SUPERCRITICAL CARBON DIOXIDE TREATMENT: EFFECT ON PERMEABILITY OF DOUGLAS-FIR HEARTWOOD[1]

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ABSTRACT

The effect of supercritical fluid treatment on superficial gas permeability of Douglas-fir was investigated by using carbon dioxide either alone or amended with methanol. Permeability increased in a majority of samples, although nearly one-third of the specimens declined in permeability. Improvements in permeability appeared to be unrelated to variations in temperature, pressure, or the presence of a cosolvent, suggesting that the conditions were uniformly suitable for extractive solubilization. Decreased permeability may reflect redeposition of solubilized extractives to positions where they again diminish permeability as conditions drop out of the critical range, a possibility that will be studied further.

Keywords: Permeability, supercritical fluids, Douglas-fir.

INTRODUCTION

Supercritical fluids (SCFs) are increasingly assessed as to their ability to extract and deposit chemicals in semiporous materials, including wood (Paulaits et al. 1982; Eckert et al., 1986; McHugh and Krukonis 1986; Johnston et al. 1989). SCFs offer a novel combination of gas- and liquid-like properties that

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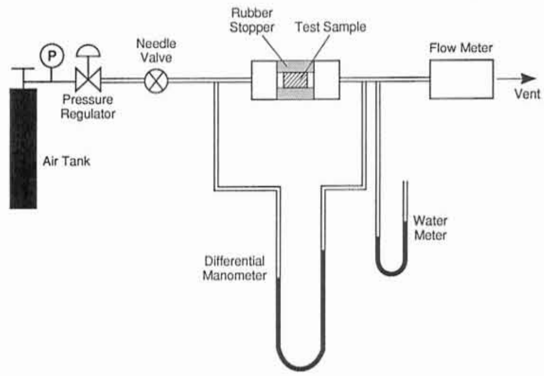

FIG. 1. Schematic of the permeability measurement apparatus.

make them unique as solvents and reaction media. Because of their abilities to penetrate wood readily, SCFs may be especially useful in wood processing, either by carrying materials that can subsequently be deposited when temperatures or pressures are varied or by solubilizing materials naturally present in the wood, such as extractives, resin acids, or fatty acids, so that they can be removed for other uses (Froment 1981; Puri and Mamers 1983; Ritter and Campbell 1991; McDonald et al. 1983; Williams 1981). Supercritical fluid extraction may also enhance permeability of wood by removing extractives clogging pit membranes or by solubilizing pits to the extent that they deaspirate. Enhancing permeability may be particularly useful in refractory species such as Douglas-fir, in some populations of which the combination of reduced pit numbers and aspiration has a dramatic effect on overall permeability (Krahmer 1961).

Removal of extractives or encrustations markedly enhances both gas and liquid permeability (Stamm 1932, 1963; Anderson and Fearing 1960; Miller 1961; Côté 1963; Thomas and Nicholas 1966; Comstock 1967). A portion of this enhancement may result from increased capillary movement through the wood cell walls, but such movement is probably overshadowed by the larger improvements in pit permeability (Côté 1963). Permeability can also be enhanced by steaming, which apparently softens pits to the point that they deaspirate (Nicholas and Thomas 1968; Naryanappa and Sharma 1990); but such treatments can have negative effects on other properties of some wood species.

Supercritical carbon dioxide (SCF-CO_2) has been used to explode lignocellulose prior to pulping, thereby enhancing the penetration of pulping chemicals. Although these effects suggest that such treatments could markedly open wood structure and improve permeability (Puri and Mamers 1993), earlier studies found no evidence of altered wood structure after SCF-CO_2 treatment at 100 C and 27.6 MPa (Ritter and Campbell 1991).

As part of a larger study evaluating SCF impregnation of wood, the trials described in this paper were performed to better quantify the effects of SCF treatment on wood permeability.

MATERIALS AND METHODS

One hundred defect-free dowels (13 mm in diam. by 10 mm long) of Douglas-fir heartwood (*Psuedotsuga menziesii* (Mirb.) Franco) were cut so that the long axis was oriented radially. The dowels were conditioned to 15% moisture content. Specific superficial gas permeability of each dowel was determined at 0.138, 0.207, 0.276, and 0.414 MPa with a flow-measurement apparatus (Fig. 1). Each dowel was inserted in a rubber stopper to help direct air flow, and air from a storage cylinder was introduced at the desired pressure at one end of the dowel. Inlet pressure was measured by connecting a differential mercury manometer, while outlet pressure was measured with a water manometer. Air flow rate was measured with a soap-film flow meter similar to that described by Siau (1971). Higher flow rates were measured with a digital flow meter (McMillan 310-3). Superficial air permeability, k_g, was determined at the selected pressures by using Darcy's Law as modified by the Klinkenberg equation (Siau 1984). The intercept and slope of the regression line of k_g vs. reciprocal mean pressure were used to calculate per-

TABLE 1. *Variables evaluated for effects of SCF treatment on average wood weight loss and permeability change.*

Treatment no.	Pressure (MPa)	Treatment time (min)	Temperature (°C)	Treatment fluid density (g/cm^3)	Methanol added	Avg. wood wt. loss (%)[a]	Avg. permeability change (%)[a]
1	20	30	40	0.841	no	2.58	179*
2	20	30	40	0.857	yes	2.92	173*
3	20	30	80	0.597	no	3.26	44*
4	20	30	80	0.608	yes	3.35	161
5	20	60	80	0.597	no	3.17	26*
6	30	30	40	0.911	no	3.03	117*
7	30	30	40	0.934	yes	2.73	170
8	30	30	80	0.747	no	3.70	87*
9	30	30	80	0.766	yes	3.37	177*
10	30	60	80	0.747	no	3.24	126*

[a] Values reflect means of 10 dowels per treatment. Permeability changes followed by an asterisk are significant at $\alpha = 0.05$ by a t-test.

meability in the absence of slip and a slip factor.

The initial permeability measurements were used to segregate 100 dowels into 20 groups of 5 with approximately similar average permeabilities. The dowels were then treated, 5 at a time, with SCF-CO_2 with or without 3 mole % methanol at various combinations of pressures, times and temperatures (Table 1). (Methanol was included because its presence increased the solubility of many nonpolar materials in SCF-CO_2.) Extraction was performed with an Isco Series 2000 SCF extraction system consisting of a dual-chamber extraction module, a 260-ml-capacity CO_2 pump, a 100-ml-capacity cosolvent pump, and a controller. Carbon dioxide continuously flowed through the extraction vessel at a rate of 0.8 g/min, and the average SCF-wood volume ratio was 3:1.

After treatment, the dowels were reconditioned to a stable moisture content at 21 C and 65% relative humidity and weighed; gas permeabilities were then measured under the same temperature/humidity conditions as described above. Permeability values before and after treatment provided a measure of the potential effects of SCF treatment on wood structure.

The resulting changes in permeability were subjected to an analysis of variance, and differences between initial and final permeabilities in individual treatments were subjected to t-tests at $\alpha < 0.05$ (Steel and Torrie 1980).

RESULTS AND DISCUSSION

Supercritical fluid treatment increased specific superficial gas permeability by an average of 133%, with a maximum increase of nearly 600% (Fig. 2). These changes were significant in 8 of 10 treatments (Table 1). Approximately 19% of the dowels had decreased permeability after the treatment. The reasons for this decrease are unclear, although they may reflect redeposition of solubilized extractives on the pit membranes as the temperature or pressure regimes dropped below the critical point (31.1

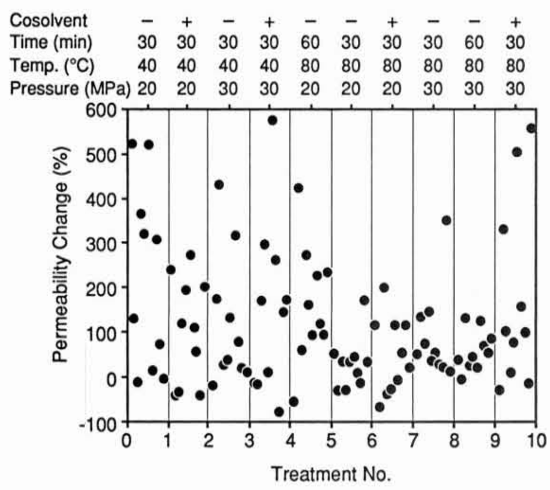

FIG. 2. Permeability changes of Douglas-fir dowels treated with SFC-CO_2 at selected temperatures and pressures with or without methanol as a cosolvent.

TABLE 2. *Analysis of variance of permeability changes in Douglas-fir heartwood dowels exposed to SC-CO_2 under differing pressure and temperature regimes with or without methanol as a cosolvent.*

Source of variation	Sum of squares	df	Mean square	*F*-ratio	Sig. level
Main effects	1.882E−5	3	6.273E−6	0.937	0.427
Permeability·pressure	9.479E−8	1	9.479E−8	0.014	0.907
Permeability·temperature	6.733E−6	1	6.733E−6	1.005	0.319
Permeability·cosolvent	9.720E−6	1	9.720E−6	1.452	0.232
Interactions	2.242E−5	3	7.474E−6	1.116	0.348
Permeability·pressure·temperature	2.611E−6	1	5.611E−6	0.838	0.373
Permeability·pressure·cosolvent	1.922E−5	1	1.922E−5	2.870	0.095
Permeability·temperature·cosolvent	4.174E−8	1	4.174E−8	0.006	0.938
Residual	4.881E−4	73	6.696E−6		
Total (corr.)	5.301E−4	79			

C, 7.353 MPa atmospheres for pure CO_2). They may also represent reaspiration of pit membranes after treatment. On the average, the dowels lost 3.32% of their weight during SCF treatment, a value comparable to that found with SCF extraction of pine or birch (Li and Kiran 1988). Permeability changes appeared unrelated to extraction weight losses, suggesting that the former reflected more subtle SCF effects on wood structure (Table 1).

Changes in temperature, pressure, and treatment time had variable effects on permeability, probably because wood permeability is itself naturally variable. High temperatures generally reduced any increases in permeability, even though high temperatures resulted in a slight decrease (4.2%) in the percentage of dowels in which permeability decreased after treatment. The ANOVA, however, indicated that changes in neither temperature nor pressure significantly affected permeability (Table 2).

Because of the complexity of the extractives in Douglas-fir heartwood, it was not possible to determine either the optimum conditions for extraction or which extractives affected permeability. It is possible that elevated temperatures reduced extractive removal, thereby reducing any improvements in permeability. Similar decreases in extractive removal with increased temperatures were observed in ponderosa pine extraction (Ritter and Campbell 1991). Extractive levels in Douglas-fir are low in comparison with those in such species as southern pine. Thus, more significant changes under different extraction regimes may be seen with these species.

The use of a cosolvent produced some improvement in permeability, especially at 80 C. Cosolvents can produce significant improvements in solubility of a wide array of compounds (Dobbs et al. 1986; Van Alsten 1986). While it is possible that methanol was not an appropriate cosolvent for extractive removal, alcohol refluxing is a standard method for removing extractives from wood. Perhaps higher concentrations in SCF-CO_2 would have boosted the improvements in permeability. Further trials with other cosolvents and treatment conditions will be required to understand these effects more fully.

CONCLUSIONS

The results indicated that SCF-CO_2 significantly improved permeability in a majority of Douglas-fir dowels tested. The improvements appeared to have little relationship to changes in treatment pressure, temperature, or time under the experimental regimes examined. Further trials to understand the nature of the permeability change better will examine pressure release rate, initial extractive level, and microdistribution of redeposited extractives in the SCF-CO_2 treated wood.

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