EFFECT OF SUPERCRITICAL CARBON DIOXIDE TREATMENT ON GAS PERMEABILITY OF *PAULOWNIA FORTUNEI* HEARTWOOD AND SAPWOOD

Huadong Xu

Associate Professor
College of Engineering and Technology
Northeast Forestry University
Harbin 150040, China
E-mail: huadongxu@yahoo.com

Hamid Reza Taghiyari

Associate Professor
Faculty of Materials Engineering and New Technologies
Wood Science and Technology Department
Shahid Rajaee Teacher Training University
Tehran, Iran
E-mail: htaghiyai@yahoo.com

Milo Clauson

Senior Faculty Research Assistant
E-mail: milo.clauson@oregonstate.edu

Michael R. Milota

Professor Emeritus
E-mail: mike.milota@oregonstate.edu

Jeffrey J. Morrell†

Professor
Department of Wood Science and Engineering
Oregon State University
Corvallis, OR 97331
E-mail: jeff.morrell@oregonstate.edu

(Received July 2018)

Abstract. Many wood species are resistant to penetration of liquids. Impermeability can affect a variety of properties including the ability to deliver preservatives, adhesive bonding, and coating applications. Developing methods for altering this characteristic could help in utilization of impermeable species. One method for altering wood characteristics is through the use of supercritical carbon dioxide (SC-CO_2) which can solubilize a wide range of organic compounds. In this report, we examined the ability of varying SC-CO_2 conditions to improve the permeability of *Paulownia fortunei*. All of the processes tested improved gas permeability and most reduced the frequency of tyloses in the vessels. The results suggest that SC-CO_2 could be used to modify the permeability of this species.

Keywords: *Paulownia fortunei,* tyloses, permeability, SC-CO_2.

INTRODUCTION

The genus *Paulownia* contains six recognized species that are native to China. The two most commonly planted members of this genus, *Paulownia tomentosa* and *Paulownia fortunei*,

* Corresponding author
† SWST member

Wood and Fiber Science, 51(1), 2019, pp. 69-73
https://doi.org/10.22382/wfs-2019-007

are both characterized by the ability to rapidly colonize open sites (Tang et al 1980). This has led to the species being used in mine reclamation or activities where other species have difficultly colonizing heavily degraded soils. At the same time, the rapid growth and ability of these trees to colonize disturbed sites has them to be considered invasive in some environments.

Paulownia produces a wood that has many potential uses, including exterior exposures. *Paulownia*, however, has little natural resistance to decay and must be supplementally treated with preservatives to perform in these environments (Tang et al 1980). Unfortunately, the wood of these species contains abundant amounts of tyloses that block flow and limit preservative penetration. Using this material in exterior exposures will require overcoming these blockages to develop an effective preservative barrier in the wood.

There are a variety of methods for improving the treatment of wood, including controlled drying, solvent drying, microwave treatment, and steaming (Coté 1963; Stamm 1963; Thomas and Nicholas 1966; Siau 1971; Togovnikov and Vinden 2010; Taghiyari et al 2014). These processes are generally aimed at altering the pits to limit aspiration or remove extractives that have been deposited on the pit membranes. Tyloses present a more formidable barrier because they are formed while the tree is alive and are not a function of postharvest processing. Although organic solvents might present one possible approach to removing or modifying tyloses, it is difficult to deliver these materials deeply into the refractory wood. They are also often costly and large quantities of the solvent will remain in the wood after treatment. One alternative to traditional liquid solvents is the use of supercritical carbon dioxide (SC-CO_2). Supercritical fluids (SCFs) have a number of advantages over traditional solvents (McHugh and Krukonis 1994). They have high diffusivities, allowing them to move through wood like a gas, coupled with excellent solvating capabilities that allow them to dissolve a variety of organic molecules at levels approaching those of a liquid solvent. The ability of an SCF to solubilize a given material can be easily adjusted by altering pressure or temperature. SC-CO_2 is frequently used in these processes because it has a relatively low critical temperature and pressure (31.1°C and 7.39 MPa, respectively). This is especially important in wood materials because excess pressure differentials can reduce the structural properties of the material.

SC-CO_2 treatment had variable effects on the permeability of Douglas-fir heartwood (*Pseudotsuga menziesii*), improving gas permeability in most specimens but decreasing it in others (Sahle-Demessie et al 1995). The variations were attributed to the inability to control redeposition of extractives within the wood as pressure was reduced below the critical pressure. Xiao et al (2009) also found that SC-CO_2 treatment with various alcohols as cosolvents improved the permeability of Masson pine (*Pinus massoniana*) and Chinese sassafras (*Sassafras tzumu*). These results suggest that some form of mild SC-CO_2 treatment might be used to improve the permeability of *Paulownia* before traditional pressure impregnation or possibly as part of a two-step SCF process whereby tyloses were removed in step one and a traditional biocide was delivered into the wood in a second step.

The potential for removing tyloses and increasing the permeability of *P. fortunei* using SC-CO_2 was investigated in the following study.

MATERIALS AND METHODS

Sapwood and heartwood boards of *P. fortunei* were obtained from a local source. Cylindrical core samples (15 mm diameter by 50 mm long in the longitudinal direction) were cut from the boards, taking care to segregate sapwood and heartwood samples. The cores were air-dried and later cut in half to produce 15 mm diameter by 25 mm long plugs that were assigned to one of five treatment groups. The cores were conditioned to a stable weight at 23°C and 65% RH before being evaluated for longitudinal gas permeability using previously described procedures (Comstock 1965, 1967, 1970; Milota et al 1995).

Each core was placed into a rubber stopper that had been drilled along its longitudinal axis to the core diameter. The stopper with the core was placed into a test jig so that flow occurred along the longitudinal axis of the core. The core was slightly compressed in the jig to limit flow around the edges of the core. Nitrogen gas was introduced to a pressure of approximately 0.138 MPa (gauge) and rotameters were used to measure flow on the downstream side of the core. The resulting data were used to calculate permeability according to previously described procedures (Comstock 1965; Comstock and Coté 1968; Milota et al 1995) as follows:

$$K_g = \frac{Q}{A} \times \eta \times \frac{L}{\Delta P} \times \frac{P}{P'} \times 10^{-2},$$

where

K_g = gas permeability, μm^2

A = specimen area, cm^2

L = specimen length, cm

Q = gas flow rate, cm^3/s

η = gas viscosity, $Pa \cdot s$

ΔP = pressure drop, MPa

P = pressure at rotameter, MPa

P' = pressure in sample, MPa

The cores were then subjected to SC-CO_2 treatment. Samples were placed into the treatment vessel, liquid CO_2 was introduced, and pressure was raised to either 7.6 or 13.8 MPa over a 3-5 min period at 40 or 80°C. Pressure was maintained at the target level for 30 or 60 min, while the CO_2 was circulated. At the end of the desired time period, the vessel was vented at a rate of 1.0 MPa/min. Ten heartwood and ten sapwood samples were evaluated per treatment condition.

The samples were then reconditioned at the same temperature and RH conditions before being retested for gas permeability as previously described.

Permeability before and after treatment was compared using a series of paired *t*-tests (α = 0.05) for each treatment. In addition, selected samples were examined microscopically on two sections per treatment. Briefly, thin cross-sections were cut 1-2 mm inward from the surface, stained with 1% safranin O, and examined under a light microscope. The presence of tyloses in the vessels was assessed on four or five fields per section by counting the number of vessels with tyloses as a percentage of the total vessels present in that field. The results were compared with examination of sections not subjected to SC-CO_2 extraction. The methodology was, admittedly subjective, but it provided some measure of any gross changes in wood anatomy associated with treatment.

RESULTS AND DISCUSSION

One of the issues associated with gas permeability measurements is the high degree of variability inherent in the process. This variability reflects differences in distribution of conducting elements throughout porous media and is especially critical in ring porous woods because the presence of larger vessels in a sample can markedly alter the permeability. As a result, comparisons between pre– and post–SCF treatment permeability represented a more direct method for assessing any treatment-associated changes.

Gas permeability values for the sapwood and heartwood samples before SCF treatment were virtually identical, averaging 0.00695 and 0.00690 KSp, respectively (Table 1). The presence of tyloses in both materials likely resulted in similar results, although there were substantial variations within individuals samples within a given treatment group.

Exposure of sapwood samples to varying SCF treatments was always associated with increased average gas permeability, although the improvements were not always significant (Table 1). For example, treatment at 7.6 MPa and 40°C for 30 min produced only a 5% increase in sapwood permeability, whereas increasing the treatment time to 60 min improved permeability by 14 0.5% and the results were significant. In both cases,

Table 1. Effects of supercritical carbon dioxide treatment on gas permeability of *Paulownia fortunei* heartwood and sapwood samples.

Temperature (°C)	Pressure (MPa)	Time (min)	Sapwood samples				Heartwood samples			
			Permeability (KSp)[a]				Permeability (KSp)[a]			
			Pretreatment	Posttreatment	Difference (%)	% Improved[b]	Pretreatment	Posttreatment	Difference (%)	% Improved[b]
40	7.6	30	0.0080 (0.0038)	0.0084 (0.0040)	5.0	70	0.0083 (0.0088)	0.0092 (0.0091)	10.8*	100
40	7.6	60	0.0055 (0.0041)	0.0063 (0.0045)	14.5*	80	0.0081 (0.0062)	0.0119 (0.0117)	46.9	100
80	7.6	30	0.0044 (0.0023)	0.0061 (0.0029)	38.6*	100	0.0098 (0.0077)	0.0109 (0.0899)	11.2	75
80	7.6	60	0.0072 (0.0045)	0.0093 (0.0070)	29.2	90	0.0042 (0.0028)	0.0069 (0.0043)	64.3*	100
80	13.8	30	0.0097 (0.0051)	0.0120 (0.0058)	23.7	90	0.0041 (0.0024)	0.0059 (0.0039)	43.9*	100

[a] Values represent means of 10 samples per treatment group and figures in parentheses represent one standard deviation. Asterisks denote that the pre- and posttreatment permeabilities differ statistically by a paired t test ($\alpha = 0.05$).
[b] Represents the percentage of samples from that treatment group where permeability increased following supercritical carbon dioxide treatment.

permeability improved in a majority of samples (70% and 80% of samples for the 30- and 60-min treatments, respectively). Increasing the treatment temperature to 80°C also improved sapwood permeability, but the improvements were only significant for the 30-min treatment time. The high degree of inherent variability in permeability made it difficult to delineate treatment differences; however, sapwood permeability increased in 70-100% of sapwood specimens for the five treatments.

Permeability in heartwood subjected to SCF treatments also improved in most samples (Table 1). Permeability tended to improve to a greater extent with either prolonged treatment time or increased pressure, although the differences were not always significant. For example, permeability increased by 10.8% and 46.9%, respectively, for the 30- and 60-min treatments at 40°C and 7.6 MPa, and 11.2% and 64.3%, respectively, for the same treatment times when the temperature was increased to 80°C. Increasing pressure to 13.8 MPa at 80°C also produced significant improvements in permeability. Permeability also improved in more heartwood specimens with 100% of the samples seeing increased permeability in four of the five treatments. These results indicate that SCF with carbon dioxide induced substantial changes in permeability of this material.

Gas permeability serves as a measure of overall permeability in the wood, but it does not provide data on what anatomical features of the wood have been affected. *Paulownia* is characterized by the presence of tyloses in the vessels that restrict fluid flow. The tremendous solvating properties of SC-CO_2 have the potential to solubilize many materials including many epoxies and other sealants (Schneider et al 2005, 2006). They could have a similar effect on tyloses. Comparisons between thin sections cut from plugs not subjected to treatments with those subjected to various SCF treatments showed a general reduction in the percentages of cells with tyloses following treatment except for the 30-min treatment of sapwood samples at 80°C and 7.6 MPa, and the 60-min treatment for heartwood

Table 2. Effect of supercritical carbon dioxide treatment on frequency of tyloses in vessels of *Paulownia fortunei*.

Temperature (°C)	Pressure (MPa)	Time (min)	Cell with tyloses (%)	
			Sapwood	Heartwood
—	—	—	60.95	72.02
40	7.6	30	45.79	55.69
40	7.6	60	48.02	56.72
80	7.6	30	66.67	50.93
80	7.6	60	50.63	67.21
80	13.8	30	44.25	42.00

samples under the same conditions (Table 2). Changes in tyloses frequency were not significant, generally less than 25% reductions, but they indicated that SC-CO_2 was capable of removing or redistributing materials associated with a general improvement in gas permeability.

The results suggest that some form of SCF treatment might be useful for altering the permeability of species such as *Paulownia*. These processes would have obvious applications for preservative deposition, and one facility in Denmark currently uses SC-CO_2 to impregnate Norway spruce. The advantage of this process is that careful selection of temperature and pressure conditions could allow treatment and extraction to occur simultaneously. Less aggressive extraction conditions could also be used to alter surface permeability to enhance properties such as resin penetration and bonding properties.

CONCLUSIONS

SCF treatment produced consistent improvements in gas permeability in *P. fortunei* that were associated with reductions in the percentage of cells containing tyloses. The results suggest that SCF treatment could be used to enhance permeability as a means of improving preservative treatment of this species.

ACKNOWLEDGMENTS

The senior author gratefully acknowledges the financial support of the Fundamental Research Funds for the Central Universities of China (2572018BL08), Research and Development Project of Application Technology in Harbin (2017RAQXJ078), and the China Scholarship Council (201706605016).

REFERENCES

Comstock GL (1965) Longitudinal permeability of green eastern hemlock. Forest Prod J 15(10):441-449.

Comstock GL (1967) Longitudinal permeability of wood to gases and non-swelling liquids. Forest Prod J 17(10): 41-46.

Comstock GL (1970) Directional permeability of softwoods. Wood Fiber Sci 1:283-289.

Comstock GL, Coté W Jr. (1968) Factors affecting the permeability and pit aspiration in coniferous sapwood. Wood Sci Technol 2:279-291.

Coté WA Jr. (1963) Structural factors affecting the permeability of wood. J Polym Sci Pol Sym 2(1):231-242.

McHugh MA, Krukonis VJ (1994) Supercritical fluid extraction: Principles and practice. Butterworth-Heinemann, Stoneworth, MA.

Milota MR, Tschernitz JL, Verrill SP, Mianowski T (1995) Gas permeability of plantation loblolly pine. Wood Fiber Sci 27(1):34-40.

Sahle Demessie E, Hasan A, Levien KL, Kumar S, Morrell JJ (1995) Supercritical carbon dioxide treatment: Effect on permeability of Douglas-fir heartwood. Wood Fiber Sci 27:296-300.

Schneider PF, Levien KL, Morrell JJ (2006) Effect of wood characteristics on pressure responses during supercritical carbon dioxide treatment. Wood Fiber Sci 38(4):660-671.

Schneider PF, Morrell JJ, Levien KL (2005) Internal pressure development during supercritical fluid impregnation of wood. Wood Fiber Sci 37(3):413-423.

Siau JF (1971) Flow in wood. Syracuse University Press, Syracuse, NY.

Stamm AJ (1963) Permeability of wood to fluid. Forest Prod J 13:503-507.

Taghiyari HR, Oladi R, Miri-Tari SM, Habibzade S (2014) Effects of diffusion drying schedules on gas and liquid permeability in *Paulownia fortunei* wood. Bosque (Valdivia) 35(1):101-110.

Tang RC, Carpenter SB, Wittwer RF, Graves DH (1980) Paulownia- a crop tree for wood products and reclamation of surface-mined land. South J Appl For 4:19-24.

Thomas RJ, Nicholas DD (1966) Pit membrane structure on loblolly pine as influenced by solvent exchange drying. Forest Prod J 16(3):53-56.

Togovnikov G, Vinden P (2010) Microwave wood modification technology and its applications. Forest Prod J 60(2): 173-182.

Xiao ZP, Lu XN, Lu JS (2009) Effect of co-solvent on supercritical CO_2 treatment on wood permeability. Journal of Fujian College of Forestry 2009(02):178-182.