites can be achieved by adding a biocide to the wood furnish, resin or other panel components prior to the hot pressing cycle or by

---

[1] Graduate Research Assistant
[2] Associate Professor, Deptartment of Forest Products.
[3] Associate professor, Department of Chemical Engineering

pressure treatment of full-sized panels with liquid preservatives. There are however, potential problems associated with each approach. Biocide addition prior to hot pressing may interfere with the curing mechanism of the resin (Kreber et al., 1991; Sahle-Demessie, 1993; Vick, 1990; Vick et al., 1990) resulting in poor adhesion and marked decreases in strength properties (Gertjejansen et al., 1989; Hall and Gertjejansen, 1982; Laks et al, 1988; Schmidt et al., 1987; Thompson, 1961). Many biocides are also chemically unstable or have high vapor pressures and can volatilize during hot pressing (Deppe, 1970; Hedley, 1976). These volatile components may cause manufacturing problems or pose potential health hazards (Anonymous, 1980). Compatibility studies between adhesives and preservatives have been performed in an effort to resolve this problem; however, no satisfactory methods have been identified to limit such effects (Gertjejansen et al., 1989; Hall and Gertjejansen, 1982; Thompson, 1961; Schmidt et al., 1987; Vick, 1980; Vick et al., 1990). Impregnation of full-sized panels, particularly with waterborne arsenical preservatives under high vacuum and pressure, leads to excessive and unrecoverable thickness swelling (Deppe, 1970; Hall et al., 1982). Warping and splitting can also occur in the subsequent drying operation (Winandy et al., 1988; Lee, 1985). Treatments with oilborne preservative systems induce less swelling, but the residual solvent may render the panels unattractive to many potential users.

Vapor phase boron treatment of wood-based composite has recently been evaluated as an alternative to conventional treatment processes (Murphy and Turner, 1989). Panels were easily treated with minimal effects on physical and mechanical properties. However, boron can leach when subjected to wetting, making this treatment less suitable for exterior exposure. Chemical modification using new generations of polymer systems may also have potential application to composite materials; however, the loadings required to effectively protect panels remain far in excess of those deemed economical (Vasishth, 1983; Vasishth and DeSilva, 1981) and these materials may still cause adverse effects on panel properties during impregnation.

Ideally, a treatment system for composites would readily penetrate the wood fiber-resin matrix without disrupting the bond structure and result in uniform chemical deposition throughout the panel. One innovative approach to this problem involves the use of supercritical fluids (SCF) as biocide carriers during impregnation (Ito et al.,1984; Morrell et al., 1993). The advantages in using SCF for treatment are derived from their unique physical properties, phase behavior and solvent properties.

2. Supercritical Fluids

A pure supercritical fluid (SCF) exists at temperatures and pressures above it's critical values (Matson and Smith, 1989)(Figure 1). Under these conditions, the liquid and the gaseous phases of the substance are indistinguishable, i.e. no phase boundary appears regardless of the pressure to which the fluid is subjected.

The physical properties of an SCF are typically intermediate between those of a gas and a liquid (Hoyer, 1985) (Table 1). The high densities of SCF's compared to those of corresponding gases at ambient pressures, result in shorter intermolecular distances with increased molecular interactions. Consequently, SCF's at densities approaching those of liquids can have significant solubilizing capacity even for solutes with low vapor pressures (Matson and Smith, 1989; Eckert et al., 1986). Furthermore, these properties can be varied by modest changes in temperature and pressure, thereby permitting the tailoring of fluid properties to suit specific applications (Ward, 1984).

Under supercritical conditions, the diffusion coefficient of a solute in the fluid is substantially greater than it is in liquid solvents (Krukonis, 1988). Thus, SCF's exhibit many properties of gases including high diffusion rates and the ability to permeate semi-porous media. In addition, SCF viscosities are commonly much lower than those exhibited by liquids, facilitating both pumping and natural convection (Eckert et al., 1986). These special properties make SCF's an ideal media for mass transfer in processes that normally utilize conventional liquids or gases, as well as other specialized applications wherein subcritical fluids are inadequate.

The technical and economic feasibility of using SCF for chemical extraction and purification of natural products have been widely studied (Krukonis, 1988; Modell, 1982 Laws et al.,, 1980; Ritter and Campbell, 1991; Ward, 1989, Zosel, 1974). Among these processes are the decaffeination of coffee, the removal of active ingredients in hops and spices, the removal of nicotine from tobacco, recrystallization of pharmaceuticals, fractionation of oils and polymers and the treatment of liquid and solid wastes.

SCF's have also been explored for wood extraction and treatment. Supercritical (SC) carbon dioxide has been used to extract wood resins, fatty acids and other extractives (Fremont, 1981; Koll et al., 1984, Larsen et al., 1992; McDonald et al., 1982, 1983; Sahle-Demessie, 1993). Other applications of SCF's in wood processes involve extraction of lignin from sulfite pulping liquors (McDonald et al., 1982) and solid wood (Beer and Peter, 1986), extraction of formaldehyde from particleboard, *in situ* polymerization of monomers into wood (Ward, 1989) and deposition of selected biocides in solid wood (Morrell et al., 1993).

SCF's were found to be useful for preservative impregnation of solid wood (Smith et al., 1993 a,b; Morrell et al., 1993), but one area with significant potential for these systems is treatment of wood-based composites. The ease of movement and ability to solubilize high levels of biocide create the potential for complete treatment of panels with little or no negative property changes.

While there is tremendous potential for using SCF's to impregnate wood with biocides, there is virtually no data on the ability of such treatments to penetrate composites or on the effects of such treatments on panel properties. In this report, we describe preliminary trials to impregnate two panel types with a single biocide.

3. Materials and Methods

Panel Type: Commercial plywood and flakeboard were used in this study (Table 2). Due to the limitations imposed by the size of the treatment vessel, panels were cut into defect-free strips (38 mm x 500 mm x panel thickness). All samples were edge sealed with two coatings of epoxy resin and conditioned to a constant weight in a chamber maintained at 65% RH and 21° C prior to treatment.

Biocide: Tebuconazole (Preventol AB), a triazole, was used in all trials (99.9% pure, pH = 4.5 from Bayer AG, Pittsburgh,PA)(Figure 2). This chemical has broad spectrum activity against wood decay fungi, is leach resistant, light and heat stable and soluble in both solvent and water-borne formulations (Exner, 1991). Previous studies had shown that this biocide also has excellent solubility in supercritical carbon dioxide (Sahle-Demessie, 1994).

Solvent and Cosolvent: Carbon dioxide (CO_2) and methanol were used as solvent and cosolvent, respectively. Carbon dioxide has favorable transport properties including low viscosity, a high diffusion coefficient and good thermal properties (Filippi, 1982; Brogle, 1982). The critical temperature (31.3° C) and pressure (1073 psig) were readily attainable with available equipment. Carbon dioxide is a safe, non-flammable and inexpensive solvent (Brogle, 1982).

Supercritical Impregnation Apparatus: Panels were treated using an impregnation device (Figure 3) in which supercritical carbon dioxide with 3% mole fraction methanol was admitted into a pre-heated saturator containing tebuconazole. The solution was then sent into a pre-heated treatment vessel (120 mm diameter and 508 mm long) containing the samples. Pressure was then increased to the desired level after which a 12 mL/min flow rate was maintained through the system. Previous trials indicated that this flow rate resulted in a saturated mixture passing through the vessel (Sahle-Demessie, 1993; Junsophonori, 1994). Flow direction through the treatment vessel was reversed at 3 minute intervals to help maintain an even distribution of biocide along the length of the vessel. At the conclusion of the pressure period, the mixture was sent through a separator (5-10 psig/sec) where the biocide was removed from solution. The sudden drop in pressure and temperature below the critical points during venting decreased biocide solubility resulting in precipitation of biocide in the panels.

Treatment Conditions and Experimental Design: Biocide solubility in supercritical fluid can be affected by temperature, pressure and the presence of cosolvents, but the effects of each variable on treatment are poorly understood. In this regard, the treatment apparatus was used to evaluate the effects of pressure (1800, 3600, 4500 psig), temperature (45°, 60°, 75°C) and treatment time (5, 15, 30 minutes) on tebuconazole retention and distribution in each panel type. Each treatment was assessed on 9 samples for each type of panel. Untreated, unexposed samples for each panel type were used as controls.

Panel Assessment: At the conclusion of treatment, the panels were removed from the vessel and carefully inspected for evidence of splits, delamination or other treatment defects. The degree of swelling and weight gain (nearest 0.01g) were also measured. Thickness was measured at three marked points and water absorption and thickness swelling were expressed as percentage of original weight and thickness, respectively.

Chemical Analyses: Tebuconazole retentions were determined after impregnation by cutting 15 mm wide sections from both ends and the middle portion of each sample (Figure 4). Distribution of biocide within each section was determined by slicing 2 mm sections from the top, middle and bottom portion of each specimen to produce 3 samples for 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 chromatograph (HPLC) according to procedures described in AWPA Standard A23 (AWPA, 1994).

Evaluation of Mechanical Properties: The potential effects of prolonged exposure to high pressure under SC conditions (12-30 times that of conventional pressure treatment) and elevated temperatures on the mechanical properties of each type of panel were evaluated using the test methods in ASTM D 1037 (ASTM, 1993). All boards were tested for static bending, internal bond (IB), water absorption and thickness swelling, although some modification in specimen size was necessary due to constraints imposed by the size of the treatment vessel (Table 3). Tests were also performed to determine plywood shear strength and wood failure (U.S. Product Standard 1-83) (APA, 1983). The results were subjected to an analyses of variance (ANOVA) and the resulting means were compared to similar tests performed on untreated samples using 95% Tukey's Highly Significant Difference (HSD) (STSC, 1993) to determine if treatment induced significant strength losses.

4. Results and Discussion

Effect of Treatment Pressure on Biocide Retention: Tebuconazole retentions for both panel types increased significantly as pressure increased from 1800 to 3600 psig when the vessel was maintained at 60° C for 30 minutes (Figure 5). Increasing pressure from 3600 to 4500 psig resulted in significant decreases in retentions for flakeboard but not plywood. Impregnation under supercritical conditions at pressures ranging from 1800 to 4500 psig resulted in mean retentions of 0.86 to 5.83 kg/m^3 (Figure 5). All values, however, exceeded the reported toxic thresholds for tebuconazole against wood degrading fungi (0.13 to 0.45 kg/m^3) (Exner, 1991).

Increased biocide uptake between 1800 and 3600 psig reflects increasing tebuconazole solubility with increasing CO_2 density (Sahle-Demessie, 1993). The cause of the decreased retention at 4500 psig for flakeboard is unclear. Interactions between pressure and other treatment parameters may have caused this effect. The limited number of observations, however, preclude further delineation of these effects.

Retentions obtained at 1800 psig were acceptable for biological performance. Hence this pressure was used as the baseline for examining the effects of other parameters on treatment.

Effect of Treatment Time on Biocide Retention: Increasing treatment time from 5 to 30 minutes increased tebuconazole retentions for both panel types treated at 1800 psig and 60°C (Figure 6). Treatment periods as short as 5 minutes resulted in mean retentions ranging from 0.07 to 1.08 kg/m^3 depending on panel type. Five of six retentions would confer protection against brown rot fungi while the 15 minute treatment of plywood resulted in an inadequate retention. The rapid chemical absorption confirms earlier reports of extremely rapid penetration of materials by supercritical fluids (Smith et al., 1993a,b).

Effect of Treatment Temperature: Increasing treatment temperature from 45 to 75°C in charges treated at 1800 psig for 30 minutes resulted in significant decreases in retention for both panel types (Figure 7). The highest biocide retentions at 1800 psig were obtained at 45°C. Mean retentions at 45°C ranged from 1.73 to 2.62 kg/m^3 for the panels, easily exceeding the reported toxic thresholds for tebuconazole (Exner, 1991).

Decreasing retentions with increasing temperature may be due to retrograde condensation wherein, tebuconazole solubility decreases due to lower fluid density even though the pressure is higher (Marentis, 1988). Since biocide solubility decreases as temperature rises, the amount of chemical available for deposition decreases.

Preservative Distribution: The excellent preservative distribution across all samples illustrated the ability of SCF's to deliver biocide through plywood or flakeboard (Figure 8). Furthermore, retention gradients from the outer to inner zones were far more uniform than would be found with conventional pressure impregnation (Mitchoff and Morrell, 1991). A steep gradient can be extremely useful where materials are unlikely to be cut or otherwise damaged in service. However, shallow gradients would be more useful for panels, since they are likely to be cut after treatment. Uniform biocide distribution would ensure adequate protection despite these cuts.

In addition to treatment variables such as pressure, temperature and time, chemical absorption may also be influenced by the structural properties of the boards i.e. density, particle size and distribution, porosity, and species composition. An ANOVA of chemical retention and panel density showed significant differences in tebuconazole concentration in boards of differing densities (p-value = 0.0053). However, no pattern of variation was detected from a plot of the data. Further study will be required to better understand the influence of board properties and other related variables such as resin distribution and added wax on biocide distribution under supercritical conditions.

Panel Assessment: No signs of splits, collapse, delamination or other treatment defects were observed for either panel type. In comparison, high pressure-liquid treatment of coniferous woods can induce collapse and other structural changes (Walters, 1967; Walters and Whittington, 1970). The absence of treatment defects suggests significant pressure gradients which would affect structural integrity were absent during treatment. All samples remained dry and clean with no significant changes in appearance. As a result, SCF treated panels could be used immediately after treatment.

Measurements following treatment showed no significant changes in specimen thickness, while sample weights increased slightly (Table 4). In contrast, excessive and unrecoverable thickness swelling results from conventional liquid treatment of wood-composites (Deppe, 1970; Hall et al., 1982). In some instances, samples in the current study experienced small weight losses after treatment. These losses may be caused by solubilization of wood extractives or resin components during exposure to supercritical conditions (Larsen et al., 1992; Ritter and Campbell, 1991; Tillman and Lee, 1990).

Traditionally, weight gain after treatment has been used as a measure of preservative absorption. However, in this study, weight gain was poorly correlated ($R^2 = 0.01 - 0.35$) with chemical absorption. Simultaneous extraction of wood extractives and other wood constituents during the supercritical treatment appears to mask biocide absorption. Combinations of weight gain and other process variables such as pressure, temperature, or treatment time were also poorly correlated with chemical absorption ($R^2 = 0 - 0.29$).

Water Absorption and Thickness Swelling: Treatment pressures and temperatures had no significant effects on water absorption or thickness swelling in panels tested after a 24-hour soak compared to untreated controls (Tables 5 and 6). The ANOVA showed that tebuconazole had no effect on water absorption or thickness swelling within the retention range obtained in this study. The results suggest that supercritical fluid conditions used in this study had no significant negative effect on dimensional stability of the treated panels. Quite the contrary, the treatment appeared to produce slight improvements in flakeboard. The nature of these changes are unclear, although they may reflect densification of the panel or, more likely, extraction of more hygroscopic components during the treatment.

Evaluation of Mechanical Properties: Effective biocide protection is essential for the performance of many panel products but equally important in this process is the impact of treatment on physical and mechanical properties of the treated product. An analysis of variance (ANOVA) of moduli of elasticity (MOE) and modulus of rupture (MOR) showed that treatment pressure, temperature, or pressure period had no significant effect on stiffness or bending strength for flakeboard compared to untreated control panels (Figure

10). Shear tests and examination of failure zones suggested that supercritical fluid impregnation induced no significant negative effects on plywood specimens (Table 7). Previous studies with liquid solvents indicate that prolonged exposure to high pressure and elevated temperatures during treatment can result in considerable mechanical damage (Walters, 1967; Walters and Whittington, 1970; Mitchell and Barnes, 1986).

Previous studies suggested that mechanical properties of wood-composites declined following conventional treatment with several wood preservatives (Boggio and Gertjejansen, 1979; Hall et al., 1982). Our results indicate that these effects are absent in supercritical fluid impregnated materials.

5. Conclusions

Supercritical carbon dioxide was capable of solubilizing and delivering acceptable levels of tebuconazole into both plywood and flakeboard without adversely affecting the physical and mechanical properties of the test samples.

Supercritical fluids provide an attractive alternative to conventional liquid treatments. This new technology avoids problems encountered with conventional fluid pressure impregnation such as excessive thickness swelling and decreased mechanical properties. However, the effects of process variables and board properties on biocide penetration and deposition must be more thoroughly understood before commercial treatment processes are developed.

Despite the need for further research, the process has demonstrated the potential for producing panel products capable of performing under a variety of conditions where conventional products would fail.

6. Literature

1. American Panel Association. 1983. U.S. Product Standard 1-83. for Construction and Industrial Plywood with Typical APA Trademarks. American Plywood Assoc. Tacoma, WA.

2. American Society for Testing and Material. 1993. Standard D 1037: Methods of Evaluating the Properties of Wood-Base Fiber and Particle Panel Materials D 1037. Annual Book of ASTM Standards. 4.09 Wood. ASTM Philadelphia, PA.

3. American Wood Preservers' Association (AWPA). 1994. Standard A23: Standard Methods for Analysis of Wood and Solutions for Propiconazole by HPLC. AWPA Book of Standards. Stevensville, MD.

4. Anonymous. 1980. Pentachlorophenol in log homes - Kentucky. Morbidity and Mortality Weekly Report. HEW Pub. No. (CDC) 78-8017.29 (9):431-432.

5. Beer, R. and S. Peter. 1986. Chem. Ing. Technol. 58(1)72.

6. Boggio, K. and E. J. Gertjejansen. 1979. Influence of ACA and CCA waterborne preservatives on the properties of aspen waferboard. For. Prod. Jour. 32(3):22-26.

7. Brogle, H. 1982. Carbon dioxide as a solvent: its properties and applications. Chemistry and Industry. June 19, pp. 385-390.

8. Deppe, H. J. 1970. The protection of sheet material against water and decay. J. of the Inst. of Wood Sci. 5(3):41-45.

9. Eckert, C. A., J.G. Alsten and T. Stoicos. 1986. Supercritical fluid processing. Environ. Sci. Technol. 20(4):319-325.

10. Exner, O. 1991. Tebuconazole - a new triaozole fungicide for wood preservation. Int. Res. Group on Wood Pres. Doc. No. IRG/WP 3629. Stockholm, Sweden.

11. Filippi, R. P. 1982. CO_2 as solvent: application to fats oils and other materials. Chemistry and Industry. June 19, pp. 390-393.

12. Fremont, H. A. 1981. U.S. Patent 4,308,200.

13. Gertjejansen, R. O., E. L. Schmidt and D. C. Ritter. 1989. Assessment of preservative treated aspen waferboard after 5 years of field exposure. For. Prod. Jour. 39(4):15-19.

14. Hall, H. J. and E. J. Gertjejansen. 1982. Weatherability of phenolic bonded Ghanian hardwood flakeboard made from ACA treated flakes. For. Prod. Jour. 29(12):34-38.

15. Hall, H. J., R. O. Gertjejansen, E. L. Schmidt, C. G. Carl, and R. C. De Groot. 1982. Preservative treatment effects on mechanical and thickness swelling properties of aspen waferboard. For. Prod. Jour. 32(11/12):19-26.

16. Hedley, M. E. 1976. Preservative requirements of exterior particleboard predicted from accelerated laboratory tests. New Zealand Journal of Forestry Sci. 6(3):457-462.

17. Hoyer, G. C. 1985. Extraction with supercritical fluids: why, how and so what? ChemTech. July, pp. 440-448.

18. Ito, N. T., T. Someya, M. Taniguchi, and H. Inamura. 1984. Japanese Patent 59-101311.

19. Junsophonori, L. 1994. Solubility of biocides in pure and modified supercritical carbon dioxide. Master's Thesis. Oregon State Univ. Corvallis, OR.

20. Koll, V. P., Brönstrup, B. and J. Metzger 1979. Thermischer abbau von birkenholz mit superkritischen gasen (organischen Lösungsmitteln) in einer hochdruck, hochtemperatur-strömungsapparatur: die verflüssigung von holz und weitere hinweise auf eine alternative zellstoffgewinnungstechnologie. Holzforshung. 33:112-116.

21. Kreber, B., P. E. Humphrey, and J. J. Morrell. 1991. Effect of polyborate pre-treatment on the shear strength development of phenolic resins to sitka spruce bonds. Holzforschung.

22. Krukonis, V. J. 1988. Processing with supercritical fluids: overview and applications. ACS Symposiun Series 366:27-43.

23. Kumar, S. and J. J Morrell. 1993. Effect of fatty acid removal on treatability of Douglas fir. The International Research Group on Wood Preservation Document No. IRG/WP/ 93-40008. Stockholm, Sweden.

24. Labracque, R., S. Kallagulne, and J. L. Grandmalson. 1984. Supercritical gas extraction of wood with methanol. Ind. Eng. Chem. Prod. Res. Dev. 23: 177-182.

25. Laks, P. E., B. A. Haatala, R. D. Palardy, and R. J. Bianchini. 1988. Evaluation of adhesive for bonding borate-treated flakeboards. For. Prod. Jour. 38(11/12):23-24.

26. Larsen, A., N. A. Jentoft and T. Geibokk. 1992. Extraction of formaldehyde from particleboard with supercritical carbon dioxide. For. Prod. J. 42(4):45-48.

27. Laws, D. R. J., Bath, N. N., Ennis, C. S. and A.G. Wheldon. 1980. U.S. patent 4,218,491.

28. Lee, A.W.C. 1985. Effect of CCA treating and air drying on the properties of southern pine and plywood. Wood and Fiber Sci. 17(2):209-213.

29. Marentis, R.T. 1988. Steps to developing a commercial supercritical carbon dioxide processing plant. Supercritical Fluid Extraction and Chromatography. B.A. Charpentier and M.R. Sevenants (Eds.). ACS Symposium Series, Washington D.C.

30. Matson, D.W. and R. D. Smith. 1989. Supercritical fluid technologies for ceramic processing applications. J. Am. Ceram. Soc. 72(6):871-881.

31. McDonald, E. C., J. Howard and B. Bennett. 1982. Chemicals from forest products by supercritical fluid extraction. ENFOR proj. C-51, Phase III. Canadian Forestry Service, Dept. of Environ. Quebec, Canada.

32. McDonald, E.C., J. Howard and B. Bennett. 1983. Chemicals from forest products by supercritical fluid extraction. Fluid Phase Equilibria. 10(2):337-344.

33. Mitchell, P. H. and H. M. Barnes. 1986. Effect of drying temperature on the clear wood strength of southern pine treated with CCA-Type A. For. Prod. Jour. 36(3):3-12.

34. Mitchoff, M.E. and J. J. Morrell. 1991. Treatment of plywood panels composed of veneers from Western State. For. Prod. Jour. 4(9):11-18.

35. Modell, M. 1982. U.S. Patent 4,338,199.

36. Morrell, J. J., K. L. Levien, E. Sahle-Demessie, S. Kumar, S. Smith and H. M. Barnes, 1993. Treatment of wood using supercritical fluid processes. Proc. Canad. Wood Preserv. Assoc. 14:6-25.

37. Murphy, R. J. and P. Turner. 1989. A vapour phase preservative treatment of manufactured wood-based board materials. Wood Sci. and Tech. 23:273-279.

38. Paulatis, M. E., J. L. Penninger, R. D. Cray Jr., and P. Davidson (Eds.). 1983. Chemical Engineering at Supercritical Fluid Conditions. Ann Arbor Science, Ann Arbor, MI.

39. Ritter, D. S. and A.G. Campbell. 1991. Supercritical carbon dioxide extraction of southern pine and ponderosa pine. Wood and Fiber Sci. 23(1):98-113.

40. Sahle-Demesie, E. 1993. Deposition of chemicals in semi-porous solids using supercritical fluid carriers. Ph.D. Thesis. Oregon State Univ., Corvallis, OR.

41. Schmidt, E. L. 1984. Test methods for mechanical and biodurability evaluation of preservative treated non-veneered wood composites. Proc. Amer. Wood Pres. Assoc. 80:56-58.

42. Schmidt, E. L., H. J. Hall, R. O. Gertjejansen and C. G. Carl. 1987. Assessment of preservative treated aspen waferboard after 30 months of field exposure. For. Prod. Jour. 37(2):62-66.

43. Smith, S. M., J. J. Morrell, E. Sahle-Demessie and K. L. Levien. 1993a. Supercritical fluid treatments: Effects on bending strength of white spruce heartwood. Internat. Res. Group on Wood Preservation Doc. No. IRG/WP. 93-20008. Stockholm, Sweden.

44. Smith, S. M., E. Sahle-Demesie, J. J. Morrell, K. L. Levien and H. Ng. 1993b. Supercritical fluid (SCF) treatment: its effect on bending strength and stiffness of ponderosa pine sapwood. Wood and Fiber Sci. 25(2):119-123.

45. STSC. 1993. Statgraphics Version 7. STSC, Inc. Rockville,MD.

46. Thompson, W. S. 1961. Diffusion of heavy metals salts into wood and their effect on selected wood properties. Ph.D. Thesis. School of Forestry, North Carolina State College, Raleigh, N.C..

47. Tillman, L. M.and Y. Y. Lee. 1990. Pulping of southern pine under low water, alkaline conditions using supercritical carbon dioxide. Tappi 73(7):140-146.

48. Vasishth,R. C. 1983. Importance of depositing polymers in wood-cell walls for wood treatment. Proc. Amer. Wood Pres. Assn. 79:129-136.

49. Vasishth, R. C. and D. P. DeSilva. 1981. U.S. patent 4,285,997.

50. Vick, C. B. 1990. Adhesion of phenol-formaldehyde resin to water-borne emulsion preservative in aspen veneer. For. Prod. Jour. 40(11/12):25-30.

51. Vick, C. B., R. C. DeGroot, and Y. Youngquist. 1990. Compatibility of nonacidic waterborne preservatives with phenolic formaldehyde adhesive. For. Prod. Jour. 40(2):27-32.

52. Walters, C.S. 1967. The effect of treating pressure on the mechanical properties of wood: I. Red Gum. Proc. Amer. Wood Pres. Assoc. 63: 166-178.

53. Walters, C. S. and L. Whittington. 1970. The effect of treating pressure on mechanical properties of wood. II. Douglas fir. Proc. Am. Wood Pres. Assoc. 66:179-193.

54. Ward, D. T. 1989. Supercritical fluid-aided deposition of methyl methacrylate into wood. M. S. Thesis, Univ. of Southern Florida, Tampa. FL.

55. Winandy, J. E., S. L., Levan, E. L., Schaffer and P.W. Lee. 1988. Effect of fire-retardant treatment and redrying on the mechanical properties of Douglas fir and aspen plywood. U.S. Department of Agric., Forest Serv., Report FPL RP-485, Madison,WI.

56. Zosel, K. 1974. U.S.patent 3,806,619.

Table 1. Typical properties of gas, liquid and supercritical fluids (SCF) (18).

Property	Gas	SCF	Liquid
Density (g/cc)	(0.6-2)x10-3	0.2-0.9	0.1-1.6
Diffusion coeff.(cm3/sec)	0.1-0.4	(0.2-0.7)x10-3	(0.2-2)x10-5
Viscosity (cP)	(1-3)x10-2	(1-9)x10-2	0.2-3

Table 2. Properties of panels used for supercritical fluid (SCF) treatment.

Board Type	Properties
Plywood	Douglas-fir face; exterior type (PF bonded) 5-ply; 0.47-0.50 g/cc density, 15 mm thick.
Flakeboard	Wafers from mixed softwood; exterior type (PF bonded); 0.60-0.65 g/cc, random orientation, 10 mm thick

Table 3. Modified sample dimensions used for evaluation of mechanical properties of SCF treated and untreated panels (ASTM D 1037).

Test	Replications	Sample Dimension
Static Bending	9	38 mm x 305 mm x panel thickness
Internal Bond (IB)	4	38 mm x 50 mm x panel thickness
Moisture Absorption	6	38 mm x 203 mm x panel thickness
Thickness Swelling	6	38 mm x 203 mm x panel thickness

Table 4. Effect of Supercritical Fluid impregnation on thickness swell and weight change in various panel types.

Panel Type	Replicates	Thickness Swelling (%)		Weight Gain (%)	
		Mean (St. Dev.)	Range	Mean (St. Dev.)	Range
Plywood	55	1.17 (0.80)	-0.336 to 3.449	2.78	-0.98 to 6.19
Flakeboard	49	1.52 (1.11)	-0.05 to 4.97	0.86 (0.70)	-0.72 to 2.86

Table 5. Effect of treatment pressure and temperature on water absorption after 24-hour soak in water (ASTM D 1037) in various panel types following impregnation with supercritical CO_2 at selected pressures at 60° C for 30 minutes or selected temperatures at 1800 psig and 60° C.

Panel Type	Water Absorption (%)[a]						
	Pressure (psig)				Temperature (°C)		
	Control	1800	3600	4500	45	60	75
Plywood	3.05 A	33.4 A	33.4 A	32.7 A	34.8 A	33.4 A	36.0 A
Flakeboard	44.0 A	27.8 AB	20.7 B	27.1 AB	46.7 A	27.8 A	29.4 A

[a] Values represent means of 6 replicates per treatment. Values followed by the same letter do not differ significantly by Tukey's HSD (= 0.05).

Table 6. Effect of treatment pressure and temperature on thickness swelling after 24-hour soak in water (ASTM D 1037) in various panel types following impregnation with supercritical CO_2 at selected pressures at 60° C for 30 minutes selected temperatures at 1800 psig and 60° C.

Panel Type	Control	Thickness Swell (%)[a]					
		Pressure (psig)			Temperature (°C)		
		1800	3600	4500	45	60	75
Plywood	3.7 A	3.7 A	3.0 A	3.2 A	3.6 A	3.7 A	3.6 A
Flakeboard	17.8 AB	9.8 B	7.5 B	10.9 A	12.8 AB	9.8 B	10.8 B

[a] Values represent means of 6 replicates. Values followed by the same letter do not differ significantly by Tukey's HSD (= 0.05)

Table 7. Effect of temperature, pressure and treatment time during supercritical fluid impregnation of plywood on shear strength and percent wood failure.

Treatment Time (minutes)	Shear Strength (psi)							Wood Failure (%)						
	Pressure (psig)				Temperature (° C)			Pressure (psig)				Temperature (° C)		
	Control	1800	3600	4500	45	60	75	Control	1800	3600	4500	45	60	75
0	134(21)A							94(4)A						
5		130(29)A							97(3)A					
15		131(24)A							94(4)A					
30		135(38)A	129(28)A	134(20)A	126(20)A	135(38)A	117(24)A		92(7)A	95(4)A	95(5)A	93(6)A	92(7)A	96(4)A

Figure 1. Phase diagram of a pure substance.

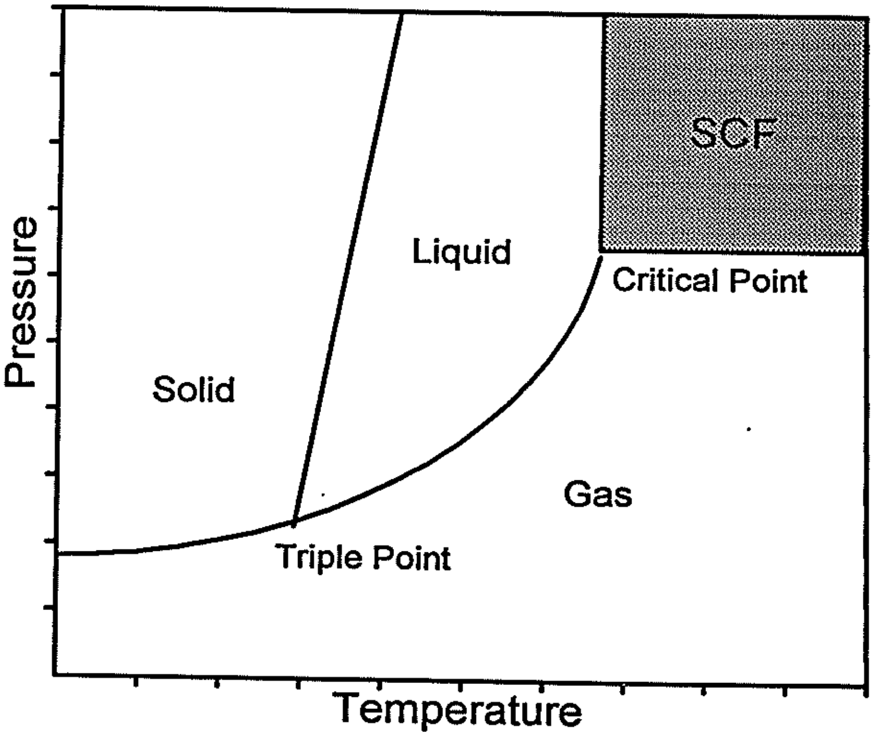


Figure 2. Chemical structure of tebuconazole (α-[2-(4-chlorophenyl)ethyl]-α-(1,1-dimethyl)-1H-1,2,4-triozole-1-ethanol) (Exner, 1991).

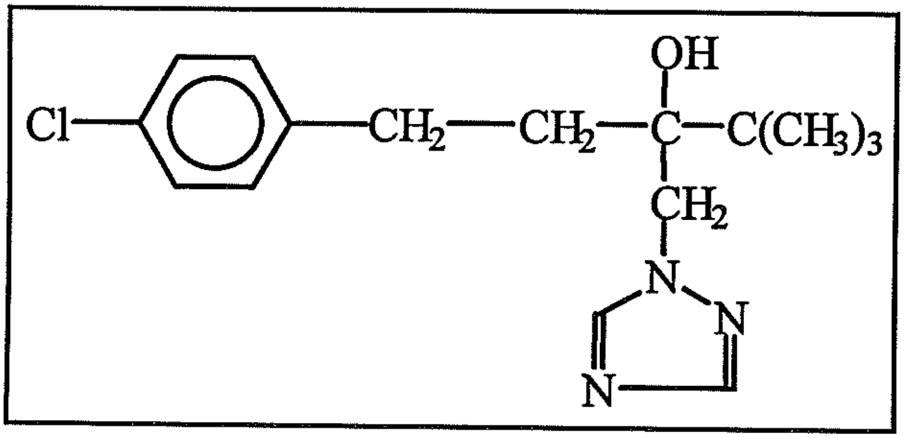


Figure 3. Device used for supercritical fluid impregnation studies.

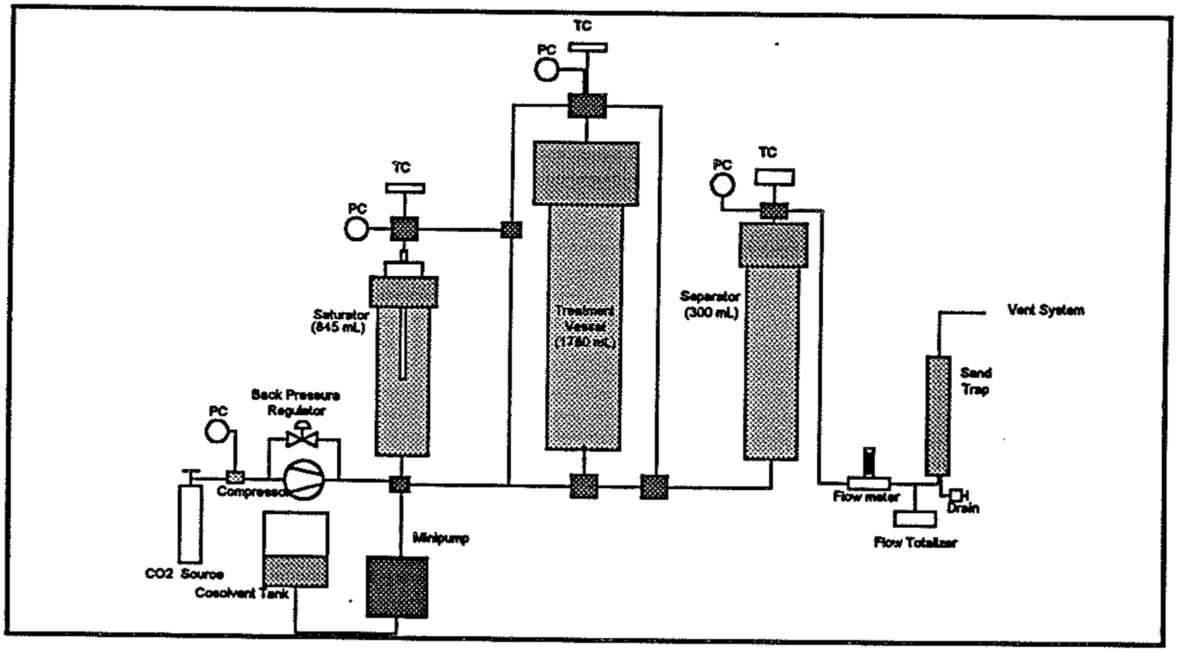


Figure 4. Sampling pattern for assessing biocide distribution and retention in SCF treated composites.

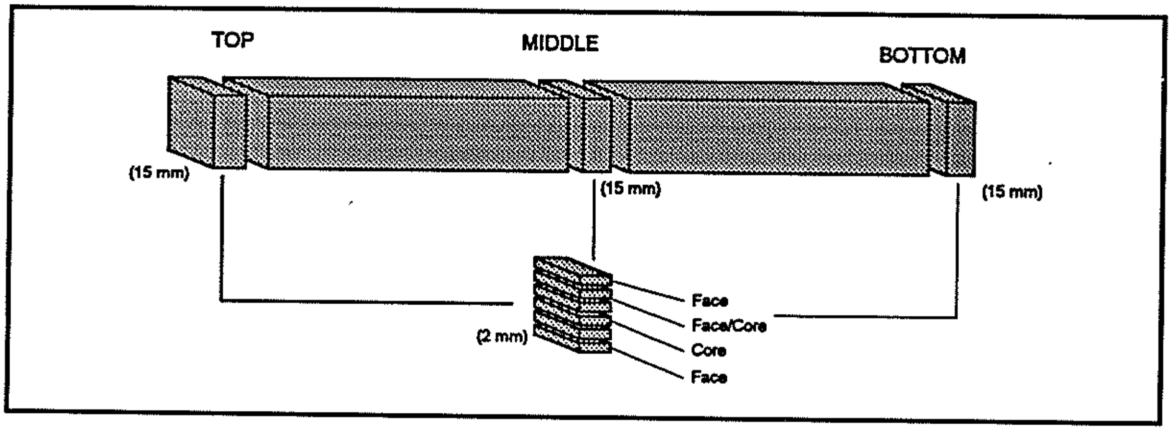


Figure 5. Effect of pressure on tebuconazole retention in various panel types during treatment with supercritical CO_2 maintained at 60°C for 30 minutes. Bars of the same panel type with the same letters do not differ significantly by Tukey's Highly Significant Difference test at $\alpha = 0.05$.

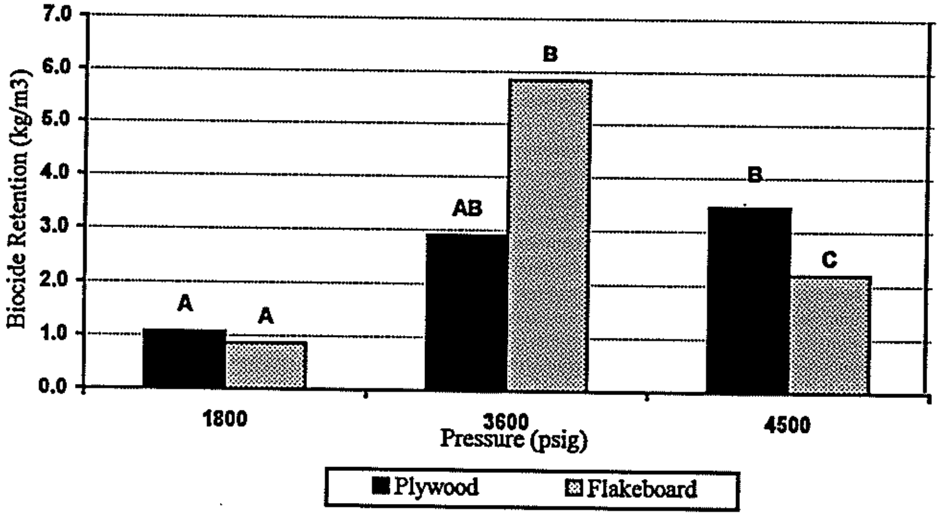


Figure 6. Effect of treatment time on tebuconazole retention in various panel types during treatment with supercritical CO_2 at 1800 psig and 60°C. Bars of the same panel type with the same letter are not significantly different by Tukey's Highly Significant Difference test at $\alpha = 0.05$.

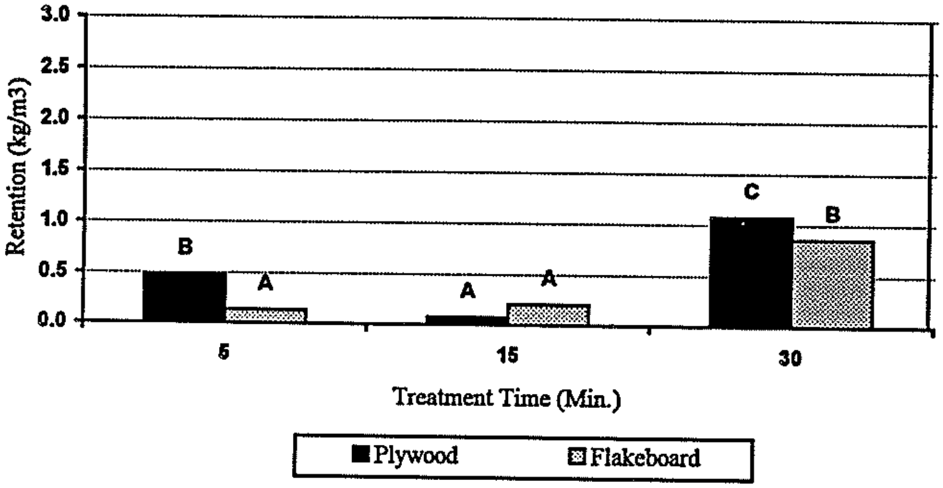


Figure 7. Effect of treatment temperature on tebuconazole retention in various panel types during treatment with supercritical CO_2 at 1800 psig for 30 minutes. Bars of the same panel type with the same letter are not significantly different by Tukey's Highly Significant Difference test at $\alpha = 0.05$.

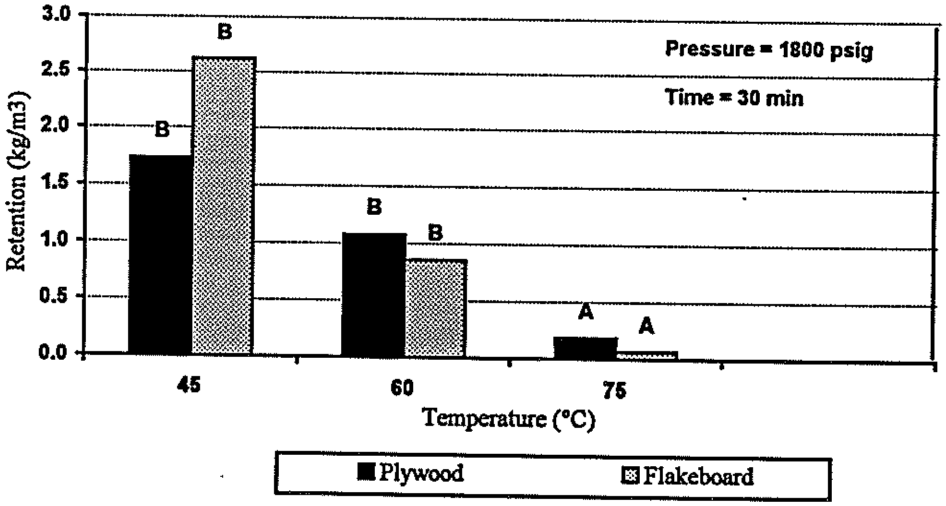


Figure 8. Tebuconazole distribution at selected depths from the surface of panels treated with supercritical CO_2 under conditions maintained at a) 1800 psig and 60°C for 30 min. b) 1800 psig and 45°C for 30 min. or c) 3600 psig and 60°C for 30 min.

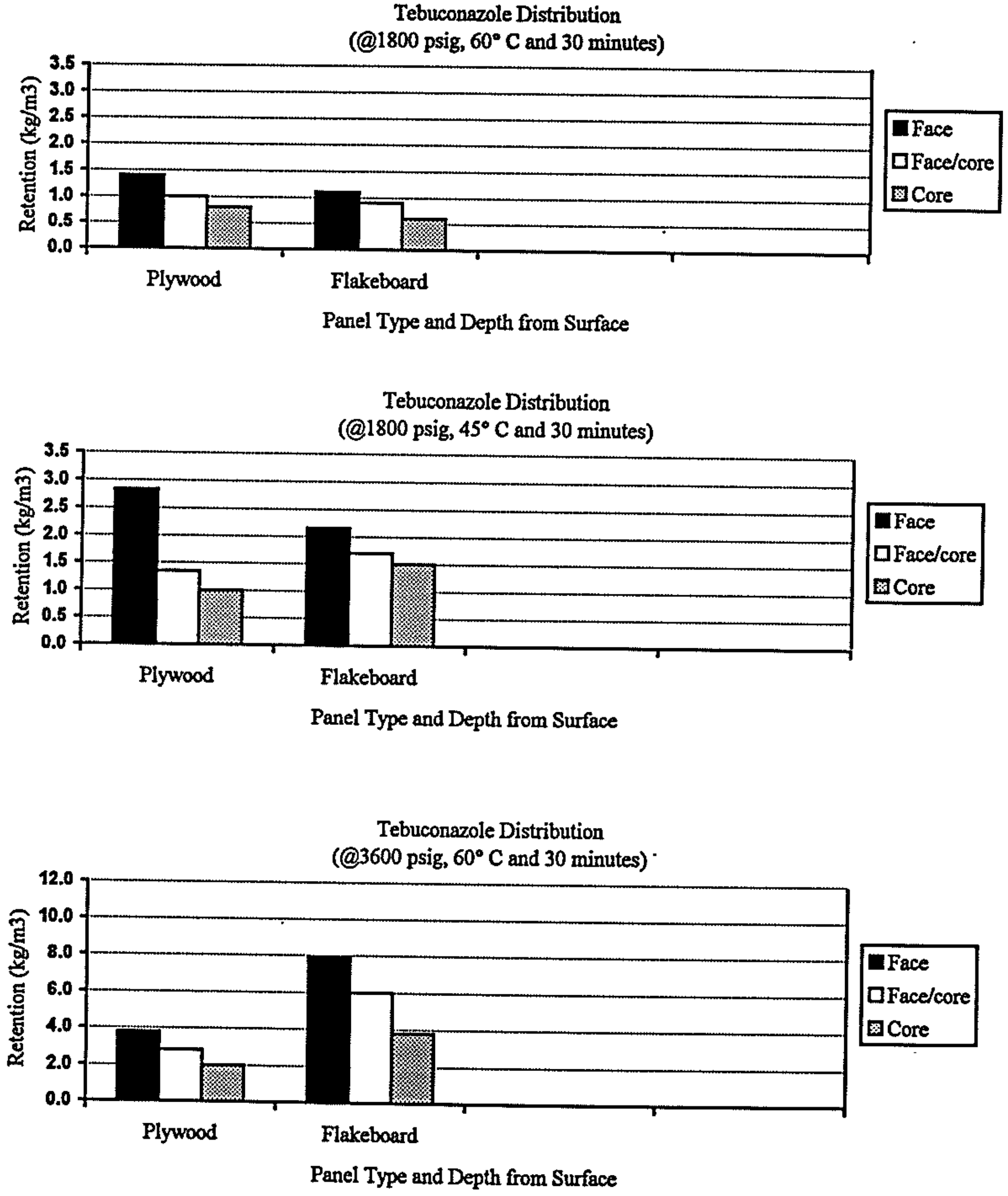
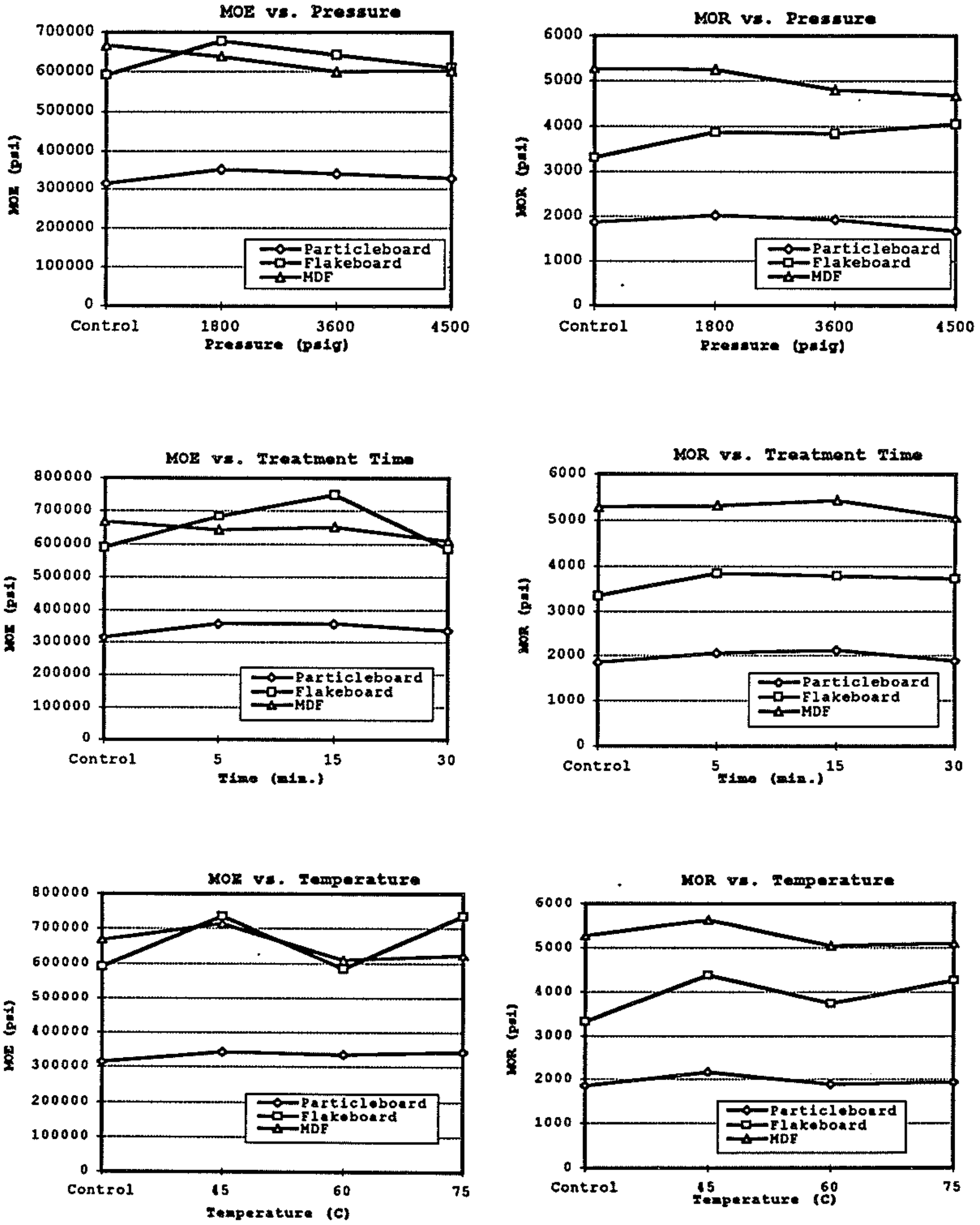
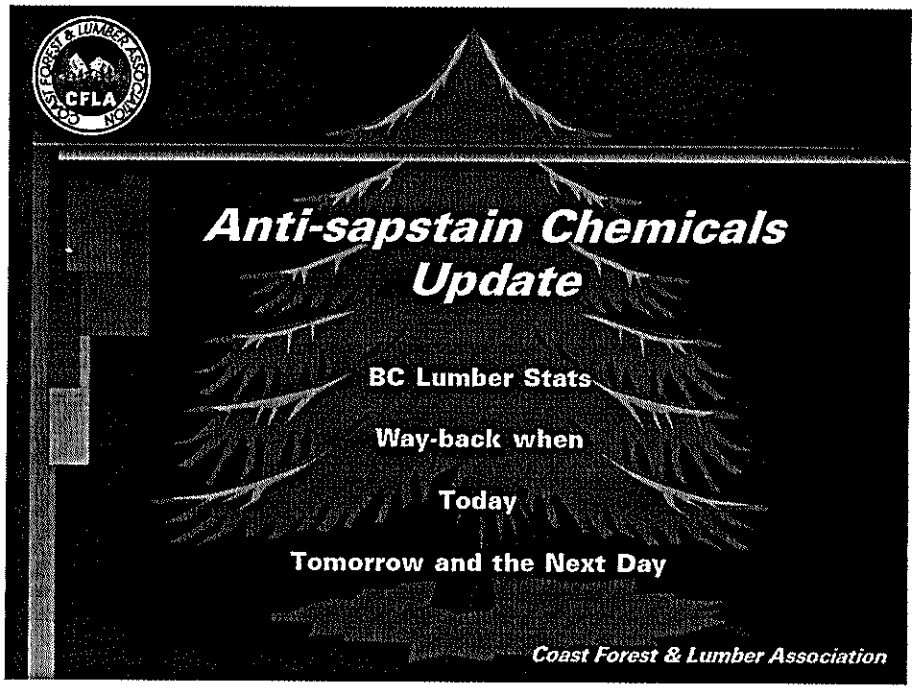


Figure 10. Effect of a) treatment pressure b) temperature, or c) pressure period on MOE and MOR of various panel types impregnated with tebuconazole using supercritical CO_2 at 60°C for 30 minutes.



UPDATE ON THE STATUS OF ANTI-SAPSTAIN TREATMENTS

B. Zack
Coast Forest & Lumber Association, Vancouver, B.C. V7T 1S7



Anti-sapstain Chemicals Update

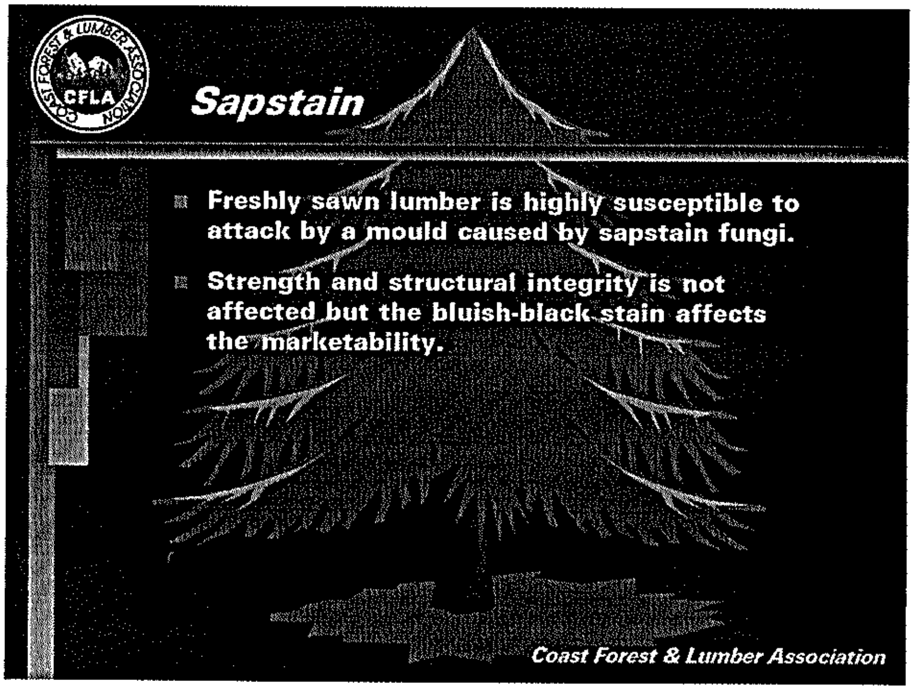
BC Lumber Stats

Way-back when

Today

Tomorrow and the Next Day

Coast Forest & Lumber Association



Sapstain

- Freshly sawn lumber is highly susceptible to attack by a mould caused by sapstain fungi.
- Strength and structural integrity is not affected but the bluish-black stain affects the marketability.

Coast Forest & Lumber Association