IN-SITU MEASUREMENT OF DIMENSIONAL CHANGES DURING SUPERCRITICAL FLUID IMPREGNATION OF WHITE SPRUCE LUMBER

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ABSTRACT

Supercritical fluids can markedly enhance preservative treatment of wood, but the high pressures employed can lead to collapse. We investigated the effects of the rates of pressure application and release on displacement of white spruce lumber during supercritical impregnation with carbon dioxide. Displacement was greatest when pressure was rapidly increased at the start of the process. Conversely, rapid pressure release at the conclusion of the treatment process resulted in the lowest level of permanent displacement. The results suggest that wood displacement during supercritical fluid impregnation can be controlled by altering process variables for a given species.

Keywords: Supercritical fluids, pressure, collapse, spruce, displacement.

INTRODUCTION

Pressure treatment of wood with preservatives provides an excellent barrier against biological degradation, but the effectiveness of such treatments requires that the barrier be maintained (Henry 1973). The depth of the preservative shell generally depends on the amount of permeable sapwood present (MacLean 1946). Numerous attempts to improve the treatment of heartwood have been made, but most have been limited by the inability to force liquids across occluded or aspirated pit membranes in the heartwood (Barnes 1985). One alternative to conventional liquid preservatives employs SCFs as carriers (Ito et al. 1984; Sunol 1991; Kayihan 1992). Supercritical fluids have diffusivities approaching those of gases, and some SCFs also have the ability to solubilize materials at levels approaching liquids (Paulaitis et al. 1983; Krukonis 1988). With these properties, SCFs have the potential to completely penetrate a liquid-impermeable material and deposit a biocide deep within the wood structure (Morrell et al. 1993, 1997; Sahle Demessie 1994; Acda et al. 1995).

Although SCFs have tremendous potential for improving wood treatment, the elevated pressures associated with impregnation processes have raised concerns about the struc-

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tural integrity of the treated material. Previous studies of high-pressure treatments with liquid preservatives show that substantial losses occur in several material properties when differential pressures develop between the interior and surface of the wood (Walters 1967; Walters and Whittington 1970). Small-scale tests on sticks of white spruce and Douglas-fir (*Pseudotsuga menziesii* [Mirb.] Franco) suggest that little or no loss in strength occurs with SCF processes (Smith et al. 1993a, b). In addition, various wood-based composites are not affected by SCF treatment (Acda et al. 1997). Nonetheless, tests on 25- × 25-mm beams suggest that some species are susceptible to collapse and splitting during the treatment process (Kim et al. 1997; Acda et al. 1999). The species that appears to be most susceptible to displacement is white spruce, a finding that is consistent with conventional treatments of this species (Willeitner 1989).

Spruce represents a substantial resource in many northern regions of the world; thus, identifying suitable SCF treatment processes for this species is important in commercial development of this technology (Willeitner 1989). A myriad of possible alternative treatment processes might potentially reduce displacement, but selecting a process is difficult without knowing when displacement occurs during the treatment process. Studying displacement at high pressures poses special challenges, because the vessels do not allow for *in-situ* observation of specimens, and examination after treatment does not show when displacement occurred. One approach to measuring displacement during treatment is to install strain gauges on wood samples that are subjected to SCF treatment. When these gauges are connected to a data acquisition system, displacement can be monitored continuously during treatment.

The objectives of this study were to determine the amount of stress during supercritical fluid impregnation and the effect of rates of pressurization and venting on this stress.

MATERIALS AND METHODS

White spruce heartwood lumber (50 × 100 mm), supplied by Forintek Canada Corp. (Vancouver, BC) and cut into specimens (38 × 50 × 200 mm), was conditioned to a stable moisture content at 25°C and 70% relative humidity. Strain gauge transducers were constructed by bonding strain gauges (series "EP," manufactured by Micro Measurements primarily for measurements of large strains) on the top and bottom of a metal watch spring (0.28 × 17.8 mm in cross section and 44.5 mm in length). One was used as an active transducer, and the other as a reference transducer. Gauges had a resistance of 120 ohms and a gauge factor of 2.0. Micro Measurements' A-12 epoxy resin was used to bond gauges to the watch spring. The gauges in a transducer were wired to a full Wheatstone bridge circuit. The active transducer was attached between two nails driven into the wide surface of the specimen so that length of transducer was perpendicular to the grain direction (Fig. 1). The reference transducer was mounted on the vessel surface to compensate for temperature effects on the active transducer during treatment.

Prior to treatment, each transducer was calibrated, and a calibration curve was developed by measuring the voltage differences caused by an induced compressive displacement of the ends of the transducer. The wood specimen with transducers was then placed in a Newport Scientific Extraction Vessel, and the transducers were connected to a Campbell Scientific 21× Micro datalogger through the wall with a high-pressure fitting. This unit collected voltage differences over the course of treatment at 2-s intervals, and these data were later downloaded to a personal computer for analysis and storage. This measuring system enabled us to evaluate the effects of the rates of initial pressure application and release on tangential dimensional changes in the spruce samples.

Specimens were subjected to six treatments, and each treatment variable was assessed on

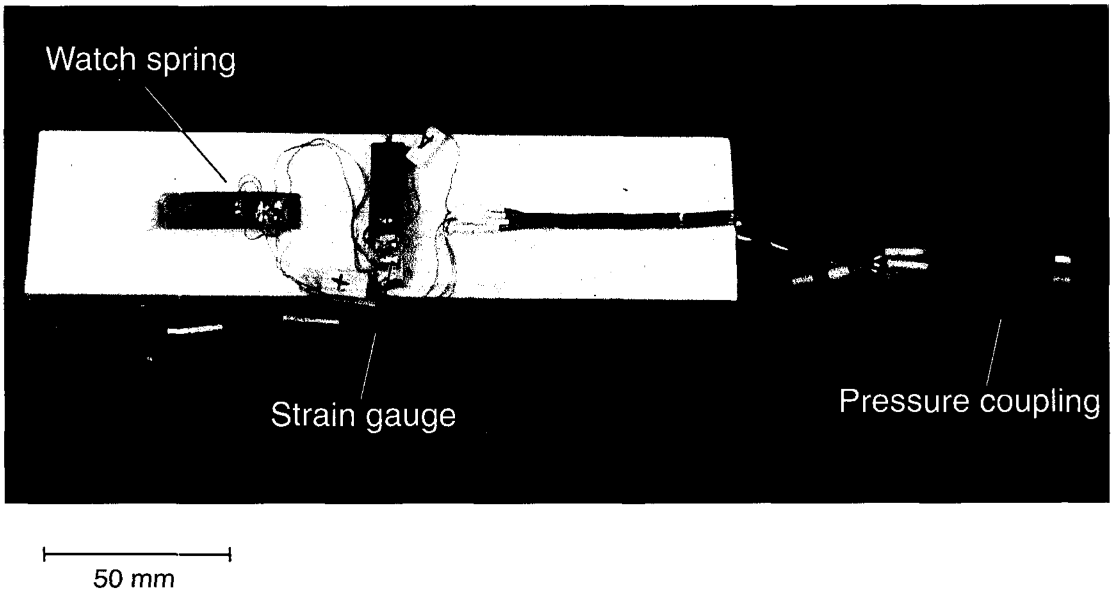

FIG. 1. System used to measure displacement on spruce wood during supercritical fluid impregnation with carbon dioxide.

five specimens. For all treatment cycles, maximum pressure was 13.8 MPa, and temperature was maintained at 60°C. In all processes, we introduced carbon dioxide into the vessel until the pressure reached 5.520 MPa; then we increased pressure to the desired final level with a pressure pump. We controlled the rate of initial pressurization first by metering the carbon dioxide, and then by adjusting the pressure pump to achieve target rates of 1.035, 2.415, and 20.700 MPa/min. Because of system constraints, actual rates were 1.028, 2.332, and 19.769 MPa/min. We also monitored the overall rate of pressurization to 13.8 MPa. The vessel, maintained at 13.8 MPa for 30 min, was then vented at a rate of 1.035 MPa/min (actual venting rates varied from 1.042 to 1.566 MPa/min).

We studied the effects of venting rate on displacement in a similar manner. The vessel was pressurized to 6.9 MPa at a rate of 8.97 MPa/min, and to 13.8 MPa at 2.898–4.092 MPa/min. At the conclusion of the process, the venting rate was adjusted to a target rate of 0.345, 2.415, or 3.450 MPa/min. Actual rates were 0.359, 2.560, and 3.788 MPa/min. The voltage changes of the transducer induced by displacement were continually monitored over the treatment process. In addition, copper constantan thermocouples attached to the surface of specimens enabled us to monitor venting rates on wood temperature. The thermocouples were fed through a high-pressure fitting outside the vessel, and then attached to the Micro datalogger. Temperature inside the vessel was monitored continuously over the process, and temperature differential from the target temperature (60°C) was reported.

Following treatment, the specimens were examined for degree of displacement. A 5-mm-thick section was cut from the center of each sample. The growth rate of the samples was categorized as slow (>10 rings/cm), medium (5–10 rings/cm), and fast (<5 rings/cm). In addition, the ring orientation of each sample was classified as flatsawn or vertical grain, and the surface was evaluated for end splits, ring separation, surface roughness, deformation around knots, and other defects that resulted from the treatment. With these data, we assessed the effect of process variables on maximum and residual displacement, as well as

TABLE 1. *Effect[a] of process variables on displacement and maximum temperature in white spruce lumber during supercritical fluid impregnation with carbon dioxide.[b]*

Treatment	PR_{69} (MPa/min)	PR_{138} (MPa/min)	Venting rate (MPa/min)	Maximum displacement (mm)	Residual displacement (mm)	TD_{max} (°C)
Low pressure	1.030 (0.133)	0.561 (0.097)	1.040 (0.066)	0.475 (0.399)	−0.023 (0.099)	—
Medium pressure	2.332 (0.128)	0.740 (0.041)	1.167 (0.175)	1.653 (0.580)	0.005 (0.227)	—
High pressure	19.766 (1.103)	2.745 (0.107)	1.567 (0.159)	6.515 (3.515)	0.880 (0.547)	—
Slow vent	8.998 (0.947)	2.904 (0.846)	0.359 (0.017)	5.077 (1.244)	1.299 (1.248)	3.3 (1.5)
Medium vent	9.288 (0.771)	4.064 (0.389)	2.557 (0.308)	3.407 (3.759)	0.337 (0.474)	19.9 (2.9)
Fast vent	9.410 (0.642)	4.092 (0.253)	3.785 (0.152)	3.727 (3.749)	−0.052 (0.355)	26.8 (2.5)

[a] Values represent means of 5 replicates per treatment. Values in parentheses represent one standard deviation.
[b] PR_{69} and PR_{138} = pressurization rate to 6.90 MPa and 13.8 MPa, respectively; TD_{max} = maximum temperature drop during ventilation.

the effects of wood characteristics on these parameters.

RESULTS AND DISCUSSION

Displacement during treatment generally increased rapidly as pressure increased, and then declined slightly as the vessel pressure reached the desired level. The time interval required to reach maximum displacement varied with charge (Table 1).

Effect of initial pressurization rate on displacement

Maximum deflection in samples used to study the initial rate of pressurization generally occurred during initial pressurization (Fig. 2). Average maximum displacement was 0.475 mm in samples pressurized at 1.028 MPa/min, 1.653 mm at 2.332 MPa/min, and 6.515 mm at 19.769 MPa/min (Table 1). Permanent displacement (defined as the displacement measured at the conclusion of the treatment cycle) followed similar trends, increasing from −0.023 mm at 1.028 MPa/min to 0.880 mm at 19.769 MPa/min. Clearly, the rate of pressure application can have substantial effects on displacement. Pressure application at relatively slow rates induced both the lowest maximum and permanent displacement, which suggests that some pressure equilibration occurred. The negative displacement at the conclusion of trials at low pressure application rates implies that the wood expanded; however, measurements of the wood did not show marked increases in dimension. We believe that these negative changes reflect some twisting of the wood that induced displacement in the watch spring. One sample subjected to the intermediate pressurization rate also had negative displacement values.

These tests indicated a tendency for samples to undergo maximum displacement early in the process, and then to recover some degree of displacement as the pressure stabilized. This rebounding effect may reflect energy trapped as the wood was compressed and deformed in the early stages of the treatment process. Recovery of the initial displacement was rarely complete, particularly as the rate of initial pressure application increased.

The slowest rate of pressurization employed would require approximately 7 min to approach the critical pressure of carbon dioxide (approx. 7.452 MPa). Although this rate may be slightly slower than those used for conventional treatment of southern pine (*Pinus* spp.), process times for more refractory species range from 2 to 6 or more h. Thus, the slower rate of pressurization necessary to reduce displacement would be of less consequence with these difficult-to-treat species. More treatable species, such as southern pine, will likely equilibrate pressure more rapidly, thus allowing for high initial rates of pressurization.

Effect of venting rate on displacement

The rates of venting at the conclusion of the treatment process could adversely affect wood integrity if the internal pressure exceeds the shear strength of the wood. At that point, the

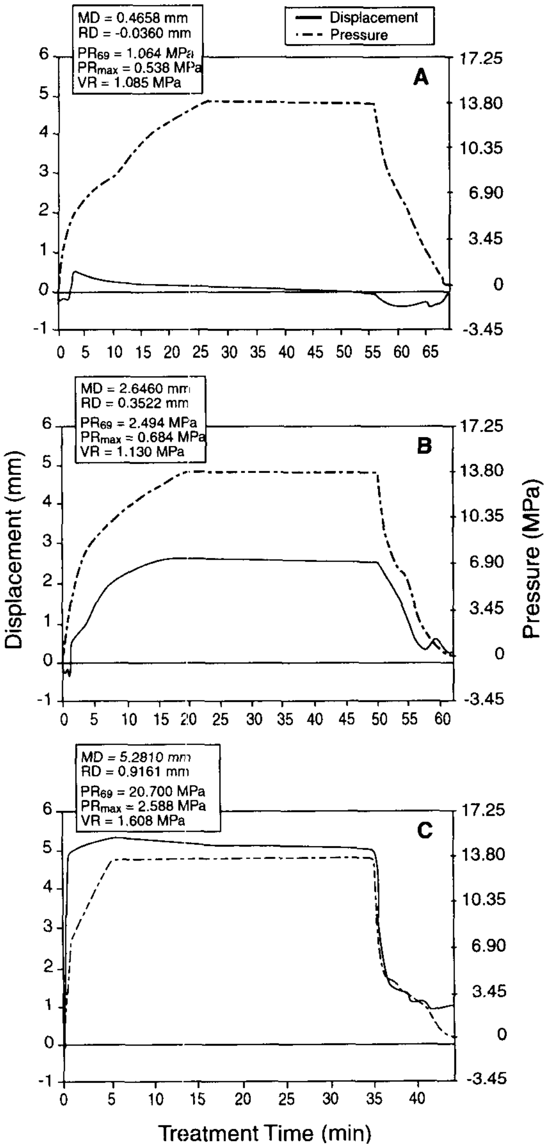

FIG. 2. Effect of rate of pressurization on deformation of white spruce lumber during supercritical fluid impregnation where the target rate of pressurization is (A) 1.035 MPa/min, (B) 2.332 MPa/min, and (C) 19.769 MPa/min. MD = maximum displacement, RD = residual displacement, PR_{69} = pressurization rate to 6.9 MPa, PR_{max} = maximum pressurization, and VR = venting rate.

wood might fail at its weakest points, likely between growth rings and along resin canals or other lines where dissimilar cells adjoin. In our studies of venting rate, we chose an initial pressurization rate that was intermediate to the medium and fast levels explored. This resulted in a modest amount of initial displacement. As in the earlier trials, maximum displacement occurred early in the treatment process as pressure was applied, and declined slightly shortly before the sample was subjected to maximum pressure (Fig. 3).

Increased venting rate had a marked positive influence on degree of permanent displacement. Permanent displacement for specimens vented at 0.359 MPa/min was 1.299 mm. Those vented at 2.560 MPa/min averaged 0.337 mm, and those vented at 3.788 MPa/min averaged −0.052 mm of displacement (Table 1). Clearly, the faster venting had a positive effect on wood displacement. There are a number of possible reasons for this effect. Whereas faster venting will increase the potential pressure differences between the interior and surface of the wood, faster venting may decrease the total period of time during which the differential exists. Alternatively, it may reduce the time during which the differential exceeds the material properties of the wood. In addition, wood tends to be more plastic under higher pressure and temperature conditions. In any case, the end result would be less displacement.

Effect of wood characterization on displacement

Neither growth rate nor ring angle had any consistent relationship with the degree of displacement of the samples. While it is possible that increasing replication might help delineate differences, our results suggest that these characteristics have less influence on dimensional change than permeability.

Effect of venting rate on temperature

One possible cause of displacement or failure during treatment is a sudden temperature change associated with either introduction of liquid carbon dioxide or venting at the conclusion of the process. In the case of our process, which introduced liquid carbon dioxide into

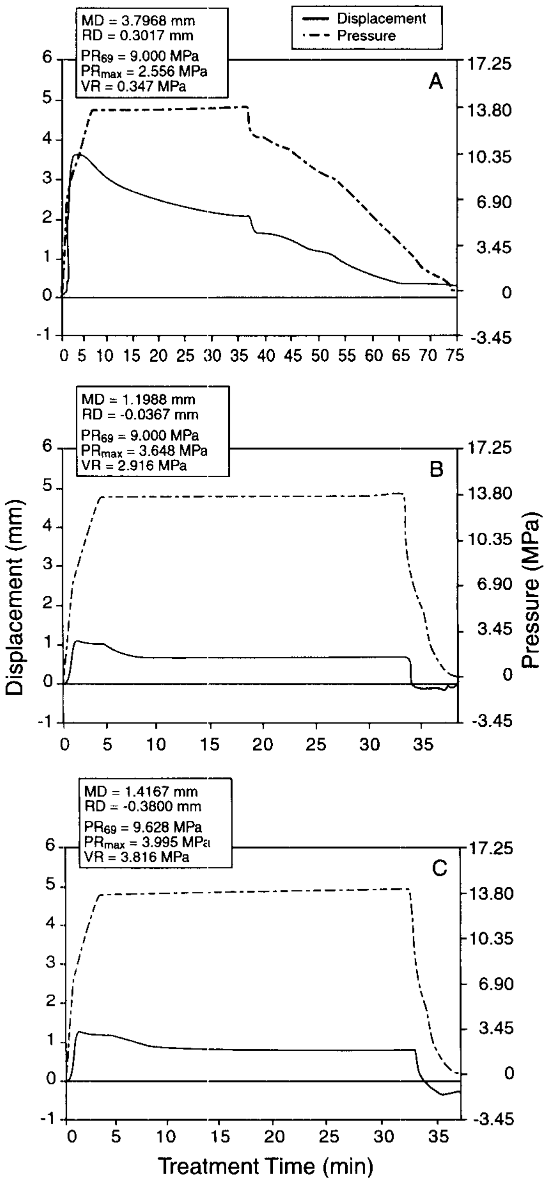

FIG. 3. Effect of venting rate on deformation of white spruce lumber during supercritical fluid impregnation with carbon dioxide when the target venting rate is (A) 0.359 MPa/min, (B) 2.560 MPa/min, and (C) 3.788 MPa/min. Measurements as defined in Fig. 2.

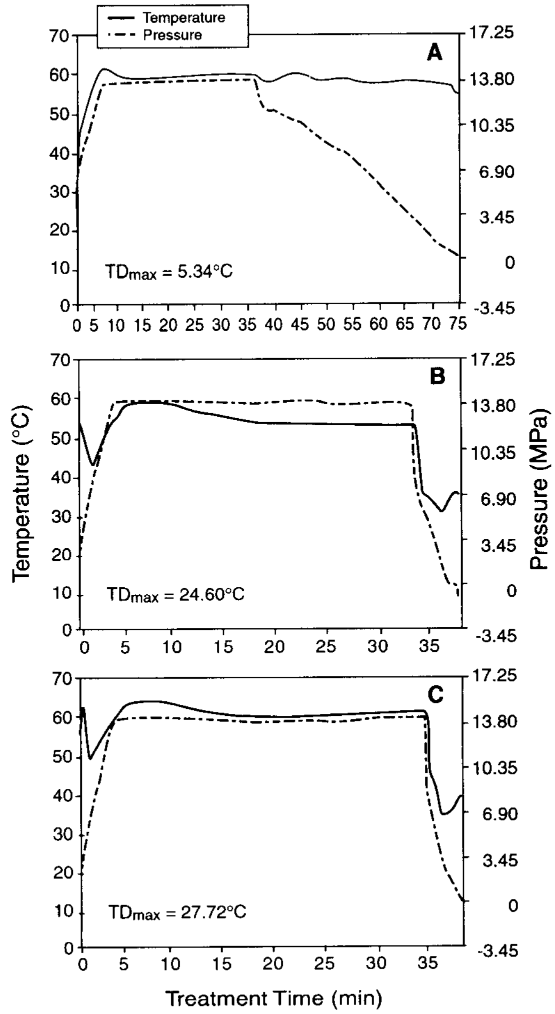

FIG. 4. Wood temperature during supercritical fluid impregnation when samples are pressurized to 13.8 MPa at a rate between 2.905 and 4.092 MPa/min at an initial temperature of 60°C, held for 30 min, and then vented at (A) 0.359 MPa/min, (B) 2.560 MPa/min, and (C) 3.788 MPa/min. TD_{max} = maximum temperature drop during ventilation.

the vessel and then used the pumps to raise the pressure above the critical temperature, the difference in temperature change at the start of the process should be relatively small. Temperature differentials in the venting experiments ranged from 8 to 14°C when an initial pressurization rate between 8.998 and 9.412 MPa/min was used to reach 6.900 MPa (Fig. 4). As a result, the initial temperature was depressed from 60°C to a minimum of 45°C during the first 5 min of the treatment cycle. The target temperature of 60°C was then recovered within 10 min. Temperature at the end of the treatment cycle depended on venting rate.

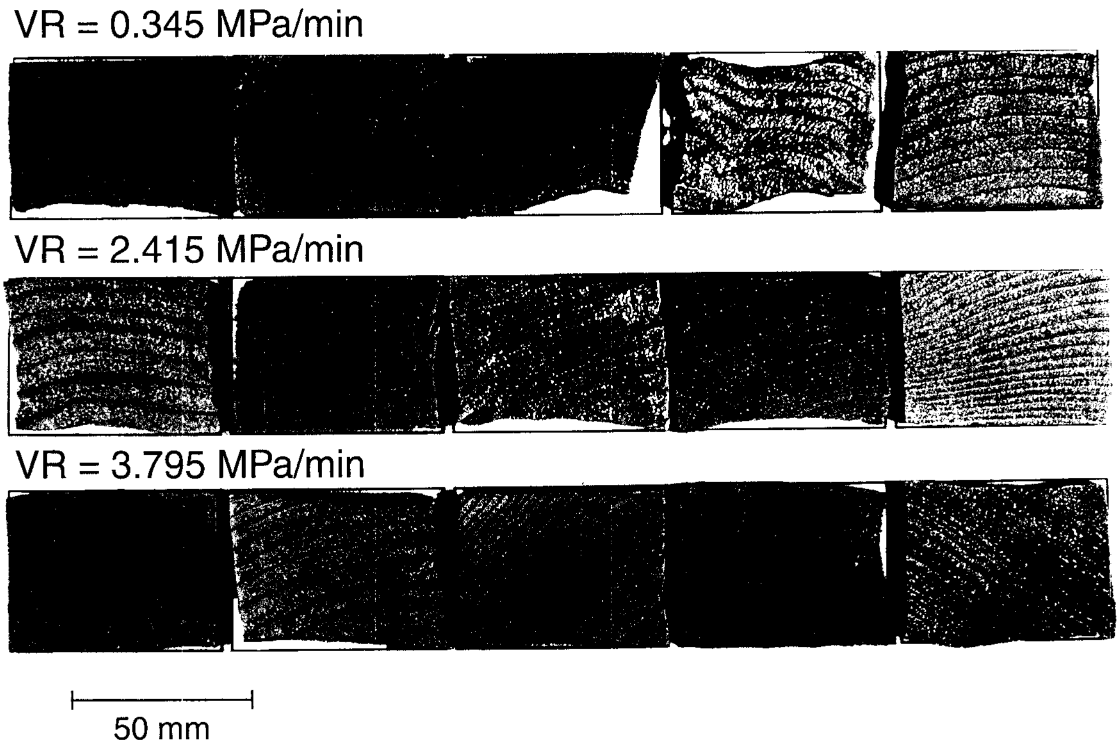

FIG. 5. Condition of selected sections cut from white spruce specimens after supercritical fluid impregnation with carbon dioxide under various initial rates of pressurization and final venting rates (VR).

Sharp temperature reductions can occur as carbon dioxide drops from the critical region and becomes a liquid, then a gas. Venting at 0.359 MPa/min from a maximum pressure of 13.800 MPa resulted in temperature drops ranging from 1.2 to 5.3°C (mean 3.3 ± 1.5°C). Venting at 2.560 MPa/min resulted in temperature drops ranging from 17.2 to 24.6°C (mean 19.9 ± 2.9°C). Venting at 3.788 MPa/min resulted in temperature drops ranging from 22.7 to 28.7°C (mean 26.8 ± 2.5°C). These results suggest that temperature differential had little influence on displacement.

IMPLICATIONS

Displacement appears to occur primarily during pressurization or venting, thus reflecting the large differentials between internal and external pressure that develop at these time points (Fig. 5). Slower rates of pressurization appear to minimize maximum displacement. Although the slower rate would increase total treatment time, the increased time is relatively short in comparison with typical treatment times now employed for conventional impregnation of refractory species. A more important outcome of slower pressurization would be a longer time in the subcritical region where biocide solubility is minimal. As a result, carbon dioxide containing little or no biocide will be forced into the wood until the pressure reaches the critical point. Slower pressurization rates would increase the likelihood that the differences between internal and external pressures remain relatively small. Once the critical pressure is reached and biocide solubility occurs, subsequent movement of biocide into the wood would depend on diffusion rather than on mass flow. Thus, a longer treatment period would be needed to achieve a given retention deep in the wood.

Venting rate at the conclusion of the treatment process may also have implications for treatment quality. Rapid drops in pressure may be desirable, not only for reducing displacement, but also for reducing solubility, thus producing higher retentions deeper in the wood. Rapid venting also reduces total process time, thus making the treatment more economical.

CONCLUSIONS

Initial rate of pressurization and venting rate at the conclusion of supercritical carbon dioxide treatment influenced the rate of displacement of white spruce samples. These results suggest that process conditions can be manipulated to reduce potential treatment effects on wood structure, while enhancing treatment efficiency.

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