TREATMENT OF WOOD USING SUPERCRITICAL FLUID PROCESSES

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Abstract

The treatment of refractory wood species poses a major challenge and limits the use of some woods under adverse environmental conditions. While researchers have labored for over 100 years to overcome the limitations of fluid flow through wood, these efforts have produced largely incremental improvements in treatment. The development of effective systems for completely treating wood will require a rethinking of impregnation strategies. One alternative to conventional treatment processes is the use of supercritical fluid treatments. Supercritical fluids behave like gases, allowing them to penetrate deep into the wood, but can solubilize chemicals at levels which approach those found with liquids. In this report, we describe trial with supercritical (SC) carbon dioxide. SC carbon dioxide had no significant effect on bending properties of white spruce heartwood samples probably because the gases rapidly equalize inner and outer pressures. A number of biocides were found to be soluble in SC carbon dioxide, including pentachlorophenol (penta), copper naphthenate and 3-iodo-2-propynyl butylcarbamate (IPBC). Solubility varied with both temperature and pressure, suggesting that retention in wood could be varied using these parameters. Laboratory decay tests of blocks treated with IPBC or penta in toluene or supercritical carbon dioxide indicated that there was no difference in performance between the two solvent systems. The results indicate that SC carbon dioxide treatment of wood is technically feasible and further studies are planned.

1. Introduction

Wood exhibits remarkable resistance to deterioration, owing to the presence of a highly integrated matrix of lignin and cellulose. The properties of these lignocellulose matrices have resulted in wood lasting hundreds of years in buildings and these properties

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continue to make wood a preferred construction material. At the same time, however, wood is a natural material which a variety of organisms have evolved to utilize under the proper environmental conditions. Some trees have responded to this attack by evolving the presence of heartwoods which are resistant to microbial or insect attack, either through the presence of silicates or the synthesis of toxic polyphenols. Builders have long known of the decay resistance of naturally durable species and their preference for these woods has led to historical depletion of supplies (Graham, 1973). Even today, there are insufficient supplies of naturally durable species to meet all wood needs. Furthermore, in many species, only old growth heartwood has high durability and society is in the midst of a heated debate on whether these forests should ever be cut.

As an alternative, less durable species can be impregnated with synthetic biocides using combinations of pressure vacuum, and temperature to force chemical into the wood. This method comprises the bulk of the wood preservation industry in North America and entails operations by over 500 treatment facilities (Micklewright, 1991). These processes depend upon the ability of fluids to move through the lumens and across the pit membranes of a non-uniform, semi-porous material. In most species, basic fluid flow is limited by pit permeability. Pits in the sapwood are generally open (unaspirated) and free of deposits which might block fluid flow. As sapwood dies, the sugars present in the ray cells undergo reactions to produce phenolic compounds which may collect on the pit membranes, occluding flow. Pits may also close or aspirate, further limiting the ability of fluids to penetrate into the wood. As a result, lumber from species such as southern pine, ponderosa pine or red pine, which have high percentages of sapwood, are more easily treated, while those with narrower sapwood bands such as Douglas-fir, lodgepole pine, and the spruces are much more difficult to treat because a higher percentage of the lumber surfaces will have exposed, heartwood faces. These differences make it difficult for western and northern treaters to compete against those dealing with more easily impregnated species and have encouraged the search for improved treatment methods.

As we examine efforts to improve treatment it is helpful to review the history of the currently used treatment systems to provide a perspective for identifying future directions for treatment research.

While there have been numerous attempts to improve wood performance by adding extractives and miscellaneous toxicants, the era of "modern" wood treatment has its origins in the 1830's patents by John Bethell of creosote as a preservative and the full cell process to deliver chemical into the wood. This process permitted controlled treatment of wood to specified depths and retentions and remains the most widely used treatment process in North America (Micklewright, 1991). Later, as treaters attempted to control treatment processes, the empty cell processes, which eliminated the initial vacuum and began the impregnation process at either atmospheric or slightly above that level were developed by Rueping and Lowry (Graham, 1973). Later developments have entailed improvements in these processes to produce incremental increases in treatment or to minimize post-treatment problems such as bleeding. Such modifications include the oscillating or alternating pressure methods, the Cellon process, and the MSU process (Barnes, 1993).

In addition to modification of treatment cycles, efforts have also been made to modify the wood to improve treatability. These efforts have resulted in the development of radial drilling or through boring of critical groundline zones of utility poles to produce more uniform treatment, the development of kerfing to control post treatment checking, and most importantly, the development of incising to increase the percentage of more permeable transverse face exposed to the treatment solution (Perrin, 1978; Graham, 1983). Incising has been the focus of extensive recent research and development as treaters attempt to improve treatment uniformity while minimizing the visual impact of the incising process (Morris et al., in press). Despite improvements in incisor technology, the effects of these practices are largely limited by the depth of individual incisions.

In general, efforts to improve treatment of thin sapwood species have been limited by an inability to move fluid through aspirated and occluded pits in the heartwood. As a result, treatments of many of these species are designed to create barriers or envelopes of treatment which surround an untreatable core. The integrity of these barriers plays a major role in performance and can severely limit the use of such treatments in extreme environments.

Continuing efforts to incrementally improve pretreatment handling or alter the treatment process are unlikely to overcome the basic inability to completely penetrate wood with conventional fluids. Overcoming these limitations will require a re-evaluation of basic methods for delivering biocides into wood.

There are two basic approaches to improving treatability: developing methods for improving the permeability of wood to fluids or altering the characteristics of treatment fluids so they can penetrate the wood. Altering wood could be accomplished by solvent treatments to open pits and remove encrustations, but the efficacy of these processes are hampered by the same limitations on basic preservative treatment (i.e. the solvent must also penetrate the wood). On a longer term basis, breeding programs could be established to identify provenances with either thicker sapwood or more treatable heartwood. Some treaters indirectly select for treatable heartwood by sourcing their wood from certain areas, but this is a terminal selection since the treatable stock is consumed. Given the relatively small percentage of lumber production from thin sapwood species which is treated (Micklewright, 1991), however, it is unlikely that extensive breeding programs will be established to produce permeable wood.

Altering the properties of the treatment fluid offers the most promising avenue for enhancing preservative penetration of wood. This approach has long been used with ammoniacal based systems where ammonia is used to solubilize copper, but also enhances treatability. Similarly, the use of liquified petroleum gas or methylene chloride as pentachlorophenol solvents was developed to produce clean, paintable finished products, but the higher vapor pressures associated with these systems also enhanced treatment. In both these instances, solvents were modified but penetration of liquid preservative was still the primary mode of treatment. If substantial improvements are to be made in wood treatment, research efforts must shift from an emphasis on liquids to the development of systems based on gaseous biocides.

The application of gaseous materials to wood has long been practiced for remedial treatment against fungi and insects, but these processes were temporary in nature and required reapplication at 5 to 15 year intervals (Morrell and Corden, 1986). Gases can also be used to dimensionally stabilize wood, however, these processes consume large quantities of costly reactant and require relatively large weight increases to produce adequate performance against biological attack (Rowell, 1993).

Two other gas phase strategies which have been less thoroughly explored are dual gas treatments and supercritical fluid treatments. In dual gas treatments, the wood is exposed to the first reactant, which diffuses throughout the wood. A second gas is introduced into the treatment vessel and the two gases react to form an insoluble precipitate as the second gas diffuses into the wood. In theory, this process would produce complete treatment of the wood at levels dictated by the concentrations of each reactant. This process is identical to the double diffusion process for fenceposts which used copper sulfate and chromic trioxide to form insoluble copper and chromium. One such gaseous system would involve carbon disulfide and methylamine, two chemicals which can react to form an insoluble carbamate in the wood. Laboratory trials to produce carbamates in wood, however, produced no noticeable improvements in decay resistance in subsequent decay tests (Lebow and Morrell, unpublished). Failures were attributed to the relatively low yield of carbamates under the acidic conditions present in most wood species. While buffering to increase pH would improve reactions, wood has a large buffering capacity which would be difficult to overcome. Furthermore, buffers would also need to be gaseous since they would need to penetrate to the reaction sites. At present, dual gas phase treatments do not appear feasible for wood protection.

Gas phase treatments are being commercially explored using trimethyl borate, a chemical with a high vapor pressure. The process involves application of a vacuum to the wood, then introduction of trimethylborate, which reacts in the presence of low moisture levels to form methanol and boric acid (Turner et al., 1990). Boron is a highly effective insecticide/fungicide, but it is not suitable for exposure of wood in direct soil contact. Furthermore, the presence of high moisture levels in the wood leads to excessive reaction near the wood surface. As a result, this process is most suitable for wood at or below 6 to 8% moisture content, a level too low for dimension lumber, but one readily attained in many composites where this process has its greatest potential. These treatments, however, will still be limited to materials in non-leaching exposures where protection from insect attack is a primary concern.

The final potential application for gaseous treatments is the use of biocides solubilized in supercritical fluids. Supercritical fluids (SCF) are created when a fluid is heated and pressurized above its critical point. Supercritical fluids have properties which lie between those of liquids and gases. These fluids have the ability to diffuse through materials in a manner similar to gases, but they have solvating powers approaching those of liquids. The low viscosity of a SCF and the relatively high diffusion properties of molecules dissolved in SCF are especially promising aspects for application to wood. A variety of compounds can be used as supercritical fluids including hydrocarbons and ammonia, but carbon dioxide is often the solvent of choice because of its safety, low cost, and relatively low critical pressure and temperature.

The possibilities for using SCF for wood impregnation were first detailed in a Japanese patent (Ito, 1985), however, the listing of potential biocides and the absence of data suggest that no successful treatments were made using the process described. Later, several papers described the use of SCF to impregnate wood with monomers which were subsequently polymerized in situ (Ward et al., 1991; Sunol et al., 1990). While complete treatment resulted, the wood samples were of dimensions which would be readily impregnated using conventional treatment processes and the rates of chemical consumption were extremely high for the final weight gains. More recently, Kayihan (1992) described a process for impregnating porous materials including wood, with preservatives, but once again the wood specimens employed for demonstration purposes were small and the patent only describes the impregnation of wood with a pigmented dye and fails to quantify the levels delivered. Interestingly, this patent claims that the method is suitable for wood preservatives but provides no data on solubility of various biocides in supercritical fluids.

It becomes readily apparent that supercritical fluid treatment of wood is a science with tremendous potential which will require considerable research to bring to commercial application. Yet, the use of SCF techniques represents one of the few technologies capable of revolutionizing wood treatment by overcoming the basic limitations of flow through wood and it is this potential which has encouraged our research program.

The development of effective systems for impregnating wood using supercritical fluids will involve studies to determine solubility of biocides in supercritical fluids, the effects of exposure to supercritical fluids on wood strength, process parameters required to achieve wood treatment, and biological performance of wood treated with biocides solubilized in supercritical fluids.

2. Materials and Methods

Strength Effects: The effects of high pressure on wood properties have been well documented (Walter and Whittington, 1970). As the pressure is raised, gradients between the outer and inner wood surfaces develop, leading to crushing and deformation. This effect is most noticeable with softer wood species such as spruce, but almost any species will eventually crush under pressure. The pressures employed with supercritical fluid treatments exceed 6.84 MPa, a pressure which can easily cause collapse in most wood species. However, SCF are believed to immediately penetrate the wood, resulting in no pressure gradient and minimal effects on strength. This possibility was evaluated using white spruce (Picea glauca) heartwood samples (2.4 by 2.4 by 54 mm long). The small sample size was dictated by the dimensions of the supercritical fluid treatment device. The samples were treated, ten at a time, under selected temperature and pressure conditions in a high pressure vessel. Conditions evaluated were 40 or 80 C, 13.68 or 24.62 MPa, and 30 or 60 minute pressure periods. The treatment cycle began with filling the vessel with carbon dioxide at a pressure of 5.47 MPa at a rate of 90 ml/minute. Pressure was increased to the target level at a rate of 13.68 MPa/minute and held for the selected time and temperature combination.

After treatment, the specimens were conditioned to 12 % moisture content in a room maintained at 20.5 C and 64 % relative humidity prior to being evaluated for static bending and stiffness using ASTM Standard D-143 (ASTM, 1983). Modulus of rupture (MOR) and modulus of elasticity (MOE) were computed for each specimen and sampling precision was calculated for the control group to assure that sampling precision varied by less than 10 percent of the mean. The MOR and MOE of the control group were compared with MOR and MOE measured for the SCF-treated group. The data for the SCF-treated group were subjected to a 3 factor analysis of variance procedure to study the main effects of temperature, pressure, and time levels (Statgraphics, 1991).

Untreated control specimens had MOR and MOE values which were within the range of previously published values for this species (USDA, 1987), and sampling precision was within the desired range.

Wood exposed to supercritical fluids exhibited no evidence of collapse which might occur if excessive pressure gradients developed between the surface and interior of the specimens. The lack of damage suggests that pressures equalized rapidly within the specimens. Specimens treated under SCF-conditions had MOR and MOE values which were not significantly different from those of the untreated controls (Table 1) and an analysis of variance showed that temperature, pressure, and treatment time had no significant effects on MOR or MOE in comparison with untreated controls (Table 2,3).

The results on small specimens indicate that exposure to supercritical fluids has little effect on wood strength when pressures are equalized. Further studies are planned on larger specimens and ultimately, these trials will be extended to larger material.

Solubility of Biocides in Supercritical Fluids: While supercritical fluids may have excellent penetrating ability in semi-porous media such as wood, their ability to solubilize significant quantities of biocide will also play a major role in the success of such treatments. Since biocide must be delivered into the wood at a specific level to confer protection, the supercritical fluid must be capable of solubilizing a chemical at that same level. For example, pentachlorophenol is typically used at solution concentrations ranging from 5 to 9 weight % in heavy oil. Equivalent concentrations in a supercritical fluid will be required for comparable performance. Solubility in supercritical fluids can be accomplished in several ways. Solubility should increase with increasing pressure or temperature, although at certain extremes, solubility improvements will be negligible. Solubility can also be improved through the use of cosolvents which are introduced along with the supercritical fluid. The choice of cosolvent depends upon the chemical nature of the biocide. The solvating effect of the cosolvent tends to increase with molecular weight and remain stable over a range of temperatures and pressures (Dobbs et al., 1986).

For our studies, the solubilities of 3-iodo-2-propynyl butylcarbamate (IPBC), copper naphthenate, pentachlorophenol, and oxine copper were evaluated. Solubility was studied using a modified dual-pump ISCO Series 2000 Supercritical Fluid Extraction system in which supercritical carbon dioxide and possible cosolvents flowed through a bed of biocide in a saturator vessel. Solubility was assessed by weight loss from the saturator vessel as well as from analysis of biocide in recovered solutions in a solvent trap.

Solid biocides were charged to the saturator with 1 mm diameter glass beads to increase bed porosity. Glass wool or metal frits were placed at the inlet and outlet of the saturator to minimize the risk of entrainment or back flow of biocide droplets or particles. A slow flow rate of supercritical fluid, between 0.5 and 0.7 ml/minute, ensured that a saturated solution was attained. The system was operated under varying pressure and temperature conditions to determine the solubility of the selected biocides under each regime.

The results indicated that of the four biocides, only IPBC was highly soluble in supercritical carbon dioxide, with solubilities ranging from 2 to 7 % at 250 bar (Figure 1). IPBC is not suitable for ground contact, but was initially chosen because its structure suggested high solubility in SCF. This chemical, however, tends to leach from the wood when placed in direct soil contact. The remaining chemicals all exhibited lower degrees of solubility, with oxine copper being the least soluble (Figure 1). In general, increasing temperature from 40 to 80 C produced slight improvements in solubility. This effect was most substantial with oxine copper. Pentachlorophenol was moderately soluble in supercritical carbon dioxide but the levels attained would not be suitable for ground contact exposure. Increasing pressure produced marked solubility increases with pentachlorophenol (Figure 2). This effect was most substantial at higher temperatures.

Copper naphthenate was moderately soluble at low temperatures (<0.3%). Increasing temperature from 40 to 80°C increased solubility over 7 fold. Solubilities at higher temperatures would be adequate for delivering sufficient quantities of chemical into wood for performance in ground contact.

The results indicate that biocides can be solubilized in supercritical carbon dioxide without modifying the fluid composition through addition of a cosolvent. The addition of a cosolvent could enhance solubility and this possibility is being explored with these and other biocides.

Development of Impregnation Processes: While the development of solubility data and the demonstration that supercritical fluids have no negative impacts on material properties are important findings, the processes required to deliver biocide solubilized in supercritical fluid to wood still require considerable research. Preliminary investigations have been performed to determine the effects of various process parameters on treatment. Defect free Douglas-fir heartwood dowels (13 mm in diameter by 40 mm long) were cut from kiln dried boards of varying ring densities. The dowels were end-sealed with an epoxy resin to restrict longitudinal flow prior to being conditioned to constant weight at 23 C and 60 % relative humidity.

The dowels were treated using the ISCO 2000 Series Dual Pump System. The wood was added along with a suitable level of copper naphthenate dissolved in dichloromethane and deposited on diatomaceous earth (Figure 3). The vessel was sealed and pressure was raised in 15 bar steps with a 5 minute equilibration period at each step. The system was evaluated at 50 or 80 C and 207 or 275 bar for 0.5, 1.0, 1.5, and 2.0 hours using supercritical carbon dioxide with a cosolvent. At the conclusion of the pressure period supercritical carbon dioxide was vented, causing an abrupt pressure drop which triggered biocide nucleation within the wood. Each treatment condition was evaluated on 4 dowels.

The dowels were first cut in half and sprayed with chrome azurol S to detect the presence of copper in the wood. The middle section of each dowel was ground to pass a 20 mesh screen and analyzed for copper using an Asoma 8620 X-ray Fluorescence Analyzer (Asoma Instruments, Austin, TX).

Copper naphthenate was detected throughout the heartwood dowels. While the samples were small, previous trials of similar material have shown that complete penetration using conventional treatment cycles would not be possible. Examination of the dowel showed no evidence of crushing or deformation due to the elevated pressures employed during supercritical treatment.

Although there was considerable variation in retention of the individual dowels, retentions tended to increase with increasing pressure period (Table 4). Retentions after two hours were generally within a range which would meet the current American Wood Preserver's Association Standards for treatment of wood poles (AWPA, 1992). Increasing pressure from 207 to 275 Bar had little effect on preservative retention, suggesting that the pressure increase did not markedly enhance solubility. Increasing temperature from 50 to 80 C produced slight increases in retention at 207 bar, but only minimal effects at the higher pressure. Higher temperature produced substantial increases in solubility of copper naphthenate in the initial solubility studies and it is unclear why this effect was not detected in the wood samples.

Biological Performance: While depositing chemical using supercritical fluids appears feasible, it is possible that the deposition of a biocide in the absence of a carrier may result in diminished performance. There are a number of reports describing the effects of various carriers on biocide performance, particularly with pentachlorophenol (Arsenault, 1973). Conversely, the higher pressures and gaseous nature of supercritical fluids may result in deeper, more uniform preservative distribution, which might enhance performance at low retentions. These possibilities were explored by treating small blocks with two biocides and exposing the treated blocks using a soil block test.

Soil blocks tests of pentachlorophenol (penta) and 3-iodo 2-propynyl butylcarbamate (IPBC) were established using SCF or toluene as the solvent. Small blocks (1.9 cm^3) were oven-dried, weighed and then treated with the respective chemicals. SCF treatments were performed using supercritical carbon dioxide with a co-solvent. Because SCF treatment results in simultaneous extraction of wood components and deposition of biocide, retentions were determined by analysis of selected blocks in each charge. Pressure and treatment time were varied with each chemical to produce retentions of 0.9, 1.25, 2.15, 2.51, and 6.90 kg/m^3 for penta and 0.381, 0.490, 0.600, and 1.560 kg/m^3 for IPBC. Comparable blocks were treated with IPBC and penta in toluene using a conventional Full Cell Process (30 minute vacuum @ 26 inches Hg followed by 125 psi for one hour) to determine if the treatment method affected performance. Retentions in these blocks were 0.80, 2.58, 3.25, 5.03, and 6.47 kg/m^3 for penta and 0.125, 0.257, 0.439, and 0.508 kg/m^3 for IPBC.

All blocks were stored under cover for 24 hours after treatment, then aerated in a hood prior to oven drying (54 C) for 24 hours. One half of the blocks were subjected to a leaching treatment as per AWPA Standard E10. The blocks were then weighed and sterilized by exposure to 2.5 MRads of radiation.

Soil bottles were prepared by placing garden loam in 454 ml glass jars along with a small feeder strip of alder (Alnus rubra). The jars were loosely capped and autoclaved for 45 minutes at 121 C. After cooling, the edge of each feeder strip was inoculated with one of three test fungi: Postia placenta, Trametes versicolor, and Gloeophyllum trabeum. The jars were incubated until the test fungus covered the feeder strip, then used in the soil block tests.

The blocks were then placed in soil bottles containing the respective test fungus and incubated for 12 weeks at 28 C. The blocks were removed, scrapped clean of adhering mycelium and oven dried (54 C) prior to reweighing to determine wood weight loss.

Additional blocks were exposed in non-sterile soil tests using garden compost to determine the resistance of the various treatments against soft rot fungi. Weight loss was used as the measure of performance for these blocks.

Soil block tests have been completed, while the soft rot burial trials are in progress. Soil block tests of wood treated with the two biocides showed that each was capable of protecting the wood, although the levels required for protection varied with the test fungi. Weight losses with T. versicolor were generally low in the controls, but high in the treated blocks particularly in IPBC blocks leached prior to fungal exposure (Table 5). It is often difficult to obtain high weight losses with this fungus when coniferous wood is used as the test media and the low weight losses in the controls reflect that difficulty. The higher weight losses in the IPBC leached treatments is perplexing as is the lack of a threshold for this chemical against this fungus. IPBC is known to be susceptible to leaching and its specification in the Standards of the American Wood Preserver's Association mandates use in environments where it is protected by a film. Our results would appear to support these recommendations.

Weight losses with penta blocks exposed to T. versicolor were generally low for both SCF and toluene treated materials suggesting little difference in performance of the biocide with different carriers. Evaluation of thresholds for the remaining fungal exposures suggests that most had thresholds which were similar for both solvents although thresholds were sometimes higher when toluene was used as a solvent (Table 6). In general, both toluene and SC treated blocks were susceptible to leaching, reflecting the absence of a heavy oil solvent which would reduce moisture uptake.

The results indicate that supercritical fluid treated blocks perform comparably with blocks treated using toluene as a solvent in a conventional treatment process. Further studies are planned to evaluate the performance of conventional and supercritical fluid treated stakes in field and fungal cellar exposures.

3. Conclusions

The initial results using a small scale treatment vessel indicate that biocides solubilized in supercritical carbon dioxide can be effectively delivered into normally refractory Douglas-fir heartwood at levels which can confer resistance to biological attack. Furthermore, these treatment processes have little effect on wood strength and do not appear to be associated with crushing or other wood deformation. Tests are currently underway to treat small wood stakes which can be exposed in field trials and tested for effects on mechanical properties. These trials, while still preliminary in nature, should permit an assessment of the potential for use of supercritical fluids for wood impregnation.

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Table 1. Bending strengths of SCF-treated and untreated white spruce heartwood.[1]

Test values	Untreated	SCF-treated	Difference[2]
MOR, psi			
n	10	79	
mean	10,349	10,332	17[ns]
variance	2.09271E+6	2.29635E+6	-0.20364E+6[ns]
MOE, psi			
n	10	80	
mean	1.1628E+6	1.2086E+6	-45,800[ns]
variance	2.47281E+10	2.88624E+10	-0.41E+10[ns]

[1] 2.4 mm by 2.4 mm by 54 mm long, tested at approximately 12% moisture content.

[2] Equality of means were tested using a t-test and equality of variances was assessed by Fisher's F-distribution. ns means there is no significant difference between test values of SCF-treated and untreated specimens at the 95% significance level.

Table 2. Analysis of variance for MOR of white spruce heartwood sticks treated using supercritical fluid processes.

Source of variation	Sum of squares	d.f.	Mean Square	F-ratio	Sig. level
Main effects	29,478,074	9	3,275,341	1.047	0.401
Temp.	5,118,545	3	1,706,181	0.545	0.651
Press.	4.738,667	3	1,579,555	0.505	0.679
Time	19,521,397	3	6,507,132	2.080	0.102
2-Factor interactions	105,423,188	27	3,904,562	1.248	0.182
Temp. Press.	51,701,696	9	5,744,632	1.837	0.059
Temp. Time	35,246,410	9	3,916,267	1.252	0.260
Press. Time	18,020,024	9	2,002,224	0.640	0.763
3-Factor interactions	78,007,392	27	2,889,162	0.924	0.578
Temp. Press. Time	78,007,392	27	1,889,162	0.924	0.578
Residual	1,773,476,533	567	3,127,824		
Total	1,986,789,642	630	3,153,634		

Note: 9 missing values have been excluded.

Table 3. Analysis of variance for MOE of white spruce heartwood sticks treated using supercritical fluid processes.

Source of variation	Sum of squares	d.f.	Mean Square	F-ratio	Sig. level
Main effects	177,793,879,304	9	19,754,875,367	0.918	0.509
Temp.	78,999,846,265	3	26,333,282,089	1.224	0.300
Press.	10,005,975,139	3	3,335,325,046	0.155	0.926
Time	88,374,533,386	3	29,458,177,796	2.369	0.251
2-Factor interactions	855,019,004,157	27	31,667,370,524	1.472	0.060
Temp. Press.	380,228,106,299	9	42,247,567,359	1.064	0.041*
Temp. Time	186,514,701,541	9	20,723,855,727	0.963	0.470
Press. Time	281,771,209,855	9	31,307,912,206	1.455	0.162
3-Factor interactions	529,318,084,950	27	19,604,373,517	0.911	0.596
Temp. Press. Time	529,318,084,950	27	19,604,373,517	0.911	0.596
Residual	1.2197999E + 13	567	21,513,226,152		
Total	1.3768942E + 13	630	21,855,463,377		

Table 4. Retention of Copper naphthenate in Douglas-fir dowels following treatment using SC-CO_2 at selected temperatures and pressures.

P (bar)	T (°C)	Treatment Period (hr)	Average Retention[a] (% Cu)	Average Retention (kg/m^3)
207	80	0.5	0.068(0.02)	0.360
		1.0	0.049(0.04)	0.294
		1.5	0.205(0.10)	0.660
		2.0	0.253(0.20)	1.518
207	50	0.5	0.036(0.02)	0.216
		1.0	0.097(0.11)	0.546
		1.5	0.074(0.04)	0.444
		2.0	0.138(0.09)	0.829
275	80	0.5	0.064(0.06)	0.384
		1.0	0.067(0.01)	0.403
		1.5	0.103(0.10)	0.618
		2.0	0.203(0.16)	1.218
275	50	0.5	0.008(0.01)	0.048
		1.0	0.164(0.06)	0.984
		1.5	0.067(0.04)	0.402
		2.0	0.177(0.12)	1.062

[a] Values represent means of 4 replicates. Values in parentheses represent one standard deviation.

Table 5. Decay resistance of ponderosa pine sapwood blocks treated with pentachlorophenol (Penta) or 3-iodo-2 propynyl butylcarbamate (IPBC) in supercritical carbon dioxide (SCF) or toluene as determined using a soil block test.

Chemical	Retention (kg/m^3)	Solvent	Weight loss (%)[a] Postia placenta Leached	Postia placenta Unleached	Trametes versicolor Leached	Trametes versicolor Unleached	Gloeophyllum trabeum Leached	Gloeophyllum trabeum Unleached
Penta	0.80	Toluene	3.70(4.25)	3.40(0.29)	2.88(0.99)	6.90(2.85)	14.22(5.26)	22.04(9.65)
	2.58		1.56(0.77)	2.97(0.14)	1.25(0.13)	3.91(1.07)	1.64(0.28)	3.00(0.14)
	3.25		1.26(0.10)	3.28(0.16)	1.18(0.18)	3.28(0.77)	2.36(0.17)	3.67(0.63)
	5.03		1.77(0.06)	2.69(0.09)	2.12(0.52)	2.69(0.09)	1.67(0.28)	2.53(0.20)
	6.47		1.81(0.11)	3.28(0.22)	1.90(0.12)	3.06(0.13)	2.02(0.29)	3.37(0.28)
Penta	0.90	SCF	1.83(0.59)	1.86(0.17)	7.99(3.86)	3.66(3.09)	2.96(1.21)	1.93(0.18)
	1.24		1.71(0.12)	2.12(0.07)	1.49(0.18)	2.20(0.13)	1.47(0.23)	2.27(0.18)
	2.15		1.64(0.28)	1.84(0.17)	3.09(2.23)	4.45(1.87)	2.27(1.03)	1.62(0.16)
	2.51		1.30(0.26)	2.15(0.14)	1.26(0.14)	2.31(0.38)	1.45(0.23)	2.12(0.18)
	6.90		1.52(0.10)	2.29(0.14)	5.61(4.39)	2.16(0.20)	2.51(1.22)	1.94(0.82)
IPBC	0.125	Toluene	10.53(7.51)	5.67(4.72)	11.95(3.72)	6.05(2.63)	35.43(6.05)	15.27(4.92)
	0.257		1.58(0.75)	3.12(0.18)	18.86(3.83)	3.60(1.13)	24.70(2.54)	10.36(4.62)
	0.439		9.83(7.14)	2.97(0.15)	13.88(4.59)	2.79(0.24)	23.57(7.56)	5.74(3.98)
	0.508		7.37(5.91)	2.61(0.10)	12.66(5.17)	2.41(0.20)	16.96(4.96)	5.73(3.63)
IPBC	0.381	SCF	19.81(7.51)	2.46(0.70)	11.05(9.19)	4.02(2.75)	39.65(8.78)	7.28(4.91)
	0.490		21.70(12.99)	2.53(0.11)	12.33(11.44)	2.27(0.11)	42.16(5.70)	5.15(2.50)
	0.600		26.99(11.83)	2.19(0.15)	7.99(1.75)	2.13(0.25)	39.70(4.87)	2.50(0.23)
	1.560		1.98(0.70)	2.84(1.30)	18.20(5.34)	2.26(0.45)	18.10(2.61)	2.50(0.16)
Control	-	SCF	24.93(3.81)	25.06(3.61)	3.51(1.96	3.23(1.74)	32.87(3.08)	38.68(3.38)
	-	Toluene	28.76(3.15)	34.50(3.53)	3.52(2.00)	4.08(2.15)	32.14(5.95)	35.66(7.81)

[a] Values represent means of 6 replicates. Values in parentheses represent one standard deviation.

Table 6. Estimated thresholds for penta and IPBC against Postia placenta, Gloeophyllum trabeum, and Trametes versicolor as measured using a soil block test.

Estimated Threshold (kg/m^3)					
Chemical	Solvent	Leaching	P. placenta	T. versicolor	G. trabeum
Penta	Toluene	yes	0.90	0.80	2.32
		no	0.81	3.00	1.90
	SCF	yes	0.90	1.20	0.90
		no	0.90	1.10	0.90
IPBC	SCF	yes	1.56	-[a]	-
		no	0.36	-	0.26
	Toluene	yes	1.65	-	-
		no	1.20	-	1.89

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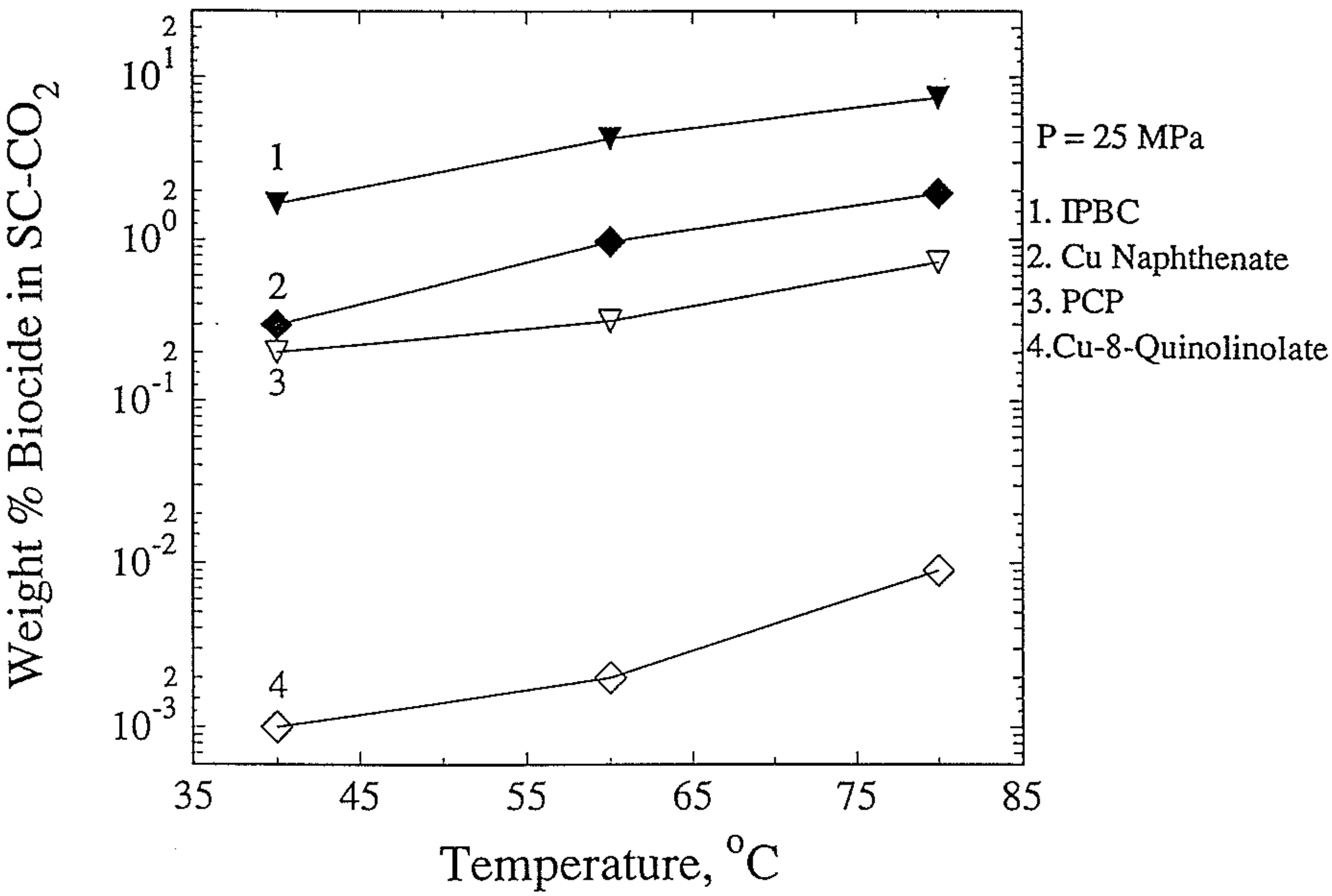

Figure 1. Solubility levels of biocides in supercritical carbon dioxide at 250 Bar and 40,60, or 80°C.

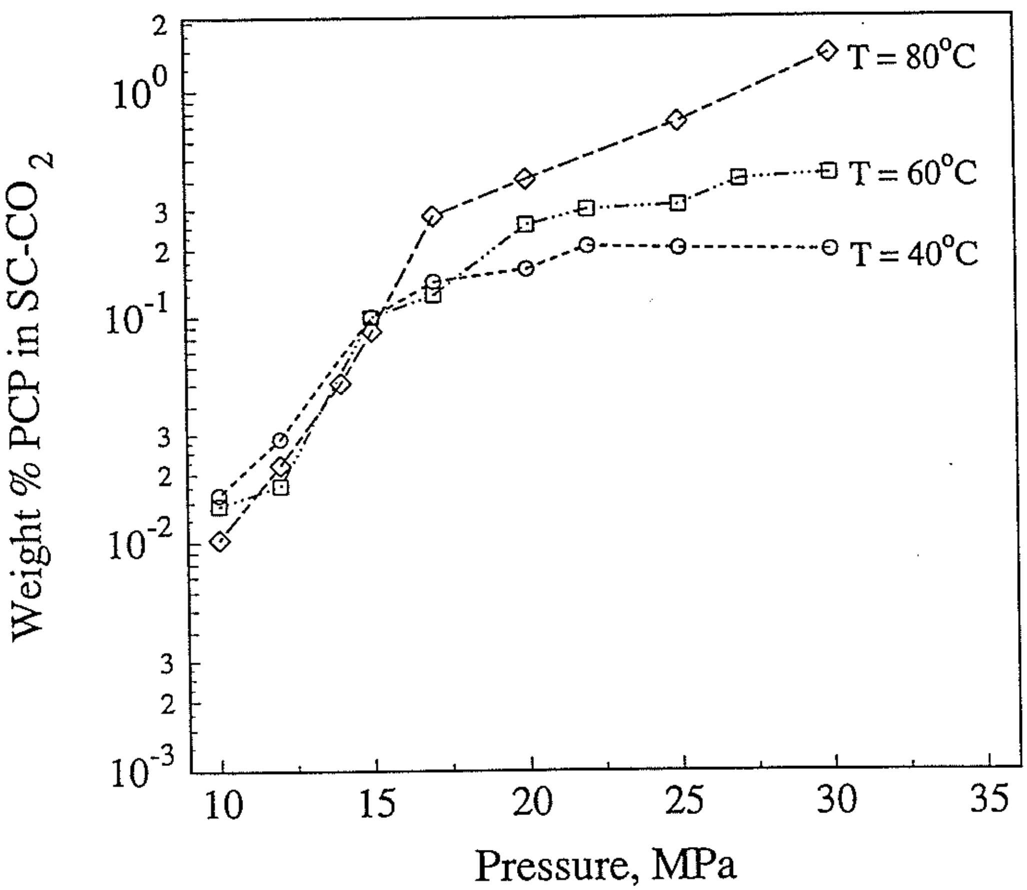

Figure 2. Solubility of pentachlorophenol in supercritical carbon dioxide at selected temperatures and pressures.

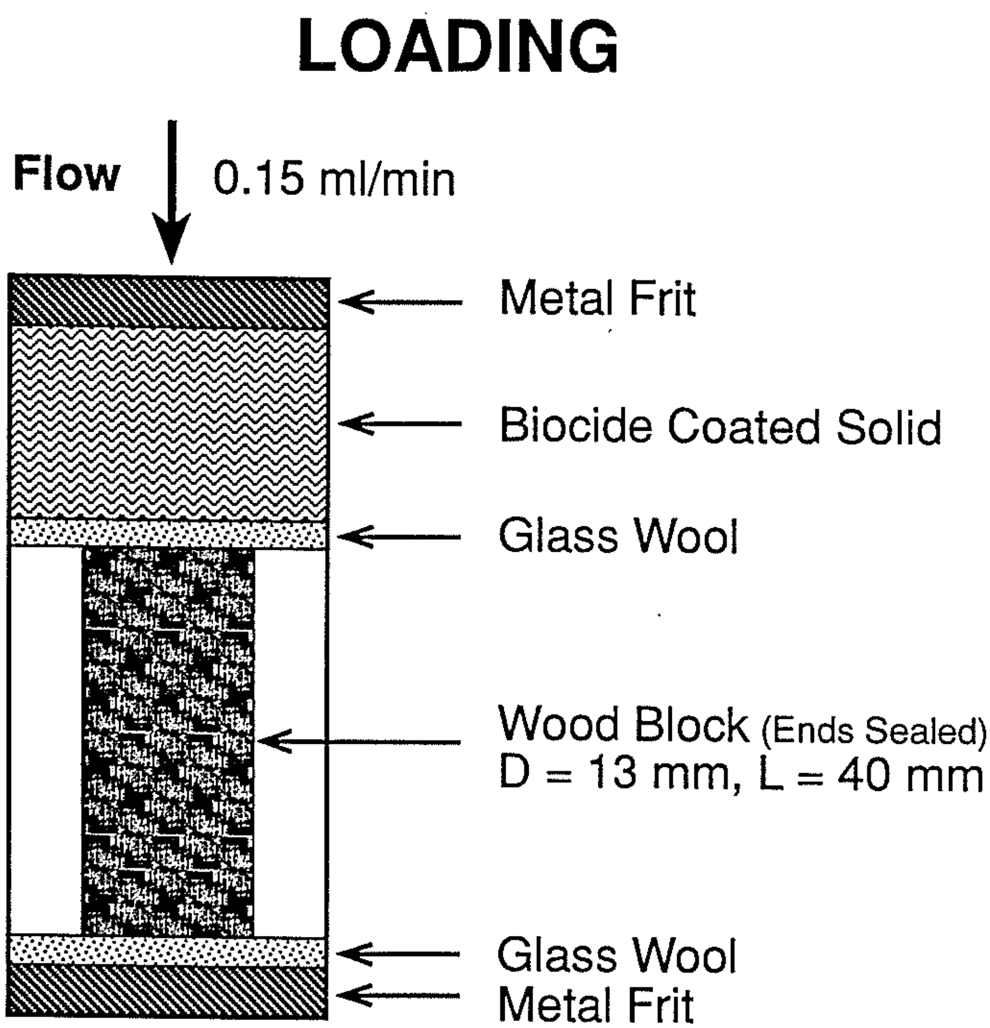

Figure 3. Vessel configuration employed for treatment of Douglas-fir dowels with selected biocides solubilized in supercritical fluids.