

# EFFECT OF WOOD CHARACTERISTICS ON PRESSURE RESPONSES DURING SUPERCRITICAL CARBON DIOXIDE TREATMENT

*Philip F. Schneider*

Former Graduate Research Assistant  
Department of Wood Science and Engineering

*Keith L. Levien*

Associate Professor  
Department of Chemical Engineering

and

*Jeffrey J. Morrell*<sup>†</sup>

Professor  
Department of Wood Science and Engineering  
Oregon State University  
Corvallis, OR 97331-5709

(Received March 2005)

## ABSTRACT

The potential for using the anatomical properties of wood to predict response to supercritical fluid impregnation was investigated using an array of hardwood and softwood species. Longitudinal resin canals were a reasonable predictor of softwood response to pressure application, while radial gas permeability and/or fiber dimensions were useful for the same predictions in hardwoods. Most other anatomical characteristics were poorly correlated with pressure response. The results suggest that there is some ability to use limited anatomical measurements to predict the receptivity of a given species to supercritical fluid impregnation, thereby reducing the need for iterative treatment trials to assess suitability of a species for use in this process.

*Keywords:* Supercritical fluids, carbon dioxide, hardwoods, softwoods, permeability, wood anatomy.

## INTRODUCTION

The treatment of wood using biocides solubilized in supercritical carbon dioxide (SC-CO<sub>2</sub>) offers tremendous potential for impregnating wood species that resist ingress of fluids using conventional pressure processes (Ito et al. 1984; Kayihan 1992). While a number of studies have shown that biocides in SC-CO<sub>2</sub> can easily penetrate a number of wood species (Acda et al. 1997, 2003; Smith et al. 1993a,b; Tsunoda et al. 1999; Ward et al. 1990; Tsunoda and Muin 2003), several of these trials have also shown that the materials are susceptible to pressure-

induced defects as well as wide variations in receptivity to treatment (Anderson 1998; Kim et al. 1997; Kim and Morrell 2000; Sahle-Demessie et al. 1995a,b; Sahle-Demessie 1994). These variations suggest that developing treatment schedules and optimizing biocide distribution for this process will be highly species-specific. These features could require repeated testing of each species to optimize treatment. While this process is possible, it is also costly and time-consuming.

An alternative approach to species-specific testing is to use measurements of gas permeability and/or anatomical features to predict pressure changes in the wood during treatments. This approach is limited because it ignores

---

<sup>†</sup> Member of SWST.

more subtle characteristics such as pit aspiration or encrustation that might also affect pressure response, but gross anatomical measurements have been correlated to the movement of liquids in wood and may have a similar application for assessing receptivity to SC-CO<sub>2</sub> treatment (Arganbright and Wilcox 1969; Behr et al. 1969; Buckman et al. 1934; Choong et al. 1972; Comstock and Côté 1968; Cooper et al. 1974; Erickson et al. 1937; Fleischer 1950; Flynn 1995; Koran 1964; Kuroda and Siau 1988; Nicholas and Siau 1973; Proctor and Wagg 1947; Sebastian et al. 1965; Venturino and Arganbright 1979; Von Werner and Liese 1975; Wardrop and Davies 1961; Wiedenbeck et al. 1990). In this report, we test the hypothesis that pressure response during SC-CO<sub>2</sub> treatment can be related to wood permeability and/or anatomy.

## MATERIALS AND METHODS

*Pressure treatments*

Kiln or air-seasoned lumber of eleven wood species was cut into five replicate blocks per species (30 × 30 × 60 mm) (Table 1). The transverse and radial faces of all samples were sealed with 2 coats of a two-part epoxy (Gluvit). A 20-mm-deep hole was drilled into one transverse face of each sample. The tip of a pressure probe (cut from 3 mm o.d. × 2 mm i.d. stainless steel tubing) was coated with epoxy and pressed to the bottom of each hole. After the epoxy cured, a drill was inserted through the probe and used to make a hole 15 mm beyond the original depth. These procedures were similar to those employed previously (Schneider et al. 2003), based upon tests at conventional pressures (Bergman 1991; Cobham and Vinden 1995;

TABLE 1. *Properties of wood species evaluated in SC-CO<sub>2</sub> treatments of this study.*

Wood	Permeability to N <sub>2</sub> (Darcy)			Mechanical values at 12% MC <sup>d</sup>		
	Longitudinal	Tangential	Radial	Specific gravity	Compression strength (kPa)	Tensile strength (kPa)
Black gum <sup>a</sup> ( <i>Nyssa sylvatica</i> Marsh.)	7.504	0.005	0.008	0.50	7,929	3,447
Douglas-fir <sup>b</sup> ( <i>Pseudotsuga menziesii</i> (Mirb.)Franco)	0.027/0.022	0.002/0.003	0.007/0.040	0.51	6,274	2,060
Engelmann spruce <sup>c</sup> ( <i>Picea engelmannii</i> Parry)	0.033			0.33	4,413	
Lodgepole pine <sup>c</sup> ( <i>Pinus contorta</i> Dougl.)	0.038			0.43	5,171	1,999
Pacific silver fir ( <i>Abies amabilis</i> Dougl.)				0.38	3,378	
Ponderosa pine <sup>b</sup> ( <i>Pinus ponderosa</i> Laws.)	0.092/0.132		0.016/0.035	0.42	5,102	2,758
Red oak <sup>b</sup> ( <i>Quercus</i> spp. ( <i>Erythrobalanus</i> group))	0.662/0.352	0.009/0.008	0.024/0.020	(0.62–0.76)	8,646	5,612
Sugar pine ( <i>Pinus lambertiana</i> Dougl.)				0.38	4,068	2,413
Western redcedar <sup>b</sup> ( <i>Thuja plicata</i> Donn)	0.042/0.095	0.001/0.000	0.001/0.013	0.33	4,206	1,517
White fir <sup>b</sup> ( <i>Abies concolor</i> Gord. & Glend.)	0.096/0.110	0.005/0.001	0.002/0.003	0.37	4,137	1,793
Yellow poplar <sup>b</sup> ( <i>Liriodendron tulipifera</i> L.)	0.935/1.084	0.012/0.018	0.012/0.011	0.43	3,999	3,585

<sup>a</sup> Choong et al. (1974) measured at a mean pressure of 121 kPa and a wood MC of 20%.<sup>b</sup> Choong et al. (1972) measured at a mean pressure of 222 kPa and a wood MC of 18% (two values given).<sup>c</sup> Markstrom and Hann (1972) measured at a mean pressure of 121 kPa and a wood MC of 0%.<sup>d</sup> Mechanical properties from Markwardt and Wilson (1935); compression and tensile strengths perpendicular to the grain.

Orfila and Hosli 1985; Peek and Goetsch 1990) and allowed us to measure surface to internal pressure differentials.

The SC-CO<sub>2</sub> treatment was applied to single blocks from two of the eleven test species in a given charge. The blocks were connected to external pressure sensors via capillary tubing fed through the vessel top. Three sensors allowed for simultaneous measurements in two samples and in the surrounding vessel. The vessel was closed and charged with CO<sub>2</sub> to raise pressure at a rate of 276 kPa/minute to a maximum pressure of 10.3 MPa. Pressure was maintained until the sample center and vessel pressures equilibrated. Pressure was then released at a rate of 276 kPa/mm until the vessel returned to atmospheric pressure. Vessel temperature was maintained at 40°C.

#### *Air permeability measurements*

Heartwood samples (12 mm dia. × 10 mm long) were cut with a plug cutter from the same lumber used to produce the treatment samples. Ponderosa pine was the only species from which a matched set of sapwood samples was included. All samples were end-trimmed by hand with a razor blade then conditioned to a constant weight at 20°C and 65% RH. Two sample sets were cut; the first was used to determine air permeability in the three grain orientations (longitudinal, tangential, and radial), and the second set was used to determine permeability in the radial direction after SC-CO<sub>2</sub> extraction. Three sample replicates were cut for each permeability determination.

The SC-CO<sub>2</sub> extraction process was performed by labeling the samples and then placing them in a bag made from fine fiberglass netting. The samples were extracted at 40°C in the treating vessel by pressing with CO<sub>2</sub> at a rate of 280 kPa/min to 10.3 MPa, holding at this pressure for 30 min with no additional CO<sub>2</sub> added, and then venting at 280 kPa/min.

Permeability was determined by measuring air flow through and pressure across individual samples at several average pressures, then calculating superficial gas permeability for these

pressure levels. Samples were individually glued with hot-melt adhesive into holes bored through the center of rubber stoppers. After the adhesive hardened, the samples were placed in the permeability apparatus using high vacuum grease to seal the region between the stopper and the sample holder walls. Air was allowed to flow through the samples so that the inlet pressure was approximately 35 kPa (gauge). Volumetric flow through the samples and pressures going into and exiting from them were measured after 30 s. Additional measurements were made using inlet pressures of 70, 140, 210, 280, and 350 kPa. When determining the longitudinal permeability of red oak and black gum, inlet pressure was restricted to a range from 15 to 140 kPa.

At each pressure condition, superficial gas permeability was determined using the following version of Darcy's law:

$$k_g = \frac{\mu Q L P_2}{A \Delta P \bar{P}} \quad (1)$$

where  $k_g$  is the superficial gas permeability in Darcy,  $\mu$  is the viscosity of air (cp),  $Q$  is volumetric air flow (cm/s),  $L$  is sample length (cm),  $P_2$  is the pressure after the sample (atm),  $A$  is the sample cross-section area (cm<sup>2</sup>),  $\Delta P$  is the difference in pressure across the sample, and  $\bar{P}$  is the average of pressure before and after the sample (atm). Superficial permeability for each sample was plotted against the reciprocal of average pressure, and a regression line was fitted to these data. The resulting equation was then used to calculate permeability at an average pressure of 125 kPa. This pressure was chosen since it was in the range applied to all samples and was similar to values used in the literature (Table 1).

#### *Anatomical measurements*

Anatomical measurements were made on the same lumber used to produce the treatment samples. Single transverse and tangential (20–50- $\mu$ m-thick) sections were cut from each species. All measurements were made either with an ocular micrometer or by analyzing com-

puterized images from a microscope camera. Ray area was determined from five fields of view (100×) on the tangential sections. Radial and tangential cellular measurements were made on the transverse sections. For the softwoods, ten tracheids in the first row of earlywood cells were measured. For the hardwoods, twenty vessels and twenty fibers throughout the earlywood were measured. In those species with resin canals, three to nine canals were measured on each 100-mm<sup>2</sup> section. Percent section area covered by resin canals was based either on the entire section for the pine species, or on an average from five fields of view for Douglas-fir and Engelmann spruce.

### Regression analysis

The results from internal pressure measurements during SC-CO<sub>2</sub> treatment for each species were quantified by the time to reach 35 kPa, time to pressure equilibrium, and maximum surface-to-center pressure differential during pressurization. Single variable regression analysis was used to judge the appropriateness of air permeability and anatomical measurements as predictors of pressure response in samples during SC-CO<sub>2</sub> treatments. The mean values for each predictor variable (permeability or anatomical measurement) were regressed against the mean

values for a single pressure response quantifier. Data were first pooled for all softwood or hardwood species and then analyzed collectively for those predictors applicable to both wood types. The coefficient of determination (*r*<sup>2</sup>) and the direction of association between the two variables for each analysis were determined.

## RESULTS AND DISCUSSION

### Pressure treatments

Internal pressure measurements were used to produce pressure response curves as well as plots showing maximum surface-to-center differences over time. Similar characteristics of these graphs for the different species were selected, and the data corresponding to these were defined as pressure response quantifiers. These unique values for the different species reflected both their permeability and anatomical differences (Table 2). Difficulties such as collapse and sealant failure resulted in fewer than five replicates of some species. In addition, meaningful values for all of the pressure response quantifiers could not be obtained for all species.

An illustration of how pressure responses can be used to categorize species susceptibility to damage during SC-CO<sub>2</sub> treatments is given by comparing the results from sugar pine to those

TABLE 2. Average internal pressure responses measurements in wood during pressurization and venting of supercritical carbon dioxide treatments at 40°C and 10.3 MPa using a 276 kPa/min pressurization and venting rate.<sup>a</sup>

Species	n <sup>b</sup>	Avg. time to 35 kPa (min)	Avg. time to equilibrium (min)	Max. ΔP during pressing (kPa)	Max. ΔP during venting (kPa)	Wood effects
Sugar pine	4	0	0.4 (0.6)	78 (51)	802 (425)	None
Lodgepole pine	4	0	0.9 (0.9)	95 (59)	1257 (649)	None
Ponderosa pine	5	0.6 (0.4)	4.7 (2.3)	268 (115)	1875 (649)	None
Douglas-fir	5	1.2 (0.7)	5.9 (2.8)	375 (214)	2187 (454)	None
White fir	5	6.7 (0.5)	104 (21.7)	2089 (204)	— <sup>c</sup>	Some collapse
Pacific silver fir	2	16.3 (1.3)	— <sup>d</sup>	7247 (1276)	— <sup>c</sup>	Collapse
Engelmann spruce	2	15.8 (4.8)	— <sup>d</sup>	6778 (800)	— <sup>c</sup>	Collapse
Western redcedar	2	12.8 (0.8)	— <sup>d</sup>	5206 (35)	— <sup>c</sup>	Collapse
Black gum	4	14.3 (8.1)	177 (23.9)	6088 (1457)	4840 (573)	Collapse
Yellow poplar	5	8.8 (0.9)	64.8 (11.4)	3130 (432)	4452 (573)	None
Red oak	2	14.0 (1.5)	421 (79.5)	6537 (297)	— <sup>c</sup>	None

<sup>a</sup> Values in parentheses are one standard deviation.

<sup>b</sup> n = number of sample replicates.

<sup>c</sup> Measurement not applicable due to sealant failure.

<sup>d</sup> Measurement not applicable due to sample collapse before pressure equilibrium.

from white fir. Plots for sugar pine illustrate relatively rapid response to pressure application and, initially, to venting (Fig. 1). During venting, internal pressure began to decrease at a rate slower than in the surrounding vessel. This lag in pressure response increased and was at a maximum by the time the vessel was fully vented. These responses resulted in little pressure differential prior to venting. As pressure was released, however, pressure differentials approached 1.25 MPa (Fig. 2). This value, while high, did not exceed the material properties of the species (Table 1) and no evidence of pressure-induced damage was detected. Similar treatment of white-fir heartwood resulted in noticeable lags in internal pressure response during both pressurization and venting (Fig. 3). These delayed responses resulted in much larger internal pressure differentials that approached the reported compression strength for this species (Fig. 4). One of the five samples experienced

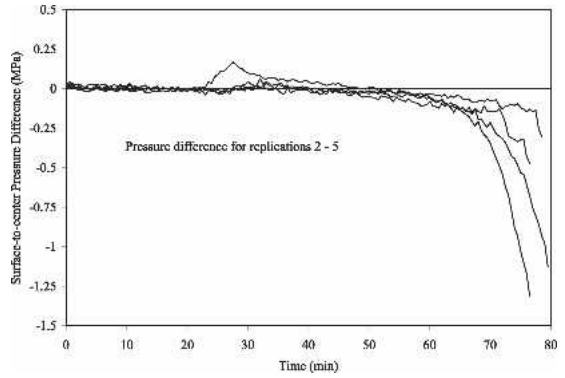


FIG. 2. Surface-to-center pressure differences in five sugar pine heartwood samples during SC-CO<sub>2</sub> treatment.

collapse, while all five had epoxy failures during venting.

The average time required to reach 35 kPa ranged from 0 to 16.3 min (Table 2). Most species showed responses that were expected based upon their permeabilities. Pines are the most

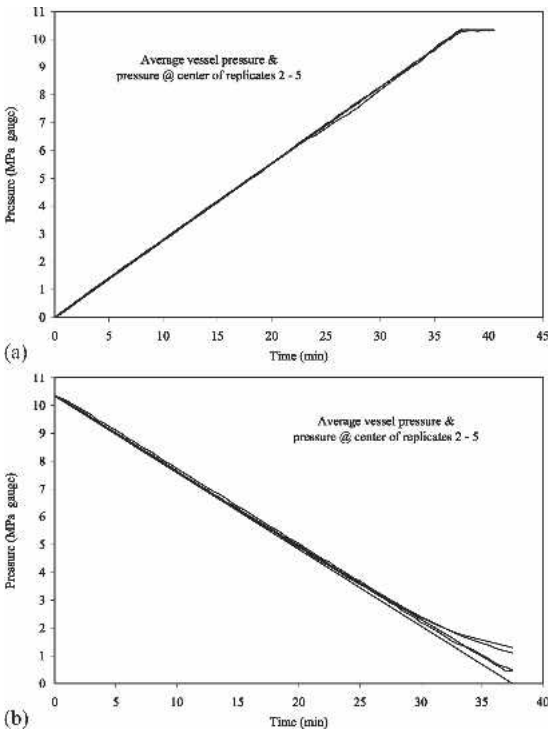


FIG. 1. Pressure measurements at the center of five sugar pine heartwood samples during (a) pressurization or (b) venting at 276 kPa/min following SC-CO<sub>2</sub> treatment.

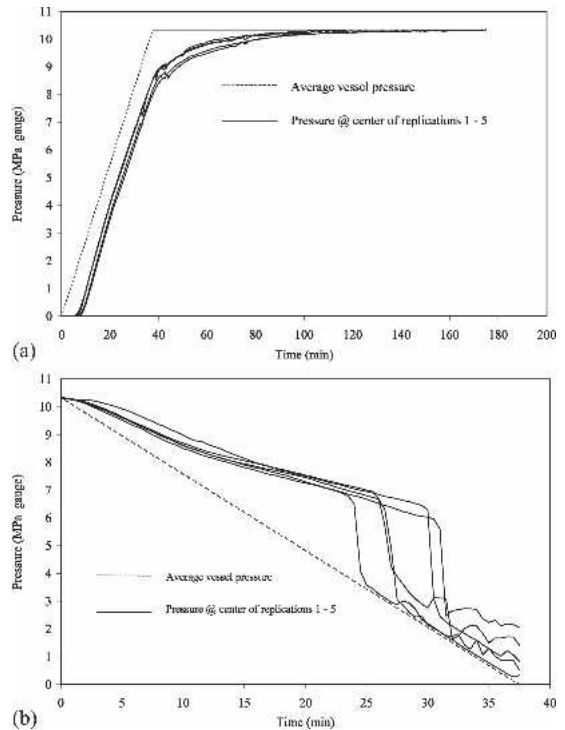


FIG. 3. Pressure at the center of five white fir heartwood samples during (a) pressurization or (b) venting at 276 kPa/min during SC-CO<sub>2</sub> treatment.

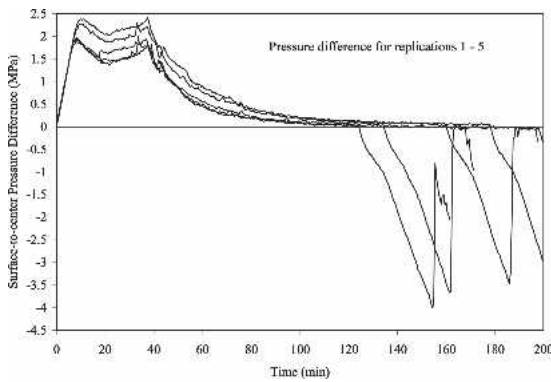


FIG. 4. Surface-to-center pressure differences in five white fir heartwood samples during SC-CO<sub>2</sub> treatment.

permeable and typically, easiest to treat. Pacific silver fir and Engelmann spruce have very low permeabilities and are nearly impossible to treat. However, it is unclear why initial pressure responses were so slow in red oak and black gum. These species are relatively treatable in conventional processes. Possibly the SC-CO<sub>2</sub> treatment reduces the permeability of these species as seen in Table 3. In addition, fluid flow in these species may be more dependent on longitudinal and tangential paths that were restricted in this experiment.

The time required for internal pressure to equilibrate with vessel pressure also varied

widely. Once again pines and Douglas-fir were extremely responsive, equilibrating within an average of 6 min. The remaining species were all much more resistant to pressure, with equalization times ranging from 64 to 420 min to reach equilibrium. Pressure equalization can have important implications such as reducing wood damage and maintaining biocide solubility during SC-CO<sub>2</sub> treatment. Steeper pressure gradients will likely lead to more damage and variable biocide distribution following treatment. Time to pressure equalization was not obtainable in three of the species due to collapse.

The maximum pressure differentials ( $\Delta P$ ) during the treating process can also provide guidance concerning possible effects on material properties of the wood as well as an understanding of the effects of process conditions on biocide solubility, and ultimately, biocide distribution in the wood. Maximum pressure values are given for all species in Table 2 even though some of the samples collapsed during pressing. In these instances, the values provide a measure of the compressive strength of the wood. Average pressure differences during pressurization of lodgepole and sugar pine heartwood were relatively small (<100 kPa), supporting the relatively rapid equilibration previously noted. Ponderosa pine and Douglas-fir developed slightly

TABLE 3. Air permeability of heartwood samples calculated at an average pressure of 125 kPa. Samples were conditioned to 20°C and 65% RH. Values are an average of three samples per species and orientation.<sup>a</sup>

Species	Permeability (Darcy)					Extractive content (%) <sup>b</sup>
	Longitudinal	Tangential	Radial		Radial permeability change (%)	
			Non-extracted	Extracted		
Sugar pine	0.611 (0.072)	0.008 (0.004)	0.014 (0.005)	0.009 (0.003)	-37	3.8
Ponderosa pine (sapwood)	0.191 (0.044)	0.001 (0.001)	0.003 (0.002)	0.031 (0.003)	907	4.4
Ponderosa pine (heart)	0.003 (0.001)	0.002 (0.002)	0.001 (0.000)	0.007 (0.003)	458	4.4
Lodgepole pine	0.266 (0.005)	0.003 (0.002)	0.005 (0.002)	0.003 (0.001)	-38	3.5
Douglas-fir	0.074 (0.015)	0.004 (0.001)	0.001 (0.008)	0.003 (0.004)	136	4.1
Engelmann spruce	0.141 (0.022)	0.023 (0.010)	0.005 (0.002)	0.007 (0.007)	61	2.8
White fir	0.107 (0.015)	0.006 (0.002)	0.003 (0.002)	0.001 (0.000)	-71	1.4
Pacific silver fir	0.037 (0.009)	0.006 (0.003)	0.030 (0.025)	0.001 (0.001)	-97	2.6
Western redcedar	0.079 (0.004)	0.024 (0.013)	0.005 (0.003)	0.008 (0.001)	42	14.1
Yellow poplar	0.339 (0.039)	0.008 (0.006)	0.033 (0.006)	0.071 (0.062)	113	16.1
Black gum	2.340 (0.138)	0.034 (0.010)	0.018 (0.006)	0.006 (0.005)	-65	11.5
Northern red oak	2.750 (0.030)	0.002 (0.002)	0.004 (0.005)	0.000 (0.000)	-93	13.2

<sup>a</sup> Values in parentheses are one standard deviation.

<sup>b</sup> Isenberg (1980 and 1981).



higher pressure gradients during pressurization (268 and 375 kPa, respectively), but these levels were still well below the point where the differences would affect wood properties (Bodig and Jayne 1982; USDA 1999). The remaining species all developed maximum pressure differentials exceeding 2000 kPa and gradients in five of seven of these species exceeded 5000 kPa. Four of the five species with the higher pressure differentials experienced collapse. The reported compression strengths for four of these species were less than the measured pressure differential, helping to explain the observed collapse. The remaining species experiencing elevated pressure differentials was red oak; however, the levels did not exceed the compressive strength of this species and no collapse was observed.

Maximum pressure differentials during venting were not reported for those species experiencing sealant failure or collapse. Although reported, those values for species with long treatment times (white fir, black gum, and red oak) are suspect of being erroneous since it was noticed that the epoxy became soft. In addition, Douglas-fir, black gum, and yellow poplar had pressure differentials that exceeded their reported tensile strengths but showed no signs of splitting. It is possible that the measurement technique resulted in erroneously high values during venting for some species (Schneider et al. 2006). As a consequence, this pressure response during venting was not used for analyses with permeability or anatomical measurements.

#### *Air permeability measurements*

About one-third of the gas permeabilities measured on samples cut from the same materials used for SC-CO<sub>2</sub> treatment were similar to those found in previous studies (Tables 1 and 3). Another third of the measurements were noticeably different from previous results. The remaining measurements from this study did not have comparison values readily available in the literature. Permeability measurements on the softwood species did not reflect internal pressure responses during treating. For the hardwoods,

the radial permeabilities did reflect the relative responsiveness of the three species.

Permeability increased in six of the twelve samples following SC-CO<sub>2</sub> treatment. The greatest increases were observed with ponderosa pine sapwood and heartwood. Permeabilities in Douglas-fir and yellow poplar heartwood more than doubled following treatment, while Engelmann spruce and western redcedar experienced moderate increases following SC-CO<sub>2</sub> treatment. Decreases in permeability were also seen as a result of the SC-CO<sub>2</sub> treatment, but they were not as dramatic. Sahle-Demessie et al. (1995a) also provided evidence for both increased and decreased permeability during similar treatments. Changes in permeability should be anticipated since SC-CO<sub>2</sub> is a reasonable solubilizer of non-polar compounds and would be expected to solubilize many extractives deposited in the heartwood. Coupled with the solubilization of extractives, internal pressure differences could lead to pit aspiration or desaturation. The net effects of these interactions on permeability remain unclear, but, the potential to use SC-CO<sub>2</sub> to improve treatment results through permeability enhancement merits further study.

#### *Anatomical measurements*

Wood anatomy can have important implications on SC-CO<sub>2</sub> treatment. Species with larger and/or more numerous passageways are likely to be more receptive to treatment compared to those with smaller or less abundant passages. Higher receptivity should be shown by more responsive internal pressure. Although all of the anatomical measurements made in this study (Tables 4, 5, and 6) were within the ranges provided by Isenberg (1980 and 1981), pressure responses did not always follow the expected trends.

In the softwoods, tracheid dimensions had little relationship with initial pressure response. For example, sugar pine contained the largest tracheids and had the most responsive initial pressure. However, lodgepole pine contained the third smallest average tracheid area but had

TABLE 4. Average tracheid dimensions and ray areas of selected coniferous species assessed for suitability for supercritical fluid impregnation.<sup>a</sup>

Species	Tangential width ( $\mu\text{m}$ )	Radial width ( $\mu\text{m}$ )	Cross section area ( $\mu\text{m}^2$ )	Length ( $\mu\text{m}$ ) <sup>b</sup>	Ray area (% field of view)
Sugar pine	43 (8)	38 (8)	1,607 (321)	5,900	8.2 (2.2)
Ponderosa pine	28 (4)	33 (6)	947 (262)	3,600	11.3 (1.5)
Lodgepole pine	31 (3)	27 (3)	827 (108)	3,100	5.9 (2.1)
Douglas-fir	37 (6)	38 (5)	1,412 (322)	3,900	10.3 (1.1)
Engelmann spruce	31 (5)	37 (5)	1,150 (267)	3,300	8.9 (0.5)
White fir	31 (3)	26 (5)	794 (159)	3,400	9.4 (0.6)
Pacific silver fir	30 (5)	27 (3)	805 (104)	3,400	8.2 (0.6)
Western redcedar	30 (5)	29 (4)	874 (200)	3,500	6.2 (0.5)

<sup>a</sup> Values in parentheses are one standard deviation.<sup>b</sup> Isenberg 1980.TABLE 5. Average resin canal diameter, frequency, and percent cross-section occupied by resin canals from single transverse and tangential sections ( $100 \text{ mm}^2$ ).<sup>a</sup>

Species	Longitudinal resin canals			Radial resin canals		
	Average diameter ( $\mu\text{m}$ )	Frequency (number of resin canals/ $\text{mm}^2$ )	Area (% cross section)	Average diameter ( $\mu\text{m}$ )	Frequency (number of resin canals/ $\text{mm}^2$ )	Area (% tangential section)
Sugar pine	238 (50)	0.23	1.07	99 (10)	0.36	0.27
Lodgepole pine	141 (22)	0.30	0.48	53 (1)	0.43	0.10
Ponderosa pine	140 (23)	0.25	0.39	42 (2)	0.44	0.06
Douglas-fir	73 (11)	0.13	0.05	29 (4)	0.90	0.06
Engelmann spruce	94 (9)	0.15	0.10	33 (2)	0.76	0.06

<sup>a</sup> Values in parentheses are one standard deviation. Measurements include epithelial cells.TABLE 6. Average cellular dimensions from microscopic observations of twenty hardwood vessels and fibers from single transverse and tangential sections ( $100 \text{ mm}^2$ ).<sup>a</sup>

Species	Earlywood vessel elements				Fibers				Rays
	Tangential width ( $\mu\text{m}$ )	Radial width ( $\mu\text{m}$ )	Cross-section area ( $\mu\text{m}^2$ )	Length ( $\mu\text{m}$ )	Tangential width ( $\mu\text{m}$ )	Radial width ( $\mu\text{m}$ )	Cross-section area ( $\mu\text{m}^2$ )	Length ( $\mu\text{m}$ ) <sup>b</sup>	Area (% field of view)
Yellow poplar	71 (12)	90 (15)	6,104 (1,626)	890	25 (6)	33 (8)	659 (283)	1,900	12.2 (1.2)
Black gum	40 (9)	52 (12)	1,680 (669)	1,330	20 (4)	28 (4)	439 (129)	1,800	16.5 (1.6)
Red oak	306 (34)	365 (39)	88,403 (16,992)	420	15 (3)	18 (4)	220 (86)	1,400	18.8 (9.8)

<sup>a</sup> Values in parentheses are one standard deviation.<sup>b</sup> Isenberg 1981.

nearly identical internal pressure responses to sugar pine. Engelmann spruce contained similar-sized tracheids to those of Douglas-fir, but the spruce was very unresponsive to pressure, whereas Douglas-fir was moderately responsive. Tracheid lengths and ray areas were similarly variable in comparison with pressure response.

Measurements showed that resin canals in sugar pine, lodgepole pine, and ponderosa pine were relatively numerous and large, explaining rapid pressure responses in these species. Douglas-fir and Engelmann spruce had

considerably fewer and smaller resin canals, but pressure responses in Douglas-fir were more similar to those in the pine samples.

In hardwoods, vessels and rays represent critical flow paths during conventional pressure treatment, while fibers in many species are extremely resistant to fluid ingress. For SC-CO<sub>2</sub> treatments, the reverse was seen. Vessel and ray measurements did not follow pressure response trends, but fiber measurements did. Red oak contained the largest vessels and greatest ray area of the three species (Table 6) yet was the least re-



sponsive when pressure was applied. The larger fiber dimensions in black gum and yellow poplar rather than vessel dimensions, appeared to more closely mirror internal pressure responsiveness.

### Regression analysis

Linear regression analyses were used to better determine if there were relationships between the pressure response quantifiers and the predictor variables (permeability and anatomical measurements). Polynomial or exponential curve-fitting procedures or the use of log and inverse transformations did not improve the ability to make associations between the available data. An analysis was considered meaningful if the coefficient of determination ( $r^2$ ) was larger than a critical value and the direction of association was logical for the two variables. For example, a negative (-) association would be expected for time to 35 kPa and radial permeability.

Results from the regression analyses for all eight softwood species are presented in Table 7. At a significance level ( $\alpha$ ) of 0.05,  $r^2$  values of 0.500 or greater indicated a significant relationship between the two variables. None of the permeability measurements and few of the anatomical

characteristics were well correlated with pressure response in softwoods. Longitudinal resin canal diameter and area and radial resin canal frequency were the only predictors that could be considered correlated to pressure response. Of these, only the longitudinal resin canal diameter and area measurements provided logical associations. Longitudinal resin canals could provide a ready path for pressure change, and all three pine species tended to be very responsive to pressure application.

Results from the regression analyses for the three hardwood species are presented in Table 8. At a  $\alpha$  of 0.05,  $r^2$  values of 0.903 or greater indicated a significant relationship between the two variables. Because only three hardwood species were analyzed, implications from the results are limited. In contrast to the softwoods, a number of permeability and anatomical measurements were highly or nearly correlated with the pressure response quantifiers in hardwoods. Of these, radial air permeability (non- or extracted) and fiber dimensions provided logical associations with the pressure response quantifiers. These results indicate that the flow of gases and SC-CO<sub>2</sub> is highly dependent on the radial connections of hardwood fibers. The po-

TABLE 7. Summary of regression analyses for various softwood characteristics against the time to reach 35 kPa, time to pressure equilibrium, and maximum surface-to-center pressure difference in heartwood samples (30 × 30 × 60 mm long) during SC-CO<sub>2</sub> treatments. Permeability and tracheid measurements pooled for eight softwood species; resin canal measurements pooled for five softwood species.<sup>a</sup>

Predictor variable	Time to 35 kPa		Time to equilibrium		Max. pressure difference	
	$r^2$	Slope	$r^2$	Slope	$r^2$	Slope
Longitudinal permeability	0.064	-	0.025	-	0.041	-
Tangential permeability	0.471	+	0.050	+	0.038	+
Radial permeability	0.205	+	0.053	-	0.088	-
Radial permeability (extracted)	0.008	-	0.435	-	0.463	-
Ray area	0.048	-	0.021	+	0.046	+
Longitudinal resin canal diameter	0.187	-	0.642	-	0.667*	-
Longitudinal resin canal frequency	0.276	-	0.132	-	0.234	-
Longitudinal resin canal area	0.233	-	0.553*	-	0.578*	-
Radial resin canal diameter	0.162	-	0.420	-	0.445	-
Radial resin canal frequency	0.236	+	0.570*	+	0.691*	+
Radial resin canal area	0.116	-	0.329	-	0.311	-
Tracheid tangential width	0.195	-	0.088	-	0.096	-
Tracheid radial width	0.062	-	0.367	-	0.323	-
Tracheid area	0.152	-	0.241	-	0.228	-
Tracheid length	0.214	-	0.097	-	0.114	-

<sup>a</sup> Values with an asterisk denote a significant relationship between the wood property and treatment parameter at  $\alpha = 0.05$ .

TABLE 8. Summary of regression analyses for various hardwood characteristics against the time to reach 35 kPa, time to pressure equilibrium, and maximum surface-to-center pressure difference in heartwood samples (30 × 30 × 60 mm long) during SC-CO<sub>2</sub> impregnation. Data pooled for three hardwood species.<sup>a</sup>

Predictor variable	Time to 35 kPa		Time to equilibrium		Max. pressure difference	
	r <sup>2</sup>	Slope	r <sup>2</sup>	Slope	r <sup>2</sup>	Slope
Longitudinal permeability	0.957*	+	0.705	+	0.999*	+
Tangential permeability	0.140	+	0.151	-	0.045	+
Radial permeability	0.732	-	0.944*	-	0.866	-
Radial permeability (extracted)	0.984*	-	0.628	-	0.998*	-
Ray area	0.849	+	0.860	+	0.949*	+
Vessel element tangential width	0.130	+	0.834	+	0.263	+
Vessel element radial width	0.127	+	0.830	+	0.259	+
Vessel element area	0.174	+	0.877	+	0.319	+
Vessel element length	0.010	+	0.468	-	0.020	-
Fiber tangential width	0.707	-	0.957*	-	0.847	-
Fiber radial width	0.523	-	0.999*	-	0.689	-
Fiber area	0.708	-	0.956*	-	0.848	-
Fiber length	0.381	-	0.985*	-	0.550	-

<sup>a</sup> Values with an asterisk denote a significant relationship between the wood property and treatment parameter at  $\alpha = 0.05$ .

TABLE 9. Regression analyses of air permeability and ray area against the time to reach 35 kPa, time to pressure equilibrium, and maximum surface-to-center pressure difference for heartwood samples during SC-CO<sub>2</sub> impregnation. Data for eight softwood and three hardwood species.<sup>a</sup>

Predictor variable	Time to 35 kPa		Time to equilibrium		Max. pressure difference	
	r <sup>2</sup>	Slope	r <sup>2</sup>	Slope	r <sup>2</sup>	Slope
Longitudinal permeability	0.151	+	0.777	+	0.823*	+
Tangential permeability	0.308	+	0.016	+	0.259	+
Radial permeability	0.127	+	0.006	-	0.093	+
Radial permeability (extracted)	0.000	+	0.024	-	0.006	+
Ray area	0.106	+	0.735	+	0.853*	+

<sup>a</sup> Values with an asterisk denote a significant relationship between the wood property and treatment parameter at  $\alpha = 0.05$ .

tential for fibers as pathways for SC-CO<sub>2</sub> is especially promising since these cells are typically difficult to uniformly treat by conventional means. Poor performance of hardwoods against soft rot fungi has long been attributed to inadequate treatment of fibers. The ability of SC-CO<sub>2</sub> to move through and deposit biocide in fibers would be a major enhancement in treatment of these species.

Results from the regression analyses of data pooled for all species are presented in Table 9. At a  $\alpha$  of 0.05, r<sup>2</sup> values of 0.362 or greater indicated a significant relationship between the pressure response and predictor variables. Although longitudinal permeability and ray area measurements were correlated with pressure response, the resulting directions of association for these measurements were illogical. This result

re-enforces the findings above that different predictor measurements will be needed to assess the suitability of different woods for SCF treatment.

## CONCLUSIONS

Internal pressure responses during SC-CO<sub>2</sub> treatments appeared to be marginally predictable using longitudinal resin canal measurements in softwoods, and radial air permeability and/or fiber dimensions in hardwoods. Time required to reach pressure equilibrium in samples tended to be the best quantifier of internal pressure response; while, maximum pressure differences provided insight to the potential for pressure induced defects. This study suggests that there is potential for developing gross anatomical predictors for applying SC-CO<sub>2</sub> impregnation pro-

cesses to new species; although, additional work is warranted on the effects of the process on wood permeability.

## REFERENCES

- ACDA, M. N., J. J. MORRELL, AND K. L. LEVIEN. 1997. Effects of process variables on supercritical fluid impregnation of composites with tebuconazole. *Wood Fiber Sci.* 29(3): 282–290.
- , ———, AND ———. 2003. Supercritical fluid impregnation of selected wood species with tebuconazole. *J. Wood Sci. Technol.* 35:127–136.
- ANDERSON, M. E. 1998. The effects of supercritical CO<sub>2</sub> on the bending properties and treatment defects of four refractory wood species. MS Thesis, Oregon State University, Corvallis, OR.
- ARGANBRIGHT, D. G., AND W. W. WILCOX. 1969. Comparison of parameters for predicting permeability of white fir. *Proc. Am. Wood-Preserv. Assoc.* 65:57–61.
- BEHR, E. A., I. B. SACHS, B. F. KUKACHKA, AND J. O. BLEW. 1969. Microscopic examination of pressure-treated wood. *Forest Prod. J.* 19(8):31–40.
- BERGMAN, O. 1991. Temperature and pressure inside wood during creosote impregnation. Document No. IRG/WP/91-3649. The International Research Group on Wood Preservation, Stockholm, Sweden.
- BODIG, J., AND B. A. JAYNE. 1982. Mechanics of wood and wood composites. Van Nostrand and Reinhold Co., New York, NY. 712 pp.
- BUCKMAN, S. J., H. SCHMITZ, AND R. A. GORTNER. 1934. A study of certain factors influencing the movement of liquids in wood. Journal Series Paper No. 1288. University of Minnesota, Agricultural Experiment Station, St. Paul, MN. 17 pp.
- CHOONG, E. T., P. J. FOGG, AND F. O. TESORO. 1972. Relationship of fluid flow to treatability of wood and creosote and copper sulfate. *Proc. Am. Wood Preserv. Assoc.* 68: 235–249.
- , F. O. TESORO, AND F. G. MANWILLER. 1974. Permeability of twenty-two small diameter hardwoods growing on southern pine sites. *Wood Fiber* 6(1):91–101.
- COBHAM, P., AND P. VINDEN. 1995. Internal pressure monitoring during the treatment of *Pinus radiata* (D. Don.). Document No. IRG/WP/95-40049. The International Research Group on Wood Preservation, Stockholm, Sweden.
- COMSTOCK, G. L., AND W. A. CÔTÉ. 1968. Factors affecting permeability and pit aspiration in coniferous sapwood. *Wood Sci. Technol.* 2:279–291.
- COOPER, P. A., G. BRAMHALL, AND N. A. ROSS. 1974. Estimating preservative treatability of wood from its air-flow properties. *Forest Prod. J.* 24(9):99–103.
- ERICKSON, H. D., H. SCHMITZ, AND R. A. GORTNER. 1937. The permeability of wood to liquids and factors affecting the rate of flow. University of Minnesota, Agricultural Experiment Station, St. Paul, MN, 42 pp.
- FLEISCHER, H. O. 1950. An anatomical comparison of refractory and easily treated Douglas-fir heartwood. *Proc. Am. Wood-Preserv. Assoc.* 46:152–156.
- FLYNN, K. A. 1995. A review of the permeability, fluid flow, anatomy of spruce (*Picea* spp.) *Wood Fiber Sci.* 27(3): 278–284.
- ISENBERG, I. H. 1980. Pulp woods of the United States and Canada: Volume I: Conifers. The Institute of Paper Chemistry, Appleton, WI. 219 pp.
- . 1981. Pulp woods of the United States and Canada. Volume II: Hardwoods. The Institute of Paper Chemistry, Appleton, WI, 220 pp.
- ITO, N. T., T. SOMEYA, M. TANIGUCHI, AND H. INAMURA. 1984. An antiseptic method for wood. Japanese Patent 59-1013111.
- KAYIHAN, F. 1992. Method of perfusing a porous work-piece with a chemical composition using cosolvents. U.S. Patent 5,094,892.
- KIM, G. H., AND J. J. MORRELL. 2000. In situ measurement of dimensional changes during supercritical fluid impregnation of white spruce lumber. *Wood Fiber Sci.* 32(1): 29–36.
- , S. KUMAR, E. SAHLE-DEMESSIE, K. L. LEVIEN, AND J. J. MORRELL. 1997. Bending properties of TCMTB-treated southern pine sapwood using supercritical carbon dioxide impregnation process. Document No. IRG/WP/97-40080. The International Research Group on Wood Preservation, Stockholm, Sweden.
- KORAN, Z. 1964. Air permeability and creosote retention of Douglas-fir. *Forest Prod. J.* 14(4):159–166.
- KURODA, N., AND J. F. SIAU. 1988. Evidence of nonlinear flow in softwoods from wood permeability measurements. *Wood Fiber Sci.* 20(1):162–169.
- MARKSTROM, D. C., AND R. A. HANN. 1972. Seasonal variation in wood permeability and stem moisture content of three rocky mountain softwoods. USDA Forest Service Research Note RM-212. USDA Rocky Mountain Forest and Range Experiment Station, Fort Collins, CO, 6 pp.
- MARKWARDT, L. J., AND T. R. C. WILSON. 1935. Strength and related properties of woods grown in the United States. Technical Bulletin No. 479. USDA, Forest Products Laboratory, Madison, WI, 99 pp.
- NICHOLAS, D. D., AND J. F. SIAU. 1973. Factors influencing treatability of wood. Pages 299–343 in D. D. Nicholas, ed. *Wood deterioration and its prevention by preservative treatments*. Syracuse University Press, Syracuse, NY.
- ORFILA, C., AND J. P. HOSLI. 1985. Pressure development in low permeable woods during the intrusion of air. *Proc. Am. Wood-Preserv. Assoc.* 81:111–124.
- PEEK, R., AND S. T. GOETSCH. 1990. Dynamics of pressure change in wood during impregnation. Document No. IRG/WP/90-3615. The International Research Group on Wood Preservation, Stockholm, Sweden.
- PROCTOR, P. B., AND J. W. WAGG. 1947. The identification of

- refractory Douglas-fir by means of growth characteristics. *Proc. Am. Wood-Preserv. Assoc.* 43:170–176.
- SAHLE-DEMESSIE, E. 1994. Deposition of chemicals in semi-porous solids using supercritical fluid carriers. PhD dissertation, Oregon State University, Corvallis, OR, 301 pp.
- , A. HASSAN, K. L. LEVIEN, S. KUMAR, AND J. J. MORRELL. 1995a. Supercritical carbon dioxide treatment: Effect on permeability of Douglas-fir heartwood. *Wood Fiber Sci.* 27(3):296–300.
- , K. L. LEVIEN, AND J. J. MORRELL. 1995b. Impregnation of wood with biocides using supercritical fluid carriers. Pages 415–428 in K. W. Hutchenson and N. R. Foster, eds., *Innovations in Supercritical Fluids: Science and Technology*. American Chemical Society, Washington, DC.
- SCHNEIDER, P. F., K. L. LEVIEN, AND J. J. MORRELL. 2003. Internal pressure measurement techniques and pressure response in wood during treating processes. *Wood Fiber Sci.* 35(2):282–292.
- , ———, AND ———. 2006. Internal pressure development during supercritical fluid impregnation of wood. *Wood Fiber Sci.* (in review).
- SEBASTIAN, L. P., W. A. CÔTÉ, AND C. SKAAR. 1965. Relationship of gas phase permeability to ultrastructure of white spruce wood. *Forest Prod. J.* 15(9):394–404.
- SMITH, S. M., J. J. MORRELL, E. SAHLE-DEMESSIE, AND K. L. LEVIEN. 1993a. Supercritical fluid treatment: Effects on bending strength of white spruce heartwood. The International Research Group on Wood Preservation, Stockholm, Sweden.
- , E. SAHLE-DEMESSIE, J. J. MORRELL, K. L. LEVIEN, AND H. NG. 1993b. Supercritical fluid treatment: Its effect on bending strength and stiffness of ponderosa pine sapwood. *Wood Fiber Sci.* 25(2):119–123.
- TSUNODA, K., AND M. MUIN. 2003. Preservative treatment of wood-based composites with a mixture formulation of IPBC-silafluofen using supercritical carbon dioxide gas. Document No. IRG/WP/03-40251. The International Research Group on Wood Preservation, Stockholm, Sweden, 8 pages.
- , M. INOUE, T. YOSHIMURA, AND A. ADACHI. 1999. Supercritical fluid application to wood preservation: Part 1: Principle of treatment and mechanical properties of treated wood. Pages 24–30. In K. Tsunoda, ed.: *Proc. 09770184; November 2–5 1998; the 4<sup>th</sup> Pacific Rim Bio-Based Composites Symposium*, Bogor, Indonesia.
- USDA Forest Products Laboratory. 1999. *Wood Handbook: Wood as an engineering material*. Agricultural Handbook 72, USDA, Washington, DC, 466 pp.
- VENTURINO, J. A., AND D. G. ARGANBRIGHT. 1979. Testing the predictability of preservative treatment of wood. *Holzforschung* 33(1):23–27.
- VONWERNER, H., AND W. LIESE. 1975. The influence of anatomical and chemical factors on the pressure treatment of spruce wood. *Holz Roh- Werkst.* 33:451–455.
- WARD, D., T. DINATELLI, AND A. K. SUNOL. 1990. Supercritical fluid-aided wood-polymer composite manufacturer. AIChE meeting, Orlando, FL.
- WARDROP, A. B., AND G. W. DAVIES. 1961. Morphological factors relating to the penetration of liquids into wood. *Holzforschung* 15(5):17–140.
- WIEDENBECK, J. K., K. HOFMANN, P. PERALTA, AND C. SKAAR. 1990. Air permeability, shrinkage, and moisture sorption of lodgepole pine stemwood. *Wood Fiber Sci.* 22(3): 229–245.