AN ABSTRACT OF THE DISSERTATION OF

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Two approaches to improving wood treatability include the modification of pressure schedules during conventional liquid treatments and the use of supercritical fluids (SCFs). In both of these techniques, pressure differences are important for transporting materials into wood. The level of pressure and its change during SCF treatments are also important for controlling the solubility of these materials. Empirical pressure measurements may be used to explain minimal or inconsistent improvements resulting from pressure schedule modifications during conventional liquid treatments and the non-uniform distribution of deposited materials and wood defects that have resulted from SCF treatments.

This investigation provided empirical data on pressure development in wood during pressure processes. Measurement techniques were developed and evaluated during conventional and supercritical carbon dioxide (SC-CO_2) treatments. A technique using probes epoxied into samples and then drilled open at the probe tips was the simplest and most effective method for assessing pressure. However, the hydraulic fluid used to transfer pressure from samples to sensors interfered with measurements during the venting phase of SC-CO_2 treatments. The effects of process parameters and wood characteristics on internal pressure development were investigated by making internal pressure measurements under different treatment conditions. Qualitative comparisons between treatments were made using pressure response quantifiers derived from the pressure measurements. Results from conventional liquid treatments indicated that minor changes in pressure schedules are not

derived from the pressure measurements. Results from conventional liquid treatments indicated that minor changes in pressure schedules are not likely to enhance the treatability of wood. Results from SC-CO_2 treatments indicated differing pressure response delays with different pressing and venting rates, wood species, and grain orientations. These delays resulted in surface-to-center pressure differences which could be used to explain preservative retention distribution, wood collapse and fracture, and wood dimensional changes observed by other investigators. Finally, a preliminary investigation showed that average air permeability and anatomical measurements were poorly correlated with pressure response quantifiers from SC-CO_2 treatments when pooled for eight softwood and three hardwood species. The pooled results for softwoods suggested that only resin canal dimensions were correlated with pressure response quantifiers.

Pressure Measurement in Wood as a Method to Understand Impregnation Processes: Conventional and Supercritical Carbon Dioxide

by

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I understand that my dissertation will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my dissertation to any reader upon request.

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Philip F. Schneider, Author

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DEDICATION

This dissertation is dedicated to my parents
Mr. and Mrs. Fred and Barbara Schneider
whose love and support has allowed me to achieve this goal.

Pressure Measurement in Wood as a Method to Understand Impregnation Processes: Conventional and Supercritical Carbon Dioxide

1 INTRODUCTION

1.1 Background

Wood has several advantages that make it an ideal material for manufacturing and construction. It is a renewable natural material that has lower financial and environmental costs than plastics, steel or concrete. It is relatively easy to machine, fasten, and finish. It is a good insulator and has a low thermal expansion coefficient. In addition, wood can be mechanically broken down and mixed with other materials to produce engineered materials with enhanced properties.

Wood also has disadvantages that must be addressed so that it can be used satisfactorily under adverse conditions. Wood can release and adsorb moisture, causing it to shrink and swell, respectively. As a result wood can warp, check, or split (Panshin and de Zeeuw, 1980). Wood exposed to moderate temperatures and moisture becomes susceptible to attack by a range of organisms. In a forest setting, decomposition is beneficial since it releases nutrients and prevents the accumulation of debris. In a structural setting, such as buildings, bridges, piling, railroad ties, or utility poles, the loss of wood integrity can be detrimental (Eaton and Hale, 1993; Zabel and Morrell, 1992).

Control strategies to protect wood include keeping it dry, isolating it from deteriorating organisms, or impregnating it with chemicals to enhance its physical properties or make it toxic to insects, fungi, and marine organisms. Drying wood soon after it has been sawn and then keeping it dry through handling and building practices should be the first approach to its protection. In general, these methods are simple, low cost, and safe. In some

situations where moisture is inevitable or insects are present that will inhabit dry wood, barriers can be used. These include vapor barriers, coatings, caps, screen, and finely crushed stone. Finally, when moisture and biological or chemical deterioration risks are great, wood must be selected that can resist these hazards. Different species of wood shrink and swell by different amounts; therefore, it may be possible to select species that are more dimensionally stable (Forest Products Laboratory, 1987). In addition, the heartwood zones of some wood species have varying degrees of resistance to biological degradation (Scheffer and Morrell, 1998). Species containing sufficient quantities of chemicals to be considered naturally resistant, however, are limited in supply and relatively expensive. Supplemental chemical treatments are the most versatile and widely used approach to enhance wood properties. Treatments that include water repellants, dimensional stabilizers, fire retardants, and biocides are applied using non-pressure methods (painting, spraying, or dipping) or pressure impregnation processes. Non-pressure methods are reviewed by Eaton and Hale (1993) and Richardson (1993); pressure impregnation processes and factors influencing them are discussed in Chapter 2.

Impregnation processes have evolved to overcome some inherent difficulties with forcing liquids into semi-porous materials. Pressure processes, including thermal and vacuum methods, offer enhanced retention and penetration over most non-pressure methods. Techniques that utilize higher pressure differentials from the surface to the interior of wood, such as the Bethell, Rüping, and Lowry processes, can further improve the receptivity of most wood to chemicals and produce more uniform treatment. The limits to improving impregnation through increased pressure seem to be dependent on the strength and permeability of the wood. The applied pressure should not exceed the crushing strength of the wood. Although, it would seem to be intuitive that elevated pressures increase uptake, this does not necessarily hold for all species. Wood is almost always dried prior to impregnation

in order to make room for the impregnating medium. However, drying can hinder flow by aspirating pits, reducing pit pore size, and forming liquid-air menisci (Stamm, 1967). Attempts to overcome flow blockage problems have led to the development of "dynamic" pressure impregnation techniques including the oscillating and alternating pressure methods (OPM and APM) and the pulsation and sonic processes. Dynamic pressure impregnation processes are not widely used, in part because of the inconsistent improvements these techniques have produced. An alternative approach to overcoming difficulties with liquid flow is the development of "modified-fluid processes". These techniques take advantage of the unique characteristics of specially tailored fluids (liquids, gases, and supercritical fluids) such as low viscosity and reduced surface tension.

One of the difficulties in assessing the value of changing pressure processes or the fluids employed is the inability to accurately understand how pressure changes inside the wood during treatment. The measurement of pressure in wood during impregnation can be used to optimize treating schedules. For example, faster pressure response can be achieved before liquid is added to the treatment vessel; therefore, it may be useful to wait for a desired pressure change in the wood before adding the treating solution. More precise control of preservative kickback (or expulsion of treating medium out of the wood) may be achieved through quantitative measure of internal wood pressure, resulting in the elimination of preservative drippage immediately after treatment. Finally, a qualitative measure of the effectiveness of treatment processes may be obtained through internal pressure measurements since the depth of liquid penetration and the solubility of a biocide in a supercritical fluid (SCF) are correlated to pressure at a given location in wood.

1.2 Research Approach

Several techniques were evaluated to measure pressure in wood during conventional and supercritical fluid impregnation processes. Once an acceptable technique was developed, the influence of process and wood variables on pressure development was investigated. Air permeability and anatomical measurements were made on samples similar to those treated with supercritical carbon dioxide (SC-CO_2) to determine if more easily measured variables could be used to predict internal pressure response during SCF treatments. Finally, internal pressure measurements made during the SC-CO_2 treatments were used to explain difficulties previously encountered in the development of SCF impregnation processes.

A pressure sampling technique must provide measurements that are representative of pressure surrounding the sampling zone, while having an acceptable response time and being relatively simple and inexpensive. The development of internal pressure measurement techniques (in Chapters 3 and 4) was based on the method used by Peak and Goetsch (1990). In this approach, a probe was placed in a wood sample and then attached to a hydraulic line leading out of the treatment vessel to a pressure sensor. A major part of technique development was obtaining an effective seal around the sampling probe. Observations of pressure response for various configurations were used along with residual pressure measurements to verify sampling technique efficacy.

Pressure measurements in wood during conventional (Chapter 3) and SC-CO_2 (Chapter 4) treatments were made to characterize the influence of process and wood variables on pressure response during treatments. Bethell, Rüping, and Lowry processes were used to impregnate ponderosa pine (*Pinus ponderosa* Dougl. ex Laws.) and Douglas-fir (*Pseudotsuga menziesii* (Mirb.) Franco) with air and a mineral spirit solution. A Lowry process using different pressurization and venting rates was used to treat Douglas-fir with SC-CO_2. Both different size samples with single pressure probes and single samples with multiple probes

were treated to examine the influence of flow length on pressure development in Douglas-fir during conventional and SC-CO_2 treatments. Finally, pressure responses during SC-CO_2 treatments were examined for wood species having different permeabilities and strengths.

It may be possible to predict internal pressure responses through the use of air permeability and anatomical measurements (Chapter 5). Air permeability and cellular dimension measurements were made on the species treated with SC-CO_2. The existence of relationships between pressure response variables and either permeability or anatomical measurements was determined.

The delay of pressure response inside wood during SC-CO_2 treatments leads to surface-to-interior pressure differences. These pressure differences were used to help explain the non-uniform preservative retentions and the collapse or fracture of wood reported in this and other SCF impregnation investigations (Chapter 6).

1.3 Research Objectives

The overall goal of this investigation was to develop a better understanding of pressure development in wood during conventional and SCF pressure impregnation processes. To achieve this goal, the following objectives were addressed:

1. To develop a method for measuring pressure in wood during pressure impregnation processes using liquid, gas, and SCF media.
2. To measure the influence of process parameters and wood characteristics on internal pressure response.
3. To identify easily measured wood properties that could be used to explain or predict internal pressure responses during SCF impregnation processes.
4. To utilize internal pressure measurements to explain difficulties encountered in the development of SCF impregnation processes.

2 LITERATURE REVIEW

2.1 Introduction

Wood preservation processes have been an important part of civilization for thousands of years. The earliest documented preservation practices were employed by the Mesopotamian people in what is now modern day Iraq. Evidence of this comes from the biblical story of Noah, when God instructs him to cover his boat with pitch. Simple non-pressure and thermal impregnation processes were likely to have been around from at least 2000 BC. Richardson (1993) theorizes that the thorough distribution of embalming salts and oil in well preserved Egyptian mummies was achieved through a thermal process. Well preserved wooden artifacts from these times were also likely to have been treated in a similar fashion. The thermal process involves placing a permeable item in a treating solution, heating this solution and allowing the item to become thoroughly heated, and then allowing the solution to cool. Air expanding inside of the material upon heating contracts upon cooling. This contraction creates a reduced pressure differential that draws the treating solution in. However without pumps and pressure vessels, the evolution of pressure impregnation processes was hindered until the 19th and 20th centuries AD.

Several pressure impregnation processes have been developed since the 1830's. One of the most recent developments employs a treating medium in its supercritical state. All of the pressure impregnation methods are dependent on the mechanism of bulk flow, which describes the relationship between factors influencing the movement of fluids under a pressure gradient through a porous medium. Continued evolution of pressure impregnation processes is dependent on the complete understanding of pressure response inside of wood as it is

treated. This knowledge can be obtained through theoretical modeling and experimental measurements.

2.2 Pressure Impregnation Processes

2.2.1 The Importance of Pressure

Vacuum: Pressures below atmospheric pressure (a vacuum) have many applications. In the beginning of a process, the application of a vacuum allows a larger pressure difference to be formed between the surface and interior of the wood, leading to faster impregnation, higher retentions, and deeper penetrations (Petty, 1978). An initial vacuum also helps to control the amount of residual pressure in the wood immediately after treating. Residual pressure causes kickback, which is the expulsion of treating medium out from the wood at the conclusion of the pressure period. The application of a vacuum/pressure cycles during a process can reverse the flow of preservative in portions of the wood that contain preservative solution. Reversing the flow may help to reverse pit aspiration in softwoods. At the end of a treatment process, vacuum again is used to control the amount of kickback, retention, and oozing of preservative out of wood immediately after it is removed from the treating vessel. In the case of oil-borne and creosote preservatives, vacuums are also used to remove excess solution from the outer regions of the wood, to limit the potential for bleeding when the wood is placed in service.

Pressure: Pressures above atmospheric are used to accelerate the transfer of treating medium into wood. The minimum amount of external pressure (static or dynamic) needed to induce liquid flow into wood is that required to overcome the surface tension of the treating medium. Siau (1971) provided a good explanation of this process and calculated that at least 1.4 MPa was needed to force water through a typical softwood pit opening having a diameter

of 0.1 μm. Increases in pressure above this minimum are linearly related to increases in liquid retention in wood (Rosen, 1975; Siau, 1970; and Walters 1967). Limits to the maximum applied pressure increases are imposed by various wood properties. Collapse will occur if the pressure gradient across wood exceeds it's crushing strength. The development of pressure gradients is primarily dependent on the permeability of the wood and the rate of pressure application. The benefits of increased pressure are also limited by the highest achievable retention. It is commonly thought that maximum retention is based on the void volume in wood. However, complete saturation of all of the void volume may be impossible. Miller (1961) failed to find improvements in creosote penetration into Douglas-fir even after extended periods of pressure application. Siau (1970) found a relationship between total parenchyma volumes in both hardwoods and softwoods and the difference between theoretical and actual liquid retentions during Bethell treatments using pressures up to 6.9 MPa. Erickson and Balatinecz (1964) and Behr et al. (1969) provide supporting evidence for the lack of fluid flow in parenchyma cells.

Strategies to improve treatability through pressure schedule modification are likely to differ for softwoods versus softwoods because of anatomical and strength differences. If pit aspiration is the limiting factor in softwood treatability, then increasing pressure on closed pits is not likely to yield beneficial results. Instead, the use of pressure cycling to open and close these valve-like structures may produce positive treatment improvements. The potential influence of flow reversal and pressure cycling on softwood pit membranes was demonstrated by Hudson and Henriksson (1956) and Kelso et al. (1963) and supported by Flynn and Goodell (1996). They found that most pits in the treated zones were aspirated in a single direction. Since hardwoods are generally more resistant to collapse from pressure gradients and since their pit membranes do not have a central impermeable region, these woods are more likely to benefit from increased static or dynamic pressure. The influence of pressure

between species of either group is likely to be dependent on the number, size, and condition of openings between cells as well as cell lumen dimensions and presence of extractives and other material that may impede fluid flow.

2.2.2 Process Development

The development of pressure impregnation processes is driven by the desire to increase penetration, control retention, obtain uniform distribution, control kickback, eliminate bleeding, and reduce treatment time. New processes must deliver material into wood in a safe and effective manner, without degrading the material properties of the wood. Processes developed through modification in pressure application techniques can be grouped into static and dynamic pressure processes. Treating medium modifications have led to a new trend in pressurized preservative delivery systems. These shall be collectively called modified-fluid processes since they employ fluids with properties that can be manipulated through temperature and pressure changes or by the addition of co-solvents.

Static Pressure Processes: Static pressure impregnation processes employ relatively slow or infrequent pressure changes. These methods include the thermal, double vacuum, sap-displacement, Bethell, Rüping, Lowry, and high pressure processes (Eaton and Hale, 1993; Richardson, 1993; and Thompson and Koch, 1981). Virtually all current commercial treaters use one of these impregnation processes.

As alluded to in Section 2.1, thermal (or hot-cold) processes date to ancient times, but a U.S. patent was issued in 1867 for this treatment method. Hot solution converts water in the wood to vapor and expands the internal moist air; upon cooling, water vapor condenses and air contracts. This contraction causes a vacuum to develop in the wood which then draws the cool treating solution inside. Advantages of the thermal process include simplicity and low

cost. Disadvantages include a relatively long treatment time and little control over penetration and retention.

The double vacuum process originated in the United States as a single vacuum treatment (Eaton and Hale, 1993), but it was further developed and adopted in Europe and Australia. In general, wood is dried and placed in a treating vessel; a vacuum is pulled for up to an hour, and the vessel is flooded with preservative. The vacuum is then released, and in some instances, a slight pressure may be applied. After a period of time, the solution is drained and a final vacuum applied. The initial vacuum is usually less than the final (20 to 80 kPa versus 10 to 20 kPa absolute). This impregnation method is restricted to applications where permeable woods are used or only a shallow penetration is required, such as for millwork.

Sap-displacement processes have not been widely adopted, but their uniqueness and potential to treat refractory species makes them worth mentioning. The Boucherie process, patented in 1838, and the Gewecke process are performed on green logs, which allows them to take advantage of a water continuum from the original tree sap that is, hopefully, free of air blockages. In the Boucherie process, a cap is fit to the butt end of the log while the top is left open. A preservative solution is allowed to flow through the cap and into the log, sometimes under a slight pressure. The treatment is stopped when preservative exudes out of the top end. In the Gewecke process, the butt end of the log is placed in a treating solution and a vacuum is applied to the top of the log to draw solution through the sapwood. Both of these processes have been successful in treating refractory wood and are relatively inexpensive and simple.

The Bethell (or full-cell) process was originally patented in 1838, but has been substantially modified since. This process is intended to provide the maximum preservative retention by filling cellular voids in the wood with preservative. Before the treating process begins, wood must be dried to below 25 to 40 % moisture content. After drying, wood is

placed in the treating vessel, a vacuum drawn, and treating solution added without breaking the vacuum. After the wood is covered, pressure is applied and maintained until adequate preservative has been forced into the wood. Pressure is then released, preservative removed, and a final vacuum applied. Typically the initial vacuum is around 35 kPa (absolute), the press phase is held between 1,000 and 1,400 kPa, and the final vacuum is around 10 kPa. Bethell treatments are typically used with water-borne preservatives, fire retardants, and dimensional stabilizers or with oil-borne preservatives and creosote in cases were high loadings are specified.

The Rüping (or empty-cell) process was developed in 1902 as a method to save on preservative solution and reduce the bleeding of preservative from finished products. This process is intended only to coat cell lumen surfaces and reduce preservative concentration. Before the treating process begins wood must be dried to below 25 % moisture content. After drying, the wood is pressurized before being flooded with a treating solution. The treating solution is added without releasing the initial pressure, and after this, pressure is increased and held constant until a target gross retention is achieved. Pressure is then released and excess preservative drained. A short vacuum period is the last phase of treatment. Typically, the initial pressure is between 170 and 400 kPa, the pressure phase is held between 1,000 and 1,400 kPa, and the final vacuum is around 40 kPa. This process allows excellent control over retention, but since an initial pressure is applied, kickback increases after wood is removed from the treating vessel.

The Lowry process (also an empty-cell technique) was patented in 1906 and is similar to the Rüping process. It differs only in that no initial pressure is applied, and the final vacuum is stronger (about 10 kPa). This process results in slightly higher retentions, but minimizes the post-treatment kickback problem. Both Rüping and Lowry processes are typically used with oil-borne preservatives. Water-borne preservatives that contain chromium

will react with sugars and various other wood extractives to form unusable precipitates. Since 40 to 60 % of the gross retention is forced back out of the wood, sludging of the treating medium can become a substantial problem (Richardson 1993). In addition, the goal of the empty cell process is to reduce solution consumption, which is much more important with oil- than water-borne solvents.

High pressure impregnation methods currently being commercially used are modifications of traditional Bethell and Lowry processes. High pressure-Bethell processes have been successfully used to treat *Eucalyptus spp.* in Australia (Ellwood, 1957). Arakawa et al. (1998) coined the name "Isostatic Compression Recovery (ICR)" to the high pressure Lowry technique they used. This is appropriate since the process involved compressing wood in a liquid medium such that equal pressure is applied to all surfaces. The wood recovers most of it's original volume when pressure is released. The success of high pressure methods depends on wood permeability, strength, moisture content, and temperature; pressure application rate and level; and on treatment time (Rosen, 1975; Walters, 1967; and Walters and Whittington, 1970). High pressure treatments have produced reduced treatment times or improved preservative retentions. Higher pressure provides a greater rate of mass transfer for permeable species. Increased pressure may have several roles for less permeable species. Higher pressure will force air into smaller pores and provide additional energy to expand air bubbles (Siau, 1971). Arakawa et al. (1998) attributed improved treatment to high pressure compression of the wood that caused pit membranes to become unaspirated or fracture. As compressed wood was allowed to expand, it sucked in the liquid treating medium. High pressure treatments can cause substantial damage to the wood, but unless the wood has been severely collapsed or fractured, bending properties are not changed to a large extent. Rosen (1975) noted that collapse occurred when white and black oak (*Quercus alba* L. and *velutina* Lam.) was pressed up to 13.8 MPa in a liquid treating medium; the severity of collapse

increased with temperature. Ellwood (1957) was not able to press Douglas-fir beyond 2.0 MPa without causing collapse; while, Walters and Whittington (1970) safely applied 5.5 MPa to Douglas-fir at a temperature of 38 °C. At 93 °C, they could only apply 1.4 MPa before collapse occurred. Arakawa (1998), Rosen (1975), and Walters and Whittington (1970) produced almost complete recovery through steaming or boiling wood following high pressure treatments.

Dynamic Pressure Processes: Dynamic pressure impregnation processes employ relatively fast and frequent pressure changes. These processes include the oscillating pressure method (OPM), the alternating pressure method (APM), the pulsation process, and sonic processes (Barnes, 1988; Eaton and Hale, 1993; Nair and Simonsen, 1995; Richardson, 1993). These processes were primarily developed to improve preservative penetration into refractory wood, but they have also produced considerable reductions in treatment time. In theory, these processes limit softwood pits from closing and/or provide the force needed to expand trapped air bubbles or force fluid through small pit openings. One of the disadvantages of these methods is the potential for sludge formation in the treating solution. With the exception of the sonic impregnation processes, wood is left in nearly a green state, at moisture contents above 50 % (wt). Higher moisture contents seem to facilitate treating medium flow into the wood, but higher moisture contents can limit the volume of preservative able to enter (Eaton and Hale, 1993).

The OPM was developed in Sweden around 1950 and is carried out by flooding wood in a treatment cylinder and then cycling pressure between a vacuum (5 kPa) and a pressure of approximately 760 kPa. The low pressure part is held to less than a minute; while, the high pressure portion is increased from under a minute to approximately 6 minutes over the course of treatment. After a sufficient quantity of preservative is taken up by the wood, the treating medium is removed and a final vacuum may be applied.

The APM evolved in New Zealand from the OPM to treat partially dried pine. It is almost identical to the OPM, but no vacuum is used. The minimum pressure is atmospheric pressure (100 kPa), and the pressure maximum is around 1,400 kPa.

The Pulsation process was developed in the 1980's. During a Pulsation process, wood is flooded with preservative, and an initial pressure of about 350 kPa is applied. After a short period, the pressure is returned to the atmospheric level for one minute followed by another press to a slightly higher magnitude. This time the pressure is not held but released for another minute. These pressure pulses are slowly increased in magnitude until a maximum of about 2,000 kPa is reached. At this point, the duration of atmospheric pressure is maintained at 1 min.; while, the period of maximum pressure is increased to about 15 minute intervals.

Sonic impregnation processes differ from the other dynamic pressure processes in that pressure is applied in a series of sharp rapid pulses (a shock wave). Each pulse applied to the liquid medium is similar to a sound wave causing a grain of sand to bounce on a speaker cone. Sonic processes may be used alone at atmospheric pressure or in conjunction with static treatment processes. Burdell and Barnett (1969) provide some insights into how these processes work. One explanation is that a shock wave causes a rapidly accelerating water column to be forced into wood. The shock wave may also travel in solution faster than in the wood causing solution to be advanced into the wood. The wave traveling through the wood then contracts the wood, forcing some of the solution back out of the wood. This back-and-forth motion of the liquid may dislodge aspirated pits. The concussion from rapidly striking waves may break up encrusted materials and dislodge stuck particles from pit openings. Sonic pressure impregnation processes date from 1949 (Avramidis, 1988). This early work showed that the application of 20 kHz shock waves to wood in a water bath could improve water penetration and resulted in a U.S. patent (in Burdell and Barnett, 1969). Burdell and Barnett used 17 Hz shock waves in combination with Bethell, Rüping, and Lowry processes to reduce

treating times by as much as 95 %. More recently, preservative absorption was improved 20 to 50 %, respectively, for ponderosa pine and Douglas-fir heartwood during Bethell treatments using a 30 Hz sonic generator (Nair and Simonsen, 1995).

Modified-Fluid Processes: Modified-fluid impregnation processes include the Cellon, Dow, vapor-phase, and supercritical fluid processes (Hashim et al., 1994; He et al., 1997; Ito et al., 1984; and Richardson, 1993). These methods use treating media that undergo at lease one phase change during the treatment process. In addition, the treating media can also be modified by adding a co-solvent to swell the wood, allowing better penetration, or improve biocide solubility in the media (Kayihan, 1992 and Sahle-Demessie, 1994). Pressure and temperature can also be used to modify treating media characteristics. The principle advantage of these impregnation techniques is the increased rate and depth of treatment penetration due to lower viscosities and surface tensions compared to liquid media. Other potential advantages include applications with composite materials, surfaces free from oily and powdery residues, and regeneration of treating media.

The Cellon and Dow processes (Richardson, 1993 and Zabel and Morrell, 1992) were developed in the 1960's by Koppers Company Inc. and Dow Chemical Company, respectively. The Cellon process involves placing wood in a pressure vessel and purging the vessel with nitrogen to remove oxygen. A Bethell or Lowry pressure schedule is then followed using a biocide dissolved in liquefied petroleum gas (LPG), usually pentachlorophenol in butane. A pressure (approximately 1,000 kPa) is applied by heating the solution to 50 °C. After adequate absorption, pressure is vented and the solution removed. A final vacuum volatilizes remaining solvent from the wood. Before removing the wood, the cylinder is purged with nitrogen to remove residual LPG. A drawback to this process is that the vaporization from a LPG is an adiabatic process, causing residual treating solution and the wood to cool. This means that additional heating is needed and a prolonged vacuum period

must be applied. Other drawbacks include fire and explosion risks and the tendency of wood treated with this process to become susceptible to surface decay in a relatively short period after treating. The Dow processes is essentially identical to the Cellon processes except that the Dow processes uses a non-flammable treating medium, methylene chloride.

Vapor-phase processes for the impregnation of wood were claimed in a 1989 British patent application (Hashim et al. 1994). The first process of this type to be developed involves placing wood in a vessel with a fixed amount of trimethylborate. The vessel is then evacuated and heated to 50 °C to vaporize the trimethylborate. Time is allowed for complete vaporization and diffusion of the trimethylborate into the wood. Releasing the vacuum helps to drive the trimethylborate further into the wood under bulk flow from atmospheric pressure. The trimethylborate vapor reacts with moisture in the wood to form boric acid, which condenses, and methanol, which is drawn off along with non-reacted trimethylborate using a final vacuum. Hashim et al. (1994) were able to dramatically reduce treating times for equivalent boric acid retentions by adding methanol with the trimethylborate. Wood composites treated with this process showed no significant change in static bending properties or internal bond strength, but impact resistance was slightly decreased (Hashim et al. 1994 and 1997). He et al. (1997) report on a second application of a vapor phase treatment. In their investigation they used Bis-[1-(dimethylamino)-2-propanolato]-copper (CuDMAP) in place of trimethylborate. Both vapor phase treatments produced retentions comparable to conventional boron and copper-based pressure impregnation processes. Unfortunately, CuDMAP is expensive to manufacture and highly reactive with water, thus eliminating it from practical consideration.

The use of a supercritical fluid (SCF) as a biocide solvent and delivery system was claimed in 1984 through a Japanese patent (Ito et al., 1984). This patent points out the advantages of rapid impregnation, ability to recycle the treating medium, and the ability to

eliminate incising and post-treatment drying. The patent did not address the fact that most commonly used biocides were not easily dissolved in the implied SCF (supercritical carbon dioxide - SC-CO_2). The Weyerhaeuser Company subsequently patented the use of so-solvents to improve biocide solubility during SCF processes (Kayihan, 1992). Considerable pioneering work has since been done at Oregon State University on treating solution characteristics and wood properties as a result of SCF treatments (Acda, 1995; Anderson, 1998; Hassan, 1995; and Sahle-Demessie, 1994). The impregnation process involves creating a solution of SC-CO_2, co-solvent, and biocide; flowing this mixture past wood at a temperature and pressure near the critical point of CO_2 (31 °C and 7.4 MPa) until the solution reaches the center of the wood; and then, precipitating the biocide in the wood by reducing the vessel pressure. SCF processes offer several advantages over methods using liquid or gas treating mediums. A SCF can penetrate wood more easily than a liquid, yet it can carry a higher preservative loading than a gas. The treating process can be set up so that extractives in the wood which may hinder SCF flow or biocide efficacy can be removed before applying the biocide. The SCF and excess biocide can be recovered. And, the process may be reversible; that is, if the biocide interaction with the wood is not stronger than with the SCF, subjecting the wood to a process similar to the original treatment can remove the biocide.

2.3 Supercritical Fluid Impregnation of Wood

2.3.1 Definition and Properties of SCFs

A supercritical fluid can be defined as the state of a material (such as a solid, liquid, or gas) that has been heated above its critical temperature (T_c) and held at a pressure greater than its critical pressure (P_c). The pressure temperature phase diagram in Figure 2.1 illustrates the different states of a material. The solid lines separating solid, liquid, and gas states indicate

that an abrupt transition of physical properties occurs between adjacent states. The dashed lines separating the SCF state indicates that material properties continuously change as pressure and/ or temperature is increased (Eckert et al., 1986). Thus, SCFs exist as a single state with no phase boundary between them and liquids or gases.

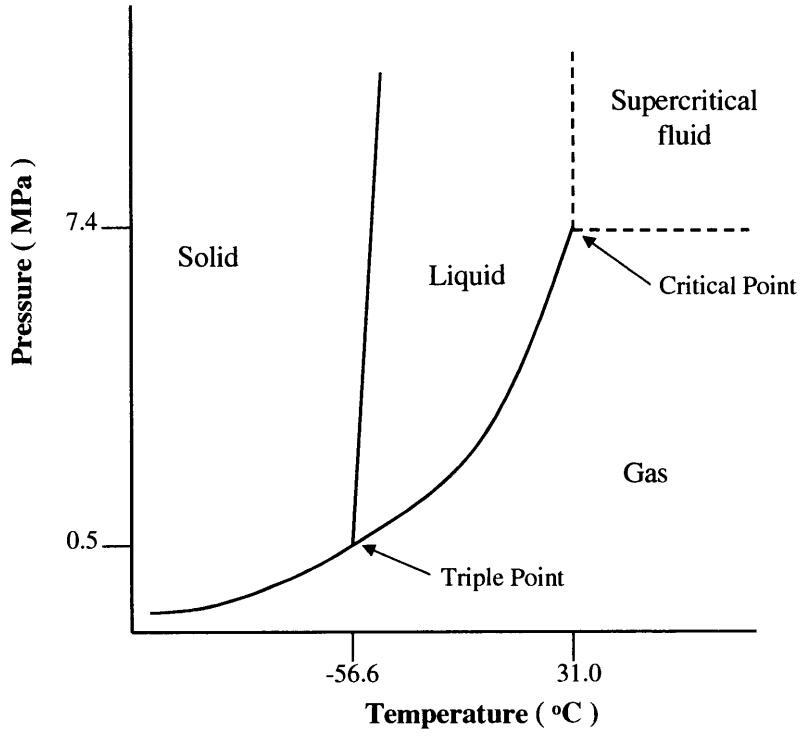


Figure 2.1 Phase diagram for carbon dioxide (Not drawn to scale).

SCFs can also be defined by their unique physical properties. These properties and the ability to change them dramatically through minor alterations of temperature and/or pressure make SCFs ideal processing media. The density, viscosity, and diffusion coefficients of typical SCFs are between those of gases and liquids (Table 2.1). Eckert et al. (1986), Hoyer (1985), and Matson and Smith (1989) provide an overview of SCFs. The relatively high densities of SCFs give them solvating powers similar to those of liquids; while, their low

viscosities and diffusion coefficients bestow good penetration and mass transport characteristics. These three properties along with the low interfacial tension, facilitate the bulk flow of materials into wood. The most dramatic change in properties occurs with temperature and pressure alterations near the critical point ($0.9 < T_r < 1.2$ and $1.0 < P_r < 3.0$), and thus, most processes are carried out under these conditions. Reduced temperature (T_r) and pressure (P_r) are defined as (ambient / critical) temperature and pressure. The high compressibility of SCFs in the near critical region, means that minor pressure or temperature changes induce large changes in fluid properties. The density of SC-CO_2 increases exponentially in this region (Ely, 1986).

Table 2.1 Physical properties of typical gases, SCFs, and liquids (Hoyer, 1985).

	Gas	SCF	Liquid
Density (g/cm^3)	$(0.6 - 2.0) \times 10^{-3}$	0.2 – 0.9	0.6 – 1.6
Diffusion Coefficient (cm^3/s)	0.1 – 0.4	$(0.2 - 0.7) \times 10^{-3}$	$(0.2 - 2.0) \times 10^{-5}$
Coefficient of Viscosity (Pa*s)	$(1 - 3) \times 10^{-5}$	$(1 - 9) \times 10^{-5}$	$0.2 - 3.0 \times 10^{-3}$

2.3.2 Solvating Power of SCFs

Because SCFs can dissolve, transport, and deposit solutes during the impregnation process, some consideration must be given to factors influencing the ability of these media to dissolve biocides and other materials. The solvating power of a SCF depends on its density, vapor pressure, and polarity as well as the vapor pressure and polarity of the solute. In addition, the presence of a co-solvent can significantly alter the ability of a SCF to dissolve a material.

Influence of Pressure and Temperature: The solvating power of a SCF increases as its density increases and as the vapor pressure of the solute increases (Hoyer, 1985). Pressure increases cause SCF density to increase; therefore, increasing pressure at a constant temperature will increase the solvating power of a SCF. Temperature increases cause SCF density to decrease and solute vapor pressures to increase. Because SCF density is more sensitive to temperature change in the near critical region, solvating power decreases with increasing temperature for pressures near the critical region. Above pressures 2 to 3 times the critical pressure, temperature increases result in increased solvating power since the affects of solute vapor pressure increases are greater than the effect of reduced SCF density (Hoyer, 1985 and Sahle-Demessie, 1994).

The polarity of SCFs tends to increase with an increase in pressure. This increase can be attributed to enhanced molecular interactions from reduced intermolecular distances (Hawthorne, 1990 and Sahle-Demessie, 1994). In the near critical region, the functionality of SCF and solute is much less important than SCF density since SCF density is affected to a greater extent (Christal et al., 1982; Diepen et al., 1953; and Johnston, 1981 in Sahle-Demessie, 1994).

Influence of co-solvents: Co-solvents are miscible compounds added in relatively small amounts to a SCF that enhance the solvating power of the SCF. Co-solvents are generally selected on the basis of having a characteristic (such as vapor pressure, polarity, or molecular weight) in between those of the SCF and the solute (Sahle-Demessie, 1994 and Sahle-Demessie et al., 1995). Co-solvents may also reduce operating pressures and temperatures, swell cellulosic materials, and assist or prevent chemical reactions in SCF media (Kiran, 1995). Sahle-Demessie (1994) and Acda (1995) have shown significant improvements in biocide retentions with the addition of co-solvents during wood impregnation processes. Vandana and Teja (1995) were able to achieve 5 to 50 fold improvements in taxol extraction

from wood. Co-solvent effects are primarily dependent on the amount and type of co-solvent and is relatively independent of operating conditions (Dobbs, 1986 in Acda, 1995).

2.3.3 Applications of SCFs

Critical pressure, temperature, and density of some SCFs are listed in Table 2-2. Carbon dioxide (CO_2) is the most commonly used SCF for several reasons. It is inexpensive, non-flammable, non-toxic, and has a relatively easy to reach critical point (31 °C and 7.4 MPa). The solvating power of SC-CO_2 changes more abruptly in the near critical region (Sahle-Demessie, 1994). This is beneficial because only minor pressure or temperature changes are needed to remove or deposit materials in wood.

Table 2.2 Critical properties of materials often used as SCFs (Matson and Smith, 1989; Sahle-Demessie, 1994).

Compound	Critical Temperature (°C)	Critical Pressure (MPa)	Critical Density (g/cm^3)
Ammonia	132.5	11.3	0.235
Benzene	288.9	4.9	0.302
Carbon dioxide	31.0	7.4	0.468
Dichlorodifluoro-Methane	111.5	4.0	0.555
Ethane	32.2	4.9	0.203
Ethanol	243.0	6.4	0.276
Ethylene	9.2	5.0	0.218
Methanol	239.4	8.1	0.272
Nitrous oxide	36.4	7.2	0.452
Water	374.1	22.0	0.322

SCFs have been applied in a wide array of processes including extraction, separation, decomposition reactions, and impregnation. SCF extraction and separation processes for several porous materials are discussed by Eckert et al. (1986), Hoyer (1985), and Matson and Smith (1989). Extraction applications for wood are presented by Acda et al. (in review), Ritter and Campbell (1991), and Vandana et al. (1995). Hoyer (1985) and Kiran (1995) discuss the use of SCFs for the decomposition of toxic materials. The impregnation of wood with monomers and biocides is discussed by Acda (1995) Acda et al. (in review), Sahle-Demessie (1994), and Ward et al. (1990). SCFs are ideal for all of these processes because their affinity for a specific compound can be carefully tailored by adjusting pressure, temperature, and co-solvent composition.

The application of SCF for wood impregnation theoretically offers several benefits including complete impregnation of refractory species, low weight gain as a result of treatment, thin uniform deposition of materials in the cell lumens, and reduced environmental impacts from the treatment process. The flow of material in wood may be enhanced by the use of SCFs. Sahle-Demessie et al. (1995) improvements in air permeability of samples subjected to a SC-CO_2 treatment. Exploratory investigations support the feasibility of this type of impregnation process. SC-CO_2 extraction results show that wood cell wall components are probably not affected by the SCF since weight losses are less than or comparable to the amount of gums, resins, and other extractives (Acda et al., in review; Li and Kiran, 1988; and Ritter and Campbell, 1991). Ritter and Campbell (1991), using a scanning electron microscope, observed no negative impacts on cell wall structure from the extraction of pine shavings. Preliminary strength evaluations on small clear samples (2.4 x 2.4 x 54 mm) of permeable and refractory woods (Smith et al. 1993a and b) and on 11 mm thick composite panels (Acda, 1995), indicated that there were no significant reductions in modulus of elasticity (MOE) or modulus of rupture (MOR) as a result of SC-CO_2 impregnation. Defects

such as collapse, fracture, or delamination were not observed in either the solid wood or composite samples. Finally, Acda (1995) and Sahle-Demessie (1994) were able to achieve preservative retentions at or in excess of threshold values for protection against fungal attack.

In spite of the studies supporting the viability of SCF impregnation of wood, concerns exist about retention and distribution of deposited materials and about the condition of large or refractory pieces of wood. Ward et al. (1990) achieved relatively constant and predictable retentions of methyl methacrylate in Douglas-fir sapwood. Acda (1995) and Sahle-Demessie (1994) showed that retentions could be increased with increasing pressure or the addition of a co-solvent. They also noted that the standard deviations of preservative retention were large in comparison to means. Since Ward used a different treating methodology than the other investigators, processing parameters may be accountable for the large variations in retention. Uneven distribution of deposited materials seems to be a characteristic of all SCF impregnation studies so far. In all cases, there are considerably higher concentrations of precipitate in the outer regions or "shell" of the wood. Sahle-Demessie (1994) found that biocide retentions in 1.3 cm diameter Douglas-fir dowels following SCF treatments were 2 to 230 fold greater in the shell regions compared to the inner core area. Using larger square samples and a different treating schedule, he was able to reduce but not eliminate shell-to-core gradients. Acda (1995) and Acda et al. (in review) also experienced 2 to 12 fold higher biocide concentrations in the shell region. In all three investigations, increased pressure resulted in higher but less uniform retentions. Sahle-Demessie showed that more permeable wood and increased treatment time produced more uniform preservative distributions.

Concerns have been raised about damage to wood as the result of SC-CO_2 treatment. Wood could be weakened by the formation of carbonic acid from carbon dioxide and water (Kiran 1995). In addition, the high pressure could easily crush it or explode the wood. Wood that was not crushed or fractured during treatment, usually had no significant change in either

MOE or MOR (Acda et al., in review; Anderson, 1998; and Tsunoda et al., 1998). In summary, wood condition seems to be influenced by both permeability and wood strength. A strong refractory wood such as Douglas-fir heartwood may be treated successfully, but a refractory species with lower crushing strength such as western redcedar will likely experience damage.

Variations in preservative retention and distribution and wood collapse and fracture may reflect insufficient pressure (inhibiting solubility), poorly controlled pressure changes (leading to a reversed flow before deposition), or excessive pressure gradients (causing mechanical failure). Measuring pressure inside wood during the impregnation process can provide insights concerning the magnitude of surface-to-center pressure differences and the factors that influence them.

2.4 Flow in Wood

2.4.1 Mechanisms of Fluid Flow

Treating media can move into wood by diffusion, capillary flow, and bulk flow mechanisms. Diffusion is the transport of materials resulting from a concentration gradient. Capillary flow is the result of stronger molecular interactions between a liquid and cell wall material compared to those within the liquid itself. Bulk flow is the transport of fluids into wood resulting from an applied pressure differential. Since diffusion is a relatively slow process and because capillary flow by itself can only produce shallow penetrations, bulk flow is the primary mechanism of fluid flow during pressure impregnation processes.

Mathematical equations can be used to provide quantitative predictions about the flow of liquids or gases into wood during pressure impregnation processes (Section 2.5) or to provide qualitative information on the influence of process and wood parameters on flow.

Because wood treating is a dynamic process, unsteady-state flow equations are needed for quantitative analyses. Derivations and solution methods for these equations are provided by Orfila and Hösli (1985), Resch (1967), Sahle-Demessie (1994), and Siau (1984). Qualitative analyses of pressure impregnation processes can be obtained through the use of steady-state flow equations.

The steady-state equations for the bulk flow of liquids and gases in wood are derived from Darcy's law. This law states that conductivity is equal to flux divided by gradient. For pressure treating processes, this may be rephrased as wood permeability is equal to the flux of fluid entering it divided by the applied pressure gradient:

$$\mathbf{k} = (\mathbf{Q} / \mathbf{A})/(\Delta\mathbf{P} / \mathbf{L}) \tag{2.1}$$

where **k** is wood permeability, **Q** is volumetric flow, **A** is the surface area perpendicular to flow, **ΔP** is the pressure difference between the surface and interior of wood, and **L** is the distance from the surface to the interior. This equation assumes that flow is viscous and linear, the fluid is homogeneous and incompressible, the wood is homogeneous and does not interact with the fluid, and that permeability is independent of the length of flow. Although careful measurements have shown departures from these assumptions (Siau, 1984), this equation shows that applied pressure and permeability are important for flow in wood. Sahle-Demessie (1994) showed that flow equations based of Darcy's law were applicable to the flow of supercritical fluid treatment solutions.

One aspect not addressed in steady-state flow equations is the occurrence of liquid-gas menisci in wood. These are of particular importance as liquid passes through a pit opening into an adjacent unfilled cell lumen or when a gas bubble becomes trapped in the passage between filled cells. In both cases, the minimal estimated pressure to bring about bulk flow is called capillary pressure, represented by:

$$(P_g - P_l) = (2\sigma \cos\theta)/r \qquad (2.2)$$

where $(P_g - P_l)$ is the capillary pressure, P_g and P_l are pressures in the gas and liquid phases, respectively), σ is the liquid surface tension, θ is the angle of wetting, and r is the radius of a circular opening (Siau and Shaw, 1971).

2.4.2 Influence of Fluid Characteristics

The approximate influences of fluid characteristics on flow in wood during pressure impregnation processes can be seen from Poiseuille's equations for flow in parallel capillaries. For liquids this equation is:

$$Q = (N\pi r^4 \Delta P)/(8\eta L) \qquad (2.3)$$

where N is the number of parallel capillaries and η is the viscosity of the fluid. Since flow of a liquid into dry wood is affected by interactions with the cell wall, the capillary flow must also be considered. For gases, and presumably supercritical fluids (Sahle-Demessie, 1994), Poiseuille's equation is modified for gas expansion due to a pressure drop along the flow path (Siau, 1984) and is expressed as:

$$Q = (N\pi r^4 \Delta P \bar{P})/(8\eta L P_2) \qquad (2.4)$$

where $\bar{P}$ is the average pressure along the flow path and P_2 is the down stream pressure (at which volumetric flow Q is measured). Equations 2.2, 2.3, and 2.4 show that flow could theoretically be increased by reducing fluid viscosity, surface tension, or angle of wetting.

Viscosity: The benefits of reducing viscosity were recognized early in the development of pressure impregnation processes. Thick coal-tar solutions were heated prior to the application of pressure. These solutions were also blended with creosote and other less viscous oils. Light organic solvents, such as mineral spirits and diesel oil, and water are used

as treating media because of their low viscosity. Mac Lean (1935) found that viscosity reductions improved penetration and retentions of creosote and aqueous treating solutions. The very low viscosities of vapor-phase and supercritical fluid processes offer the potential for improved preservative penetration.

Although Petty (1978) found a simple inverse relationship between retention and silicon oil viscosity, there has been empirical evidence that viscosity is not as important for flow as predicted in the steady-state flow equations. Rosen (1975) and Buckman et al. (1934) found no predictable relationship between the viscosity of polar and non-polar liquids and the degree of impregnation. Siau (1970) found that the reduction of silicon oil viscosity from 1.0 to 0.05 poise resulted in retention improvements, but further reduction to 0.009 poise had no effect. In addition, over the influential range, Siau determined that the viscosity term of Equation 2-3 should be raised to a power of less than one.

Surface Tension and Angle of Wetting: Surface tension is the net result of cohesive forces between molecules within a liquid. When a liquid comes in contact with the walls of a capillary, it may be drawn into the capillary to a depth that is dependent on the relative strengths of adhesive forces between the liquid and capillary and the cohesive forces in the liquid. The angle between a tangent to the liquid surface and the capillary wall (angle of wetting) is a measure of the net result of these forces. If the angle is between 0 and 90 °, the capillary is said to be "wet" by the liquid, and the liquid is drawn into the capillary. If the angle is greater than 90 ° (indicating that the cohesive forces within the liquid are greater than the interactions between the liquid and the capillary wall), the liquid will not wet the capillary and an external force will be needed to move the liquid into the capillary. A surfactant (or wetting agent) can be added to the liquid to reduce its surface tension, thus reducing the cohesive forces relative to the adhesive forces. This decreases the contact angle and helps to wet the wood. In non-pressure methods, that rely on capillary flow, caution must be used not

to reduce the surface tension too much since this would limit capillary pressure and hinder fluid flow (Richardson, 1993). For pressure impregnation processes, however, benefits from increased wetting are probably less important than reductions in surface tension since the driving force for flow is provided by an external pressure. In application, surfactants in pressure processes may not improve the treatability of refractory wood (Kumar and Morrell, 1992).

2.4.3 Influence of Wood Anatomy

The Cellular Structure of Wood: Only a brief description of wood structure is provided here; for a more complete description see Côté (1964), Panshin and de Zeeuw (1980), Siau (1984), and Zabel and Morrell (1992). The cellular structure of wood can be described in terms of softwoods (from gymnosperms or coniferous trees) and hardwood (from angiosperms or deciduous trees). Softwoods are composed of tracheids and parenchyma. According to Panshin and de Zeeuw (1980) longitudinally oriented tracheids make up 93 % of the volume of a typical softwood. Radially oriented groups of parenchyma and tracheids, forming rays, make up 6 % of softwood volume. Some rays, such as those in true firs (*Abies spp.*), consist entirely of parenchyma. In certain species, tubular bundles of parenchyma forming resin canals make up 1 % of softwood volume. When present, longitudinally oriented resin canals may be found in the early- or latewood of an annual growth-ring. Radially oriented resin canals are located at the center of rays. Only a relatively small portion of rays contain resin canals. Rays with resin canals are called fusiform rays; those without resin canals are called uniseriate rays. Resin canals may form open pipe-like passages or be partially or completely occluded by resin and/or epithelial cell outgrowths, called tylosoids.

Cell types in hardwoods include vessel elements (longitudinally stacked on top of one another to form vessels), fibers, parenchyma, and tracheids. Vessels comprise approximately

30 % of hardwood volume. They are either distinctly arranged from large to small diameter across an annual growth-ring in "ring porous" woods, are the same size throughout a growing season in "diffuse porous" woods, or decrease only slightly in diameter in "semi-diffuse porous" woods. Fiber cells are also longitudinally oriented and comprise about 50 % of hardwood volume. Parenchyma cells makeup from 1 to 20 % of hardwoods and are oriented both longitudinally and radially. Those oriented in the longitudinal direction are found adjacent to vessels or grouped throughout a growth-ring. The radially oriented parenchyma cells are bundled into rays, which are comprised entirely of parenchyma and make up about 17 % of hardwood volume. Tracheids are not very abundant in hardwoods but are found scattered amongst or just beyond the latewood vessels or surrounding the earlywood vessels.

Connections Between Cells: Softwood cells are connected to one another through pits, which are small channels passing through the walls of each cell with a diaphragm, or membrane, separating the two cells. Simple, semi-bordered, and bordered pits are found in both softwoods and hardwoods. In simple pits, the passage from one cell to the next has a consistent diameter. In semi-bordered pits, one of the cell walls extends over the pit chamber forming a dome-shaped structure with a small aperture at its top. In bordered pits, both cell walls are extended, forming a chamber with an elliptical cross section. Pitting between parenchyma cells is simple; pitting between parenchyma and tracheids is semi-bordered; and pitting between tracheids is bordered. In hardwoods simple pits connect adjacent parenchyma cells. Pitting between parenchyma and all other cell types is semi-bordered, and pitting between vessels, fibers, and tracheids is bordered with the exception of between adjacent vessel elements. In the junction between two vessel elements is a perforation plate. The openings in this plate are so large that adjacent elements are considered a single capillary tube, or vessel.

Pit membranes are thought to originate from modifications of the primary cell walls of adjacent cells and the middle lamella region between them (Liese, 1965). Simple and semi-bordered pit membranes in most softwoods and all hardwood pits closely resemble the primary and consist of a randomly oriented tightly woven net of cellulose microfibrils (Liese, 1965 and Panshin and de Zeeuw, 1980). Most microscopic observations show no openings in these membranes (Krahmer and Côté, 1963 and Panshin and de Zeeuw, 1980), but the flow of materials through them indicates that the membranes are porous (Behr et al.,1969; Murmanis and Chudnoff, 1979 (in Siau 1984); Wardrop and Davies, 1961). Most softwood bordered pit membranes, excluding western redcedar, have an open web of cellulosic microfibrils radially oriented like the spokes of a wheel. At the hub of these fibers is a non-permeable dome-shaped structure extending out on both sides of the membrane, the torus. The web area between the torus and pit wall is called the margo.

Membrane dimensions, pore size, and condition affect the flow of materials in wood. Softwood bordered pit membranes range from 6 to 30 μm in diameter and from 0.1 to 0.5 μm in thickness (Siau, 1984). Simple and semi-bordered pit membranes are smaller but thicker than those in bordered pits. Pit membranes in latewood are generally smaller than those in earlywood. Hardwood pit membrane diameters are smaller than those in softwoods (average diameter is 6 μm), but have about the same thickness.

Pit membrane pore sizes are difficult to obtain because of the flexible three-dimensional structure of pit membranes and their hygroscopic nature. In addition, flow through wood is determined by the net effect of several membrane openings. Therefore, an "effective" pore size is often determined by indirect means, such as through permeability measurements. Siau (1984) and Stamm (1967) list conservative values of 0.02 to 4 μm for softwood bordered pit membrane pore diameters and 0.005 to 0.17 μm for hardwood pit pore diameters. Because of their similar structure, simple and half-bordered pit membrane pores in

softwoods are likely to have similar dimensions to those of hardwood pit pores. Liese (1965) and Krahmer and Côté (1963) provide direct measurement methods, that were similar to the ranges listed by Siau. The effective opening size decreases with increasing sample length and moisture content in the hygroscopic range (Stamm, 1967).

The condition of pit membranes can be altered by the deposition of metabolic materials during heartwood formation, aspiration from liquid withdrawal upon drying or the forced flow during impregnation, and reduction of pore size from drying in the hygroscopic range. Pit aspiration accounts for the majority of flow reduction. Several studies have shown a direct correlation between the number of aspirated pits and reduced flow of materials in softwoods (Fleischer, 1950; Miller, 1961; and Sebastian et al., 1965). The aspiration of pits during drying may be prevented by displacing sap (predominantly water) with liquids having lower surface tensions and/or lower polarities, a process referred to as solvent drying (Comstock and Côté, 1968). Although the majority of pit membranes may become aspirated, those in the latewood are often not aspirated because of their rigid structure. There are conflicting conclusions on the ability to reopen aspirated pits. Krahmer and Côté (1963) and Liese (1965) were unable to deaspirate pits using solvent extraction methods. Flynn (1995), summarizing the work of several authors, also came to the conclusion that softwood pits held closed by hydrogen bonding and hydrophobic extractives could not be opened. Contrary to these findings, Thomas and Nicholas (1966) deliberately aspirated pits in earlywood samples by air drying them. Then they re-soaked some of these samples in water and dried them a second time using a solvent drying technique. They found that pits (most likely to have been aspirated during the initial air drying) were no longer aspirated. Aspirated pits must have been reopened by saturating originally dried material in experiments by Buckman et al. (1934) since permeability measurements using water produced the same results for green and dried samples. Henriksson (1958, in Peek and Goetsch, 1990) found that reversing air flow could

recover decreased permeability during air permeability measurements. And, Kelso et al. (1963) showed that reversing water flow restored flow rates that had decreased over time. Although Kelso et al. attributed the reduced flow to blockage from air bubbles, reduced flow during air permeability measurements support the idea that pits may become aspirated if flow is continued in a single direction regardless of the presence of air-liquid menisci. Finally, improvements in fluid impregnation during sonic treatments have been attributed to freeing closed pit membranes (Burdell and Barnett, 1969). Aspiration does not occur in hardwoods, since these pits do not have a torus. Reduced flows in these woods most likely occur from deposition of gums and other metabolic materials (Behr et al., 1969) and from reductions in membrane pore size from drying in the hygroscopic range.

Flow Paths in Wood: Fluids under pressure differences can move through cell lumens, pit membranes, and cell wall capillaries. Stamm (1967) showed that flow through cell wall capillaries was negligible compared to that through pit membranes, and the static pressure drop through cell lumen was negligible compared to that through pit membranes. Therefore, pit membranes control fluid flow in wood. In addition, the direction of flow is controlled by the largest effective pit opening for parallel paths and the smallest opening in series along a single path.

Behr et al. (1969) and Wardrop and Davies (1961) provided microscopic examinations of the advancement of oil and water based solutions in softwoods during pressure impregnation. Longitudinal tracheids were the primary entry points for fluids; although, rays may play an equal or greater role for relatively long samples. The importance of rays seemed to be greater for water-based solutions compared to oil solutions or creosote; this was attributed to the higher viscosities and non-polar nature of the latter solutions (Behr et al., 1969). Once inside wood, the flow of fluids is greatest in the longitudinal direction because of the large open tracheids and lower number of pits to cross per unit length of flow

(Stamm, 1967). The relative importance of tangential and radial flows is difficult to determine. Since tracheids make up about 93 % of softwood volume and almost all inter-tracheal pitting is on the radial walls (facilitating flow in the tangential direction) and since rays represent only about 6 % of total wood volume, it seems logical that flow in the tangential direction would dominate. However, Behr et al. (1969) provided strong evidence that fluids flow from rays into adjacent tracheids. In addition, Wardrop and Davies (1961) found that rays were more important than tracheids for the movement of fluid into an untreated region when fluid entry was restricted to the radial direction, as in poles and large timbers. The degree of flow enhancement from resin canals is questionable since they are not in all softwood species and may be partially blocked by resin and/or tylosoids. When present and clear, flow through resin canals in the radial direction can be greatly improved. These passageways are larger in the longitudinal direction compared to those in the radial direction. In general, fluid flow in dried softwood is greatest in the longitudinal direction followed by the tangential and then radial directions (Smith and Redding, 1964).

Behr et al. (1969) and Wardrop and Davies (1961) showed that vessels were the primary conduits for fluid flow through hardwoods. Flow in fibers and tracheids is equally likely; although, fibers are generally far more abundant. Flow in parenchyma is least likely, especially with creosote and oil solutions. Longitudinal flow dominates because of the large open perforation plates between consecutive vessels. Transverse flow may become more important when vessels are blocked by dense tyloses. Flow in the radial direction generally is greater than that in the tangential direction for a given species, but when averaged for several hardwood species, flow is similar in these two directions (Choong et al., 1974). Radial flow is assisted by the greater number of pits in this direction (Panshin and de Zeeuw, 1980). Although hardwoods contain a large proportion of rays (comprised entirely of parenchyma cells), the effectiveness of these cells for conducting fluids is questionable. Behr et al. (1969)

found that flow occurred in some rays, but continuous flow was often blocked by gum and other metabolic deposits. Rays were only filled after all cells surrounding them were filled with treating solution. Wardrop and Davies (1961) showed that rays (and parenchyma cells in general) played an important role in fluid transport. They showed fully impregnated rays leading out of the treated zones and into untreated wood. In conclusion, it seems that fluids enter hardwoods primarily through vessels and then pass into adjacent fibers, parenchyma and tracheids at approximately the same rate. Fluids also enter through rays and pass into adjacent cells in relatively long samples or when tyloses are abundant.

2.5 Pressure Response Models and Measurements during Pressure Treatments

Pressure is the driving force required for transporting treating medium into wood, and it governs the properties of SCFs. Pressure inside wood during treatment processes can be better understood through its prediction and measurement. Only a few attempts at prediction have been made (Orfila and Hösli, 1985 and Sahle-Demessie, 1994) and limited experimental measurements are available (Bergman, 1991; Cobham and Vinden, 1995; Kyte and Sanders, 1978; and Peek and Goetsch, 1990).

2.5.1 Models of Internal Pressure Response

Models of Pressure during Conventional Pressure Processes: Orfila and Hösli (1985) used finite elemental analysis with incremental time and distance to calculate pressure from a partial differential equation describing unsteady-state flow. This differential equation was based on equations of continuity and motion for viscous flow in a porous medium and was modified to account for slip flow. Although this model was only supported with a single

experimental vacuum treatment, preliminary results from this investigation and work by Kyte and Saunders (1978) support the theoretical results it provided.

Simulations were run for pressure development at three depths along the radial axis of dried white spruce (*Picea glauca*) during the initial phases of Bethell and Rüping treatment processes with air. Simulations showed that faster application of vacuum or pressure resulted in more rapid internal pressure response. This significantly reduced treatment times and indicated that insufficient internal pressure changes occurred if treatment schedules are rushed. These simulations also show that interior pressure equalizes with treatment vessel pressure, given sufficient time, but the time requirement for a significant pressure change in refractory woods was exceedingly long. Simulated pressure results showed that more than three days was required for pressure at a depth of 1 cm into spruce heartwood to reach that of the treatment vessel. Most significantly, these theoretical calculations suggested that common industrial treatments did not significantly affect pressure deep in wood.

Models of Pressure during SCF Treatments: Sahle-Demessie (1994) derived differential equations to explain the effects of pressure, density, viscosity, compressibility, and biocide solubility during impregnation with a biocide (2-thiocyanomethylthio benzothiazole (TCMTB)) in SC-CO_2. He used numerical procedures to approximate the solutions to these equations. Treatment pressure, time, and wood characteristics were incrementally changed to assess their influence on biocide retention and distribution.

A comparison of experimentally and mathematically calculated results indicated that the modeling methods provided a rough approximation of the effects of process and wood variables on treatment. The importance of internal pressure response was shown by comparing SCF characteristics at a fixed location at two times during a theoretical treatment. Increasing treatment time from 15 to 45 minutes resulted in a pressure rise from 5 to 21 MPa.

This pressure change resulted in a 7.5 fold increase in fluid density and a corresponding 7 orders of magnitude increase in biocide solubility.

2.5.2 Measurements of Internal Pressure Response

Methods of Pressure Measurement: Two general approaches have been used to measure pressure in wood during impregnation processes. Arganbright and Resch (1970), Bergman (1991), Cobham and Vinden (1995), and Kyte and Saunders (1978) placed pressure sensors directly into wood samples and fed electrical cables outside the treating vessel to data recorders. The ability to minimize time delays between pressure change and when this change is detected is an advantage to this method. The latter two papers used micro-pressure transducers to maximize sensitivity. This method requires the sensors to be able to withstand pressures up to 1,400 kPa in a liquid environment as well as physical damage from loading and unloading a treatment charge or attaching and detaching them from the wood. The second internal pressure measurement approach offers protection for the pressure sensors and facilitates sample preparation. Peek and Goetsch (1990) epoxied tubing into their samples and connected the tubing to hydraulic lines leading out of the treatment vessel to external pressure sensors. Hydraulic lines were filled with silicone oil before each treatment run, taking care to exclude air bubbles. Both approaches are time consuming and plagued with the potential for leaks. As a result, empirical data on pressure changes during treatment are limited, and widespread application of pressure measurement as a method for monitoring wood impregnation has not occurred.

Pressure Response in Wood during Impregnation Processes: Pressure has been measured in wood to quantify the importance of process and wood characteristics during Lowry, Rüping, Bethell, and SCF impregnation processes. These studies have shown the importance of process parameters and wood characteristics on pressure development.

The difficulty of using liquid versus gas media to deliver biocides was clearly shown by the hindered internal pressure responses when water or creosote solutions were applied to wood instead of air. A 40 fold increase in time was needed to achieve similar pressure conditions in dry pine sapwood during Lowry treatments with water versus air (Peek and Goetsch, 1990). Internal pressure responded quickly to changes in treatment vessel pressure during the initial air evacuation or press phases of Bethell and Rüping processes, respectively. Pressure response slowed as soon as the liquid medium was added (Cobham and Vinden, 1995 and Bergman, 1991).

Pressure in permeable radiata pine (*Pinus radiata*) sapwood took only a few minutes to equilibrate with vessel pressure after flooding and pressurization. Pressure in refractory Douglas-fir took almost 3 hr to reach equilibrium (Cobham and Vinden, 1995). Suggestive but inconclusive evidence was also given for a direct correlation between pine heartwood permeability and pressure response. Peek and Goetsch (1990) used a Lowry process to treat pine (*Pinus spp.*) and spruce (*Picea spp.*) sapwood. Pressure inside the more permeable pine sapwood sample equilibrated within 3 hr while a pressure response was not detected in the spruce even after 8 hr. Similar results for pine and spruce were shown by Kyte and Saunders (1978).

Preliminary measurements for this investigation showed that pressure in ponderosa pine, sugar pine, and Douglas-fir samples responded more quickly to SC-CO_2 treatment pressure changes when flow was restricted to the radial versus tangential direction. This is the opposite of what is expected from observations with liquid treatments in Chapter 3 and by Smith and Redding (1964). In addition, it is also contrary to what would be expected from anatomical characteristics since the majority of intercellular connections are in the tangential direction. Rays would not be expected to contribute much to pressure response because they only occupy about 6 % of the total wood volume and are often occluded by extractives and

tylosoids (Panshin and de Zeeuw, 1980). The removal of extractives (Sahle-Demessie et al., 1995) and breaking up of tylosoids are possible explanations for the observed results.

In hardwoods, pressure changes are expected to be more rapid when treating media flows along the radial versus tangential directions since a larger portion of inter-vessel pitting is in this direction and rays occupy a substantial volume of hardwoods (Panshin and de Zeeuw, 1980). However, as with preliminary measurements in softwoods, pressure in black gum samples responded in a manner opposite of expected. That is, pressure rose more quickly when SC-CO_2 flow was restricted to the tangential versus radial direction. Because these contrary results could not be easily explained, further study needs to be conducted comparing internal pressure responses when treating media flow is restricted to a single longitudinal or transverse direction.

The measurement of pressure inside wood during pressure impregnation processes may allow the optimization of treating processes by being able to better quantify the effects of process and wood variables. In addition, internal pressure measurements can be used to verify pressure response models. These models, in turn, could help to explain difficulties encountered during process development and may be used to develop treatment schedules for previously untested wood species or treating media.

3. INTERNAL PRESSURE MEASUREMENT TECHNIQUES AND PRESSURE RESPONSE IN WOOD DURING CONVENTIONAL IMPREGNATION PROCESSES: BETHELL, RÜPING, AND LOWRY

3.1 Introduction

Conventional wood treating processes (Section 2.2.2, "Static Pressure Processes") typically involve three stages. In the first, wood is subjected to a vacuum, a slight pressure elevation, or no pressure change. In the second, the wood is then flooded by a liquid treating solution and pressure is increased to about 1,000 kPa. After an acceptable amount of solution is impregnated into the wood, pressure is released, and the third stage involves pulling a vacuum on the wood. Although a desired preservative retention is usually assured by these processes, there is no way to tell for certain how deep the preservative has penetrated into the wood without some form of destructive sampling. This is especially troublesome for species that contain wood having a wide range of permeabilities such as Douglas-fir (Miller, 1961; Erickson and Estep, 1962). Not only is penetration likely to be shallow or non-existent, but it is likely to vary widely in comparison to more easily treated woods. Another potential problem with retention-based monitoring of treating processes is the uncertainty about residual pressure in the wood after treatment. Residual pressure, or back-pressure, is often used when low preservative retentions are desired. But, the magnitude of residual pressure at any given time is poorly understood. In some instances residual pressure can be troublesome. Preservative forced back out of wood (kickback) can create unsightly surface deposits and is a potential risk to people handling the wood and to the environment. Quantitative measurements of pressure inside of wood during the treating process could help develop improved treating schedules and provide ways to monitor treating processes so that penetration and back-pressure concerns can be minimized.

Bergman (1991), Cobham and Vinden (1995), Kyte and Saunders (1978), and Peek and Goetsch (1990) studied pressure levels inside wood during treatment. Most studies used pressure sensors embedded directly in wood that was placed inside the treating vessel. Potentially corrosive environments at pressures of 1,000 to 1,400 kPa and difficulties with inserting and sealing sensors limit the reproducibility of these techniques. Peek and Goetsch (1990) sealed a capillary tube in their samples and fed this tube to an external pressure transducer.

Process and wood variables can influence the flow of materials into wood during impregnation processes, and thus, these variables are likely to influence pressure response in wood during processing. Pressure schedules, including the sequence and rate of pressure change, are more likely to produce dramatic treatment effects when applied to liquid versus gas treating media during conventional processes. This is because air trapped in the wood hinders liquid flow. Differences in treating media characteristics can be exemplified by comparing internal pressure responses for a liquid and a gas. Liquids have much higher viscosities and surface tensions that hinder flow into small capillaries. In an ideal case, the rate of fluid flow into wood should be independent of the length of flow. However, Kuroda and Siau (1988) provide evidence of non-linear flow in wood. It is difficult to predict whether pressure response would also show a departure form linearity. Since permeability is a measure of the ability of fluids to flow through wood, wood that is more permeable should treat easier and more easily treated wood should show faster internal pressure responses during treatment.

Previous investigations have shown limited data on the response of internal pressure to changes in vessel pressure during air and liquid treatments. Most of these studies have evaluated pressure in pine sapwood, although Cobham and Vinden (1995) measured pressure in a single Douglas-fir sample. Douglas-fir is an abundant structural timber source but its

liquid permeability, particularly in the heartwood, ranges from very refractory to permeable (Miller, 1961). Developing information on internal pressure response during treatment could be used to improve treatment cycles or better control kickback.

3.2 Objectives

The following are the objectives of this study:

1. To develop and evaluate techniques for measuring pressure in wood during conventional pressure treatments.
2. To make qualitative internal pressure response comparisons between samples receiving treatments that differ in either pressure schedule, treating media, or wood permeability and between pressure responses measured at different radial depth into single samples.

3.3 Methods

3.3.1 Investigative Framework

The methods used in this investigation were intended primarily to develop techniques for measuring pressure in wood during conventional pressure impregnation processes and to evaluate these techniques with pressure treatments having different process and wood variables. No attempt was made to compare the different techniques under a standard set of variables nor was there any attempt to use a fixed experimental design for comparing the influences of these variables on internal pressure development during the various treatments. Nevertheless, useful information may be obtained to help characterize internal pressure response during pressure treatments involving different process and wood variables.

Over one hundred and fifty pressure probes were evaluated under different treatment conditions (Appendix A). During each treatment application (or run), up to four pressure probe measurement techniques were evaluated. Pressure measurements from all of these treatment applications were grouped first by pressure-probe and sealant method and then subsequently by pressure process, treating medium, species, and sample size. This was done so that qualitative comparisons could be made between the collective pressure responses in samples that received similar treatments to the collective responses in samples receiving treatments differing in either pressure process, treatment medium, species, or pressure probe depth. Data sets for comparison purposes were assembled only from treatments applied long enough for internal pressure to rise and either level off below the treating vessel pressure or approach equilibrium with vessel pressure.

In this investigation, a "treatment" or a "treating run" refer to the specific pressure schedule, treating medium, wood species, and wood sample size employed at a given time. A "sample" refers to a piece of wood in which pressure measurements were made. During a given treatment, up to four separate pressure probes could have been used. Most of the time, only a single pressure probe was placed in a sample; however, up to three probes were occasionally used.

3.3.2 Equipment

Internal pressure was monitored in a 0.3 m diameter by 3.0 m long treating vessel. A second vessel of similar volume was used to store treating solution when vacuum or air treatments were applied. Both vessels were equipped with electronic sight-gauges (that allowed observation of fluid level) and pressure sensors. The treating vessel was equipped

with an internal shelf and small tank that allowed liquid treatments of small samples. A vacuum pump and air compressor provided a pressure range from 12 to 800 kPa (gauge). However, there was no method to control the rate of pressure or vacuum application.

Pressure measurements in samples were made with four sample pressure transducers. The transducers were OMEGA PX302-200AV pressure sensors with a pressure range of 0 to 1,400 kPa (absolute) and an accuracy of ± 3.4 kPa. The sensors were calibrated with a dead-weight test apparatus, and calibration curves were made to convert sensor output signal to a pressure value. A comparison of sensors over the treating vessel pressure range showed that they provided identical readings (Figure 3.1).

The data were collected using a Campbell 21x data logger. This unit was programmed to provide excitation voltage, measure signal voltage, and convert the mV signal to a pressure value sequentially for all sensors at fixed intervals ranging from 10 to 300 seconds. The pressure data was then transferred to a personal computer for later analysis.

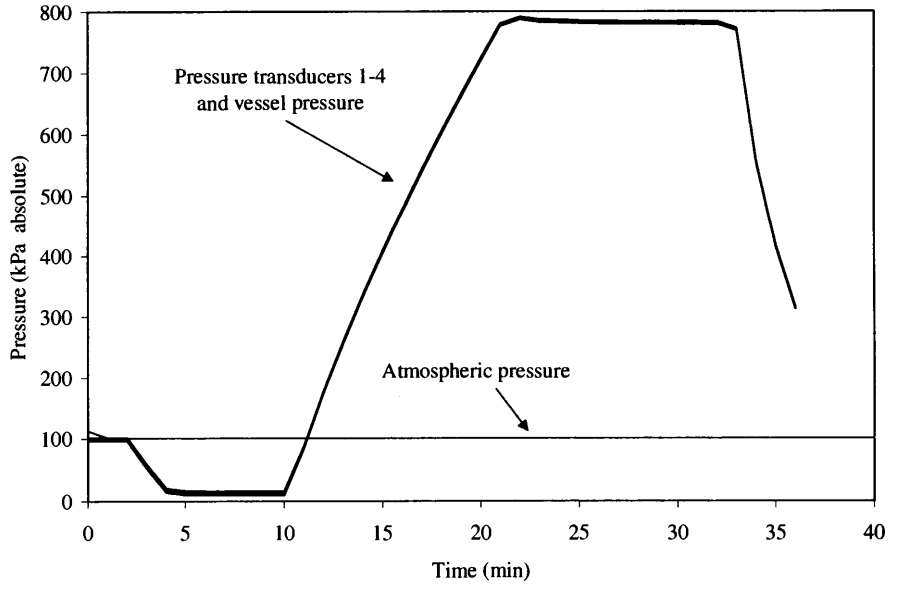


Figure 3.1 Pressure transducer comparison showing similarity in response between all transducers used to measure internal pressure of wood and retort pressure.

3.3.3 Sample Preparation and Treating Solution

All experimental work was performed using Douglas-fir (*Pseudotsuga menziesii* (Mirb.) Franco) heartwood or ponderosa pine (*Pinus ponderosa* Laws.) sapwood. Douglas-fir heartwood has low permeability and resists fluid flow, making it difficult to treat with liquid preservatives. Ponderosa pine sapwood is highly permeable. It was used in this investigation because of the large permeability difference between it and Douglas-fir heartwood and because internal pressure responses could be compared to those in previous studies (Bergman, 1991; Cobham and Vinden, 1995; Kyte and Saunders, 1978; and Peek and Goetsch, 1990). Samples were cut from dried boards purchased from a local lumber yard, end coated with Gluvit (a two-part epoxy by ITW Philadelphia Resins; Montgomeryville, PA), and conditioned at approximately 20 °C and 65 % RH to a constant moisture content prior to use. Sample dimensions along the radial, tangential, and longitudinal axes, respectively, were 90 x 90 x 600 mm (for samples that had probes pressed or epoxied inside of them), 25 x 25 x 76 mm (for samples that were placed in single-probe holders), and 50 x 50 x 76 mm (for samples that were placed in double- and triple-probe holders).

The treating medium was either air or a solution of Cu-8 in mineral spirits. The solution contained less than 1 % by weight of Cu-8 and was reused for all treatments. This chemical was chosen because it is safe to work with and can be easily seen in treated wood. The green color and copper content of this solution assisted in determining if pressure-probe seals were effective and allowed the depth of treating medium penetration to be measured.

3.3.4 Pressure Measurement Techniques

Pressure Transducer Attachment: Pressure in wood during conventional treating processes was monitored using sensors mounted outside of the treating vessel (Figure 3.2).

Four 1.6 mm stainless steel tubes were fed through a bulkhead into the vessel. This tubing was filled with DOT 5 silicone based brake fluid that acted as a hydraulic fluid. Before each treatment, or treating run, the hydraulic lines were refilled and air bubbles removed by individually separating the lines from their pressure transducers and forcing hydraulic fluid through them using a large syringe. After filling, the line was reconnected to its pressure transducer and a sample was placed on the other end in the treating vessel. Compression-fitting type unions were used on the hydraulic line ends in the vessel. This simplified sample attachment and allowed lines to be plugged when not in use. No attempt was made to fill the hydraulic line in the sample with hydraulic fluid or prevent the hydraulic fluid from leaving the lines and entering the samples. Once the samples were connected to the hydraulic lines, they were allowed to hang freely in the vessel (for air treatments), submerged and weighted in a small tank of treating solution (for oil treatments using Lowry or Rüping press cycles) or weighted in the bottom of the treating vessel (for oil treatments using a Bethell press cycle).

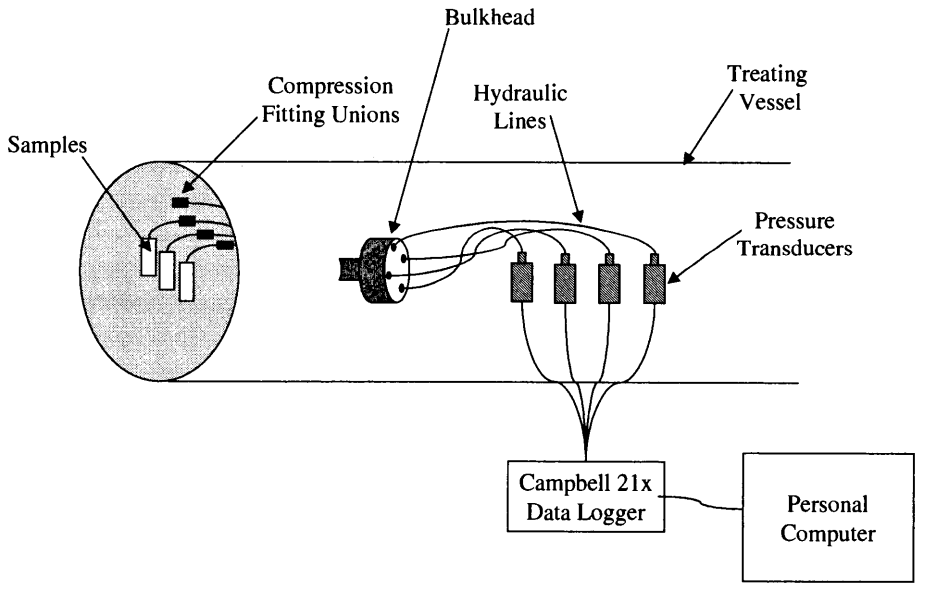


Figure 3.2 Schematic showing placement of wood samples, hydraulic lines, and pressure transducers used to measure internal pressure of wood during pressure treatments.

Pressure Probe and Sealing Techniques: Nine pressure probe and sealing techniques used to measure pressure inside of wood during pressure treatments were tested. The first two techniques used probes pressed or epoxied into Douglas-fir samples having dimensions of 90 x 90 x 600 mm (Figure 3.3). Holes for the probes were drilled perpendicular to the samples' longitudinal axes, located mid-way along their lengths, and to a depth of 45 mm. In the first technique, two holes per sample were drilled one 15 mm from the edge and the second at 45 mm. The holes were drilled with a beveled piece of wire just greater than 1.6 mm in diameter. Pressure probes were made out of 75 mm long stainless steel tubing (1.6 mm OD, 0.76 mm ID) and tapped into the tight fitting holes. In the second technique, a 6 mm in diameter was drilled 45 mm from the edge of each sample and to a depth of 30 mm. A 1.6 mm diameter hole was centered in the bottom of the first and extended to a total depth of 45 mm. A probe was then tapped in the pilot hole so that a 5 mm air chamber remained below the tubing. Sawdust was packed around the probe for about 1.0 cm of the larger hole, and then, the probe above the sawdust was back-filled with epoxy ("2-Ton Epoxy" by ITW Devcon; Danvers, MA). For both techniques, a compression-fitting nut and new ferrule had to be placed on the probe ends so that they and their samples could be attached to the hydraulic lines.

The remaining seven techniques for sampling internal pressure involved placing Douglas-fir and ponderosa pine samples in specially designed holders with probes that penetrated pre-drilled holes in the samples (Figure 3.4). Single-probe holders were made for samples approximately 30 x 30 x 80 mm. Double-probe and triple-probe holders were made for 50 x 50 x 80 mm samples. The top and bottom plates of each holder were made from 3 mm thick steel. The top plates had 1.6 mm diameter stainless steel tubing set through them to a depth of 30 mm and silver soldered in place. The tubing of the single-probe holder was placed so that it would extend longitudinally into a hole centered in the end of a sample.

Based on a sample having a 25 mm square cross section, this probe setup provided pressure measurements at a transverse depth of about 12 mm. Double-probe holders had probes placed to reach a point near the sample surface and at its center representing, respectively, 6 and 24 mm transverse depths in a sample with a 50 mm cross section. Triple-probe holders had an additional probe placed to measure pressure at a depth representing 12 mm. (Note: Vessel pressure was recorded with a separate transducer and this data was used to calculate transverse "surface-to-center" pressure differences for the different depths representing flow paths of 6, 12, and 24 mm.) A groove to hold an o-ring was milled in the bottom face of the single-probe sample holder tops. A compression-fitting nut and ferrule were pressed on the top end of the tubing to attach the sample holder probes to the hydraulic lines in the treating vessel.

The pressure-probe sample holder techniques for measuring internal pressure required a sealant be used as an integral part of each method. O-rings and several gasket materials were tested alone and in combination for their ability to prevent the treating fluid from leaking into the sample probes and producing false pressure measurements. Solid rubber gaskets were cut from 1.6 and 3.2 mm thick rubber sheets so that they were large enough to overhang the sample edges. The solid rubber gaskets were used by themselves in the double- and triple-probe holders and either alone or in combination with an o-ring in the single-probe holders. In some cases, silicone adhesive (Dow Corning Auto/Marine Sealant by Dow Corning Corp.; Midland, MI) was used in combination with a 3.2 mm gasket in the single probe holders.

Holder assembly was performed by drilling 2 mm diameter holes longitudinally through the end coating of the samples to their centers. Padding (made of 1.6 mm thick rubber sheeting) was placed in the holders first, followed by the wood sample, a sealant, and the top plate of the holder. The entire assembly was held together with threaded rods screwed into the bottom plate and held in place with nuts above the top plate. The sealant material encircling each pressure probe was pressed against the epoxied sample surface by tightening the sample

holder nuts. In most cases, the sample holder nuts were tightened by hand until the sealant material was no longer compressible. In the last few treatment applications, a torque-wrench was used in an attempt to more uniformly tighten the sample holder assembly. Torque settings of 2.9, 4.0, and 5.7 Nm were used.

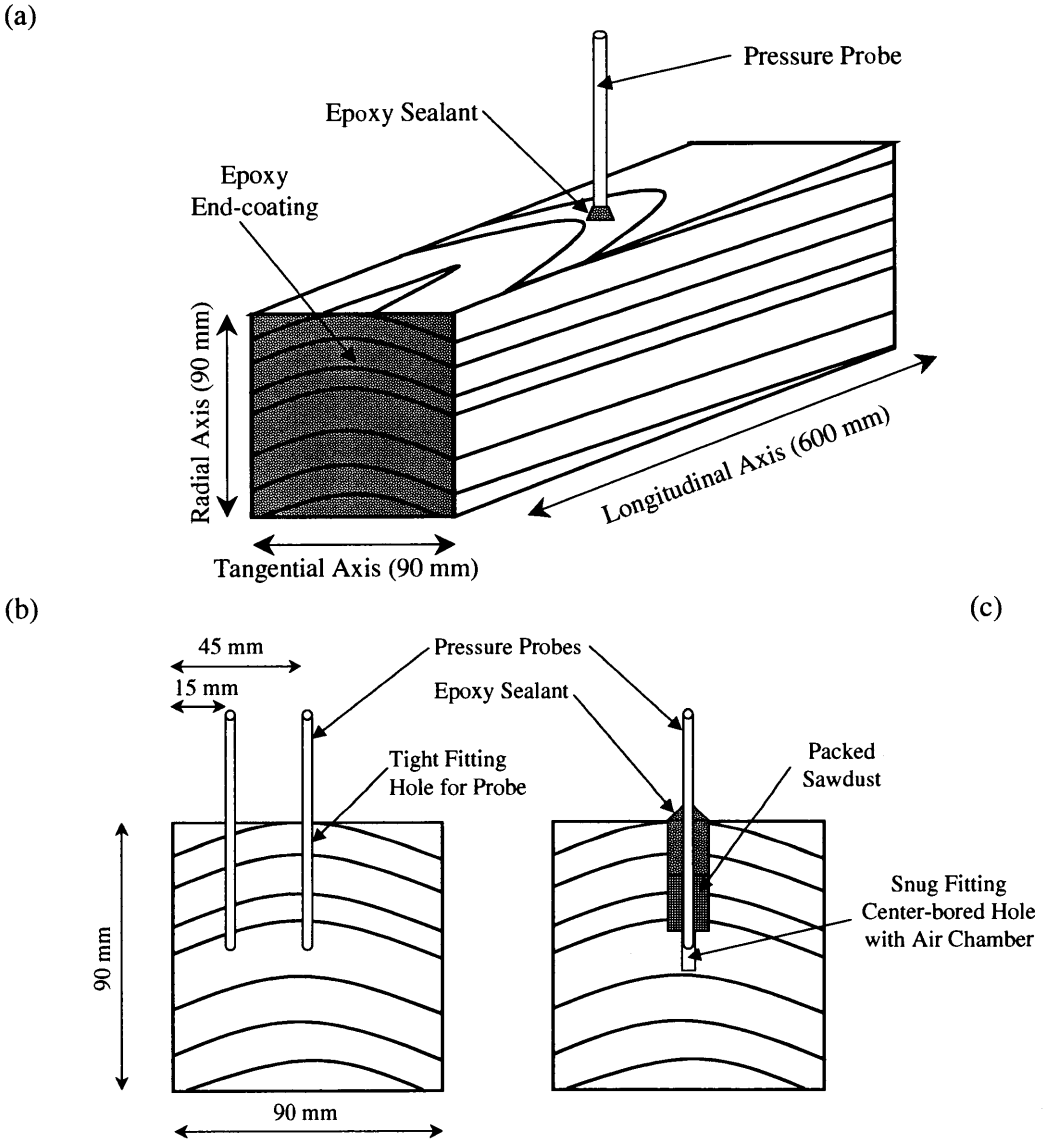


Figure 3.3 Pressure probes (1.6 mm tubes) set in place with epoxy are shown in the overall configuration of a single epoxied probe (a), in the cross section of a sample with two probes pressed in tightly fitting holes (b), and in the cross section of a two-stage-hole technique (c).

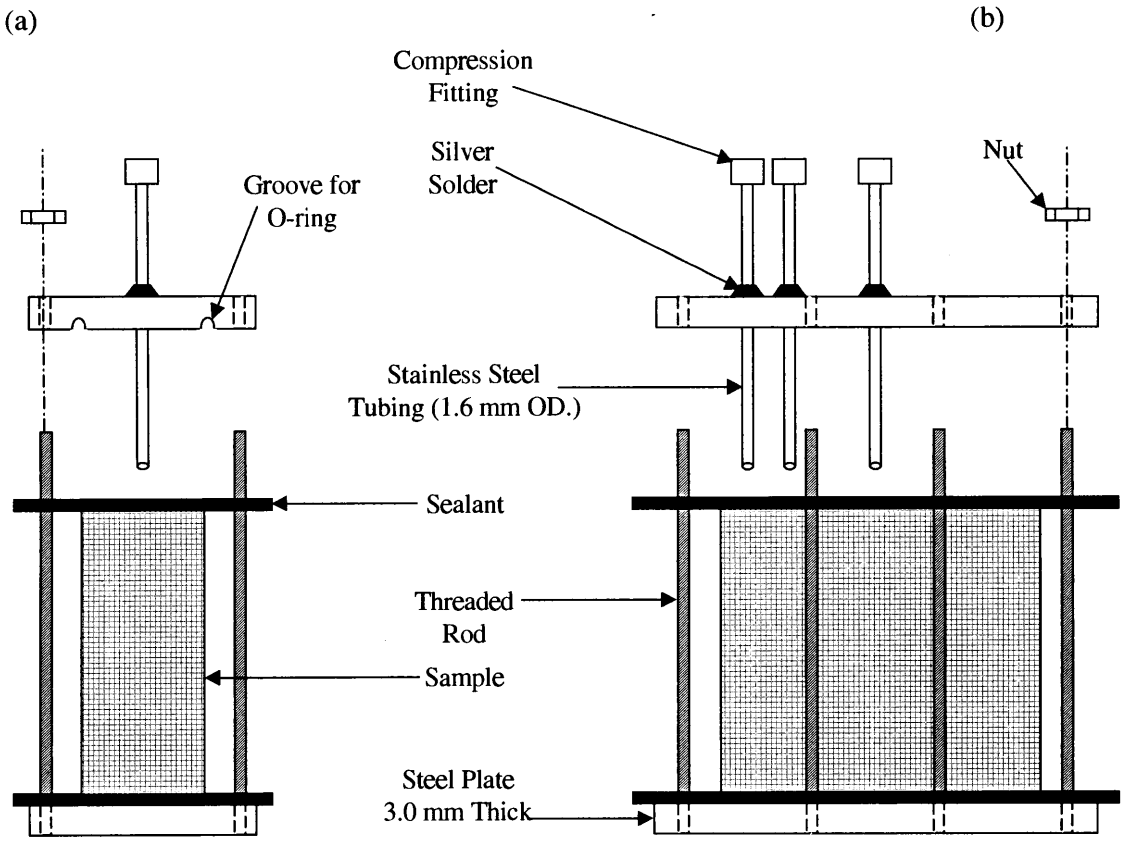


Figure 3.4 Examples of sample holders, (a) a single-probe sample holder and (b) a double-probe sample holder, used to measure pressure changes in wood during pressure treatments

3.3.5 Process and Wood Effects on Internal Pressure Response

Although many treatment runs were conducted (as discussed in Section 3.2.1), the following section provides the methodology used for those treatments from which pressure measurement data sets were used to compare the influence of specific process and wood variables.

Pressure Schedules: The influence of pressure treating schedules on pressure changes in wood during treating may be characterized by using two sets of internal pressure measurement data. In the first, internal pressure was measured in Douglas-fir mixed heart- and sapwood samples (90 x 90 x 600 mm) treated in air by modified Lowry or Rüping

processes. A single modified Lowry treatment with air was conducted by placing four samples in a treating vessel, applying a pressure of 720 to 790 kPa (absolute) for two hours, and then venting. Four modified Rüping treatments with air were conducted with four samples per treatment. The samples were placed in a treating vessel and an initial pressure of either 170 kPa or 310 kPa (absolute) was applied for 10 or 30 min followed by a 2 h press at 720 to 790 kPa. Internal pressure measurements were made every 10 s using the single-epoxied-probe method.

In the second set of pressure measurement data, comparisons were made between Douglas-fir heartwood samples treated in Cu-8 solution with either a modified Lowry or modified Bethell process. The Lowry process was as described above but was continued until internal pressure no longer seemed to increase. In the Bethell process, an initial vacuum (12 kPa absolute) was applied for 30 to 60 min before flooding the samples with Cu-8 solution and increasing pressure to between 720 and 790 kPa (absolute). When internal pressure no longer appeared to increase, pressure was released and solution drained. In one of the Bethell treatments, a sample was submerged in the solution before the initial vacuum was applied. Internal pressure measurements were made every 120 s with single-probe sample holders using either a thick gasket or a thick gasket and o-ring combination to seal the pressure probes.

Treating Media and Wood Permeability: Internal pressure data sets from the same experimental setup and samples were used for characterizing the influences of treatment media and wood permeability on pressure changes. Eight Douglas-fir heartwood and eight ponderosa pine sapwood samples (25 x 25 x 76 mm) were treated by a modified Lowry process using air or Cu-8 solution. Four of the Douglas-fir samples were treated with air and the remaining four were treated using Cu-8 solution. All eight pine samples were treated first in air and then, after allowing internal pressure to return to atmospheric pressure, submerged in Cu-8 solution and pressed. All samples were placed in single-probe sample holders using a

thick rubber gasket seal. Internal pressure was measured at 10 s intervals for the air treatments and at 120 s intervals for the liquid treatments. The samples were placed, four at a time, in the treating vessel and pressed to between 720 and 790 kPa (absolute) until their internal pressure no longer increased.

An additional comparison of treating media affects on internal pressure response can be made with data collected from two matched Douglas-fir heartwood samples (25 x 25 x 76 mm) treated at the same time using a Bethell process. One sample was placed in a tank of Cu-8 solution the other was kept out of the treating solution. The pressure schedule consisted of a 60 minute vacuum followed by a pressure period continued until internal pressure no longer increase. Internal pressure measurements were made every 120 s with single-probe sample holders using a thick (3.2 mm) gasket and o-ring combination to seal the pressure probes.

Transverse Depths: The internal pressure response at 6, 12, and 24 mm depths into wood along the radial axis was characterized using pressure measurement data from Douglas-fir heartwood samples treated with Cu-8 solution in multi-probe sample holders. Two modified Lowry treatments have data available when double-probe sample holders were used, and one treatment has data available from a triple-probe holder. One modified Bethell run treatment has data available when a double-probe holder was used and another when a triple-probe holder was used. Samples treated with a modified Lowry process were flooded with treating solution and pressed to between 760 and 790 kPa (absolute) until internal pressure no longer increased. Samples treated by a modified Bethell process had an initial vacuum applied before flooding and pressing until internal pressure leveled off. Pressure measurements were made at 120 s intervals.

3.3.6 Data Analysis

Internal pressure measurements are presented in graphic form only for those samples which did not appear to have pressure probe occlusions or leaks and that had pressures either approaching equilibrium with vessel pressure or that leveled off after a period of increase. Because of the disjointed nature of the replicates, no statistical analysis was possible. Instead, the data provide a guide to pressure response. To facilitate making comparisons between treatment variables, such as pressure processes or treating media, measurements or "quantifiers" were made on the internal pressure data. These measurements were selected on the bases of potentially indicating important aspects in the treatment process.

Each sample, regardless of the method of pressure application, experienced a time delay before an internal pressure response was noted. This delay may be attributed to the times required for the treating medium to enter a sample, for gas compression (treating gas and/or air in the sample), and the delay associated with the pressure measuring technique. To quantify this delay, the **time for a 35 kPa pressure rise** was recorded in the summary tables for each sample. For each pressure process, timing of this period was started when maximum treatment pressure was applied. Therefore, timing was started at the beginning of the Lowry treatments, after the initial pressure phase of the Rüping treatments, and at the initiation of the pressure phase during the Bethell treatments. In the case of the Bethell treatments, the delay prior to internal pressure response represented the time to recover atmospheric pressure after the initial vacuum phase and not time for a 35 kPa pressure increase.

Following the initial delay, pressure increased at a fairly constant rate until the majority of pressure rise was achieved. **The constant pressure increase rate** appeared to be unique to each sample. Kyte and Saunders (1978) suggested that the rate of pressure rise was correlated to the movement of preservative into wood based on the principle that the preservative volume displaces or compresses air in the wood, thus reducing the original

volume of material in wood and, correspondingly, increasing internal pressure. Pressure increases after this point were usually minimal, suggesting that the end of this period may be an efficient point to terminate the pressure phase of a treating schedule.

Total time to equalization (of pressure) was measured as a guide to how long it would take to process each sample to a fixed pressure endpoint. This time period started when the treatment was started and concluded when internal pressure no longer continued to rise. When a treatment was not continued long enough for pressure equilibrium to be reached, time was estimated by extrapolating graphs of pressure data beyond the time of treatment. In some cases, however, time to equilibrium may not be applicable since internal pressure leveled off below vessel pressure (Bergman, 1991; Peek and Goetsch, 1990).

The surface-to-center pressure difference after the constant pressure increase period (**ΔP after constant pressure increase**) might be used as a measure of wood treatability or thoroughness of liquid impregnation by a given process, since pressure increase after this point was usually minimal. Air pockets may become isolated in wood and prevent complete penetration of a treating medium. This isolation can be continuous, in highly refractory wood, or in small pockets, as in earlywood of moderately treatable wood. A larger total volume of isolated areas should result in a larger surface-to-center pressure difference after the constant pressure increase period.

Back-pressures or surface-to-center pressure differences immediately after vessel venting (**ΔP after venting**) were noted. Back pressure is an indication of residual pressure in the wood resulting from the treatment process. This pressure is often indirectly regulated in commercial process by the application of an initial pressure and/or a final vacuum.

3.4 Results and Discussion

Before evaluating internal pressure measurement techniques or the influences of process and wood variables on internal pressure response during pressure treatments, a few points must be considered. The same samples were used to evaluate both internal pressure measurement techniques and the influence of process and wood variables on internal pressure response. In addition, different pressure measurement techniques were occasionally used when comparing different process and wood parameters. Therefore, it is impossible to separate the pressure measurement data acquired during the evaluation of a particular measurement technique from numerical data used to help show the influence of a particular process or wood parameter on internal pressure response This dilemma was addressed by providing a qualitative evaluation of the pressure measurement techniques and reserving numerical data for a graphical and tabular representation of internal pressure response to process and wood variables.

3.4.1 Pressure Measurement Techniques

Difficulties with Pressure Measurement Evaluations: Aborted treatment runs, runs stopped before pressure increased, and the highly permeable pine sapwood complicated the evaluation of pressure measurement techniques. Treatments were sometimes aborted due to equipment failures or immediate seal leakage. Because these runs were not used for evaluating pressure measurement techniques, the effectiveness presented for a technique may be biased. Several runs were terminated before pressure inside the samples rose substantially. During the initial treatments, the absence of internal pressure increases during liquid treatments of Douglas-fir was thought to have indicated that a pressure probe was blocked. But, based on later work showing that pressure development was exceedingly slow in some

samples, information from these runs was latter assumed to indicate effective probe installation. Highly permeable pine sapwood (allowing rapid internal pressure response) and relatively long pressurization times (due to the large treating vessel volume) made it difficult to determine if pressure probe and sealant combinations were effective with this species. It was found that 100 % penetration could be achieved in ponderosa pine sapwood samples (2.5 x 2.5 x 7.6 cm) which were placed in an oil treating solution and either evacuated for 25 min. followed by a 5 min soak or pressed to 480 kPa over a five minute period. The time required to reach treating pressure (710 – 790 kPa) during Lowry treatments used in this investigation was about 9 min. Thus, the pine samples were likely to have been completely treated before processing pressures were fully applied.

Determination of Pressure Probe Leaks: Arganbright and Resch (1970) and Cobham and Vinden (1995) stated that pressure probe leaks could be detected by a sudden rise of internal pressure. While this was evident in this work, a sudden rise due to leakage was difficult to delineate from the rapid treatment of highly permeable pine sapwood samples, where internal and external pressures followed similar trends with little time delay. Also complicating the delineation of success versus failure in a technique was the potential for leaks occurring at a point in a treatment cycle when pressure increase was expected, such as after vessel pressure increased following a vacuum period or for slow leaks. A more careful evaluation of pressure sampling techniques can be performed by comparing several factors. In addition to sudden pressure changes, the absence of a characteristic internal pressure phase seen during a typical treatment under similar conditions was used as an indicator of the presence of a leak. In treatments where preservative penetration in the wood did not reach the pressure probe, the presence or absence of solution intrusion around the probe was also used as an indicator of sealant effectiveness.

The detection of leaks during internal pressure measurements can be assisted by making comparisons between pressure responses from samples that did not have probe leaks and responses from samples that did. Figure 3.5 shows pressure measurements at the centers of three Douglas-fir heartwood samples treated in oil by a Bethell process. When the initial vacuum was pulled on the empty treating vessel, pressure in the sample quickly decreased. After 30 min, the vessel was flooded with an oil solution and pressure applied. Pressure within the samples then took from 170 to 370 min before it returned to the atmospheric level. After this, internal pressure rose at almost a constant rate until approaching that of the treating vessel. So, the characteristic internal pressure phases for this treatment are a reduced pressure during the vacuum, an extended period of vacuum after vessel pressure has been increased, a relatively constant pressure increase period, and a leveling off near vessel pressure.

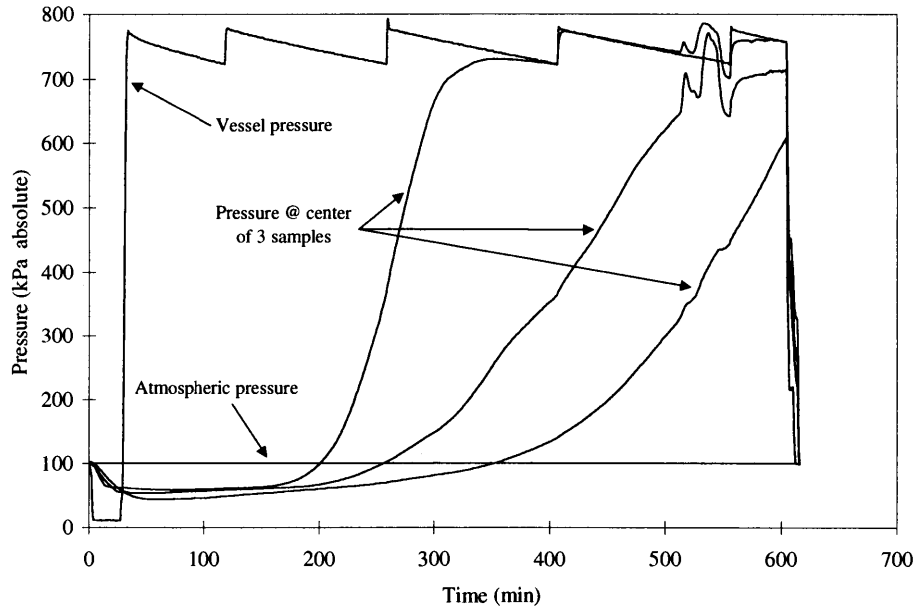


Figure 3.5 Pressure measurements at the center of three Douglas-fir samples (2.5 x 2.5 x 7.5cm) treated with Cu-8 in mineral spirits (oil) by a modified Bethell process. Pressure probe sealant appears to be good.

Figure 3.6 shows two similarly treated Douglas-fir samples which contained pressure probes that clearly leaked. In one of the samples, internal pressure abruptly increased after the application of vessel pressure. In the second, there was no extended vacuum period.

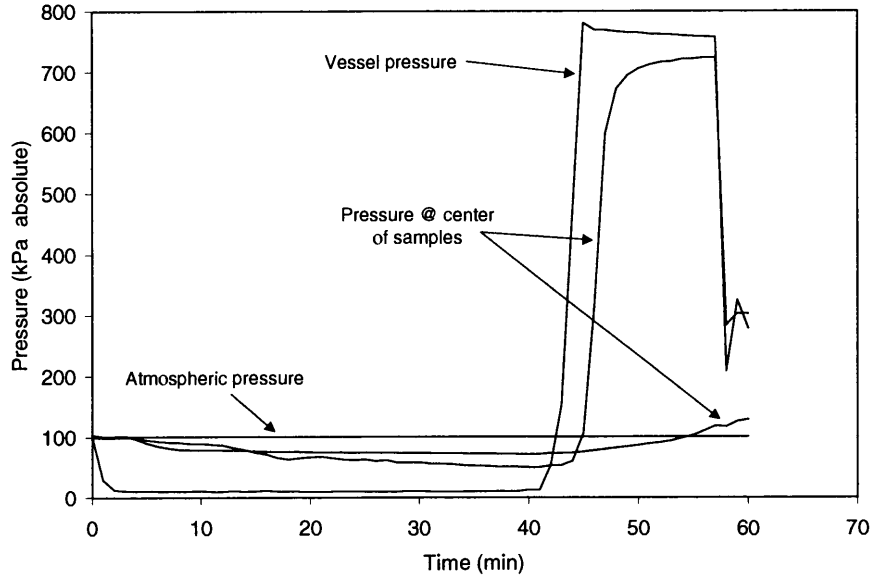


Figure 3.6 Pressure measurements at the center of two Douglas-fir samples (2.5 x 2.5 x 7.5cm) treated with Cu-8 in mineral spirits (oil) by a modified Bethell process. The sealant has leaked around both probes.

Figure 3.7 helps to depict the difficulty of delineating internal pressure responses due to probe leaks versus variations in sample permeability. By looking at the two pressure responses in these samples, it initially appears that there were no leaks. However, upon closer comparison to pressure responses in the similarly treated Douglas-fir samples of the previous two figures, there are indications that leaks did occur. The extended vacuum period ranges only from 30 to 45 min versus 170 to 370 min for the samples in Figure 3.5, and pressure rise after the extended vacuum in these sample is almost as sudden as it was in the sample probe that abruptly failed in Figure 3.6. Uncertainty still remains, though, because if the samples in

Figure 3.7 were considerably more permeable than those in Figure 3.5 then more rapid pressure response would be expected. Samples in these three figures were, however, made from the same source board. In summary, these three graphs show that the presence of pressure probe leaks can be determined from pressure response comparisons in similarly treated samples.

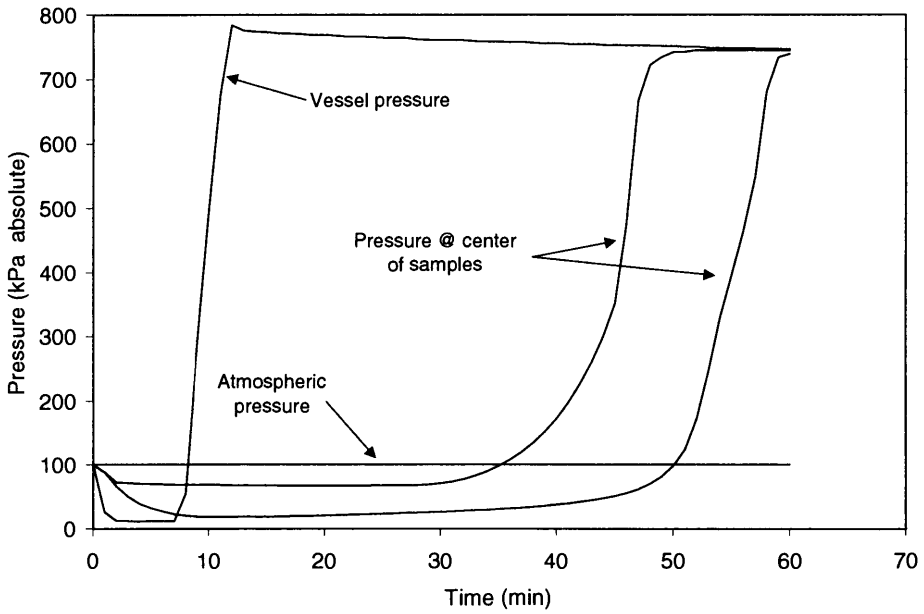


Figure 3.7 Pressure measurements at the center of two Douglas-fir samples (2.5 x 2.5 x 7.5cm) treated with Cu-8 in mineral spirits (oil) by a modified Bethell process. Pressure probe sealant has likely leaked.

Pressure Measurement Technique Evaluations: Internal pressure measurement techniques were evaluated for their ability to provide internal pressure readings without leaking and the practicality of their use as a measurement technique. All probe techniques, treatment conditions during which the probes were evaluated, and the condition of the probes during each treatment are listed in Appendix A. Table 3.1 summarizes this appendix by listing

the number of probes evaluated for each probe/sealant technique, the condition of these probes, and the technique effectiveness. The technique effectiveness is the percent of good probes in each technique.

Small tubes pressed in tight fitting holes represented the simplest internal pressure measurement technique. However, this method was not successful since all six probes that were tested showed the presence of air or oil leaking around the probes. Attempts to modify this technique by brushing epoxy on the tubes before placing them in slightly enlarged holes was also unsuccessful since the epoxy settled in the bottom of the holes and blocked the probe openings.

A two-staged hole with a sawdust barrier was developed to keep epoxy away from the open end of the pressure probe while allowing epoxy to seal around the probe sides. This technique was fairly simple, but probe position relative to sample hole depth had to be observed during sample preparation. This and the previous method required that compression fittings be placed on each pressure-probe tube adding cost to the procedure. Four of the twenty samples seemed to provide representative pressure measurements without being blocked (an effectiveness of 20 %). The lack of probe blockage during air pressing and the occurrence of little or no pressure rise during liquid treatment support the effectiveness of this pressure probe and sealant technique. When these samples were treated in air, it was difficult to tell which samples were effectively sealed and which leaked since pressure responses were similar. The long pressure equalization period after maximum vessel pressure was reached and the presence of back-pressure in the air treated samples support effective sealing; however, no initial time delay was detected. When the samples were later treated with Cu-8 in mineral spirits, to compare air and liquid treatments, fourteen of the twenty samples leaked (shown by the presence of preservative around the embedded probes and an unusually rapid internal pressure increase).

Table 3.1 Effectiveness of various techniques for sealing pressure probes in wood samples for the measurement of internal pressure during conventional pressure treating processes. [1]

Pressure Probe Type	Sealing Method	Number of Probes in each Probe/Sealant Technique	Condition & Number of Probes			Technique Effectiveness (Percent of Good Probes)
			Blocked	Leaked	Good	
2 Probes	Pressed in tight fitting holes	6	0	6	0	0
Single probe	Two stage hole with epoxy	20	0	16	4	20
Single-probe Holder	O-ring	8	0	5	3	38
	O-ring with 1.6 mm gasket	8	1	7	0	0
	O-ring with 3.2 mm gasket	55	2	18	35	64
	3.2 mm gasket	45	2	11	32	71
	3.2 mm gasket with Si adhesive	4	0	0	4	100
Double-probe holder	3.2 mm gasket	5	0	1	4	80
Triple-probe holder	3.2 mm gasket	6	0	0	6	100

[1] Results from runs aborted due to immediate equipment failure and/or seal failure are not included. Results from air and oil treatment mediums are combined for each sampling technique.

No intruding solution was seen around the probes that appeared to be giving representative pressure measurements. It was also found that the probes which had leaks could be removed easily by pulling on them, thus, confirming poor adhesion between the epoxy and the probes. This poor adhesion was undoubtedly the source of the observed leaks. Further use of epoxy as a sealing method will require that the probes are first rubbed with sandpaper to roughen their surfaces and then washed with a solvent.

Single-probe sample holders combined with five different sealing methods provided mixed success. A definite advantage of these techniques was the ability to re-use pressure probes and compression fittings since these were a permanent part of the sample holders. Unfortunately, these pressure sampling techniques did not eliminate the need for wood samples to be drilled and epoxied; in fact, additional sample preparation care was needed to make the epoxy coated ends as flat and parallel as possible. These sampling techniques were further complicated by the difficulty of uniformly tightening the assembled holders. The seal surrounding the probe leaked if the probe-holder top was not tightened enough or was not squarely tightened. Non-uniform tightening caused the samples to twist so that their end-surfaces were no longer parallel to the holder surfaces. The twisting, coupled with possible shifting of the sealant upon tightening, allowed the treating medium access to the pressure probe without traveling through the wood. Also, twisting of the sample caused shear stresses in the wood. In one case, a sample was split along a growth ring from excessive non-uniform tightening. If the top was tightened squarely, but with too much force, sample ends would be crushed.

The single-probe holder with only an o-ring had an effectiveness of only 38 %. An o-ring, which fit in the groove of the sample holder top, probably did not provide enough sealant material between the sample and the holder top. Upon tightening, especially if done so non-uniformly, spaces could result between the holder top and the sample. The use of a thin

rubber gasket (1.6 mm) in combination with the o-ring proved to be completely ineffective. The thin gasket wrinkled under the holder top preventing uniform tightening and creating gaps in the sealant. It is unclear why one of the probes using this technique was blocked. Possibly the probe hole was not drilled deep enough causing the probe tip to be compressed in the bottom of the hole when the sample holder top was tightened in place. Sealant effectiveness improved when thicker (3.2 mm) gaskets were used. Of the 55 probes tested using this technique 64 % were effective in providing pressure measurements. The use of only the thick gasket seemed to provide even better sealing (71 % effectiveness). But, it is unclear whether the lack of an o-ring, which may sporadically confound the sealing method, or use of a torque wrench to assist in tightening the holders lead to the improved performance of this technique. A torque wrench was only used with the thick gasket sealing method. A torque setting of 5.7 Nm crushed the earlywood bands in the end of the Douglas-fir samples, while settings of 4.0 and 2.9 Nm did not hurt the wood. Although one of the samples using the highest torque setting was split along a growth ring, the remaining three had probes that did not leak. Six out of eight samples with the 4.0 Nm setting had non-leaking probes, while only one of four samples with the 2.9 Nm setting appeared to be effectively sealed. The use of a silicone adhesive between the sample and gasket was very effective. Although gaskets were cut slightly by holder tops, the lack of gasket shifting and the added sealant layer prevented leakage. Adding silicon adhesive increased preparation time and might not be effective for long treatment times since the material was partially dissolved in the mineral spirits-based treating solution.

The double- and triple-probe sample holders were only used with thick (3.2 mm) gaskets. Both of these pressure sampling techniques were very effective. The additional bolts in these holders reduced the tightening problems associated with the single-probe holders. One of the samples on which the double-probe technique was tested had a check leading to the

center probe that was not detected until after treatment. Therefor, this probe was not used in evaluating the technique effectiveness.

3.4.2 Process and Wood Affects on Internal Pressure Response

Pressure Schedules: Two sets of internal pressure measurements were used to make comparisons between pressure responses in samples treated either by modified Lowry or Rüping processes, in the first set, or by modified Lowry or Bethell processes, in the second set. Pressure measurements form the first data set are shown in Figures 3.8 to 3.12 and summarized in Table 3.2.

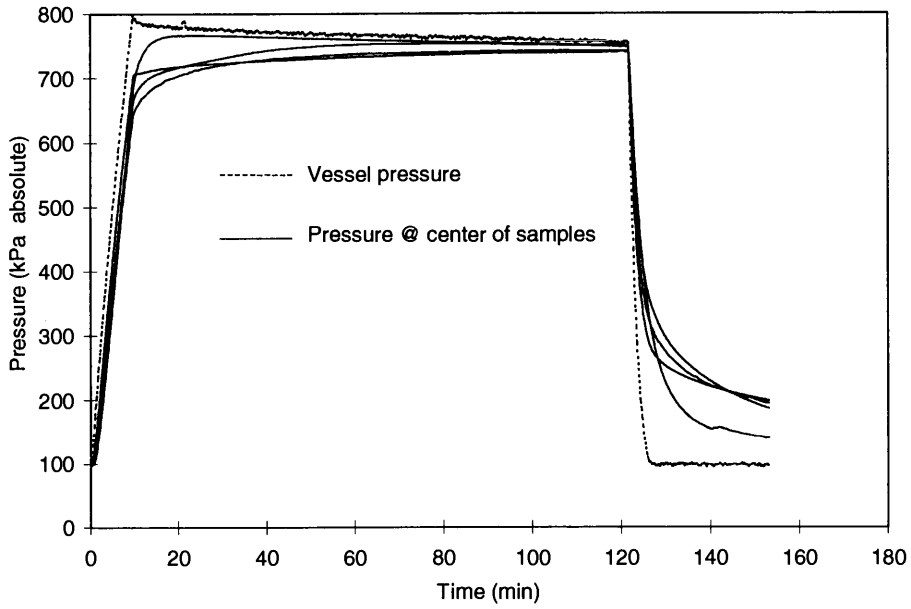


Figure 3.8 Internal pressure measurements at the center of four Douglas-fir heartwood samples (90 x 90 x 600 mm) treated with air by a modified Lowry process (120 min @ 760 – 790 kPa absolute).

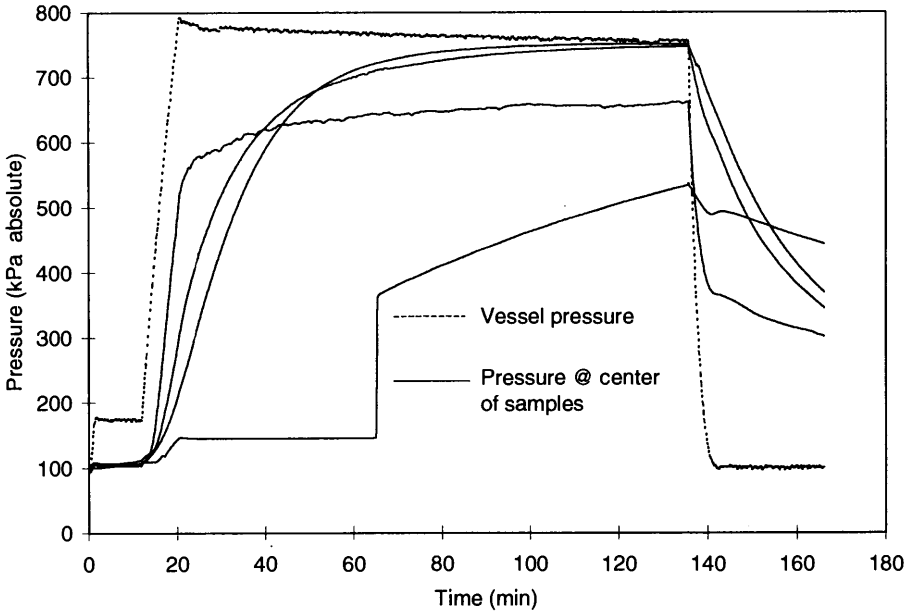


Figure 3.9 Pressure measurements at the center of four Douglas-fir heartwood samples (90 x 90 x 600 mm) treated with air by a modified Rüping process (10 min @ 170 kPa, then 120 min @ 760 – 790 kPa absolute).

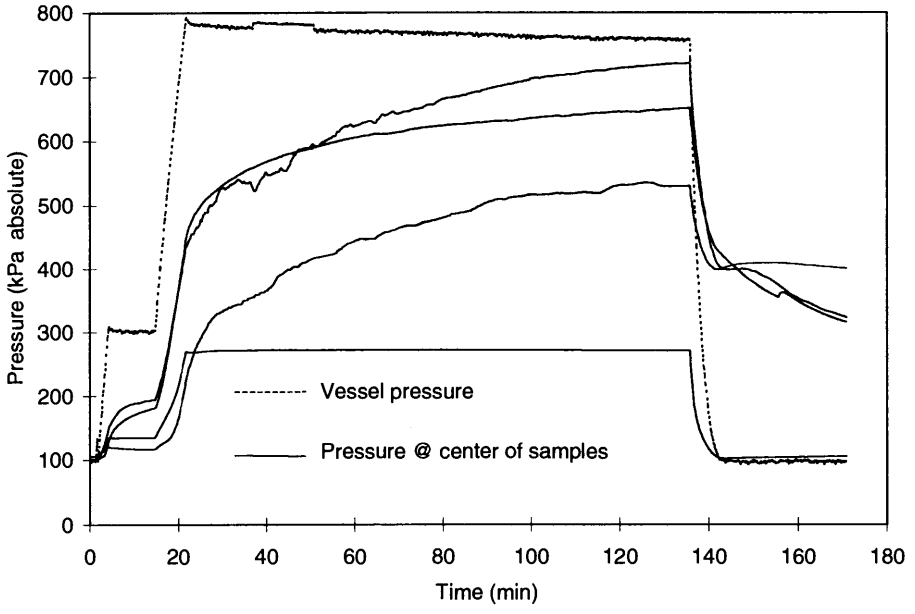


Figure 3.10 Pressure measurements at the center of four Douglas-fir heartwood samples (90 x 90 x 600 mm) treated with air by a modified Rüping process (10 min @ 310 kPa, then 120 min @ 760 – 790 kPa absolute).

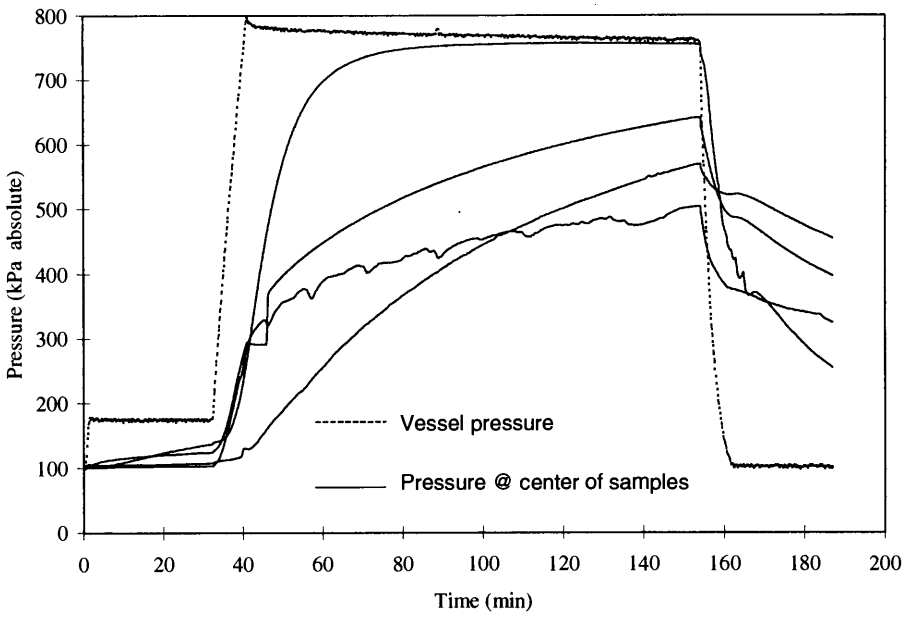


Figure 3.11 Pressure measurements at the center of four Douglas-fir heartwood samples (90 x 90 x 600 mm) treated with air by a modified Rüping process (30 min @ 170 kPa, then 120 min @ 760 - 790 kPa absolute).

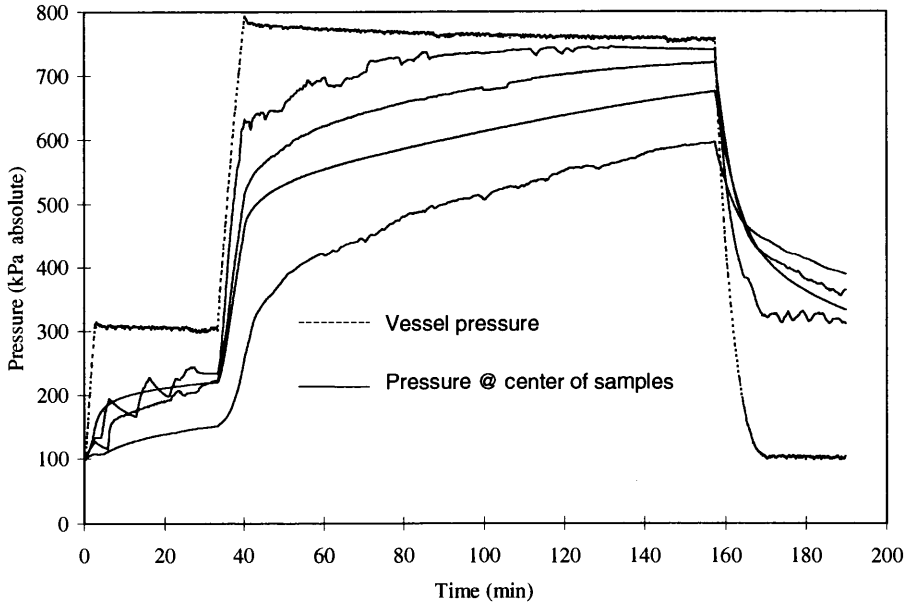


Figure 3.12 Pressure measurements at the center of four Douglas-fir heartwood samples (90 x 90 x 600 mm) treated with air by a modified Rüping process (30 min @ 310 kPa, then 120 min @ 760 - 790 kPa absolute).

Table 3.2 Internal pressure response quantifiers from pressure measurements at the center of Douglas-fir heartwood samples (90 x 90 x 600 mm) treated in air by modified Lowry or Rüping processes. [1] This data was used to compare the influences of pressure schedule on internal pressure response.

Treatment	Time for 35 kPa Rise [2] (min)	Total Time to Equalization (min)	Constant Pressure Increase Rate (kPa/min)	ΔP after Constant Pressure Increase (kPa)	ΔP after Venting (kPa)
(Lowry – **Figure 3.8**) Pressed @ 74 kPa/min to 750 – 800 kPa for 120 min	1.4 (0.2)	137 (15)	65 (2)	125 (20)	-212 (24)
(Rüping – **Figure 3.9**) Pressed to 170 kPa for 10 min then @ 72 kPa/min to 750 – 800 kPa for 120 min	5.1 (1.5)	219 (109)	40 (17)	151 (55)	-433 (118)
(Rüping - **Figure 3.10**) Pressed to 310 kPa for 10 min then @ 70 kPa/min to 750 – 800 kPa for 120 min	2.4 (1.4)	304 (50)	36 (8)	387 (75)	-310 (8.2)
(Rüping - **Figure 3.11**) Pressed to 170 kPa for 30 min then @ 97 kPa/min to 750 – 800 kPa for 120 min	5.3 (3.4)	270 (106)	21 (10)	327 (122)	-353 (57)
(Rüping - **Figure 3.12**) Pressed to 310 kPa for 30 min then @ 80 kPa/min to 750 – 800 kPa for 120 min	1.6 (1.1)	212 (16)	45 (14)	297 (103)	-301 (47)

1 Values represent the average of four samples. Numbers in parentheses represent one standard deviation. All pressure values are in kPa absolute.

2. Time started after initial pressurization period in Rüping treatments.

Caution must be used with this first set of data because the integrity of their pressure-probe seals remains questionable. Although leaks were detected in fourteen of these samples when they were treated with a Cu-8 solution; the leaks may have been small enough that they did not affect the air treatments initially carried out on these samples. Pressure responses during air treatments were similar for those samples that did and did not leak during the Cu-8 treatments.

The time for the 35 kPa pressure rise, the constant pressure increase rate, and the total time to equalization for the Lowry treatment indicated that air must have entered the samples more quickly, causing a faster pressure response than for any of the Rüping processes. The smaller surface-to-center pressure difference immediately after the constant pressure increase period and after venting may indicate more complete transfer of air into and out of the Lowry treated samples compared to those treated with the four Rüping processes. Slower and more varied pressure responses and larger pressure differences in the Rüping samples could be attributed to air forced into the samples during the initial pressure application. The initial air press may aspirate pit membranes and/or increase the amount of air that must be compressed during treating before a pressure change can be detected in the wood. Reduced air permeabilities with the continued application of air pressure were noted during the determination of air permeability in Chapter 5. This finding supports pit aspiration as a possible explanation for delayed pressure response. Within the Rüping treatments, an initial pressure of 170 or 310 kPa for 10 or 30 min did not produce consistent internal pressure response differences.

In the second set of data used to compare the influence of pressure schedules on internal pressure response, samples were treated with Cu-8 in mineral spirits using a modified Lowry or Bethell process. Pressure measurements from this data set are shown in Figures

3.13 and 3.14 (summarized in Table 3.3) for the Lowry treatments and in Figures 3.15 to 3.17 (summarized in Table 3.4) for the Bethell treatments.

Comparison between initial pressure responses are not easily made due to the fact that the Bethell treatments involved an initial vacuum. Slower internal pressure increase (averages of 0.1 kPa/min versus 3.3 kPa/min) and longer average time to pressure equalization (11,400 min versus 1,142 min) indicate that the pressure response during the Lowry treatments was considerably slower than during the Bethell treatments. An interesting comparison was noticed with the surface-to-center pressure differences after the constant pressure increase periods. Internal pressure in two of the three Lowry samples leveled off around 350 and 500 kPa, even after an extended treatment period. Only one of the six Bethell samples showed a similar pressure plateau around 500 kPa. The leveling of pressure considerably below the surrounding vessel pressure, resulting in a large surface-to-center pressure difference, may be attributed to a discontinuity in the flow of treating medium to the pressure probe resulting from trapped air. Kelso et al. (1963) demonstrated reduced flow caused by the formation of air bubbles. The application of an initial vacuum during the Bethell treatments would remove air from the samples, possibly allowing more complete oil penetration. This, in turn could explain the lower average pressure differences. The surface-to-center pressure difference after constant pressure increase period may, therefore, be an indicator of treatment thoroughness or treatability of wood. The initial vacuum also appeared to reduce the back-pressure remaining in samples immediately after treatment, but the lack of measurements during Lowry treatments hinders the ability to make comparisons between the two treatments.

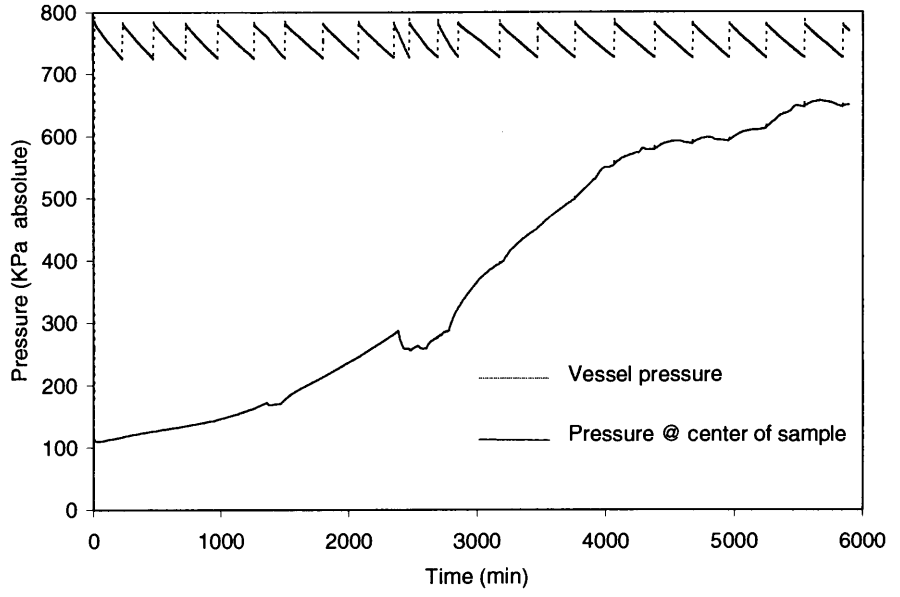


Figure 3.13 Pressure measurements at the center of a Douglas-fir heartwood sample (25 x 25 x 76 mm) treated with oil by a modified Lowry process.

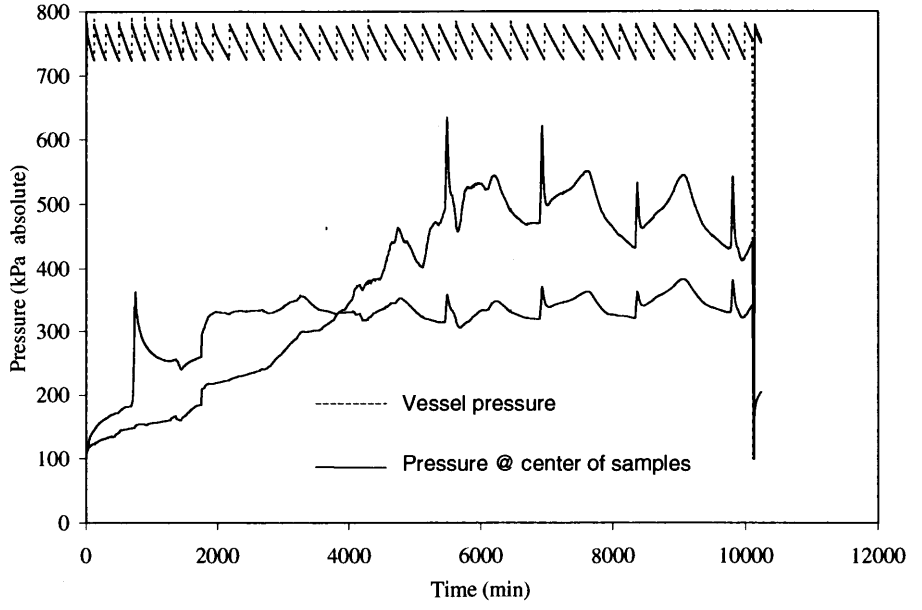


Figure 3.14 Pressure measurements at the center of two Douglas-fir heartwood sample (25 x 25 x 76 mm) treated with oil by a modified Lowry process.

Table 3.3 Internal pressure response quantifiers from pressure measurements at the center of three Douglas-fir heartwood samples (25 x 25 x 76 mm) treated with oil by a modified Lowry process at 720 – 790 kPa. This data was used to compare the influences of treatment variables including pressure schedule, treating medium, and wood permeability on internal pressure response. [1]

Treatment (Run) Conditions	Time for 35kPa Rise (min)	Total Time to Equalization (min)	Constant Pressure Increase Rate (kPa/min)	ΔP after Constant Pressure Increase (kPa)	ΔP after Venting (kPa)
(Figure 3.13) Initial Press Rate: 72 kPa/min Treatment Time: 6,735 min	1,000	11,400 [2]	0.2	183	-261
(Figure 3.14) Initial Press Rate: 114 kPa/min Treatment Time: 10,226 min	455	— [3]	0.1	302	— [4]
	70	— [3]	0.1	425	— [4]
Average (Std.)	508 (382)	11,400	0.1 (0.05)	303 (99)	-261

1 All pressure values are in kPa (absolute).
2 Total time to equalization obtained by extrapolating graphed data beyond actual treatment.
3 Internal pressure plateaued below vessel pressure.
4 No data were recorded for this measurement.

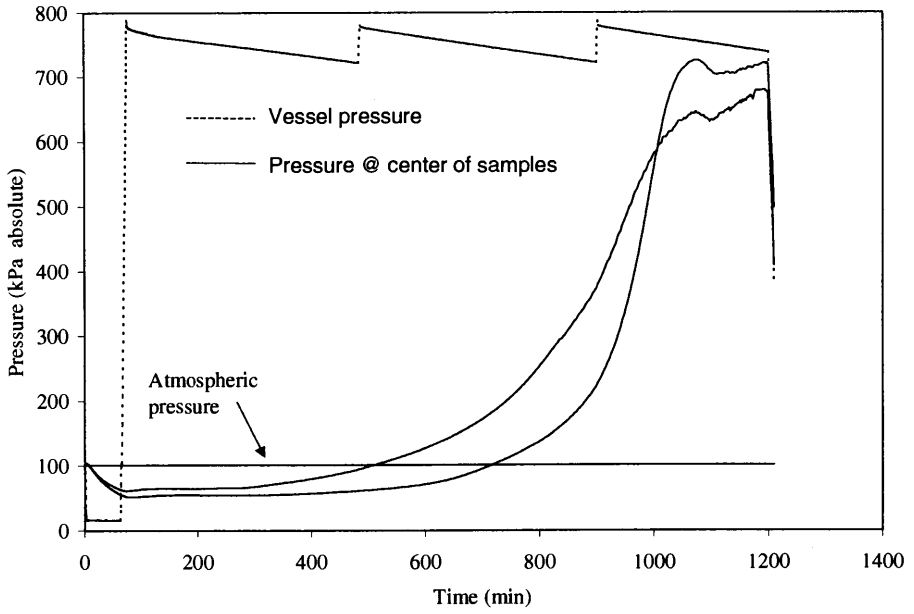


Figure 3.15 Pressure measurements at the center of two Douglas-fir heartwood samples (25 x 25 x 76 mm) treated with oil by a modified Bethell process.

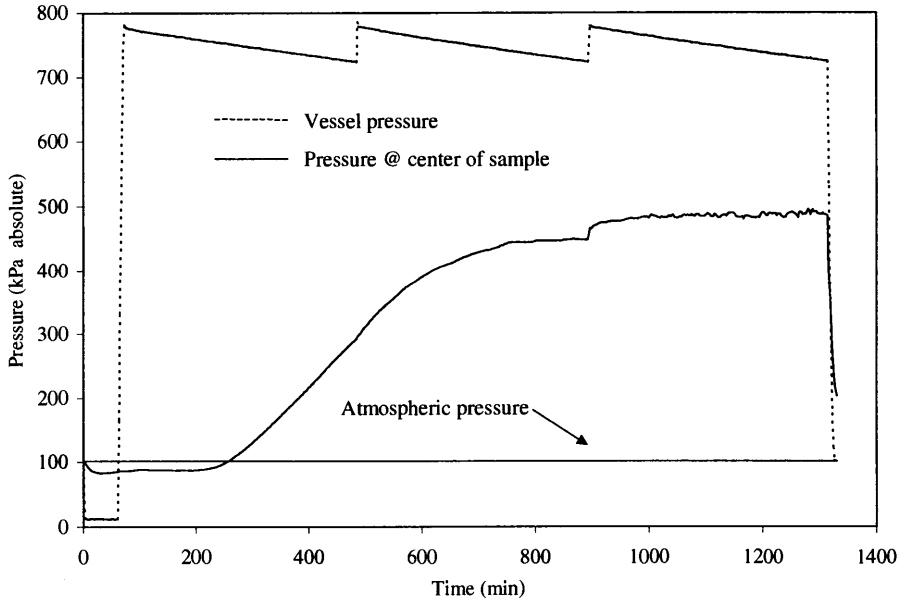


Figure 3.16 Pressure measurements at the center of a Douglas-fir heartwood sample (25 x 25 x 76 mm) treated with oil by a modified Bethell process.

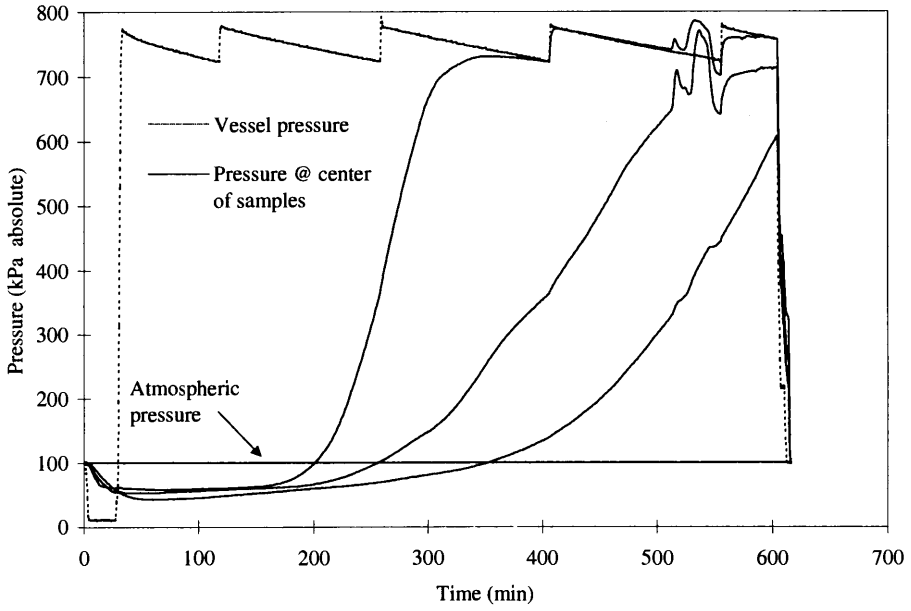


Figure 3.17 Pressure measurements at the center of three Douglas-fir heartwood samples (25 x 25 x 76 mm) treated with oil by a modified Bethell process.

Table 3.4 Internal pressure response quantifiers from pressure measurements at the center of six Douglas-fir heartwood samples (25 x 25 x 76 mm) treated with oil by a modified Bethell process at 720 – 790 kPa. This data was used to compare the influences of pressure schedules on internal pressure response. [1]

Treatment (Run) Conditions	Time to Atmospheric Pressure (min)	Total Time to Equalization (min)	Constant Pressure Increase Rate (kPa/min)	ΔP after Constant Pressure Increase (kPa)	ΔP after Venting (kPa)
(Figure 3.15) Vacuum: 24 kPa for 60 min Initial Press Rate: 63 kPa/min Treatment Time: 960 min	465	2,280 [2]	2.1	149	— [5]
	661	1,644 [2]	4.6	58	— [5]
(Figure 3.16) Vacuum: 14 kPa for 60 min Initial Press Rate: 72 kPa/min Treatment Time: 1,260 min	190	— [3]	0.9	355	-112
(Figure 3.17) Vacuum: 12 kPa for 30 min Initial Press Rate: 205 kPa/min Treatment Time: 564 min	322	740 [2]	2.9	— [4]	-231
	174	407	6.9	56	-141
	230	640 [2]	2.3	68	-173
Average (Std.)	340 (174)	1,142 (707)	3.3 (2.0)	137 (114)	-164 (44)

1 All pressure values are in kPa (absolute).
2 Total time to equalization obtained by extrapolating graphed data beyond actual treatment.
3 Internal pressure plateaued below vessel pressure.
4 This run was terminated too early.
5 No data were recorded for this measurement.

The application of a vacuum before solution is added to the treatment vessel during Bethell processes seems to be important. A single Bethell sample (Figure 3.16) was submerged before the vacuum was applied. As a result, only a limited vacuum was able to develop inside of the sample (83.4 kPa versus 43.9 to 61.4 kPa absolute). The rate of pressure increase in this sample resembled that seen in the Lowry treatments, and as with two Lowry samples, internal pressure reached a plateau far below vessel pressure. The limited vacuum and the similarity of pressure response to that seen in wood treated by the Lowry process, support the importance of eliminating air from wood before the application of liquid treating media.

The process by which pressure is applied to wood can influence the flow of a treating medium into the wood and thus the amount of time it takes for the transfer of the applied pressure into the wood. The initial vacuum in the Bethell processes removed air from the wood and allowed treating oil to enter with ease, resulting in relatively short treatment times and small surface-to-center pressure differences. The Rüping processes used an initial pressure application to force additional air into the wood. This air appeared to hinder the flow of air into and out of the wood during the remainder of the process and resulted in relatively large surface-to-center pressure differences. The Lowry processes, which used no initial vacuum or pressure, resulted in internal pressure responses in between those for the Bethell and Rüping treatments.

Treating Media: The influence of treating media on internal pressure response was compared using two sets of internal pressure measurements. In the first set, comparisons were made on data from Douglas-fir heartwood samples treated in either Cu-8 solution or air. Data for samples treated in the Cu-8 solution has already been presented (Figures 3.13 and 3.14 and Table 3.3) Data for samples treated in air are presented in Figures 3.18 and 3.19 (summarized Table 3.5).

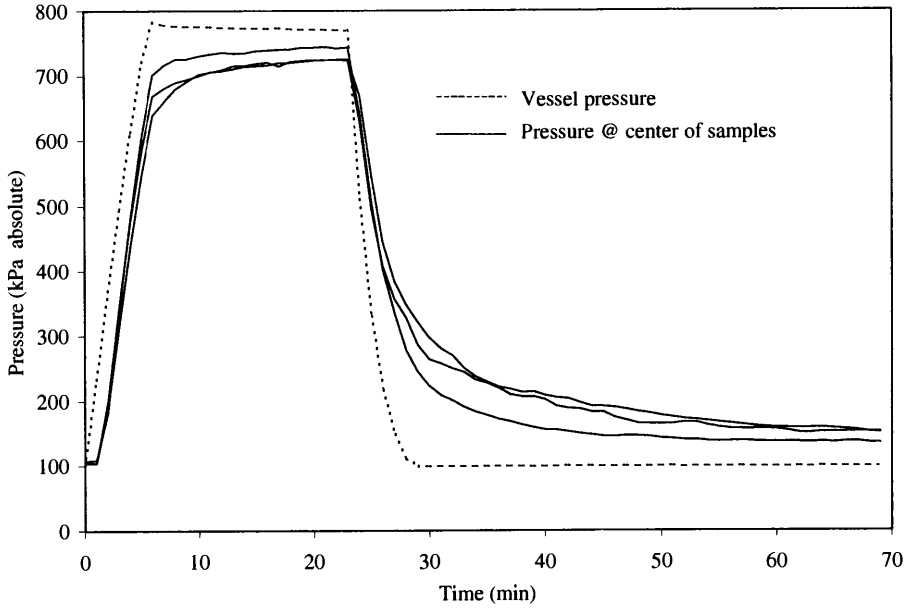


Figure 3.18 Pressure measurements at the center of three Douglas-fir heartwood samples (25 x 25 x 76 mm) treated with air by a modified Lowry process.

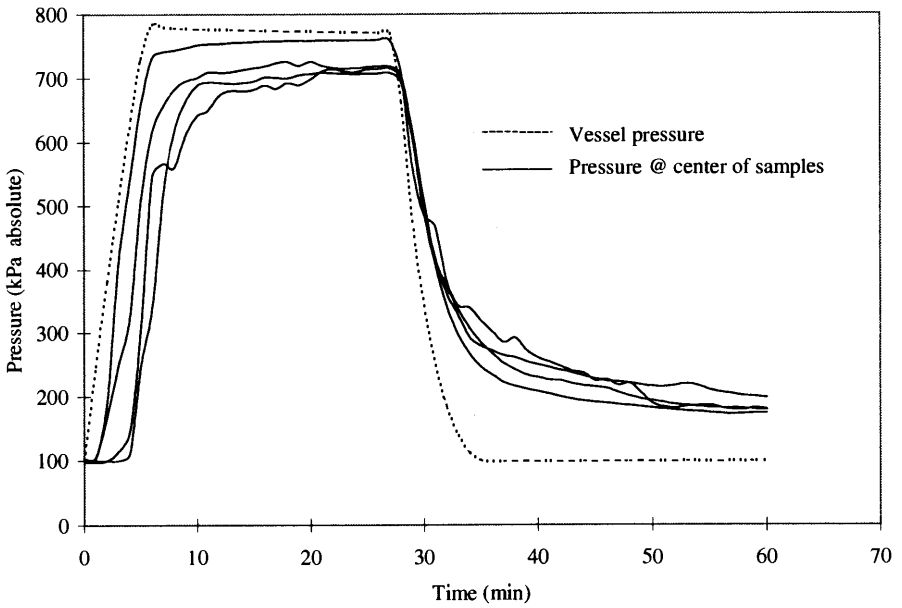


Figure 3.19 Pressure measurements at the center of four Douglas-fir heartwood samples (25 x 25 x 76 mm) treated with air by a modified Lowry process.

Table 3.5 Internal pressure response quantifiers from pressure measurements at the center of seven Douglas-fir heartwood samples (25 x 25 x 76 mm) treated with air by a modified Lowry process at 720 – 790 kPa. This data was used to compare the influences of treatment variables including treating medium and wood permeability on internal pressure response. [1]

Treatment (Run) Conditions	Time for 35kPa Rise (min)	Total Time to Equalization (min)	Constant Pressure Increase Rate (kPa/min)	ΔP after Constant Pressure Increase (kPa)	ΔP after Venting (kPa)
(Figure 3.18) Initial Press Rate: 130 kPa/min Treatment Time: 23 min	1.4	45 [2]	118	110	-188
	1.4	36 [2]	130	77	-146
	1.4	36 [2]	113	140	-222
(Figure 3.19) Initial Press Rate: 130 kPa/min Treatment Time: 27 min	3.6	46 [2]	299	103	-179
	4.2	72 [2]	97	89	-146
	1.5	72 [2]	221	95	-185
	1.4	36 [2]	139	53	-219
Average (Std.)	2.2 (1.2)	50 (14)	159 (68)	95 (25)	-183 (28)

1 All pressure values are in kPa (absolute).

2 Total time to equalization obtained by extrapolating graphed data beyond actual treatment.

Internal pressure response during treatments with air can be considered almost "instantaneous" compared to those with a Cu-8 solution. Average times for the initial 35 kPa pressure increase and total times to pressure equalization for the air versus oil treatments were 2.2 and 50 min versus 508 and 11,400 min, respectively. This 230 fold increase in response time clearly reflects the faster flow of a gas versus a liquid into dry wood. Bergman (1991) and Peek and Goetsch (1990) similarly reported almost instantaneous internal pressure response when treating in air and delayed responses when using a liquid medium. For one of the air treatments, the constant pressure increase rate was actually faster than that of the vessel pressure rise. The reason for this is unclear. The average surface-to-center pressure differences in the air treated samples was only 95 kPa versus 303 kPa in the oil treated samples after the constant pressure increase and only -183 kPa versus -261 kPa immediately after venting. These differences did not reflect the dramatic differences in rates of pressure change. Due to the lower viscosity and lack of hindrance from liquid menisci, the air treating media most likely had more uniform and complete access to the void space in the samples.

The second set of data used to compare the influence of treating media on internal pressure response came from two matched Douglas-fir heartwood samples treated in air or oil by a Bethell process (Figure 3.20 and Table 3.6). Internal pressure responses were much more rapid and proceeded closer to equilibrium in the air medium versus the Cu-8 solution during the Bethell treatment, as was seen in the Lowry treatments. The time needed for internal pressure to return to atmospheric pressure after vessel pressure was applied was 6 versus 190 min in the sample receiving the air versus oil treatment. Total time to pressure equalization was 86 min in the air sample, but pressure in the oil sample leveled off after about 800 minutes. The constant pressure increase rate was much faster for the air treatment, 88 versus 1 kPa/min. The greater back-pressure for the air treatment is explained by the fact that, while

the rate of pressure decrease in the air sample was slightly faster, pressure in the oil sample was much lower just prior to venting.

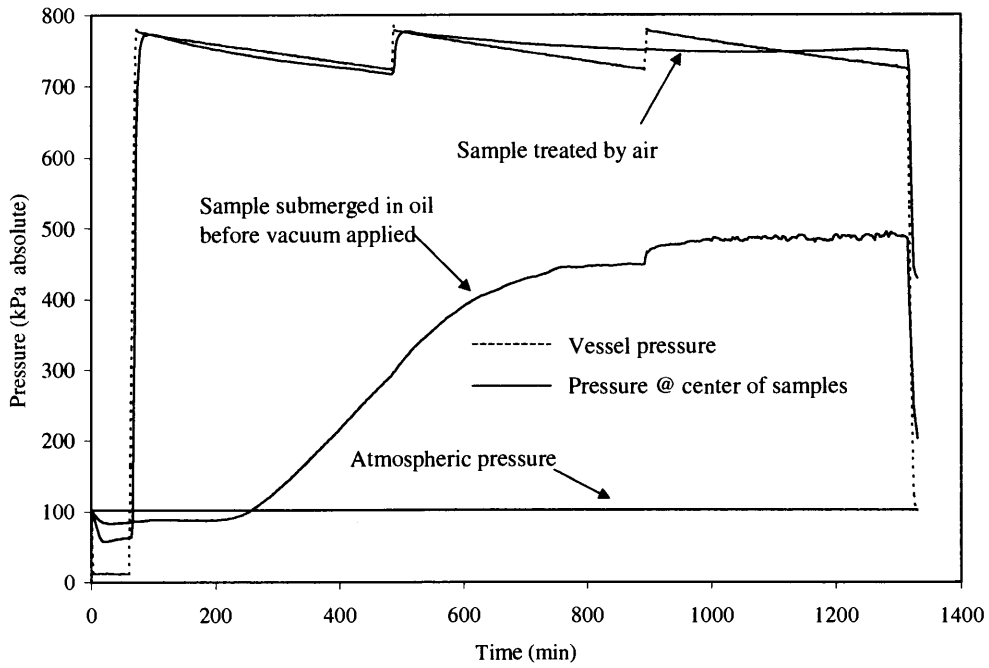


Figure 3.20 Pressure measurements at the center of two Douglas-fir heartwood samples (25 x 25 x 76 mm) treated with either Cu-8 in mineral spirits (oil) or air.

Table 3.6 Internal pressure response quantifiers from pressure measurements at the center of two Douglas-fir heartwood samples (25 x 25 x 76 mm) treated with Cu-8 in mineral spirits (oil) or air by a modified Bethell process at 720 – 790 kPa. This data was used to compare the influences of treating medium on internal pressure response. [1]

Treatment (Run) Conditions	Treating Media	Time to Atmospheric Pressure (min)	Total Time to Equalization (min)	Constant Pressure Increase Rate (kPa/min)	ΔP after Constant Pressure Increase (kPa)	ΔP after Venting (kPa)
(Figure 3.20) Vacuum: 14 kPa for 60 min Initial Press Rate: 72 kPa/min Treatment Time: 1,260 min	Oil	190	[2]	0.9	355	-112
	Air	6	86	88	173	-331

[1] All pressure values are in kPa (absolute).

[2] Internal pressure plateaued below vessel pressure.

Wood Permeability: The influence of wood permeability on internal pressure response was investigated using Douglas-fir heartwood and ponderosa pine sapwood samples. Although permeability measurements were not made, anatomical and extractives content differences between these sample groups gave rise to substantial permeability differences. Two sets of internal pressure measurement data were used to make comparisons.; in the first, samples were treated with Cu-8 solution (oil). Data for the Douglas-fir samples has already been presented in Figures 3.13 and 3.14 (Table 3.3). Data for the ponderosa samples was presented in Figures 3.21 and 3.22 (summarized in Table 3.7).

Internal pressure responses during the oil treatments of pine samples were exceedingly fast compared to responses in the Douglas-fir samples. Time for 35 kPa pressure and time to obtain pressure equalization ranged from 3.2 to 6.5 and 16 to 51 min for the pine samples versus a range of 70 to 1000 min and a single time to equalization of 11,400 minutes for the Douglas-fir sample. This data suggests that the oil solution only took a few minutes to flow into the pine samples whereas several hours were needed for comparable flow in the Douglas-fir. The constant pressure increase rate ranged from 49 to 274 kPa/min for the pine samples and from 0.1 to 0.2 kPa for the Douglas-fir samples. In one of the pine treating runs (Figure 3.21), pressure in the samples increased faster than vessel pressure was applied. Since a pressure period of only 5 minutes was required to saturate a pine sapwood sample in a preliminary treatment, it is likely that the oil reached the pressure probes soon after maximum vessel pressure was reached, and the fluid then allowed a rapid pressure transfer. The treatment of the more permeable wood resulted in lower surface-to-center pressure differences after the constant pressure increase period and immediately after venting, 43 to 104 kPa and -39 to -125 kPa versus 183 to 425 kPa and -261 kPa. Pressure immediately after venting was not recorded in two of the Douglas-fir samples.

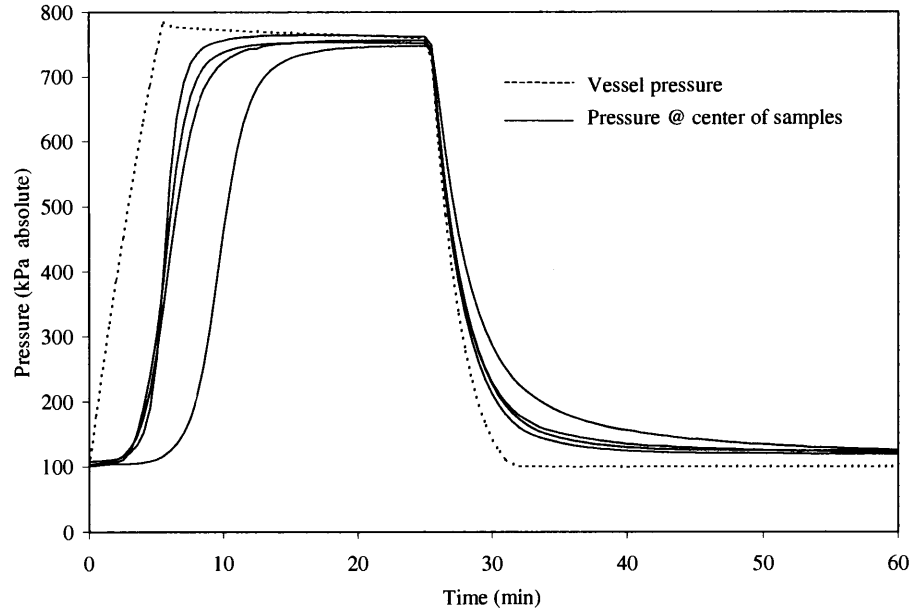


Figure 3.21 Pressure measurements at the center of four ponderosa pine sapwood samples (25 x 25 x 76 mm) treated with oil by a modified Lowry process.

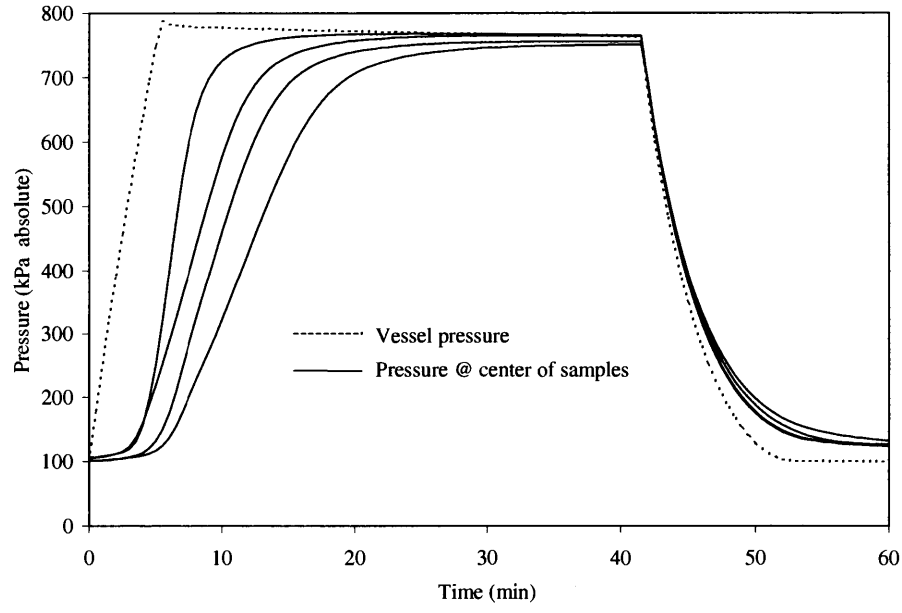


Figure 3.22 Pressure measurements at the center of four ponderosa pine sapwood samples (25 x 25 x 76 mm) treated with oil by a modified Lowry process.

Table 3.7 Internal pressure response quantifiers from pressure measurements at the center of eight ponderosa pine sapwood samples (25 x 25 x 76 mm) treated with oil by a modified Lowry process at 720 – 790 kPa. This data was used to compare the influences of treatment variables including treating medium and wood permeability on internal pressure response. [1]

Treatment (Run) Conditions	Time for 35kPa Rise (min)	Total Time to Equalization (min)	Constant Pressure Increase Rate (kPa/min)	ΔP after Constant Pressure Increase (kPa)	ΔP after Venting (kPa)
(Figure 3.21) Initial Press Rate: 123 kPa/min Treatment Time: 25 min	3.2	27 [2]	174	78	-59
	6.5	32 [2]	133	104	-125
	3.6	16	274	55	-72
	3.3	27 [2]	143	94	-78
(Figure 3.22) Initial Press Rate: 124 kPa/min Treatment Time: 41 min	5.9	51 [2]	49	75	-61
	5.1	49 [2]	65	75	-50
	3.5	32	71	74	-39
	3.7	25	129	43	-41
Average (Std.)	4.4 (1.2)	32 (11)	130 (26)	75 (18)	-66 (26)

1 All pressure values are in kPa (absolute).

2 Total time to equalization obtained by extrapolating graphed data beyond actual treatment.

In the second set of internal pressure measurement data used to compare wood having different permeabilities, samples were treated with a Lowry pressure process using air as the treating medium. Data for the air-treated Douglas-fir samples has already been presented in Figures 3.18 and 3.19 (Table 3.5) Data for the air treated ponderosa samples is presented in Figures 3.23 and 3.24 (summarized in Table 3.8).

Internal pressure response during the air treatment of pine sapwood could be considered instantaneous under the treating and pressure measurement conditions used in this investigation. Except for a few second delay in time to 35 kPa, internal pressure responses were inseparable form changes in treating vessel pressure. Time for the initial 35 kPa internal pressure increase, time to equalization, and the constant pressure increase rate in the Douglas-fir samples ranged from 1.4 to 4.2 min, 36 to 72 min, and 97 to 299 kPa/min. The constant pressure increase rates in most of the Douglas-fir samples were greater than those in the pine. This is the opposite of what was expected since the more permeable pine should have resulted in faster rates of pressure increase. The slightly faster vessel pressing used with the Douglas-fir samples may help to explain this discrepancy. It is also possible that slow leaks developed in the sample holder seals of the Douglas-fir samples having pressure increases greater than vessel pressurization. Although pressure responses looked similar for all Douglas-fir samples (Figures 3.18 and 3.19). If the seals leaked, pressure in the vessel would force treating media into the pressure probes causing a premature pressure rise to be recorded. Surface-to-center pressure differences were negligible in the pine samples, where as moderate pressure differences were found in the Douglas-fir samples (53 to 140 kPa after the constant pressure increase period and -146 to -222 immediately after venting). Pressure response differences between pine and Douglas-fir during the air treatments did not seem as large compared those during oil treatments.

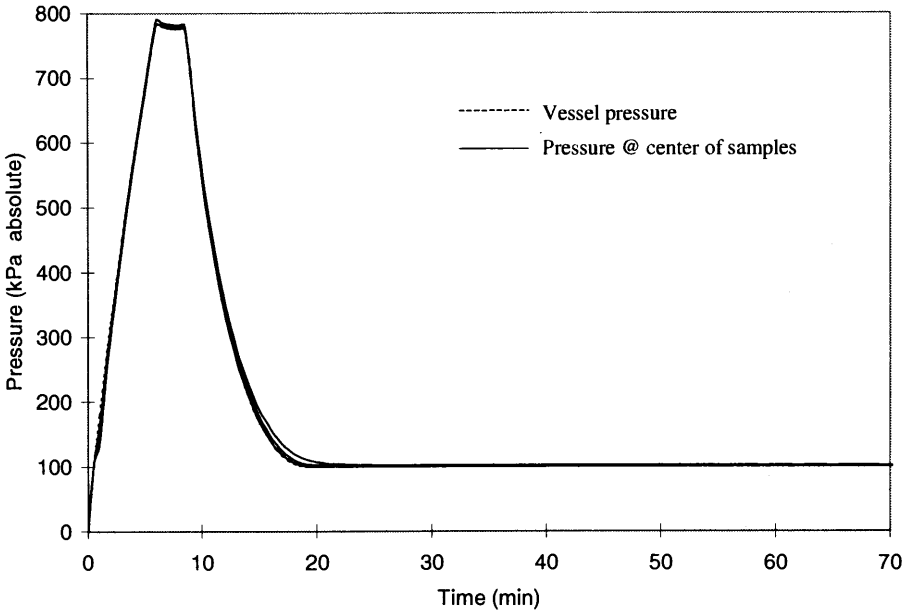


Figure 3.23 Pressure measurements at the center of four ponderosa pine sapwood samples (25 x 25 x 76 mm) treated with air by a modified Lowry process.

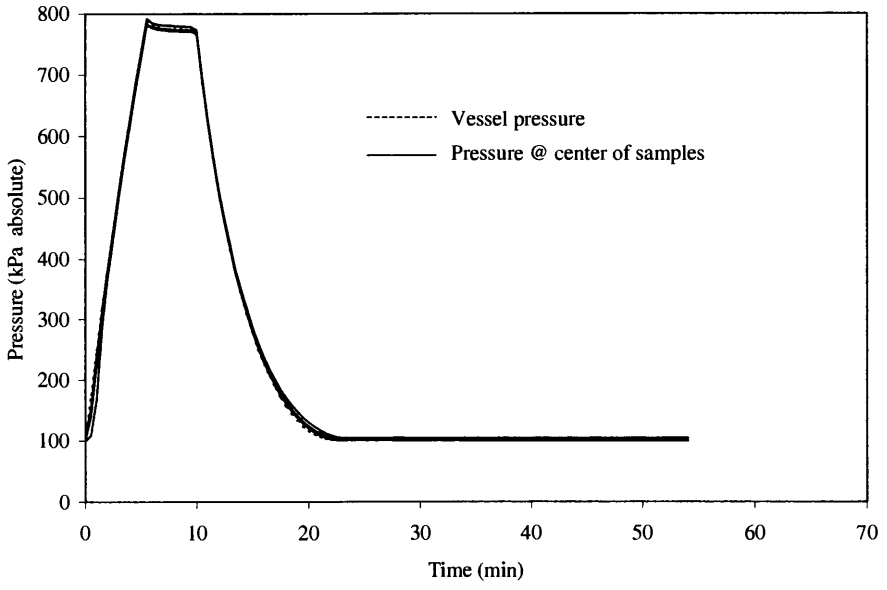


Figure 3.24 Pressure measurements at the center of four ponderosa pine sapwood samples (25 x 25 x 76 mm) treated with air by a modified Lowry process.

Table 3.8 Internal pressure response quantifiers from pressure measurements at the center of eight ponderosa pine sapwood samples (25 x 25 x 76 mm) treated with air by a modified Lowry process at 720 – 790 kPa. This data was used to compare the influences of treatment variables including treating medium and wood permeability on internal pressure response. [1]

Treatment (Run) Conditions	Time for 1st 35kPa Rise (min)	Total Time to Equalization (min)	Constant Pressure Increase Rate (kPa/min)	ΔP after Constant Pressure Increase (kPa)	ΔP after Venting (kPa)
(Figure 3.23) Initial Press Rate: 121 kPa/min Treatment Time: 12 min	0.5	—[2]	121	0	-10
	0.3	—[2]	121	0	0
	0.4	—[2]	121	0	-15
	0.3	—[2]	121	0	-3
(Figure 3.24) Initial Press Rate: 122 kPa/min Treatment Time: 10 min	0.5	—[2]	122	0	-1
	0.8	—[2]	122	0	-7
	0.5	—[2]	122	0	-5
	0.6	—[2]	122	0	-4
Average (Std.)	0.5 (0.2)	—	122 (0)	0	-5 (5)

1 All pressure values are in kPa (absolute).

2 Pressure equalization obtained before maximum vessel pressure reached.

Transverse Depths: The influence of distance from the surface on pressure response was investigated by comparing pressure measurements at depths of 6, 12, and 24 mm along the radial axis of individual samples. Data from two sample sets were used. Results for the first set, treated by a Lowry process, is shown in Figures 3.25 and 3.26 (summarized in Table 3.9).

Time required for the first 35 kPa pressure rise at the 24 mm depth was about 6.5 times that for the 6 mm depth in both samples (3,390 and 6,520 min versus 540 and 990 min). But, time to 35 kPa at the 12 mm depth was only 3.5 times that for the 6 mm depth (3,810 versus 990 min). Total time to pressure equalization was about 1.5 times longer at the 24 mm depth versus the 6 mm depth (8,400 and 13,800 min versus 5,760 and 10,200 min). Equalization times for the 12 and 6 mm depths were estimated to be the same (10,200 min). The rates of pressure rise during the constant increase period and the surface-to-interior pressure differentials at the end of this period were similar for the different depths. This may indicate that these variables depend on the pressure schedule and wood characteristics and are independent of depth. Surface-to-interior pressure differences after venting appeared to increase with depth (-159, -191, and -394 kPa respectively for the 6, 12, and 24 mm depths).

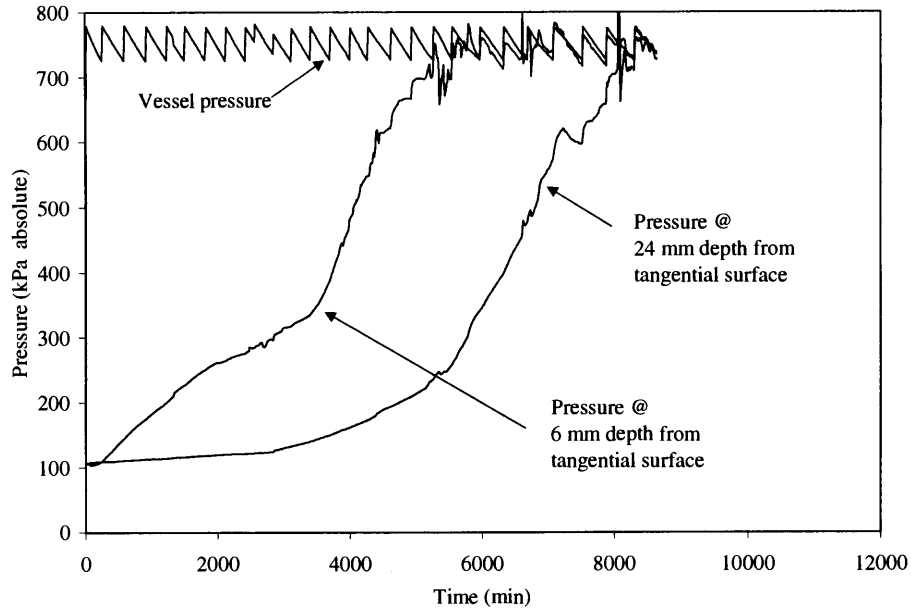


Figure 3.25 Pressure measurements at 6 and 12 mm depths along the radial axis of a Douglas-fir heartwood sample (50 x 50 x 76 mm) treated with oil by a modified Lowry process.

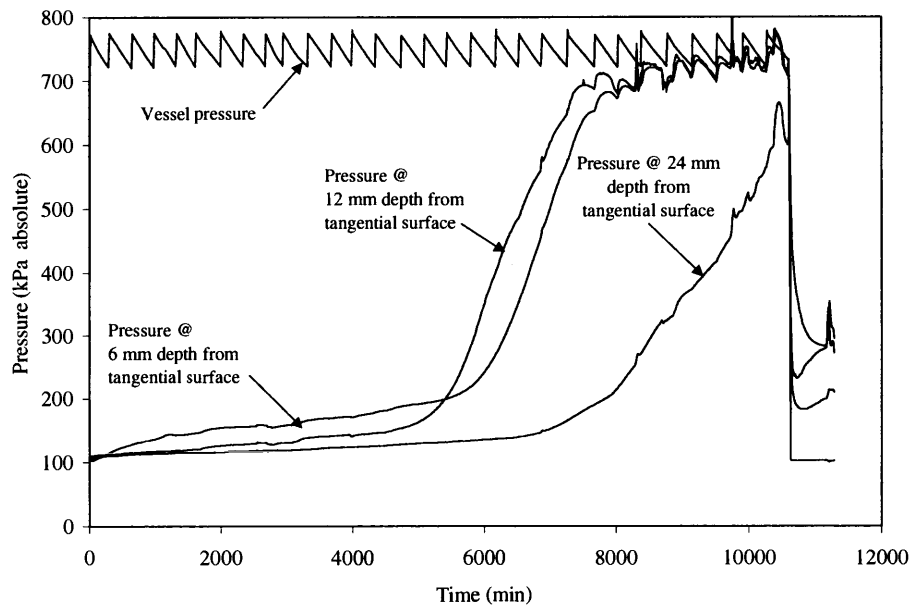


Figure 3.26 Pressure measurements at 6, 12, and 24 mm depths along the radial axis of a Douglas-fir heartwood sample (50 x 50 x 76 mm) treated with oil by a modified Lowry process.

Table 3.9 Internal pressure response quantifiers from pressure measurements at 6, 12, and 24 mm depths along the radial axes of two Douglas-fir heartwood samples (50 x 50 x 76 mm) treated with oil by a modified Lowry process at 720 – 790 kPa. This data was used to compare the influences of transverse depth on internal pressure response [1]

Treatment (Run) Conditions	Measurement Depth (mm)	Time for 35 kPa Rise (min)	Total Time to Equalization (min)	Constant Pressure Increase Rate (kPa/min)	ΔP after Constant Pressure Increase (kPa)	ΔP after Venting (kPa)
(Figure 3.25) Initial Press Rate: 69 kPa/min Treatment Time: 8,630 min	6	540	5,760	0.1	61	[4]
	24	3,390	8,400	0.2	60	[4]
(Figure 3.26) Initial Press Rate: 68 kPa/min Treatment Time: 1,0625 min	6	990	10,200	0.3	101	-159
	12	3,810	10,200	0.3	63	-191
	24	6,520	13,800 [2]	0.2	[3]	-394

1 All pressure values are in kPa (absolute).
2 Total time to equalization obtained by extrapolating graphed data beyond actual treatment.
3 This run was stopped too early.
4 No data were recorded for this measurement.

Similar trends of internal pressure response for different depths were seen with pressure measurements from a single Bethell treatment (Figure 2.27 and Table 3.10). Time for internal pressure to regain atmospheric level after vessel pressure was applied, increased for sequentially deeper locations in this sample (1,005, 1,520, and 3,215 min respectively for the 6, 12, and 24 mm depths). Total time to pressure equalization was similar for the first two depths but increased from 3,235 min at the 12 mm depth to an estimated 5,624 min for the 24 mm depth. Interestingly, the constant pressure increase rates and the surface-to-interior pressure differences after the pressure increase period for all depths were similar (0.4 kPa/min and about 40 kPa). This supports the idea (presented for the Lowry samples having multiple probes) that these pressure response quantifiers may be independent of flow length and instead are influenced by pressure process and wood characteristics.

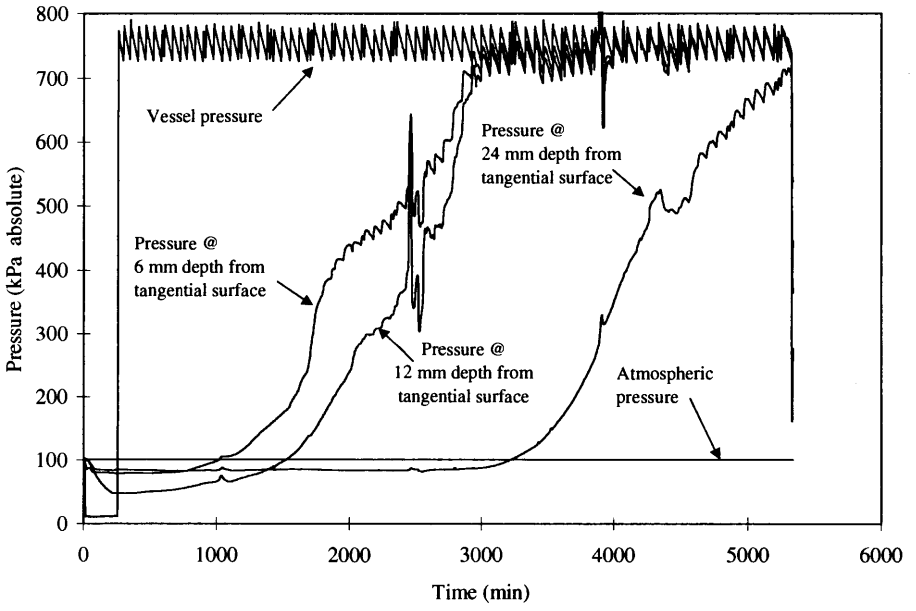


Figure 3.27 Pressure measurements at 6, 12, and 24 mm along the radial axis of a Douglas-fir heartwood sample (50 x 50 x 76 mm) treated with oil by a modified Bethell process.

Table 3.10 Internal pressure response quantifiers from pressure measurements at 6, 12, and 24 mm depths along the radial axis of a Douglas-fir heartwood sample (50 x 50 x 76 mm) treated with oil by a modified Bethell process at 720 – 790 kPa. This data was used to compare the influences of transverse depth on internal pressure response. [1]

Treatment (Run) Conditions	Measurement Depth (mm)	Time to Atmospheric Pressure (min)	Total Time to Equalization (min)	Constant Pressure Increase Rate (kPa/min)	ΔP after Constant Pressure Increase (kPa)	ΔP after Venting (kPa)
(Figure 3.27) Vacuum 11 kPa for 240 min Initial Press Rate: 70 kPa/min Treatment Time: 5,076 min	6	1,005	3,235	0.4	34	-259
	12	1,520	3,235	0.4	42	-230
	24	3,215	5,624 [2]	0.4	[3]	-374

1 All pressure values are in kPa (absolute).
2 Total time to equalization obtained by extrapolating graphed data beyond actual treatment.
3 This run was stopped too early.

Surface-to-interior pressure difference immediately after venting was greater for the 24 mm depth than the 6 mm depth (-374 versus -259 kPa), but, without a logical explanation, the residual pressure at the 12 mm depth was the lowest (-230 kPa).

Pressure response differences were seen at the different radial depths; however, comparisons between depths may have been compromised from the tangential flow of the treating media since no attempt was taken to prevent flow along this direction. Results from these two data sets suggest that the initial internal pressure response is dependent on depth within a sample, but further pressure increases seem to be less influenced by depth and possibly governed instead by process and wood characteristics.

3.5 Summary

This investigation was exploratory in nature and was intended to set the framework for experimentation with supercritical carbon dioxide in Chapter 4. The objectives of this study were to develop and evaluate methods for measuring pressure in wood during conventional pressure impregnation processes and to characterize the influence of process and wood variables on internal pressure response. These objectives were simultaneously met by measuring pressure at the center of samples while evaluating different pressure measurement techniques under different treatment conditions. Internal pressure measurements were then segregated into data sets first by pressure measurement technique and then by pressure process, treating medium, and wood species. Data from the same samples were often used for more than one treatment variable comparison. Because no attempt was made to work in a controlled experimental design or to provide adequate replication of pressure measurements, statistical analyses could not be made but qualitative comparisons were. Further, it is difficult to conclude whether trends seen in the data are representative of a given treatment variable or are simply experimental variations.

Several pressure measurement techniques were evaluated using different pressure-probe and sealant combinations. The first two methods utilized small tubing either pressed into tight fitting holes or epoxied into a two-staged hole drilled in the samples. The remaining methods used pressure-probe sample holders and a sealant. Although most techniques provided useful results, inconsistent performances and difficulties preparing samples imply that further development of measurement techniques is warranted, especially if higher treatment pressures are used. Considerable care was needed to ensure that pressure probes were not blocked and were effectively sealed. The probe surface had to be roughened and cleaned of all contaminants when probes were placed into samples with adhesive. Squarely cut sample ends and tightening holder tops uniformly were essential when sample holders were used.

Some generalizations can be made about the pressure response in wood during pressure treatments. A consistent pattern of pressure development occurred that lead to the creation and use of pressure response quantifiers, which facilitated making qualitative comparisons between treatment variables. There was an initial delay period followed by a period of relatively constant pressure increase to near vessel pressure. In most cases, pressure increase slowed but continued to approach vessel pressure. There was a distinct surface-to-center pressure difference immediately after the period of constant pressure increase. Immediately upon venting, a residual pressure remained in the samples, which diminished at a progressively slower rate. When treating with Cu-8 in mineral spirits, liquid appeared to reach the pressure probes before noticeable pressure increase were recorded. This may have resulted from the condensation of vapors ahead of the mineral spirits (Stamm, 1967).

The pattern of pressure change in wood during treating appeared to be influenced by pressurization schedule, treating medium, wood permeability, and transverse depth into wood. The use of a Lowry process (directly applying pressure to and holding at a maximum) with an

air treating medium allowed faster and more complete pressure response compared to the use of a Rüping process, which uses an initial low pressure application before full pressurization. Applying an initial vacuum before adding the treating medium and pressing (a Bethell process) substantially reduced pressure response time and surface-to-center pressure differences compared to the Lowry or Rüping pressure schedules. The use of air as the treating media resulted in internal pressure responses that were one to three orders of magnitude quicker compared to the use of a mineral spirits solution. And, surface-to-center pressure differences were less with the air treatments. These differences were accentuated with the less permeable Douglas-fir samples. Wood permeability (represented by highly permeable ponderosa pine sapwood and relatively refractory Douglas-fir heartwood) appeared to have similar affects on pressure response as did treating media differences. Under the treatment and pressure measurement conditions used in this investigation, the pressure response in the pine samples can be considered instantaneous when gas treatments are applied. The initial internal pressure response and the surface-to-interior pressure differences after were dependent on the depth at which measurements were made. However, the rate of constant pressure increase and the surface-to-interior pressure difference after the pressure increase period did not appear to be dependent on depth.

3.6 Implications

In spite of the low number of treatment replications that were successfully completed without pressure probe leaks and the fact that probe leaks could not be detected easily with the pine samples, a number of implications may be made.

1. The methods for measuring internal pressure of wood employed herein could be used to measure pressure at a specific depth to monitor the treatment of large timbers of refractory species. Also pressure begins to rise, preservative solution is likely to have reached

the area surrounding a pressure probe. More precise treatment schedules could be developed by knowing the influence of treating vessel pressure application rates, levels, and durations. Internal pressure monitoring could be used to adjust these processing variables. Treatment schedules optimized through internal pressure measurements could thus result in improved control over preservative kickback and reduced processing time.

2. The relatively long time for liquid treating media to penetrate Douglas-fir heartwood indicates that treating vessel pressure changes involving short pressure cycles are unlikely to influence treating results of refractory species.

3. The inability to achieve impregnation of all void volume during liquid treatments, may be indicated by internal pressure leveling off below vessel pressure. If the amount of surface-to-center pressure difference were related to the volume of unfilled voids, the measurement of internal pressure might be used as a method of measuring the amount of liquid in wood relative to the total void volume of the wood. This implication was based on the fact that evacuating samples prior to treating with an oil solution tended to result in smaller differences between vessel pressure and pressure at the center of samples during treatment.

4 INTERNAL PRESSURE MEASUREMENT TECHNIQUES AND PRESSURE RESPONSE IN WOOD DURING SUPERCRITICAL CARBON DIOXIDE TREATMENTS

4.1 Introduction

Pressure development in wood during processing with supercritical fluids (SCFs) could be used to control solubility and transport of materials in or out of the wood. Although theoretical models exist for determining pressure in wood during SCF treatments (Sahle-Demessie, 1994), empirical data were not found. A better understanding of pressure changes at a given point in wood over time and the factors that influence these changes could be used to develop more effective SCF processes for impregnating wood.

Techniques to measure pressure in wood during treating were developed in Chapter 3 but needed further improvements to withstand the higher pressures developed in the SCF treating vessel. In addition, supercritical carbon dioxide (SC-CO_2) at a temperature of 40 °C may soften or interact and degrade sealants and epoxies.

Based on Darcy's Law for the flow of fluids into wood (Siau, 1984), the transport of CO_2 and SC-CO_2 into wood and the resulting internal pressure response should be influenced by the magnitude of pressure differences going into wood, the distance through which the SCFs must flow, and the wood's permeability. The magnitude of pressure difference can be controlled by the rate of pressure application. Preliminary tests indicated that faster pressing and venting rates led to larger surface-to-center pressure differences, and this phenomenon was accentuated in less permeable woods. Wood can be easily damaged if the surface-to-center pressure differences exceed the crushing strength during pressing or cleavage limit during venting (Markwardt and Wilson, 1935). In preliminary tests, a pressing and venting rate of 690 kPa/min crushed and/or split Douglas-fir heartwood samples; while a rate of 170 kPa/min produced minimal damage. In an ideal case, (uniform permeability, constant pressure

difference, and single directional fluid flow) doubling the flow length for a gas in a porous medium should double the time needed for a given pressure rise. The influence of wood permeability on internal pressure development during SC-CO_2 treatment may be evaluated by measuring pressure at the center of samples from different species representing a broad range of permeabilities. In addition, since permeability of a given species is dependent on grain orientation, the influence of wood permeability on internal pressure response may also be shown from pressure measurements at the center of samples where the flow of CO_2 was restricted to either the radial or tangential direction.

4.2 Objectives

The following are the objectives of this research:

1. To develop and evaluate methods for measuring pressure in wood during SCF treatments.
2. To characterize internal pressure responses in wood during SC-CO_2 treatments.
3. To investigate the influence of process and wood characteristics including pressing and venting rates, flow length into a sample, and wood permeability on internal pressure response during SC-CO_2 treatments.

4.3 Methods

4.3.1 Equipment

The high-pressure equipment used in this investigation consisted of an electronic instrument cabinet, CO_2 source, gas compressor, back-pressure regulator, treatment vessels, vessel heaters, heating tapes, tubing, metering valves, and ball valves (Figure 4.1). Standard

grade carbon dioxide was purchased from Industrial Welding Supply Inc. in 23 kg gas cylinders. A single-stage diaphragm compressor (Fluitron Model A1-400) was used to move CO_2 from the gas cylinders to a high pressure storage vessel. Pressure in the storage vessel was controlled using a back-pressure regulator (Tescom Model 26-1722-24). Two metering valves, having flow coefficients of 0 to 0.04 and 0 to 0.37, were used to control CO_2 flow to the treating vessel from the storage vessel and from the treating vessel to outside the building during venting. The cylindrical storage and treating vessels, supplied by High Pressure Equipment Co. Inc., had inside diameters of 15 and 10 cm, respectively, and lengths of 60 cm. The temperature of each vessel was controlled through a cascading loop. A slave controller, (West Model 2072) measured the vessel thermal well temperature and sent a signal to the master controller, (West Model 3100) which measured vessel surface temperature. If both controllers called for heat, the master controller turned on a heating blanket surrounding the pressure vessel. The stainless steel tubing connecting the two vessels and leading from the vessels out the vent was wrapped with heating tape to maintain the desired temperature during fluid transfer.

Temperature inside the treating vessel was measured with a Type K thermocouple. Thermocouples made from 24 gauge Type K thermocouple grade wire have a response time of about 3 s and an error limit of 2.2 °C (OMEGA Engineering, 1995). Temperature readings were measured as thermocouple potential in mill-volts using a Campbell 21x data logger and were stored in a personal computer.

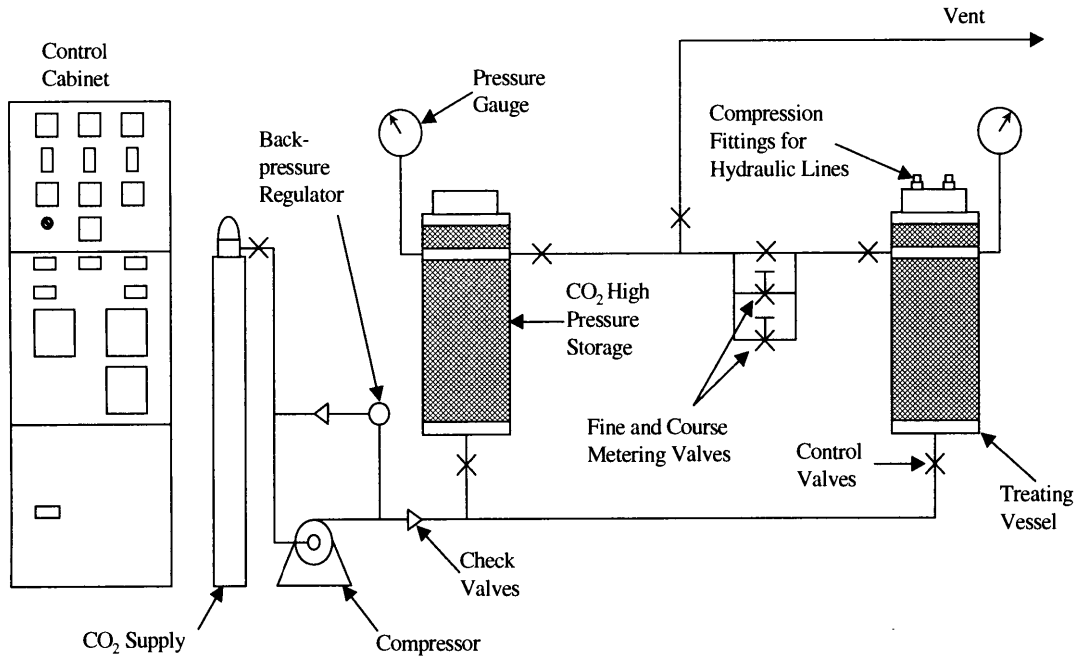


Figure 4.1 Supercritical fluid treating vessel used to apply SC-CO_2 treatments.

Pressure measurements were made using OMEGA PX 420-5K GI pressure transmitters. These pressure transmitters have error ranges of 0.5 % of full-scale readings and were individually calibrated using a Heise test gauge with a pressure range of atmospheric to 41.368 MPa divided into 35 kPa divisions. Because the pressure sensors produce an output signal of 4 to 20 mA, a precision resistor was placed in series with each sensor, and a Campbell 21x data logger measured the voltage across this resistor. The transmitters were then connected to a common pressure vessel and their responses compared with each other to confirm proper installation and calibration. An analog-to-digital converter meter was also placed in series with each vessel's pressure transmitter. This meter was adjusted so that its zero and span corresponded to zero and the maximum gauge pressure readings from the pressure transmitters. The digital meters were used for determining vessel pressure during pressing and venting.

4.3.2 Pressure Measurement Techniques

Pressure Transmitter Attachment: Because of the high pressures generated in the treating vessel, the pressure transmitters were placed on the outside and hydraulic lines were fed into the vessel top. The hydraulic line apparatus (Figure 4.2) was constructed using stainless steel tubing (3.2 mm OD) and stainless steel compression fittings. The tubing was connected to the pressure transmitters outside the treating vessel and fed through the vessel top. Pressure probes in the samples were attached by a union to the tubing extending below the vessel top. A tee union was placed at the highest point of the hydraulic line outside of the vessel allowing attachment of a hydraulic fluid reservoir.

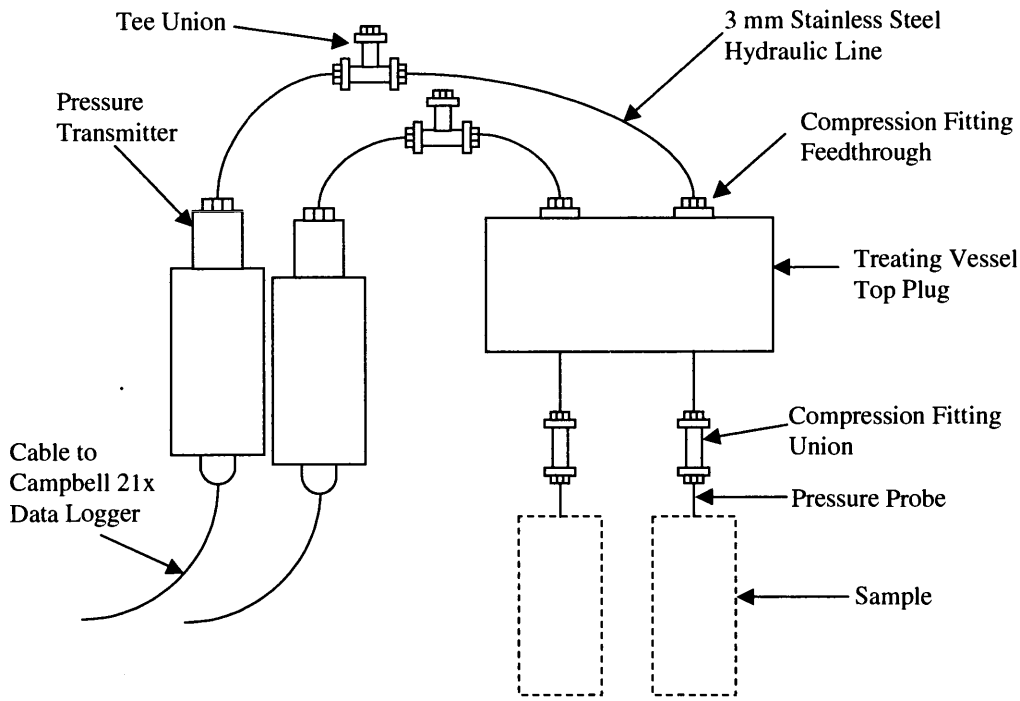


Figure 4.2 Sample configuration used to measure pressure changes in wood during SC-CO_2 treatments showing pressure transmitters, hydraulic lines, and samples.

Pressure Probe Techniques: The techniques used to measure internal pressure changes in wood during SC-CO_2 processing were similar to those used for the conventional treating processes discussed in Chapter 3. Because of the success experienced with pressure-probe sample holders (Figure 3.4), they were also evaluated with SC-CO_2 treatments. Rubber and Teflon® gaskets , respectively 3.2 and 1.6 mm thick, and High Temperature RTV Silicone were used as sealants with single- and double-probe sample holders. Gasket material was placed at the bottom of the sample holder, followed by the sample, a second gasket, and, finally, the sample holder top. The bottom gasket served as padding for the sample while the top gasket prevented treating medium from leaking around the pressure probe(s) and into the sample. The assembled holder was held together with bolts and the nuts tightened using a torque wrench. In some sample holder evaluations, silicone high temperature gasket sealant was applied above and below the sample in place of the gaskets. For these treatments, the holder's top was tightened only to the point were excess sealant oozed from the assembly. Assembled sample holders with silicone were allowed to cure for 24 h prior to use.

An alternative to the pressure-probe techniques involved gluing pressure probes directly into wood. Unlike a similar technique in Chapter 3, larger diameter tubing was used for the probes to prevent epoxy blockage. Probes were made from stainless steel tubing (3.2 mm OD, 2.1 mm ID) cut to 50 mm lengths, roughed with sandpaper, cleaned with alcohol, and set into the samples with Gluvit epoxy. Holes for the probes were centered in the end-grain and drilled to a depth of 20 mm with a 3.9 mm bit. After the epoxy cured, a 1.9 mm drill bit was used to bore through the epoxy at the bottom of the tubing creating a 10 mm long pressure chamber below the tubing (Figure 4.3).

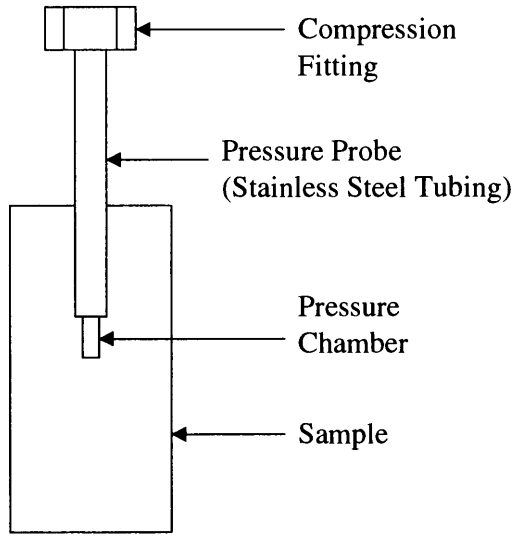


Figure 4.3 Schematic showing the pressure probe arrangement used to measure internal pressure near the center of wood samples during SC-CO_2 treatment.

Douglas-fir heartwood samples cut from locally purchased lumber were conditioned to approximately 12 % moisture content. Sample dimensions were approximately 25 x 25 x 76 mm for the single-probe sample holders and 60 x 60 x 80 mm for the double-probe sample holders. For the epoxied-probe samples, dimensions ranged from 25 to 60 mm along the radial and tangential axes and 60 to 80 mm along the longitudinal axis. All samples were end-coated with Gluvit epoxy, and some had their radial faces epoxied to restrict the flow of CO_2 treating medium to along their radial axes. Several treating schedules were used because the samples used to evaluate internal pressure measurement techniques were also used to determine acceptable pressing and venting rates that would not destroy the samples. In addition, the different pressing and venting rates were experimented with to become familiar with the SCF equipment. Sample preparation and treating conditions for all samples used to evaluate pressure measurement techniques are listed in Appendix B.

Sealant Tests: Adhesives, epoxies, and sealants were used to seal sample ends and faces and to set pressure probes into samples. Although most of these materials, collectively

termed "sealants", were not affected by CO_2 gas, they may become softened when exposed to SC-CO_2. Because of the potentially large pressure differences between the sample interior and surface; this softening can lead to sealant failure. Sealants were evaluated using two methods. In the first method, an experiment was specifically carried out to compare various sealants on wood blocks. One coat of each sealant (listed in Table 4.2) was placed on the end-grain of Douglas-fir heartwood samples (25 x 25 x 100 mm). The sealants were allowed to cure for 48 h prior to treatment with SC-CO_2 using a slow press to 13.8 MPa, holding for 20 min, and slowly venting.

Table 4.1 Sealants evaluated for use with wood during SC-CO_2 treatments.

Sealant Name	Manufacturer
2-Tone Clear Epoxy	ITW Devcon; Danvers, MA
3145 RTV Silicone Adhesive	Dow Corning Corp.; Midland, MI
A-12 Epoxy Adhesive Kit	Armstrong Products CO.; Easton, MA
Beats the Nail Adhesive	DAP Inc.; Dayton, OH
Epoxy Plus 25	ITW Devcon; Danvers, MA
Fix-All	NCH Corporation; Irving, TX
Gacoflex Neoprene	Gaco Western Inc.; Seattle, WA
High Temp RTV Gasket/Sealant	Permatex; Rock Hill, CT
Multi-temp Glue Sticks	Adhesives Technologies Inc.; Hampton, NH
Plumbers Goop Adhesive/Sealant	Eclectic Products, Inc.; Eugene, OR
Super Mend Epoxy Putty	Titan Corp.; Lynnwood, WA
The Welder Adhesive/Sealant	DIY Products; Chicago, IL

In the second method of evaluating the compatibility of sealants with SC-CO_2, sealants were tested indirectly as they were applied to samples used in other investigations.

Three treatment groups with five samples each were sealed and treated two samples at a time in SC-CO_2 at 40 °C by applying pressure at 276 kPa/min to 10.3 MPa and maintaining this vessel pressure level until internal pressure equilibrated with it. The vessel was then vented at 276 kPa/min. In the first treatment group, five Douglas-fir heartwood samples (60 x 30 x 60 mm; radial x tang. x long.) were coated on the end-grain and radial faces with Gluvit epoxy (ITW Philadelphia Resins, Montgomeryvill, PA). Then, the end-grain was coated a second time with Scotch-Weld 2216 B/A epoxy (3M; St. Paul, MN). In the second treatment group, five Douglas-fir heartwood samples (90 x 30 x 60 mm; radial x tang. x long.) were coated on the end-grain and radial faces with Gluvit followed by High Temperature RTV Silicone (by Permatex). In the third treatment group, black gum heartwood samples (30 x 30 x 60 mm; radial x tang. x long.) were coated using 5 sealant variations. One sample was coated with three layers of Gluvit with thick aluminum foil embedded in the first layer, the second was coated with Scotch-Weld 2216 B/A, the third was coated with Gluvit followed by a layer of High Temperature RTV Silicone, the fourth received only two coats of Gluvit, and the fifth sample was coated in a similar manner to the first sample, but thin foil was used.

Hydraulic Media Tests: Two investigations were performed to evaluate pressure response measurements. In the first, air, silicone grease, and silicone-based brake fluid were evaluated as hydraulic media. Each medium was placed in two hydraulic lines open to the treating vessel and in a piece of glass tubing set in a beaker on the bottom of the vessel. The medium sample in the glass tubing was used to determine if the medium would be solubilized by the SC-CO_2. Each material was evaluated in one treatment cycle (10.3 MPa, 40 °C, 5 min). Pressure in the hydraulic lines and vessel were recorded every 10 s.

In the second investigation, hydraulic medium comparisons between air in one line and silicone oil in the other were performed simultaneously with wood samples attached to the open end of the hydraulic lines inside of the treating vessel. The amount of air that had to be

compressed in the hydraulic line was reduced by using a short piece of 1.6 mm (OD) steel tubing, which gave a total air volume for the tubing and pressure sensor of about 3.6 cm^3. Samples were cut (30 x 30 x 60 mm; respectively radial, tangential, and longitudinal axes) from kiln dried lumber, sealed on four sides with Gluvit epoxy so that only radial or tangential flow occurred during treatment, and then conditioned to approximately 12 % moisture content before treating. Pressure probes were epoxied into the wood as discussed in the pressure probe techniques section below. The wood was treated at 10.3 MPa and 40 °C for 10 min. Pressing and venting rates were 690 kPa/min and pressure at the sample centers was recorded every 10 s.

Three sets of wood samples were used in this investigation evaluating the hydraulic media. In the first, Douglas-fir samples, two sapwood and two heartwood, were sealed to allow only radial flow. These samples were treated with one sapwood on the hydraulic line with air and one heartwood on the line with the oil medium, then in a second treatment, the remaining sapwood on the oil line and the remaining heartwood on the air line. The second set consisted of two ponderosa pine sapwood samples experiencing only tangential flow. These samples were individually treated one per treatment on either the air or oil filled line. The third set of wood samples used to compare air and oil hydraulic media consisted of ten ponderosa pine sapwood samples experiencing SC-CO_2 flow in the radial direction only. Five treating runs were made with one sample on each of the hydraulic lines.

Internal Pressure Verification: Preliminary tests showed that residual pressures in Douglas-fir heartwood samples immediately after venting the treating vessel were as high as 4 MPa. Pressures this high should have caused the wood to split since this species has a tensile strength perpendicular to the grain of between 2.1 and 2.3 MPa (Markwardt and Wilson, 1935). However, several samples did not show fractures. To confirm the seemingly high residual pressures and to verify that measurement techniques provided representative pressure

data, three experiments were performed. In each experiment, residual pressure throughout each sample was determined using a pressure bomb. These residual pressures were then compared to pressure measured with a probe at the center of similarly treated samples immediately after venting the treating vessel.

In the first experiment, five ponderosa pine sapwood samples (30 x 30 x 60 mm) were epoxied on the end-grain and radial faces, allowing only radial flow. The samples were conditioned to 12 % moisture content before being individually treated in SC-CO_2 by pressing at 690 kPa/min to 10.3 MPa, holding for 10 min @ 40 °C and then venting at the same rate. Each of these samples were simultaneously treated with two other matched samples for the evaluation of hydraulic media. After each treatment, the residual pressure sample was quickly removed and placed in a pressure bomb (Figure 4.4).

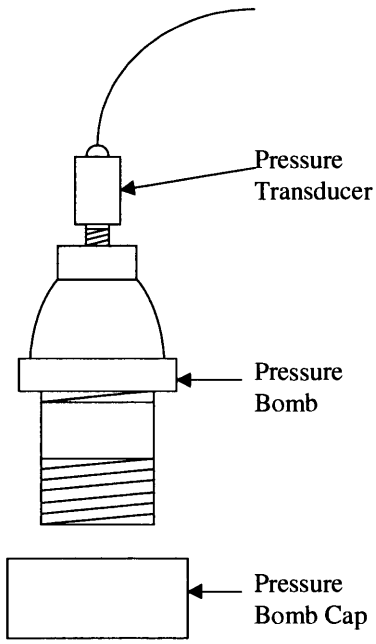


Figure 4.4 The pressure bomb that was used to measure residual pressure in wood samples following SC-CO_2 treatments was assembled from pipe fittings and had an internal volume of 270 cm^3.

In the second experiment, two ponderosa pine sapwood samples (30 x 30 x 79 mm) were prepared and treated in a manner similar to those in the previous experiment except that flow was restricted to the tangential direction, and the samples had pressure probes in them (using air in one and oil hydraulic media in the other) to measure pressure during the SC-CO_2 treatment. These samples were individually treated and immediately after treatment, they were placed in the pressure bomb.

In the third experiment, five yellow poplar heartwood samples (30 x 30 x 60 mm) were prepared in the same way, but their tangential faces were coated, allowing only tangential flow. These samples were individually treated in SC-CO_2 by pressing at 280 kPa/min to 10.3 MPa, holding this pressure for 60 min @ 40 °C, and then venting at the same rate as pressing. Residual pressure from these samples, determined from pressure bomb measurements, was compared to pressure measurements made during the evaluation of grain orientation influence on internal pressure response in matched samples.

The samples were placed in the pressure bomb as soon as possible after the end of the treatment cycle. The bomb was sealed and allowed to equilibrate either at room temperature (20 °C) or at 40 °C in a water bath. Only the yellow-poplar samples were equilibrated in the water bath. In a few cases, the bomb was vented and resealed to see if the initial bomb equilibrium pressure could be calculated from a second equilibrium pressure.

Residual pressure was determined using the combined gas law for real gases:

$$\mathbf{PV = nRTZ} \tag{4.1}$$

where **P** is pressure (kPa absolute), **V** is volume (cm^3), **n** is the amount of gas (moles), **R** is the gas constant (8,314 cm^3 kPa/mole K), **T** is temperature (K), and **Z** is the gas compressibility factor. For the determination of pressure before and after pressure equilibrium in the bomb, this equation may be written as:

$$(P_1V_1/T_1Z_1)=(P_2V_2/T_2Z_2) \tag{4.2}$$

were subscripts **1** & **2** represent state conditions before and after equilibrium. In this experiment, the pressure system consists of gas in the wood void volume (subscript **w**) and gas in the pressure bomb (subscript **b**). Initial pressure in the wood P_{1w} can then be determined from:

$$\left(\frac{P_{1w}V_{1w}}{Z_{1w}T_{1w}}\right)+\left(\frac{P_{1b}V_{1b}}{Z_{1b}T_{1b}}\right)=\left(\frac{P_{2w}V_{2w}}{Z_{2w}T_{2w}}\right)+\left(\frac{P_{2b}V_{2b}}{Z_{2b}T_{2b}}\right) \tag{4.3}$$

The compressibility factor is dependent on temperature and pressure and may be obtained by interpolation from tabulated data. Values for the compressibility factor of CO_2 are available in Perry's Chemical Engineers' Handbook (Perry and Green, 1984). The compressibility factor for the gas in the wood Z_{1w} was determined by first estimating the initial pressure using the gas law without the compressibility factor, treating the CO_2 as an ideal gas.

The volume of gas in the wood V_w was calculated by multiplying sample volume by the wood void volume fraction (Siau, 1984):

$$vvf = 1-G_w(0.685+0.01M/G_s) \tag{4.4}$$

were **vvf** is the void volume fraction, G_w is the wood specific gravity, **M** is the wood moisture content (% wt), and G_s is the specific gravity of water sorbed to wood cell wall material. Volume of gas in the pressure bomb V_b was calculated by subtracting the volume of the entire sample from the bomb volume.

4.3.3 Process and Wood Affects on Internal Pressure Response

Sample Preparation: All samples were cut so that the growth rings were parallel to the tangential faces and their dimensions are given using the following orientation: radial x

tangential x longitudinal axes. All samples were conditioned to a stable weight at 20 °C and 65 % RH prior to use, resulting in an equilibrium moisture content between 8 and 12 % depending on wood species and previous drying history. Pressure probes (3.2 mm steel tubing) were epoxied in each sample as described in the Pressure Measurement Techniques section, and the samples were attached to hydraulic lines leading out of the treating vessel to pressure transmitters. Silicone-based DOT 5 brake fluid tinted with copper naphthenate was used as the hydraulic medium since it responded quickly to pressure changes, allowed air bubbles to be easily bled, was not dissolved by the SC-CO_2, and could be easily seen in the wood. The pressure probe in each sample and the hydraulic lines were filled with hydraulic fluid before each treatment run, being careful to eliminate air bubbles. Pressure inside the samples was measured by recording the pressure on the hydraulic fluid at 30 s intervals using a Campbell 21x data logger and relaying this data to a personal computer. All treatments were conducted at 40 °C

Characterization of Internal Pressure Response: Two experiments were performed to characterize internal pressure measurements in wood during SC-CO_2 treatments. In the first, a single yellow-poplar heartwood sample (30 x 30 x 60 mm) was cut from a kiln-dried board and coated on its end and tangential faces with two layers of Gluvit epoxy and allowed to cure 24 h between coats. A 20 mm deep hole was drilled longitudinally at the center of one end of the sample and a stainless steel pressure probe (9.53 mm OD x 6.22 mm ID x 60 mm long) was epoxied in the hole. After approximately 48 h, a 5.88 mm diameter hole was drilled through the epoxy at the tube bottom extending an additional 10 mm into the wood.

In the second experiment, five samples (30 x 60 x 60 mm) were cut from a single kiln-dried Douglas-fir heartwood board. The end-grain and radial faces of each sample were coated with two layers of Gluvit epoxy and allowed to cure for 24 h between coats. Two 20 mm deep holes were drilled, 15 mm apart, along the radial axis 30 mm from one of the

tangential faces. A stainless steel pressure probe (3.18 mm OD, 2.13 mm ID) was set with epoxy in each hole extending out of the sample's end. After the epoxy hardened, a 1.97 mm diameter hole was drilled through the epoxy at the tube bottom extending an additional 15 mm into the wood.

In both experiments, the samples were treated by individually placing them in a treating vessel, applying compressed CO_2 at a rate of 276 kPa/min to 10.3 MPa (gauge), and maintaining this pressure until pressure at the center of each sample equilibrated with the vessel. The pressure was then vented at a rate of 276 kPa/min.

Pressing and Venting Rates: Fifteen samples (30 x 30 x 60 mm) cut from a single kiln-dried Douglas-fir heartwood board were coated on the end-grain and radial faces with two layers of Gluvit epoxy. A 20 mm deep hole was drilled longitudinally on one transverse face of each sample and a stainless steel pressure probe (3.18 mm OD x 2.13 mm ID) was epoxied in place so that it extended out of the sample. After the epoxy hardened, a 1.97 mm diameter hole was drilled through the epoxy at the tube bottom extending an additional 15 mm into the wood.

Samples were treated by placing them in a treating vessel, applying compressed CO_2 at rates of 138, 276, or 827 kPa/min to 10.3 MPa (gauge), and maintaining this pressure until pressure at the sample centers equilibrated with the vessel. The pressure was then vented at the same rate as it was applied. This treatment was applied to two samples using the 138 kPa/min rate and five samples each at the 276 and 827 kPa/min rate.

Flow Lengths: A single kiln-dried Douglas-fir heartwood board was used to produce fifteen total samples with five each having radial dimensions of 30, 60, or 90 mm; all had dimensions of 30 and 60 mm in the tangential and longitudinal directions, respectively. The end-grain and radial faces were coated with two layers of Gluvit epoxy; then a 20 mm deep hole was drilled longitudinally at the center of one end of each sample and a stainless steel

pressure probe (3.18 mm OD x 2.13 mm ID) was epoxied in place so that it extended out of the sample. After the epoxy hardened, a 1.97 mm diameter hole was drilled through the epoxy at the tube bottom extending an additional 15 mm into the wood.

Samples were treated by placing them in a treating vessel, applying compressed CO_2 at a rate of 276 kPa/min to10.3 MPa (gauge), and maintaining this pressure until pressure at the sample centers equilibrated with the vessel; then pressure was vented at a rate of 276 kPa/min.

Wood Species (Permeability): Because of limited availability, test samples (30 x 30 x 60 mm) were cut from both air- and kiln-dried heartwood lumber having a broad range of physical properties (Table 4.2). The end-grain and radial faces of all samples were sealed. Samples were sealed with the Gluvit epoxy (a Travaco product). A 3M epoxy was used on the red oak and one of the black gum samples (Scotch-Weld 2216B/A gray Epoxy Adhesive Tube Kit). Permatex High Temp RTV Silicone Gasket/Sealant was applied on one of the black gum samples initially coated with Gluvit. In addition, aluminum foil was placed in the wet Gluvit of two black gum samples. In all cases where Gluvit was used, the first coat was cured for 24 h before a second layer was applied. A 20 mm deep hole was drilled longitudinally at the center of one end of each sample and a stainless steel pressure probe (3.18 mm OD x 2.13 mm ID) was epoxied in place so that it extended out of the sample. After the epoxy hardened, a 1.97 mm diameter hole was drilled through the epoxy at the tube bottom extending an additional 15 mm into the wood.

Samples were treated, two species at a time, by applying compressed CO_2 at a rate of 276 kPa/min to 10.3 MPa (gauge). Pressure was held until pressure at the sample centers equilibrated with the vessel; then it was vented at a rate of 276 kPa/min. This rate of pressure change was selected to limit the amount of collapse found during preliminary studies at 689 kPa/min.

Table 4.2 Properties of wood species used in this investigation (Markwardt and Wilson, 1935).

Wood	Permeability to N_2 (Darcy) [1]			Specific Gravity (green / 12% mc)	Compression Strength [2] (kPa)	Tensile Strength [3] (kPa)
	Longitudinal	Radial	Tangential			
Black gum (*Nyssa sylvatica* Marsh.)	7.504	0.0008	0.0005	0.46 / 0.50	7,929	3,447
Douglas-fir (*Pseudotsuga menziesii* (Mirb.) Franco)	0.027 (0.020) 0.022 (0.013)	0.007 (0.006) 0.040	0.002 (0.001) 0.003	0.45 / 0.51	6,274	2,060
Engelmann spruce (*Picea engelmannii* Parry)	0.033			0.31 / 0.33	4,413	
Lodgepole pine (*Pinus contorta* Dougl.)	0.038			0.38 / 0.43	5,171	1,999
Pacific silver fir (Abies amabilis *Dougl.)*				0.35 / 0.38	3,378	
Ponderosa pine (*Pinus ponderosa* Laws.)	0.092 (0.017) 0.132 (0.002)	0.016 (0.017) 0.035		0.38 / 0.42	5,102	2,758
Red oak (*Quercus* spp. (Erythrobalanus group))	0.662 0.352	0.024 0.020	0.009 0.008	(0.51-0.61) / (0.62-0.76)	8,646 [3]	5,612
Sugar pine (*Pinus lambertiana* Dougl.)				0.35 / 0.38	4,068	2,413
Western redcedar (*Thuja plicata* Donn)	0.042 0.095	0.001 0.013 (0.017)	0.001 0	0.31 / 0.33	4,206	1,517
White fir (*Abies concolor* Gord. & Glend.)	0.096 (0.035) 0.110	0.002 (0.001) 0.003 (0.001)	0.005 (0.006) 0.001 (0.001)	0.35 / 0.37	4,137	1,793
Yellow-poplar (*Liriodendron tulipifera* L.)	0.935 1.084 (0.277)	0.012 (0.009) 0.011 (0.001)	0.012 (0.006) 0.018 (0.003)	0.38 / 0.43	3,999	3,585

1 Choong and Fogg, (1972); Choong et al. (1974); and Markstrom and Hann, (1972). Chong et al. listed two values for permeability.
2 Compression perpendicular to the grain as stress at the proportional limit (@ 12 % mc).
3 Maximum tensile strength perpendicular to the grain (@ 12 % mc).

Grain Orientation (Permeability): Yellow-poplar was chosen to study the effect of grain orientation because it is moderately permeable to carbon dioxide, producing easily recognizable surface-to-center pressure differences during treatment. Samples that were too permeable would make it difficult to detect orientation influences on pressure development. Yellow-poplar also has relatively thin latewood regions that provided potential for more uniform internal pressure measurements when material flow was restricted to the tangential direction.

Ten heartwood samples (30 x 30 x 60 mm) were cut from kiln-dried lumber and end-grain sealed with Gluvit epoxy. Five samples each were sealed on their radial or tangential faces. A 20 mm deep hole was drilled longitudinally at the center of one end of each sample and a stainless steel pressure probe (9.53 mm OD x 6.22 mm ID) was epoxied in place so that it extended out of the sample. After the epoxy hardened, a 5.88 mm diameter hole was drilled through the epoxy at the tube bottom extending an additional 10 mm into the wood.

Two samples, one sealed radially and one tangentially, were treated in each treatment run. Pressure was applied at a rate of 276 kPa/min to 10.3 MPa (gauge) and was held at this level until pressure at the sample centers equilibrated with that of the vessel. Pressure was vented at a rate of 276 kPa/min.

4.3.4 Approach to Data Analysis

Data collected on the pressure response in wood during SC-CO_2 treatment were presented graphically, and pressure response quantifiers from each sample in a treatment group were assembled in accompanying tables. The time for an initial pressure increase (**time to reach 35 kPa**) and **time to equilibrium after vessel reached maximum pressure** provided a relative measure of the ease that CO_2 entered the wood. Time to equilibrium may also indicate time needed for processing wood under similar treatment conditions. The

maximum surface-to-center pressure difference (**max. ΔP during pressing**) and **back-pressure** level provided indications of the mechanical forces wood samples were subjected to during treatment. The data from treatment groups were averaged for comparison, but the small number of replicates limited the potential for statistical analysis. Thus, these data should be viewed as qualitative indicators of internal pressure changes in wood during SCF treatment.

4.4 Results and Discussion

4.4.1 Pressure Measurement Techniques

Pressure Probe Techniques: Results for pressure probe effectiveness are given in Table 4.3, summarized from Appendix B. Because of the low number of treatment replications for the evaluation of some techniques, it is difficult to compare techniques solely on the percent of probes which did not leak.

The pressure probe sample holders provided leak free pressure measurements under certain conditions, but in general they were too cumbersome and unreliable. Tightening the holders to the proper level was difficult, and leaks occurred around the pressure probes when the holder tops became skewed or were too loose. Conversely, earlywood on the end-grain was crushed when holders were too tight. It appeared that a torque of approximately 5 Nm on the four sample holder nuts worked best with a rubber gasket. Silicon RTV adhesive simplified sample preparation, but the technique of using it in combination with the single-probe sample holders resulted in a low percentage of effectively sealed probes.

An interesting sample defect occurred in most of the samples that had the RTV adhesive as a sealant. Diamond shaped dimples were found in the earlywood of the end-grain

of most samples. These dimples have been caused by gas pockets that formed beneath the adhesive during venting and were subsequently forced back into the wood by the restraining top and bottom plates of the sample holder. Or, these failures may have resulted from the restrained longitudinal expansion, which most likely occurs as samples are compressed in the transverse direction by the application of the SC-CO_2 treatment. Bubbles in the coating without dimple shaped wood defects were noticed on test samples where RTV adhesive was used without a sample holder in preliminary experiments.

Carefully prepared tubing epoxied into a sample proved to be the best technique for making pressure probes that remained functional throughout the treatment process. Leaks seldom occurred even when samples were crushed or blown up.

Sealant Tests: Sealants used on wood samples during SC-CO_2 treatments were evaluated in two investigations. Results from the first investigation are shown in Table 4.4. The A-12 epoxy provided the best resistance to damage during treatment; while, the other three epoxies softened and allowed bubbles to form and break open. Unfortunately, the rigidity of A-12 made it susceptible to cracking as sample dimensions change during the pressing and venting portions of a treatment cycle. The Super Mend Epoxy Putty may have failed as a result of the use of an old partially used supply. Silicon based adhesive/sealants were flexible and allowed samples to change dimensions. These materials remained intact but blistered as gas pockets formed between the end-seal layer and the wood. The Neoprene based Gacoflex looked promising but a thicker or second layer would be needed. The remainder of the materials bubbled and blistered at some point during treatment.

Table 4.3 Effectiveness of pressure probe techniques for the measurement of internal pressure during SC-CO_2 treating processes. [1]

Pressure Probe Type	Sealant (Torque on sample holder nuts)	Number of Probes in each Probe/Sealant Technique	Condition & Number of Probes		Technique Effectiveness (Percent of Good Probes)
			Leaked	Good	
Single-probe Sample Holder	Rubber Gasket (2.8 Nm)	2	1	1	50
	Rubber Gasket (4.5 Nm)	1	1	0	0
	Rubber Gasket (5.1 Nm)	1	0	1	100
	Rubber Gasket (5.6 Nm)	3	1	2	67
	Rubber Gasket (9.0 Nm)	1	0	1	100
	Silicone RTV	10	4	6	60
Double-probe Sample Holder	Rubber Gasket	2	0	2	100
	Silicone RTV	6	4	2	34
3.2 mm Stainless Steel Tubing	Epoxy	16	0	16	100

[1] This table only includes pressure probes that were used to collect internal pressure measurements and which were in samples that were not severely crushed during the pressing phase of applied treatments.

Table 4.4 Sealants evaluated for use with wood during SC-CO_2 treatments.

Sealant Name	Sealant Condition
2-Tone Clear Epoxy	Softened, wood resin bubbled through
3145 RTV Silicone Adhesive	Blistered slightly
A-12 Epoxy Adhesive Kit	Good adhesion, no blistering
Beats the Nail Adhesive	Bubbled and blistered
Epoxy Plus 25	Softened and bubbled
Fix-All	Bubbled and blistered
Gacoflex Neoprene	Coating too thin, resin bubbled through
High Temp RTV Gasket/Sealant	Blistered but still adhered to the wood
Multi-temp Glue Sticks	Bubbled and blistered
Plumbers Goop Adhesive/Sealant	Bubbled and blistered
Super Mend Epoxy Putty	Bubbled and blistered
The Welder Adhesive/Sealant	Bubbled and blistered

In the second investigation, sealants used on samples in three other experiments were evaluated. In the first experimental group, Gluvit epoxy used alone on the radial faces and with a top coat of Scotch-Weld epoxy on the end-grain provided excellent sealing with only some small non-broken blisters in the Gluvit. No blistering occurred on the end-grain where both epoxies were used. Larger blisters occurred in the second experimental group of samples, which were first coated with Gluvit epoxy and then with RTV silicone sealant. Some blisters erupted and hydraulic oil from the pressure probes could be seen on the end-grain of some samples. The less rigid silicone may have allowed the larger blisters to form; whereas, the Scotch-Weld in the first group of samples contained the Gluvit. Apparently, after two to three hours of SC-CO_2 exposure, the Gluvit becomes too soft to withstand out-gassing of the samples during venting. It may be that the Gluvit became too soft after the 3.5 h treatment. As a result, gas leaving the samples during the venting phase of treatment caused the blisters to form. The third experimental group of samples to have their sealants evaluated exhibited a mixture of results that were complicated by wood collapse. Samples coated only

with Gluvit or with Gluvit followed by a coat of RTV silicon sealant had extensive blistering, and blisters on the end-grain ruptured. The foil was partially delaminated on the two samples with aluminum foil embedded in Gluvit, but the epoxy below was only mildly blistered even after the 3.5 h treatment. The samples coated with Scotch-Weld alone had the fewest number of blisters, and thus, this epoxy appeared to hold up best in the SC-CO_2 treating medium.

Hydraulic Media Tests: Two investigations were performed to evaluate the suitability of air, silicone oil, and silicone grease as pressure transfer media. The first investigation compared these media in hydraulic lines open to the treating vessel. Before evaluating different media in the hydraulic lines, a comparison was made of the two pressure transmitters attached to the hydraulic lines and the one connected to the treatment vessel. Since the hydraulic lines were open to the vessel, this treatment corresponds to the evaluation of air as a hydraulic medium. Data for this comparison shows that the three pressure sensors responded identically (Figure 4.5).

Pressure measurements made during a SC-CO_2 treatment with silicone oil in the hydraulic lines similarly showed no delay between vessel pressure and the pressure indicated by the pressure sensors on the two oil filled lines (Figure 4.6). However, the use of silicone grease filled hydraulic lines resulted in considerable delay before vessel pressurization was detected (Figure 4.7). The rates of pressure increase measured by the grease filled lines were slower than vessel pressure increase, and the pressure response in one line was noticeably different than in the other. The hindered responsiveness of silicone media can be attributed to its high viscosity and tackiness. Also, the presence of air bubbles trapped in the grease would contribute to delayed pressure transfer as they were compressed.

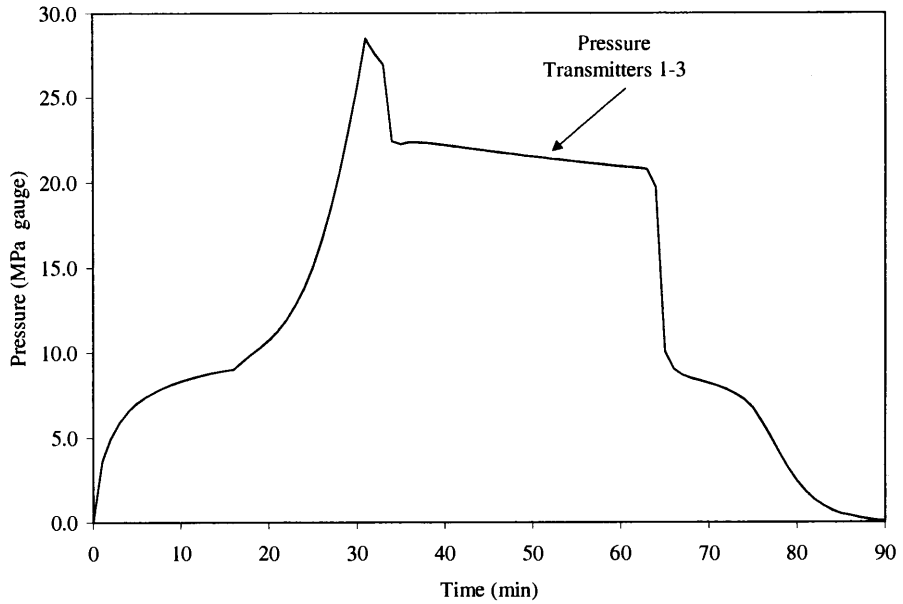


Figure 4.5 Pressure measurements made with three pressure transmitters during a SC-CO_2 treatment. The hydraulic lines attached to the sensors were left open to the treating vessel ("air" hydraulic medium").

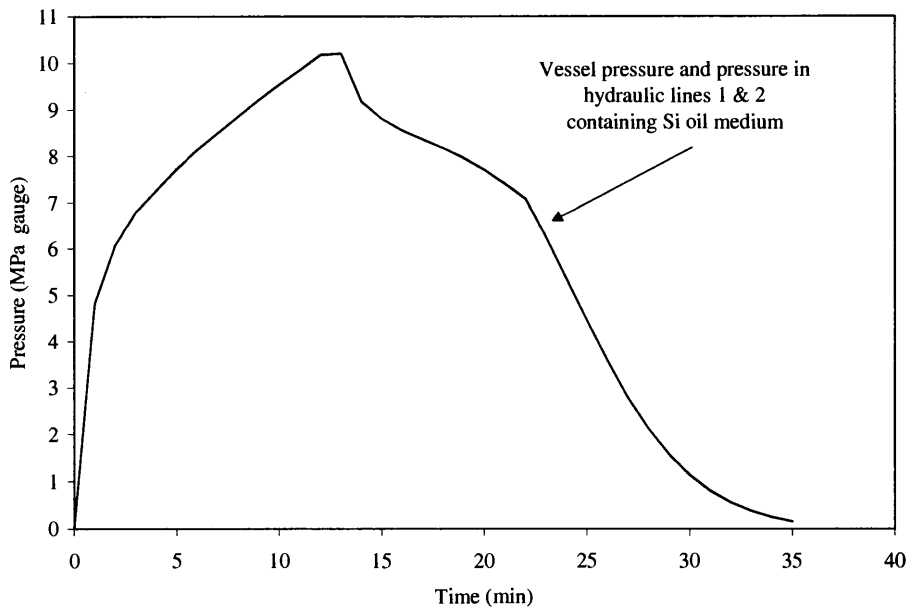


Figure 4.6 Pressure measurements made on two silicone oil filled hydraulic lines and in the treatment vessel during a SC-CO_2 treatment.

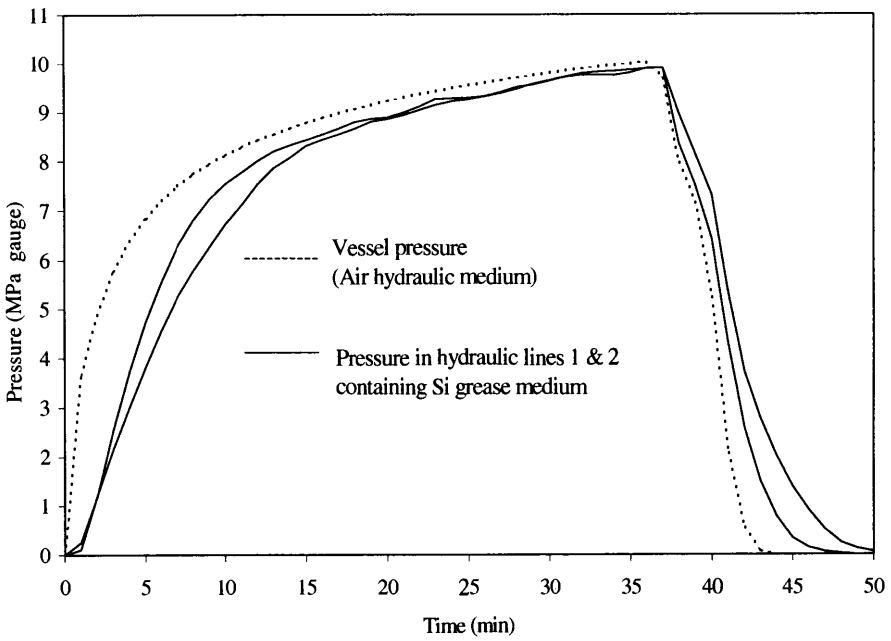


Figure 4.7 Pressure measurements made on two silicone grease filled hydraulic lines and in the treatment vessel during a SC-CO_2 treatment.

The second investigation evaluated air and oil pressure transfer media using three sets of wood samples attached to the hydraulic lines inside of the pressure vessel. The addition of samples to the end of the hydraulic lines was done to more closely represent the pressure measurement conditions to be carried out in future investigations. Results from the first sample set, comparing pressure measurements at the center of Douglas-fir samples, are shown in Figure 4.8. Pressure measurements were similar when the same hydraulic medium was used, regardless of whether a heartwood or sapwood sample was placed on the hydraulic lines. Excluding an initial delay, pressure measurements using the oil filled lines more closely followed vessel pressure changes. The sporadic pressure readings closely following vessel pressure measured in the heartwood sample on the oil filled line may have been caused by pressure probe leaks. In addition, this sample collapsed during treatment.

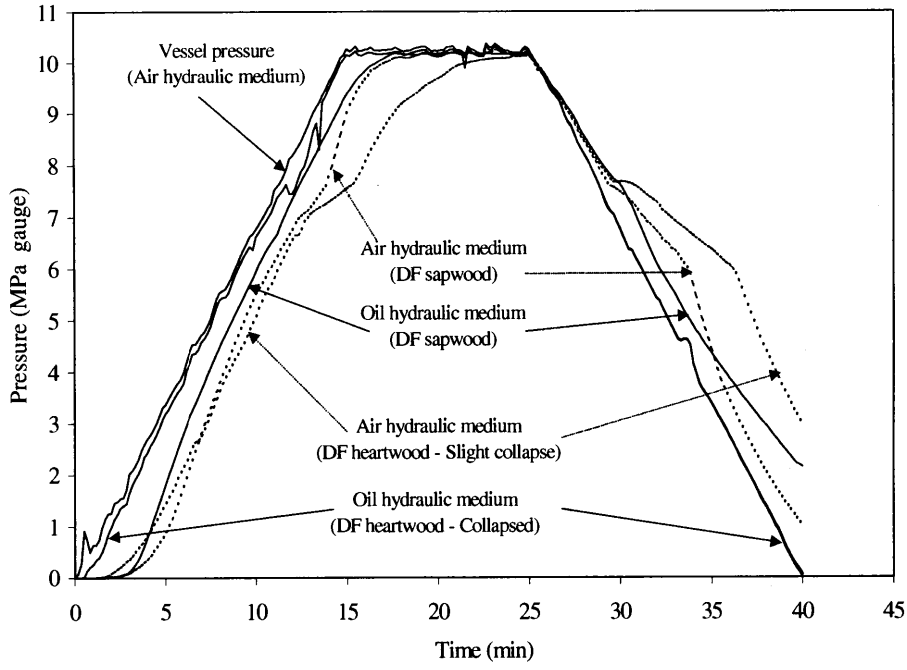


Figure 4.8 Pressure measurements in Douglas-fir heart- and sapwood samples made during SC-CO_2 treatments with either air or oil filled hydraulic lines (CO_2 flow was restricted to the radial axis).

Pressure measurements using the air filled hydraulic lines showed an initial delay in internal pressure response, as seen with the oil filled lines, but there was a second delay when internal pressure approached 7.0 MPa. This delay continued until a pressure of about 7.7 MPa was achieved at the centers of both heartwood and sapwood samples. Because the critical pressure of CO_2 is 7.4 MPa, this pressure range corresponds to the period of high compressibility. This second delay, therefore, must correspond to the time required to compress the gas filling the hydraulic lines and pressure sensors. After this compression period, the air filled lines show internal pressure increasing again to eventually equilibrate with the treatment vessel. During the vessel venting period, the air filled hydraulic lines again show a delay as internal pressure drops through the near critical zone (7.7 to 6.2 MPa). An important difference between using oil versus air hydraulic media is seen with the sapwood

samples at the very end of vessel venting. Pressure remaining in the oil filled line is almost three times that in the air filled line, possibly indicating that the oil hindered the release of pressure from the hydraulic line through the pressure probe tip. An interesting point to note is that the pressure in the Douglas-fir sample on an air filled line exceeded 4.2 MPa during venting. This internal pressure was nearly twice the tensile strength of this wood perpendicular to the grain. As a result this sample fractured completely along a growth ring near its surface. It is also interesting to note that internal pressure responses were slower for the less permeable heartwood samples.

The second sample set used to evaluate air and oil media in the hydraulic lines compared pressure measurements at the center of ponderosa pine sapwood samples sealed to allow only tangential flow of CO_2 (Figure 4.9).

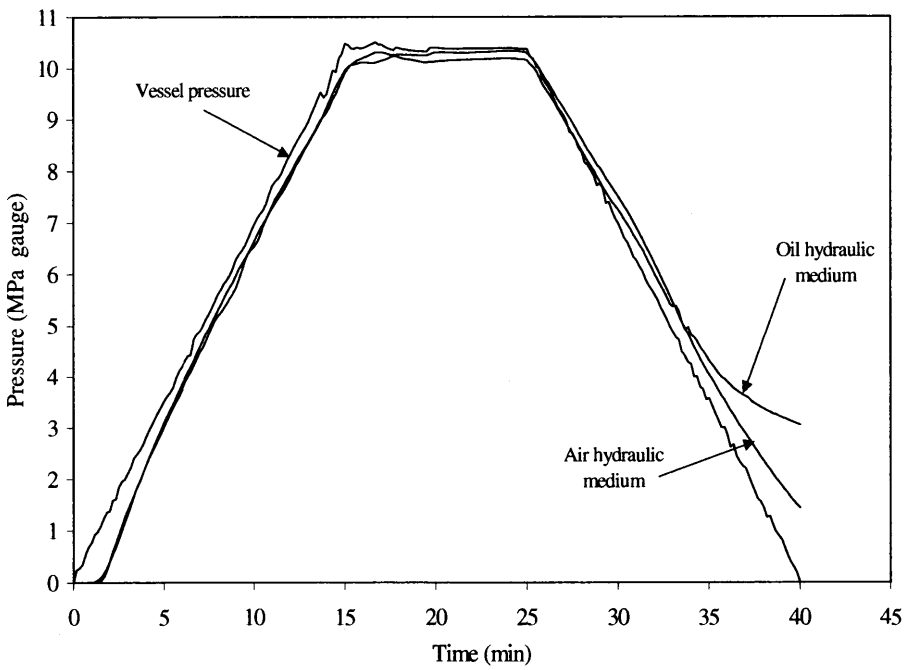


Figure 4.9 Pressure measurements at the center of ponderosa pine sapwood samples made with either air or oil filled hydraulic lines during a SC-CO_2 treatment (CO_2 flow was restricted to the tangential direction).

Pressure measurements at the centers of these samples were nearly identical for both the oil and air filled hydraulic lines during the pressing and equalization phases of treatment. However, during venting, pressure loss from the oil filled hydraulic line became progressively slower, and by the end of the treatment, measured pressure in the sample on the oil filled line was twice that in the air filled line. For the air filled line, there were no pressure delay periods associated with the near critical region as seen in the Douglas fir samples. This may be because the more permeable pine allowed a large amount of CO_2 to flow into the tubing, during the period of high compressibility, minimizing the delay of internal pressure response.

The third wood sample set used to evaluate air and oil media in the hydraulic lines compared pressure measurements at the centers of ponderosa pine sapwood sealed to restrict CO_2 flow to the radial direction. Since pressure measurements were nearly identical for the five replications, data from only one treatment is shown in Figure 4.10.

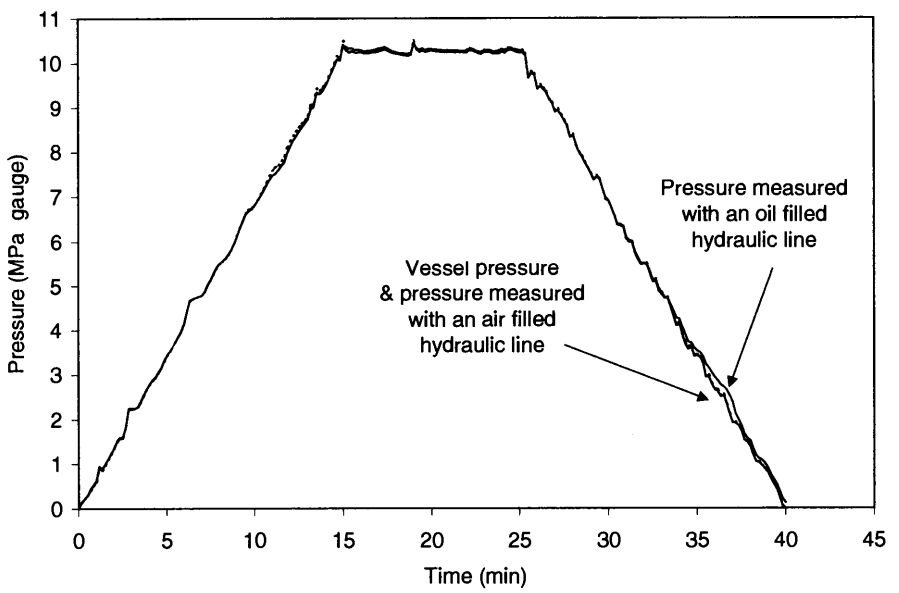


Figure 4.10 Pressure measurements at the center of ponderosa pine sapwood samples made with either air or oil filled hydraulic lines during a SC-CO_2 treatment (CO_2 flow was restricted to the radial direction).

Internal pressure measurements made with gas or oil hydraulic media were identical during the pressing and equilibrating phases of treatment. Upon venting however, measurements made with the oil filled line were noticeably higher than those made with the air filled lines. Because radial flow of the CO_2 treating medium was so rapid, better comparisons between pressure responses using the two hydraulic media may be made from difference in pressure between the vessel and the samples' interior, "surface-to-center pressure difference" (Figure 4.11).

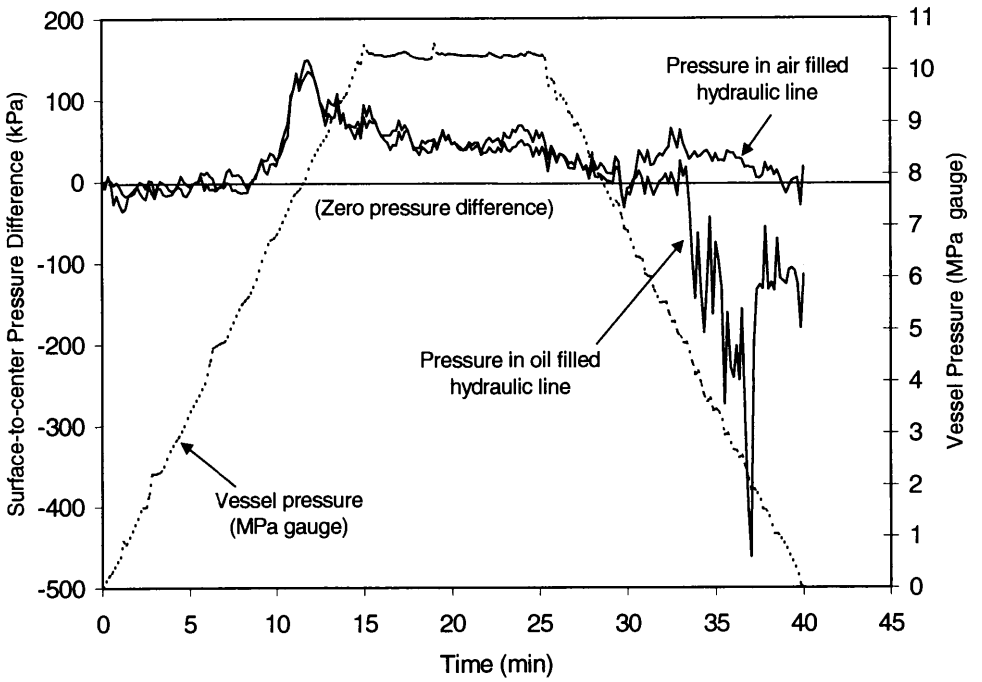


Figure 4.11 Surface-to-center pressure differences for two ponderosa pine sapwood samples made with either air or oil filled hydraulic lines during a SC-CO_2 treatment (CO_2 flow was restricted to the radial direction).

Pressure in the oil filled hydraulic line during and immediately after vessel venting was considerably higher than in the air filled line (see Table 4.5 in the Internal Pressure Verification section for numerical data). Interestingly, pressure measured with the air filled line was lower at the sample center than in the vessel as vessel pressure dropped below 7 MPa. Pressure was expected to be higher in the sample's interior, creating a negative surface-to-center pressure difference. The reason for this positive pressure difference was not known. Additional concern with pressure measurements using the air hydraulic medium arose from the fact that there was no measurable back-pressure immediately after venting. Despite the high radial permeability of the pine samples, the existence of back-pressures was shown by the release of bubbles from samples immersed in water immediately after treatment.

In summary, the accuracy of air filled lines in representing true pressure response as a result of the SC-CO_2 treatment remains questionable during both the pressing and venting phases of treatment. When air filled lines are used, it is unclear whether delayed pressure response measurements actually existed or were caused by the sampling technique (i.e. delay due to hindered transfer of gas into the wood or from compression/expansion of gas in the hydraulic line). Also the use of air filled lines may result in pressure measurements during venting that are artificially low. The use of silicone grease produced unacceptable time delays throughout SC-CO_2 treatments and thus can not be used as a hydraulic medium. The oil filled hydraulic lines seem to show pressure measurements that are representative of pressure in wood during pressing. However, during venting the oil medium seems to interfere with the release of pressure, resulting in measurements that are falsely greater than the actual internal pressure. Mike Milota (personal communication) suggested that the hindered pressure release from oil filled hydraulic lines may be due to CO_2 dissolved in the oil hydraulic media during treatment. When treatment pressure was released, CO_2 coming out of solution could force the

hydraulic fluid into the surrounding wood. Dye placed in the hydraulic oil could be seen impregnated directly below the pressure probe opening supporting this idea.

Internal Pressure Verification: Residual pressure measurements were used as a qualitative measure of how well internal pressure measurements provided representative data, especially at the end of a treatment. Pressures measured immediately after treatment, using pressure probes placed at the center of samples, were compared to residual pressures calculated from matched samples that did not have pressure probes but were individually placed in a pressure bomb immediately after treatment (Table 4.5). The calculated values represent total pressures in the samples, total residual pressure, not just the central pressure. The pine samples used to measure internal pressure were also used to assess the hydraulic medium, so two sets of pressure-probe measurements were given.

Residual pressure calculations confirmed the existence of artificially lower or higher internal pressure measurements during the venting phase of treatments when air or oil hydraulic media were used, respectively. However, the use of oil hydraulic medium with pine samples where flow was restricted to the radial direction appeared to provide representative internal pressure measurements. This suggests that the negative influence of the oil hydraulic medium may be dependent on the sample's permeability.

The calculation of residual pressures between 1.3 and 1.9 MPa in the yellow-poplar samples suggests that high internal pressures do exist. Since measured and calculated residual pressures appear to increase with less permeable wood, care should be taken to reduce surface-to-center pressure differences during venting, especially with woods having low tensile strength perpendicular to the grain.

Table 4.5 Comparisons of pressure measured at the center of wood samples immediately after SC-CO_2 treatment to total residual pressure in matched samples calculated from pressure bomb measurements. [1]

Sample [2]	Internal Pressure-probe Measurement using Different Hydraulic Media (kPa) (absolute)		Calculated Residual Pressure from Bomb Equilibrium Pressure (kPa absolute)
	Air	Oil	
Pine – R	110	359	474
Pine – R	111	538	517
Pine – R	111	367	629
Pine – R	112	346	569
Pine – R	112	236	556
Avg. (Std.)	111 (1)	369 (97)	549 (51)
Pine – T	1,297	—[3]	1,243
Pine – T	—[3]	3,096	1,308
Avg. (Std.)			1,276 (33)
Poplar – T	—[3]	3,627	—[3]
Poplar – T	—[3]	4,399	1,618
Poplar – T	—[3]	3,544	1,579
Poplar – T	—[3]	—[3]	1,279
Poplar – T	—[3]	—[3]	1,916
Avg. (Std.)		3,857 (385)	1,598 (226)

1 Except for the pine having tangential CO_2 flow, separate samples were used for probe and pressure bomb measurements.

2 R and T represent samples with either radial (R) or tangential (T) flow of CO_2 during treatment. In all but the Pine – T samples, separate samples were used for pressure-probe and pressure bomb measurements.

3 No sample for this treatment combination.

The reliability of residual pressure calculations was assessed by venting and resealing the pressure bomb after pressure from a treated sample had initially equilibrated (Table 4.6). Calculation of the initial equilibrium based on a second equilibrium pressure produced results that differed from 5 to 20 %. These differences (higher and lower) may have resulted from not allowing the pressure to fully equilibrate initially or during the second measurement. Small leaks in the pressure bomb may have occurred, but in most cases, none were detected. In conclusion, it appears that the pressure bomb provided relatively accurate measurements of the total residual pressure in wood samples immediately after treatment.

Table 4.6 Evaluation of the method used to calculate residual pressure based on recalculating equilibrium pressures.

Sample	Initial Equilibrium Pressure (kPa)	Calculated Initial Equilibrium Pressure Based on a Second Equilibrium in the Pressure Bomb (kPa)
Poplar-T-2	436	396
Poplar-T-3	424	444
Poplar-T-4	365	347
Poplar-T-5	400	472

4.4.2 Process and Wood Affects on Internal Pressure Response

Data Limitations: Complete pressure measurement data sets were not made on all samples. In most cases, five replicates of each treatment group were evaluated, however, some samples were accidentally destroyed. Because of the long sample preparation and treatment periods, these samples were not replaced. Three of the eleven wood species that were evaluated collapsed under relatively mild treatment conditions (vessel pressure changes of 276 kPa/min), and therefore only two replicates of Engelmann spruce, Pacific silver fir, and western redcedar were treated. Because of the exceedingly long time (over 9 hr) to reach

pressure equalization at the center of red oak, only one treatment run of two samples was performed.

Variations in treatment applications may have influenced pressure measurement results. The intent of the treatment schedule employed in the following investigations was to pressurize the treatment vessel at a controlled rate, hold pressure until pressure equilibrated in the samples, and then vent the vessel at the same rate as pressurization. For some of the ponderosa pine and all of the black gum samples, internal pressure came close but did not equilibrate with the treatment vessel pressure because the vessel was vented too early. This was accidentally done as the result of improperly adjusted pressure indicators on the equipment control cabinet. These indicators provided a visual indication of pressure inside of the samples and were used to initiate venting. As a consequence, time to reach equilibrium for these species should be slightly longer than indicated in the summary tables. Due to the difficulty maintaining a constant maximum pressure, especially just after reaching this level, vessel pressure occasionally went 30 – 60 kPa above the target pressure for a short period. This caused a reduction in the time to achieve pressure equilibrium in the samples.

Pressure response quantifiers used to make comparisons between treatments have some limitations. Time to reach 35 kPa may not be an appropriate quantifier on internal pressure response for samples that had rapid responses during treatment. This is because pressure measurements were made on 10 second intervals. These may have been too slow or out of sync with incremental treatment vessel pressure increases. Time to equilibrium and maximum pressure difference can not be used for samples that collapsed during treatment. Samples that collapsed included Engelmann spruce, Pacific silver fir, and western redcedar. Finally, sampling anomalies causing artificially high internal pressure readings during venting (discussed in the sub-section on Internal Pressure Verification in Pressure Measurement

Techniques, Section 4.4.1) excluded the use of the back-pressure quantifier in comparisons between SC-CO_2 treatments.

Characterization of Internal Pressure Response: Pressure response in wood during treatment may be characterized on the basis of changes at a given location with time or on the basis of pressure at different locations at a given time. The former case is exemplified in Figure 4.12 with pressure measurements in a single yellow-poplar sample.

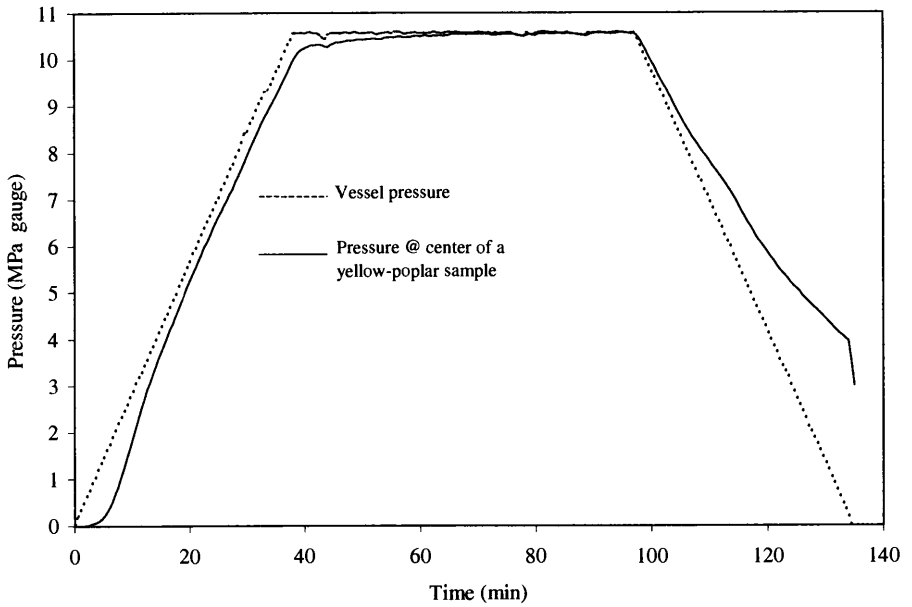


Figure 4.12 Internal pressure measurements at the center of a yellow-poplar sample during SC-CO_2 treatment (CO_2 was restrict to tangential flow).

As vessel pressure was increased, there was an initial delay in pressure rise at the center of this sample followed by a period of relatively constant pressure increase in response to increasing vessel pressure. The initial delay may be explained by the time needed for CO_2 to flow into the sample center In addition, there may be a delay associated with the compression of CO_2 in the wood. After vessel pressure reached the maximum, the rate of

pressure increase in the sample decreased dramatically, and a considerable amount of time was needed for internal pressure to reach equilibrium with that in the vessel. As vessel pressure was decreased, internal pressure decreased at a progressively slower rate. This pattern of internal pressure decrease most likely resulted from a combination of factors including delayed flow of CO_2 through the wood, the expansion of CO_2, and interference from the hydraulic oil. During the SC-CO_2 treatment, gas may be dissolved in the hydraulic medium; upon venting, the expansion of CO_2 from the hydraulic oil could force some of the oil out into the surrounding wood. Since the wood was not easily impregnated by the oil, release of pressure from the probe would likely be hindered. As a result, artificially high pressure measurements would have been made during the venting phase of this treatment. The magnitude of discrepancy between actual pressure and that indicated by the pressure probe was not known, but based on other experimental work (see the Internal Pressure Verification portion above in this section), it likely to have increased as the ability of the hydraulic medium to move into the wood was hindered by decreased wood permeability. The sudden internal pressure drop near the end of venting this sample was most likely caused by wood or sealant failure around the pressure probe.

Figure 4.13 shows the difference in pressure between the vessel and the center of the yellow-poplar sample presented in Figure 4.12 (the surface-to-center pressure difference). This alternative representation of internal pressure response more easily shows the stresses which the wood is subjected to and the magnitude of the driving force causing material to flow into or out of the wood. The initial delay in pressure response at the sample center noted above resulted in a relatively large (1.3 MPa) surface-to-center pressure difference. If the wood was less permeable or not as strong, the initial pressure response delay could have resulted in collapse. As pressing continued, the movement of CO_2 into the wood relaxed the surface-to-center pressure difference. As vessel pressure reached the critical level (7.4 MPa),

the surface-to-center pressure difference increased again, this time due primarily to the high compressibility of CO_2 at this pressure. The density of CO_2 increases exponentially in the transition through the near critical region (Ely, 1986). While the treating vessel was held at a constant pressure, the internal pressure equilibrated and thus, the surface-to-center pressure difference diminished. Vessel pressure dropped faster than that in the wood during venting, causing a negative pressure difference to develop. In most cases, the largest surface-to-center pressure difference occurred at the end of the vessel venting. Again, excessive pressure differentials could cause wood failure (fracture) during the venting phase of treatment.

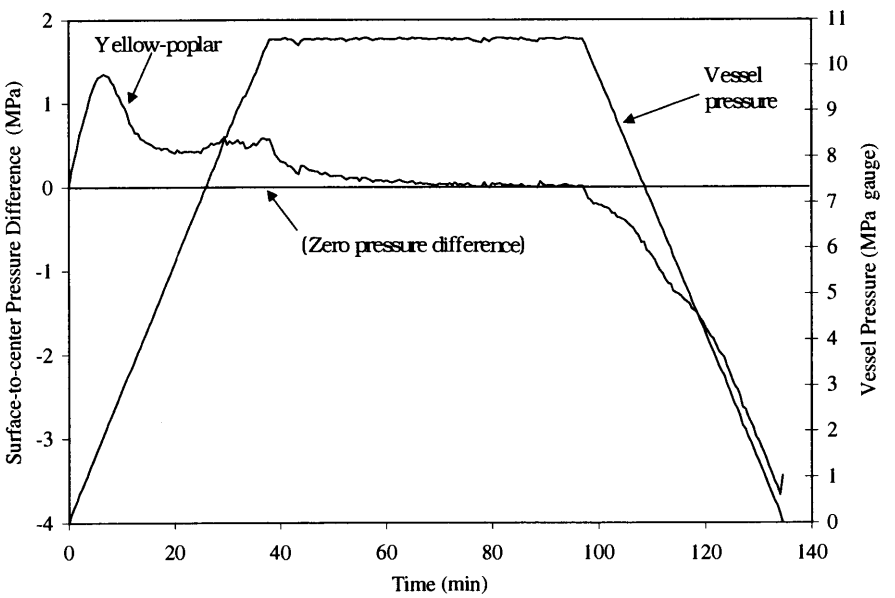


Figure 4.13 Surface-to-center pressure differences during SC-CO_2 treatment in a yellow-poplar sample sealed to restrict flow to the tangential direction.

The second basis for characterizing pressure response in wood during SC-CO_2 treatment is to provide pressure measurements at two locations at a given time. Measuring pressure at two depths, or distances along the CO_2 flow path, in a sample provides information

about the surface-to-center pressure profile (pressure gradient). Figures 4.14, 4.15, and 4.16, summarized in Table 4.7, show simultaneous pressure measurements at depths of 15 and 30 mm along the radial axes of 60 mm thick samples. The initial delay in pressure response was almost twice as long at the 30 mm depth, but after this delay, pressure at the center increased faster. The difference in pressure at these two depths was eliminated as vessel pressure reached 5 MPa. Increasing pressure into the critical region (above 7.4 MPa) resulted in a similar delay in pressure response at the two depths. Average time to reach equilibrium was only slightly longer for the increased depth (8.7 versus 6.3 min).

In four of the five treatment replications, pressure initially decreased slightly faster at the 15 mm depth during venting, but then decreased faster from the center location, leaving a larger back-pressure at the 15 mm probe immediately after venting (Figures 4.15 and 4.16). Shortly after the treating vessel was vented, pressure at the 15 mm depth dropped below that measured at the center of the sample (Figure 4.17). In one of the five treatment runs, pressure at the 15 mm location continuously remained below that at the 30 mm location, as expected. The unusual pressure measurements seen during venting of the four treatment replications may be due to a combination of anomalies in the pressure sampling method. When the samples were split open hydraulic fluid could be seen around the pressure probe region, traveling slightly in the transverse direction and completely penetrating the sample longitudinally below the probe. This indicated that hydraulic fluid was forced out of the probes. Resistance from the wood to the impregnation of hydraulic oil could cause the delayed release of pressure from the pressure probe even though the surrounding pressure in the wood became less than that in the hydraulic line (See the discussion at the end of the sub-section on Hydraulic Media Tests, Section 4.4.1).

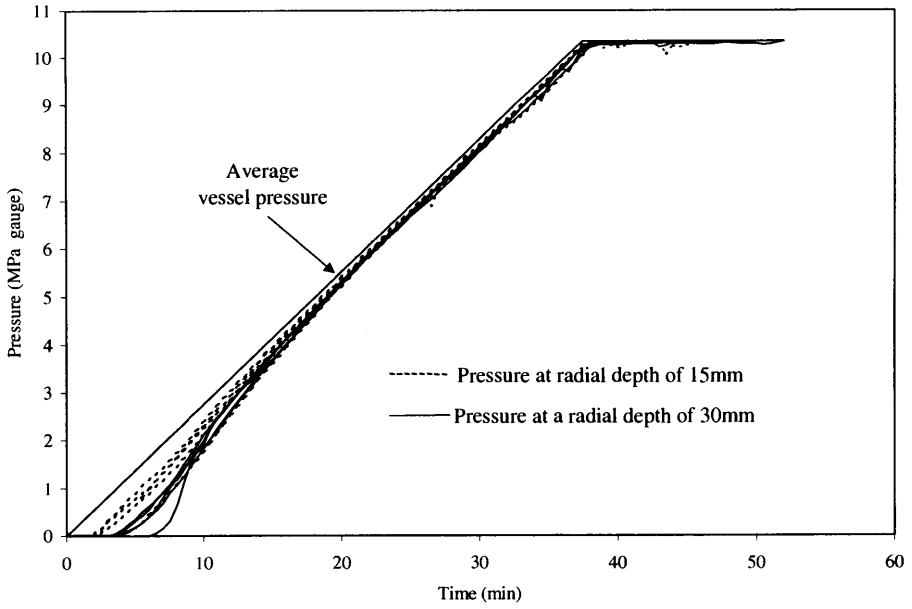


Figure 4.14 Internal pressure measurements simultaneously recorded at depths of 15 and 30 mm along the radial axes of five Douglas-fir heartwood samples during the pressing phase of SC-CO_2 treatments with one sample per treatment application.

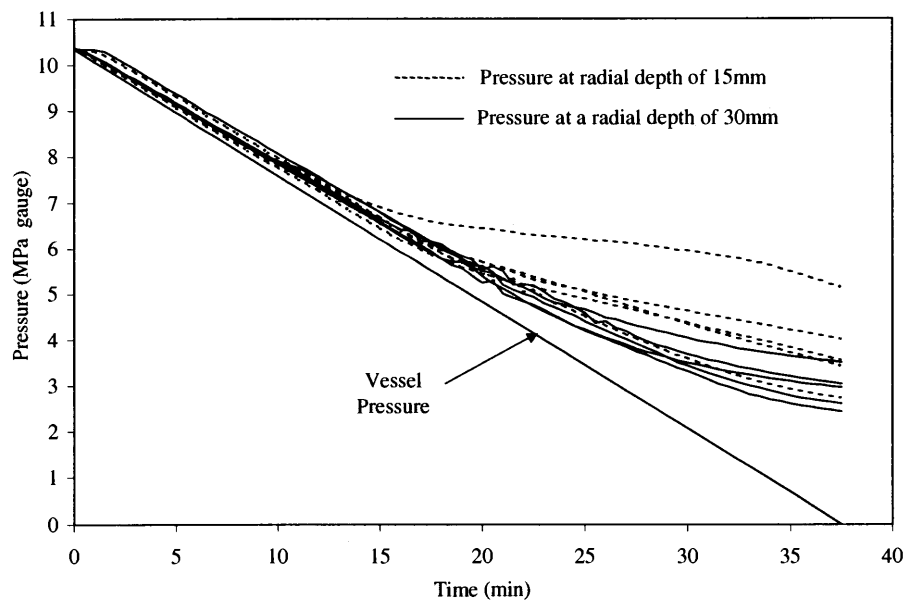


Figure 4.15 Internal pressure measurements simultaneously recorded at depths of 15 and 30 mm along the radial axes of five Douglas-fir heartwood samples during the venting phase of SC-CO_2 treatments with one sample per treatment application.

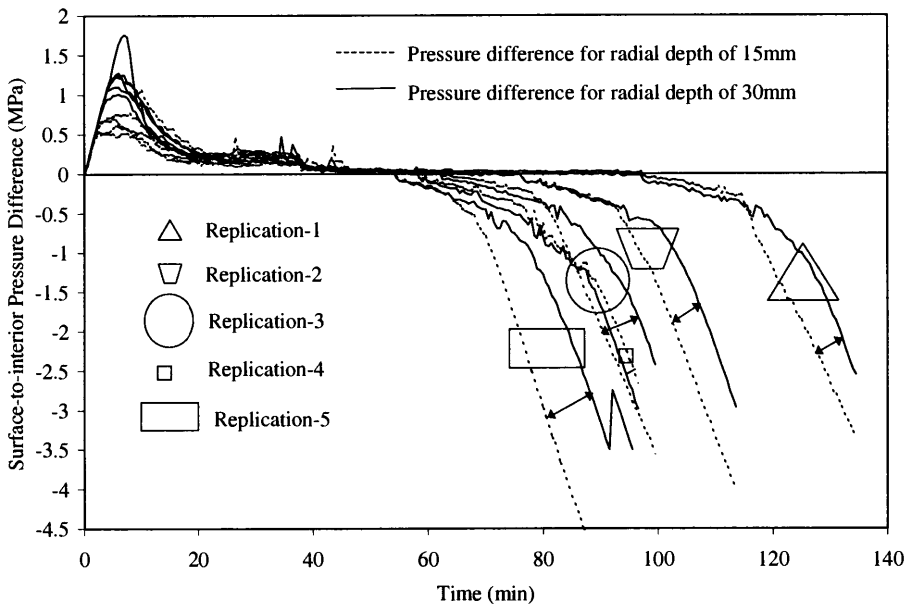


Figure 4.16 Surface-to-interior pressure differences for pressure measurements simultaneously recorded at depths of 15 and 30 mm along the radial axes of five Douglas-fir heartwood samples during SC-CO_2 treatments with one sample per treatment application.

Table 4.7 Simultaneous pressure measurements at two depths along a radial flow path in Douglas-fir heartwood samples during SC-CO_2 treatment.

Sample & Depth of Pressure Probe (mm)		Time to Reach 35kPa (min)	Time to Equilibrium after Vessel Reached Maximum Pressure (min)	Max. ΔP during Pressing (kPa gauge)	Back-pressure (kPa gauge)	Wood Condition
Sample 1-15		2.0	9.0	614	-3,323	Good [1]
Sample 1-30		3.5	9.5	1,007	-2,544	Good
Sample 2-15		2.5	3.5	710	-4,006	Good
Sample 2-30		6.5	7.0	1,765	-2,958	Good
Sample 3-15		2.0	5.5	531	-3,558	Good
Sample 3-30		3.5	7.0	1,103	-2,427	Good
Sample 4-15		2.0	5.0	758	-2,654	Good
Sample 4-30		4.0	12.0	1,241	-2,985	Good
Sample 5-15		4.0	8.5	1,227	-5,143	Good
Sample 5-30		4.0	8.0	1,276	-3,503	Good
Average (Std.)	15 mm	2.5 (0.8)	6.3 (2.1)	768 (242)	-3,737 (828)	
	30 mm	4.3 (1.1)	8.7 (1.9)	1,278 (261)	-2,883 (380)	

[1] (Good) Means no evident wood failures due to either tensile or compressive forces.

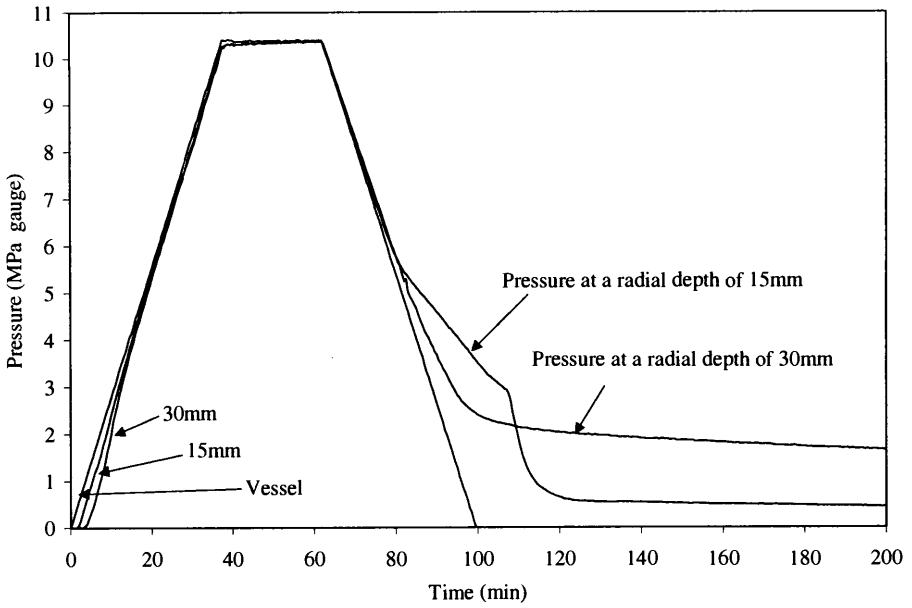


Figure 4.17 Pressure measurements at depths of 15 and 30 mm radially from the surface of Douglas-fir samples during SC-CO_2 treatment showing an unusual pressure drop at the 15 mm depth just after venting.

In addition to the delayed pressure loss from both probes, voids created by displaced liquid in the 15 mm probes would allow CO_2 leaving the center probes to accumulate. As a result, pressure would decrease more quickly at the center probes compared to the probes at 15 mm. The sudden drop in pressure at the 15 mm probe location shortly after vessel pressure was released is most likely the result of a leak in the epoxy near the 15 mm probe. It is not clear why the epoxy failed in these cases since this pressure measurement technique has proven to be effective in similar applications. Possibly, a combination of softened epoxy and high surface-to-center pressure difference (approximately 3 MPa) resulted in this failure.

The suspicion that one probe interfered with the other led to the comparison of pressure measurements recorded at the 30 mm depth in these samples to measurements made at the same depth in matched samples containing only a single centered probe (Figures 4.18 and 4.19).

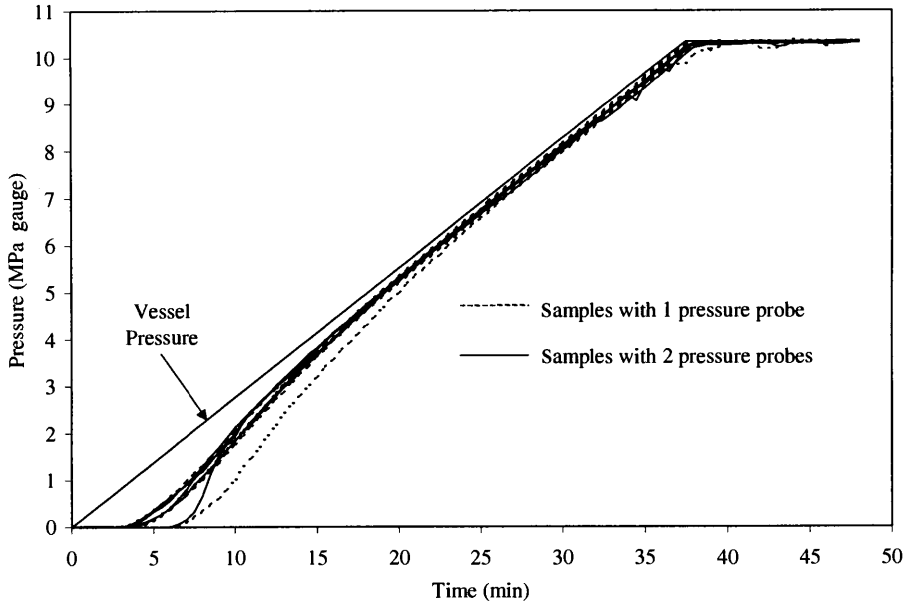


Figure 4.18 Pressure measurements 30 mm radially from the surface (i.e. at the sample center) of Douglas-fir heartwood samples containing either one or two pressure probes during the pressing phase of SC-CO_2 treatments.

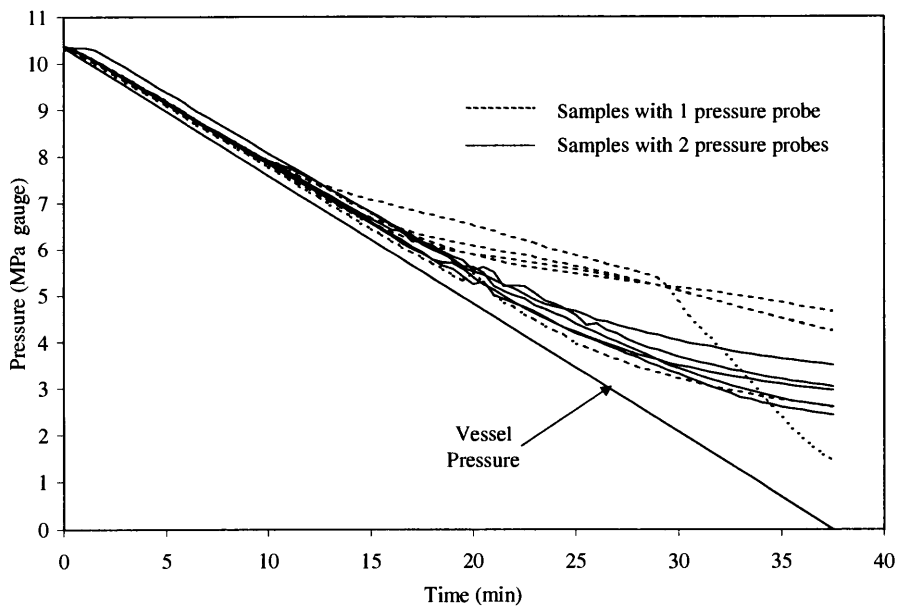


Figure 4.19 Pressure measurements 30 mm radially from the surface (i.e. at the sample center) of Douglas-fir heartwood samples containing either one or two pressure probes during venting following SC-CO_2 treatments.

The presence of a second probe did not interfere with pressure measurements during the pressing phase of treating. During venting, however, lower pressures at the sample centers occurred with the two probe configuration. This supports the possibility that gas from the center probe region may have moved outward more quickly due to the presence of void volume created in the 15 mm pressure probe hydraulic line as fluid was previously forced out of it during venting.

Pressing and Venting Rates: Differentiation of internal pressure responses during treatments using pressing and venting rates of 138, 276, and 827 kPa/min was confounded by the higher permeability of the Douglas-fir heartwood chosen for this investigation compared to that preliminary trials.

Figures 4.20 through 4.28 show internal pressure measurements recorded during pressing and venting of samples at three rates. Table 4.8 summarizes these results. Faster press rates decreased the average time before noticeable pressure increases occurred at the sample centers (3.5, 1.2, and 0.7 minutes, respectively for the 827, 276, and 138 kPa/min pressurization rates). Conversely, the faster press rates resulted in longer times to pressure equalization after maximum vessel pressure was reached. Figures 4.23, 4.26, and 4.29 show that the surface-to-center pressure differences increase with increasing rate of pressure change. Therefore, the longer time to pressure equalization seems to have resulted from the formation of larger pressure differences across the sample. Maximum surface-to-center pressure differences during pressing did not seem to differ for the two slower rates, but they increased from an average of 375 kPa to 791 kPa when press rate was increased from 276 to 827 kPa/min. Back-pressure immediately after venting did not seem to differ with venting rate, possibly reflecting difficulties in measuring pressure during the venting phase of treatment. In summary, faster pressing reduced overall treatment times, but this benefit could be outweighed if surface-to-center pressure differences exceed the strength of the wood.

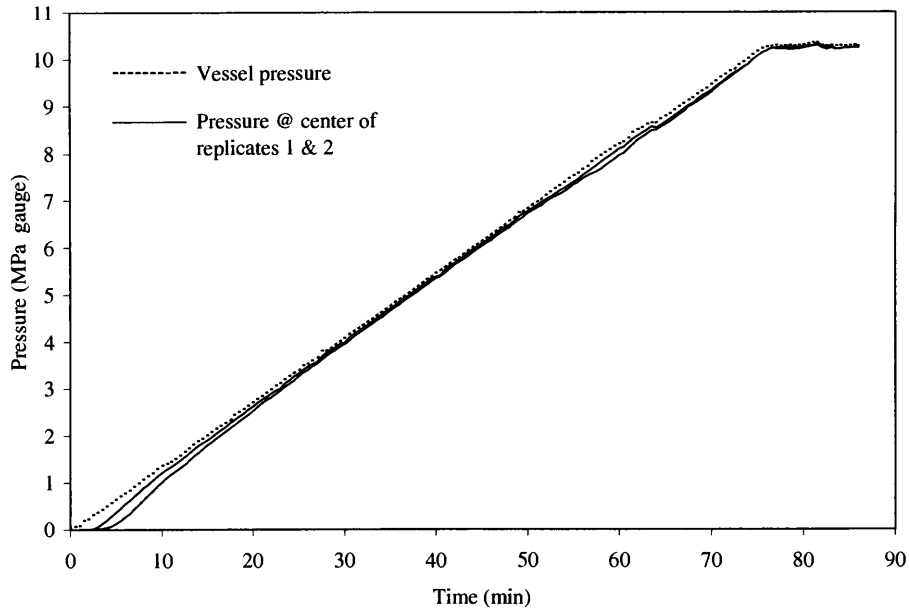


Figure 4.20 Pressure measurements at the center of Douglas-fir heartwood samples during SC-CO_2 pressing @ 138 kPa/min.

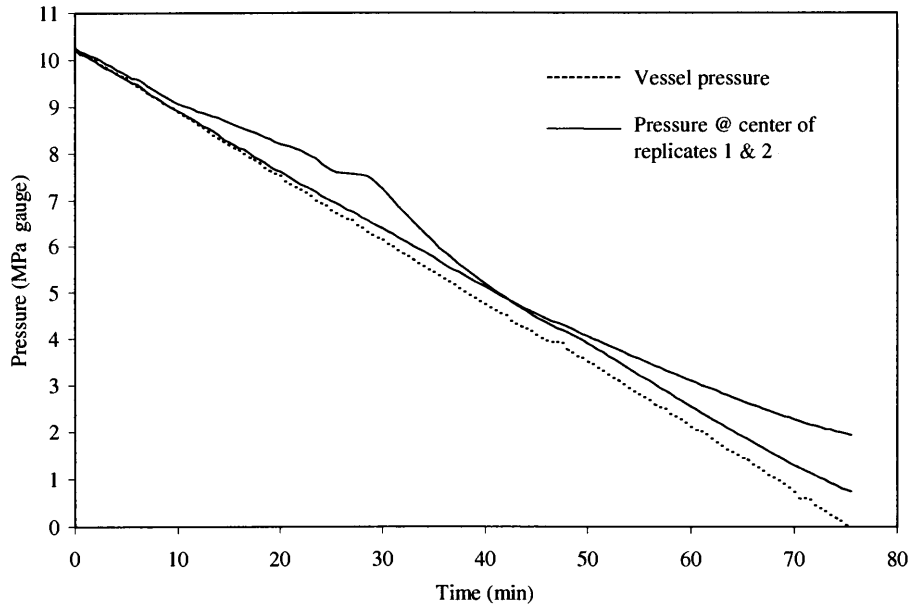


Figure 4.21 Pressure measurements at the center of Douglas-fir heartwood samples during venting @ 138 kPa/min following SC-CO_2 treatment.

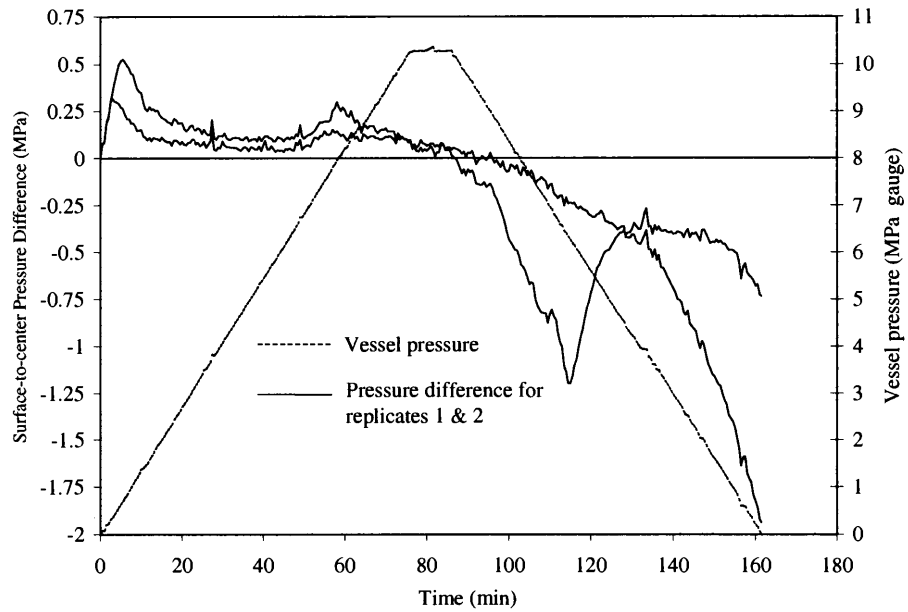


Figure 4.22 Surface-to-center pressure differences in Douglas-fir heartwood samples during SC-CO_2 treatment when pressure was applied and vented at 138 kPa/min.

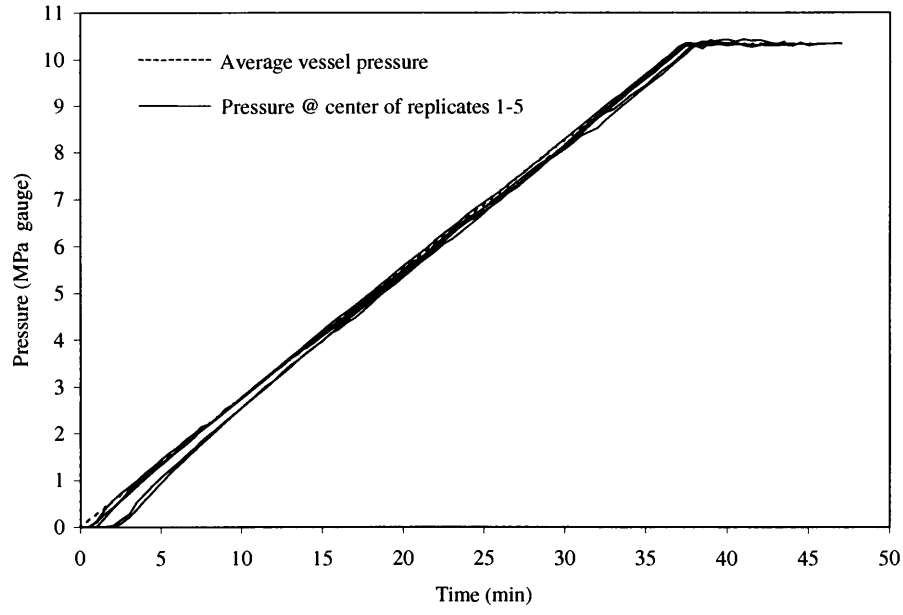


Figure 4.23 Pressure measurements at the center of Douglas-fir heartwood samples during SC-CO_2 pressing @ 276 kPa/min.

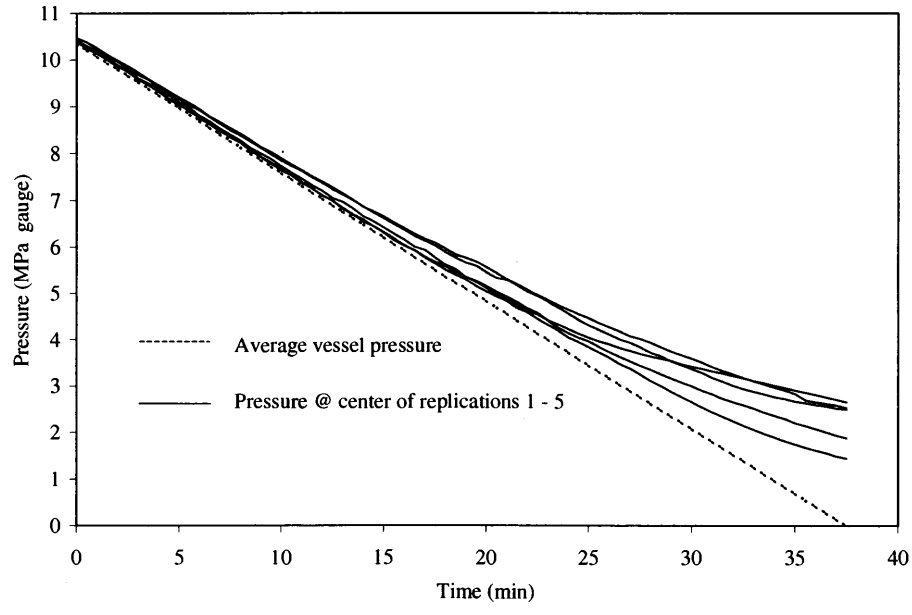


Figure 4.24 Pressure measurements at the center of Douglas-fir heartwood samples during venting @ 276 kPa/min following SC-CO_2 treatment.

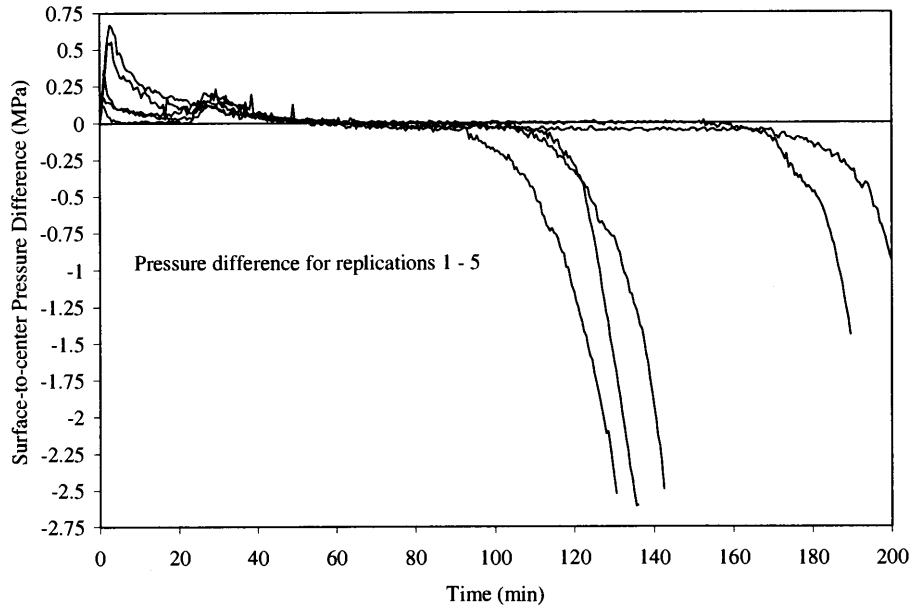


Figure 4.25 Surface-to-center pressure differences in Douglas-fir heartwood samples during SC-CO_2 treatment when pressure was applied and vented at 276 kPa/min pressing & venting.

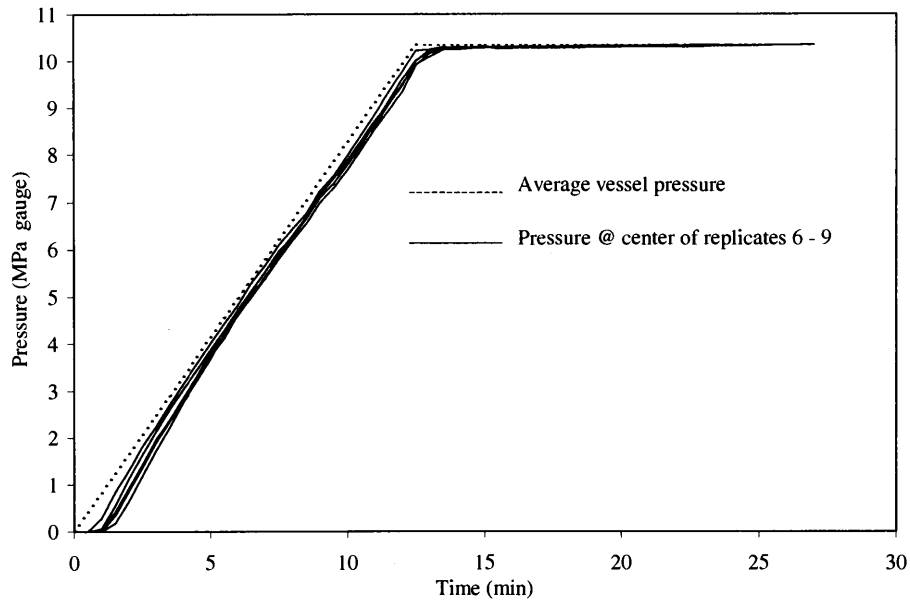


Figure 4.26 Pressure measurements at the center of Douglas-fir heartwood samples during SC-CO_2 pressing @ 827 kPa/min.

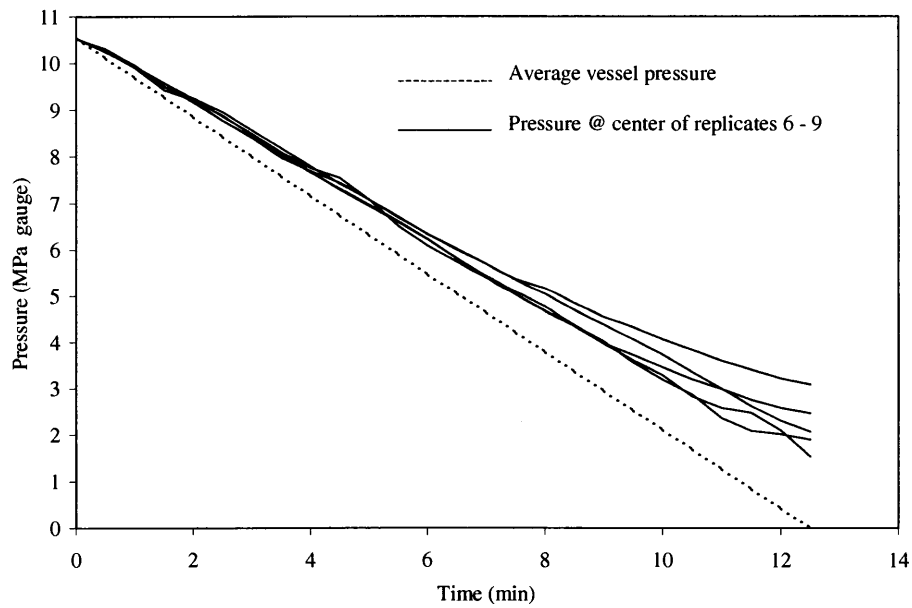


Figure 4.27 Pressure measurements at center of Douglas-fir heartwood samples during venting @ 827 kPa/min following SC-CO_2 treatment.

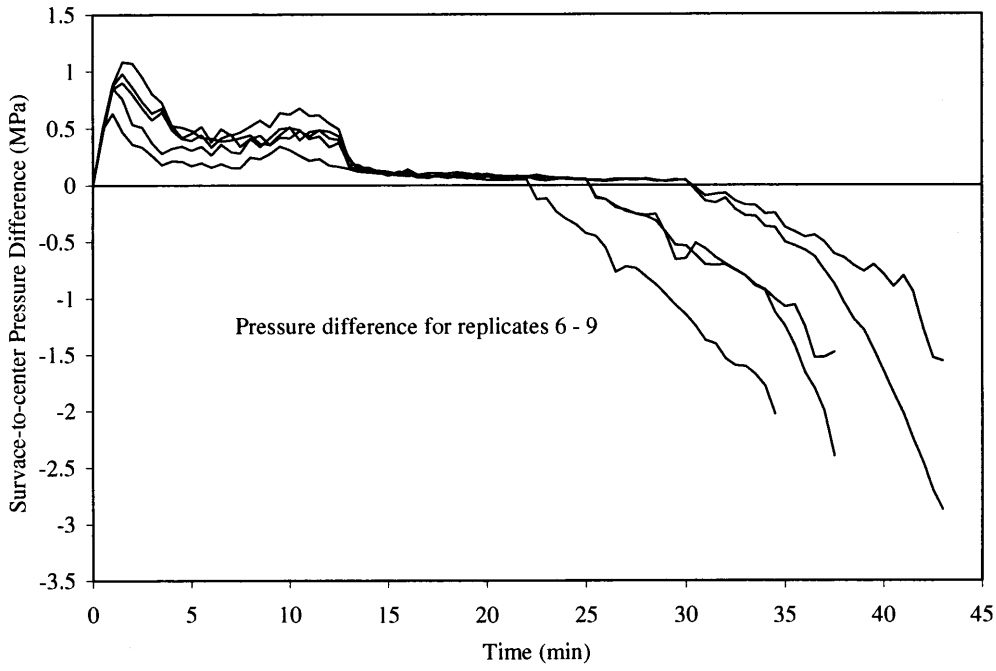


Figure 4.28 Surface-to-center pressure differences in Douglas-fir heartwood samples during SC-CO_2 treatment when pressure was applied and vented at 827 kPa/min.

Table 4.8 Effect of pressing and venting rates during SC-CO_2 treatment on time to reach 35 kPa and vessel pressure at sample center, maximum surface-to-center pressure difference, pressure difference after treatment, and wood condition of Douglas-fir heartwood samples.

Pressing & Venting Rate (kPa/min)	Time to Reach 35kPa (min)	Time to Equilibrium after Vessel Reached Maximum Pressure (min)	Max. ΔP during Pressing (kPa gauge)	Back-pressure (kPa gauge)	Wood Condition
138	3.0	4.5	317	-1,937	Good [1]
	4.0	5.0	531	-731	Good
Avg. (std.)	3.5 (0.5)	4.8 (0.3)	424 (107)	-1,334 (603)	
276	0.5	8.5	117	-2,599	Good
	0.5	2.5	172	-1,441	Good
	2.0	3.0	669	-2,523	Good
	2.0	6.0	558	-2,496	Good
	1.0	9.5	359	-1,875	Good
Avg. (std.)	1.2 (0.7)	5.9 (2.8)	375(214)	-2,187 (454)	
827	0.5	20.0	586	-2,151	Good [1]
	1.5	20.0	1,193	-2,965	Good
	0.5	— [2]	476	-1,427	Good
	0.5	— [2]	372	-1,965	Good
	0.5	13.5	634	-1,558	Good
	0.5	14.0	855	-2,868	Good
	1.0	10.5	903	-1,503	Good
	1.0	11.0	979	-2,420	Good
	0	10.0	1,082	-2,027	Good
	1.0	11.0	827	-4,327	Good
Avg. (std.)	0.7 (0.4)	13.8 (3.8)	791 (253)	-2,321 (838)	

1 (Good) Means no evident wood failures due to either tensile of compressive forces.

2 Samples did not reach equilibrium; therefore, values were not used with the average.

Flow Length: Pressure measurements recorded at the center of samples having single directional flow lengths of 15, 30, and 45 mm are shown in Figures 4.29 through 4.37 and summarized in Table 4.9. Doubling flow length from 15 to 30 mm resulted in a nearly four fold increase in the time needed for the first 35 kPa pressure increase at the sample center. And, increasing flow length from 30 to 45 mm resulted in slightly less than a threefold increase in time required for the first 35 kPa increase. Thus regardless of the depths investigated, time required for an initial pressure response increases approximately twofold for each increment of length. After maximum vessel pressure was reached, the time to reach pressure equilibrium between the vessel and the sample centers was similar for the samples having 15 and 30 mm flow lengths. Time for equalization was approximately tenfold longer for the samples having a 45 mm flow length. Average maximum surface-to-center pressure differences increased proportionally to the time needed for the initial pressure response. Although surface-to-center pressure differences did not exceeded the compressive strength of these samples, two of the five Douglas-fir samples with 45 mm flow lengths showed signs of collapse in the radial direction. Back-pressure measurements did not seem to be related to flow length. These results suggest that pressure response is directly related to flow length, but they do not conclusively indicate the magnitude of this relationship.

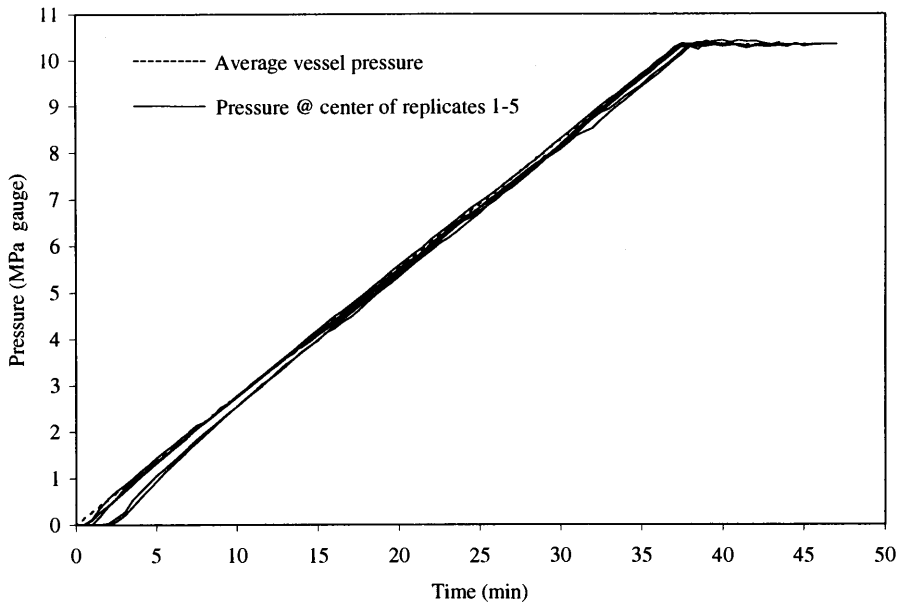


Figure 4.29 Pressure measurements at the center of Douglas-fir heartwood during SC-CO_2 pressing of samples with a 15 mm CO_2 flow length.

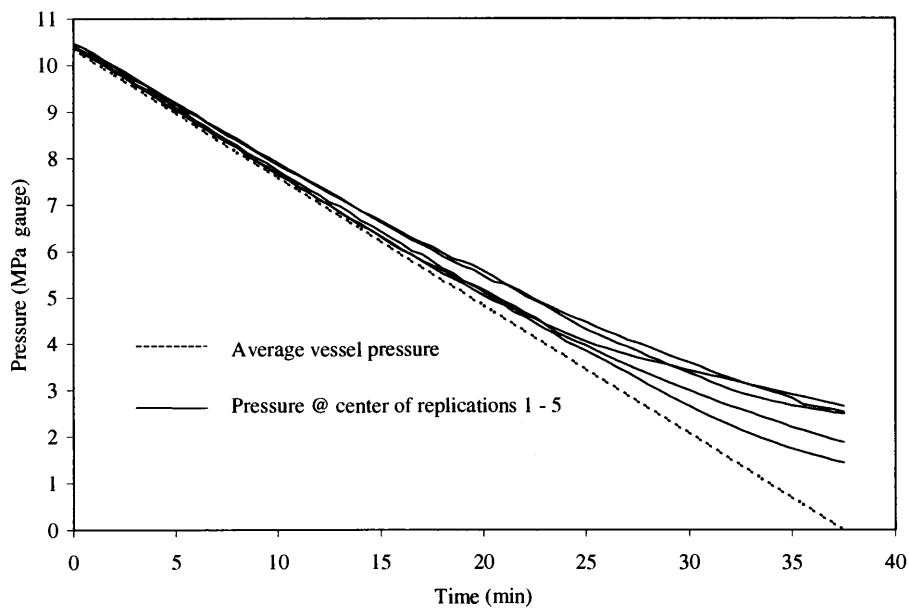


Figure 4.30 Pressure measurements at the center of Douglas-fir heartwood during venting following SC-CO_2 treatment of samples with a 15 mm CO_2 flow length.

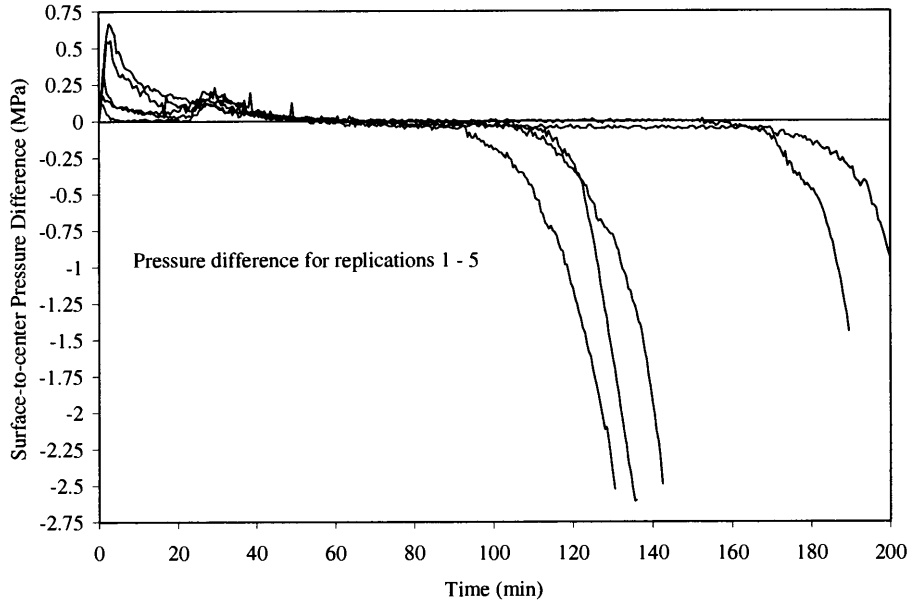


Figure 4.31 Surface-to-center pressure differences in Douglas-fir heartwood during SC-CO_2 treatment of samples with a 15 mm CO_2 flow length.

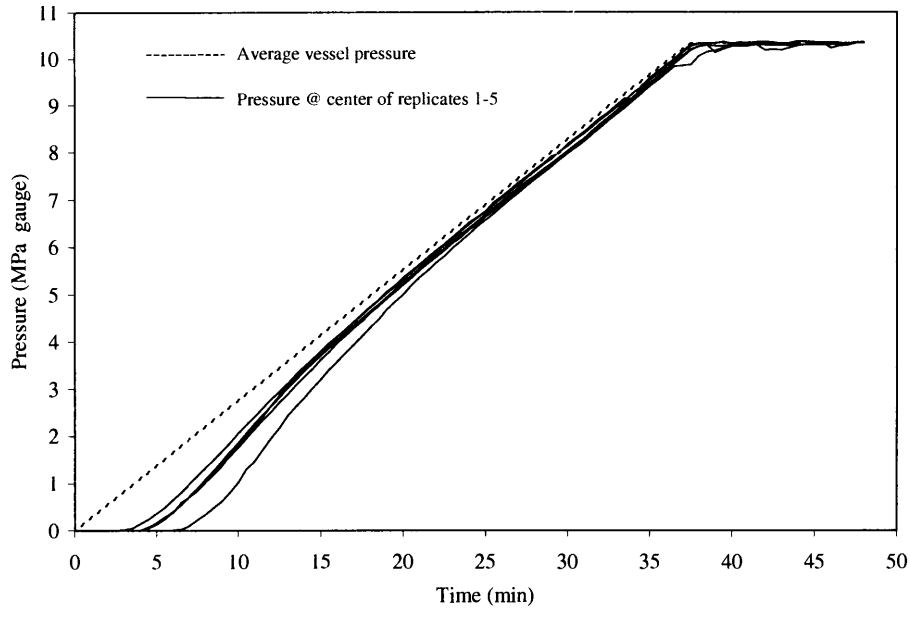


Figure 4.32 Pressure measurements at the center of Douglas-fir heartwood during SC-CO_2 pressing of samples with a 30 mm CO_2 flow length.

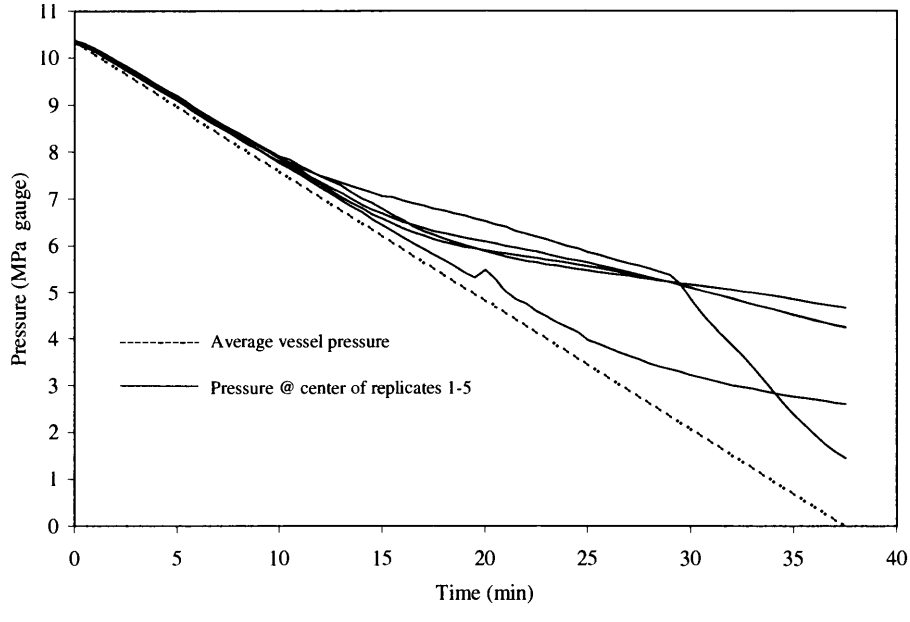


Figure 4.33 Pressure measurements at the center of Douglas-fir heartwood during venting following SC-CO_2 treatment of samples with a 30 mm CO_2 flow length.

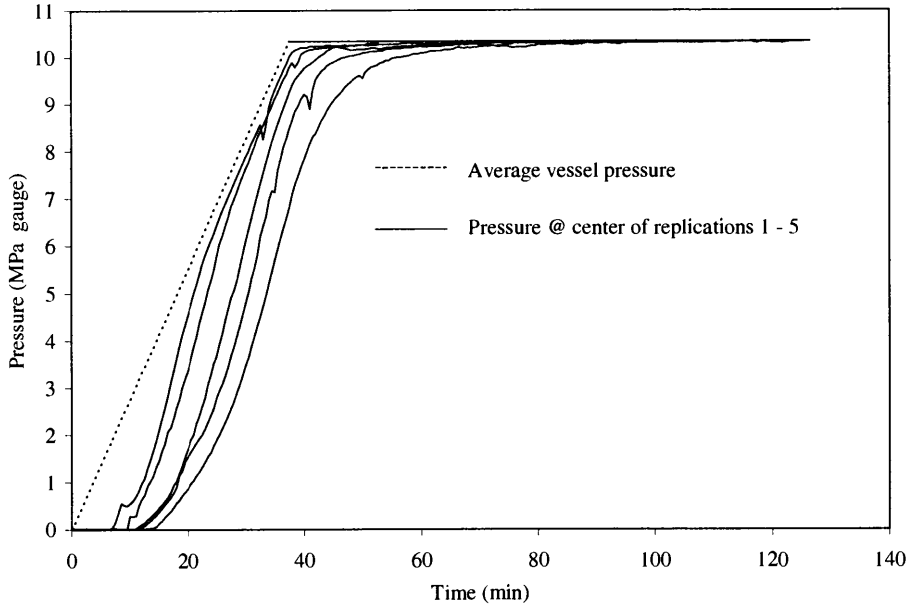


Figure 4.35 Pressure measurements at the center of Douglas-fir heartwood during SC-CO_2 pressing of samples with a 45 mm CO_2 flow length.

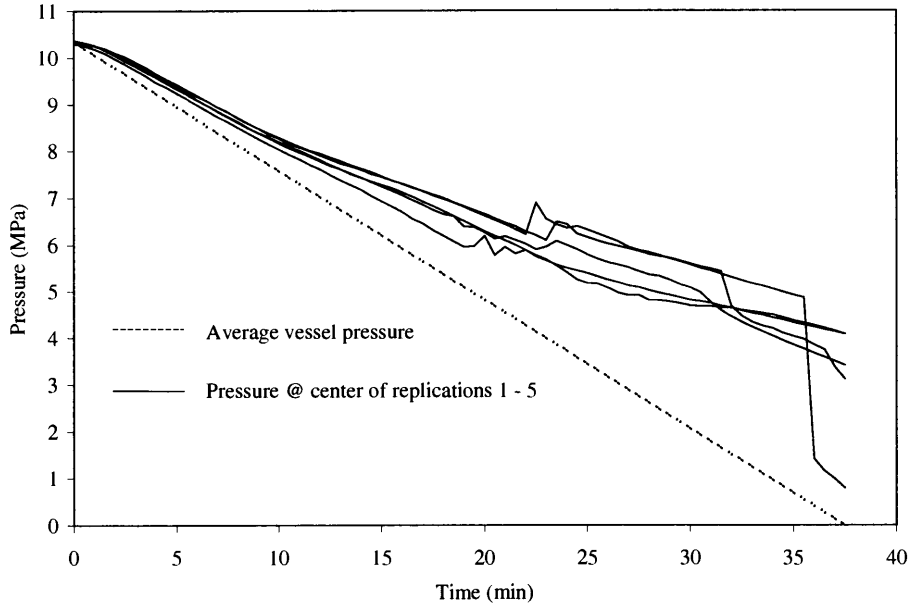


Figure 4.36 Pressure measurements at the center of Douglas-fir heartwood during venting following SC-CO_2 treatment of samples with a 45 mm CO_2 flow length.

Table 4.9 Data showing the effects of flow length on pressure response at center of Douglas-fir heartwood samples treated with SC-CO_2 by pressing at 276 kPa/min, holding at 10.3 MPa and 40 °C until pressure equilibrated in the sample, then venting at 276 kPa/min.

Depth of Pressure Transmitter Probe [Surface to sample center] (mm)	Time to Reach 35kPa (min)	Time to Equilibrium after Vessel Reached Maximum Pressure (min)	Max. ΔP during Pressing (kPa gauge)	Back-pressure (kPa gauge)	Wood Condition
15	0.5	8.5	117	-2,599	Good
	0.5	2.5	172	-1,441	Good
	2.0	3.0	669	-2,523	Good
	2.0	6.0	558	-2,469	Good
	1.0	9.5	359	-1,875	Good
Avg. (std.)	1.2 (0.7)	5.9 (2.8)	375 (214)	-2,181 (451)	
30	6.5	13.0	1,862	-4,661	Good
	4.0	10.0	1,234	-1,448 [2]	Good
	4.0	2.0	1,048	-4,247	Good
	4.0	6.5	1,282	-2,599	Good
	4.0	6.5	1,269	-4,289 [2]	Good
Avg. (std.)	4.5 (1.0)	7.6 (3.7)	1,339 (275)	-3,949 (796)	
45	11.5	59.5	4,226	-3,103	Collapsed
	11.0	89.0	3,978	-786	Good
	14.0	78.0	5,081	-4,082	Collapsed
	9.5	44.0	2,765	-3,413	Good
	7.0	— [1]	2,358	-4,082	Good
Avg. (std.)	10.6 (2.3)	67.6 (17.2)	3,682 (993)	-3,670 (426)	

1 Samples did not reach equilibrium; therefore, values were not used with the average.

2 Samples had pressure probe sealant failure during venting; therefore, values were not used with the average.

Wood Species (Permeability): Results from pressure measurements for eleven species are shown in Figures 4.38 through 4.67 and summarized in Table 4.10, page 174. Heartwood from sugar and lodgepole pines showed no measurable resistance to CO_2 flow. Samples from ponderosa pine showed a slight delay before an initial pressure response (35 kPa rise). The time required for this response increased from 1.2 to 16.3 min respectively for Douglas-fir followed by white fir, yellow-poplar, western redcedar, red oak, black gum, Engelmann spruce, and Pacific silver fir. The average time required for pressure inside of the wood to equilibrate after maximum vessel pressure was reached was less than one minute for sugar and lodgepole pine samples. Ponderosa pine and Douglas-fir samples took approximately 5 min to equilibrate. Yellow-poplar, white fir, black gum, and red oak respectively required averages of 65, 105, 177, and 421 minutes to reach pressure equilibrium. Equalization times were not available for Engelmann spruce, Pacific silver fir, and western redcedar because they collapsed during the pressing phase of treatment. The average maximum surface-to-center pressure differences during pressing occurred in all of the pine samples while the CO_2 was passing into the critical region. These values were 78, 95, and 268 kPa respectively for sugar pine, lodgepole pine, and ponderosa pine. Maximum pressure difference occurred during the beginning of pressing for Douglas-fir, white fir, yellow-poplar, black gum, and red oak respectively 375, 2,089, 3, 130, 6,088, and 6,537 kPa. Western redcedar, Engelmann spruce, and Pacific silver fir had maximum pressure differences of 5,206, 6,778, and 7,247 kPa, which corresponded to the average forces which caused them to collapse. The average back-pressure values followed the same relative order of magnitudes as the maximum surface-to-center pressure differences, but due to sealant failures and collapse, data was available on fewer species. Long treatment times required for the red oak and black gum samples caused the epoxy sealant around the pressure probes to soften and fail during venting.

None of the pine, Douglas-fir, yellow poplar, and red oak samples experienced treatment damage. One of five white fir samples crushed slightly. All of the black gum samples were moderately crushed; while, all of the Engelmann spruce, Pacific silver fir, and western redcedar samples were severely crushed (Table 4.10). Except for the white fir sample, all samples which were crushed developed surface-to-center pressure differences that exceeded their crushing strengths (Table 4.2) (Markwardt and Wilson, 1935).

The internal pressure response differences seem to be correlated to differences in radial gas permeability (Choong et al., 1972). Unfortunately, radial permeability values are not readily available for all of the species tested (Tables 4.2).

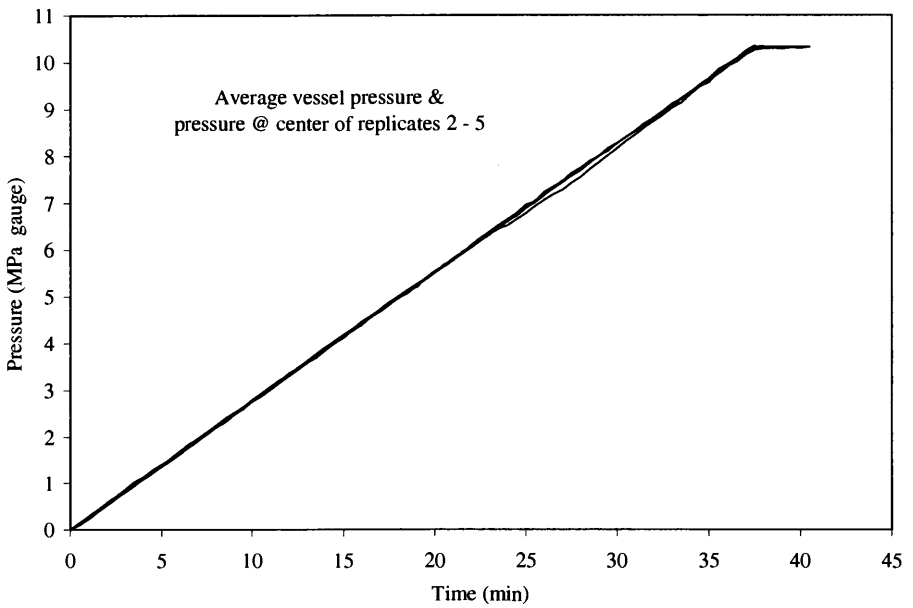


Figure 4.38 Pressure measurements at the center of sugar pine heartwood samples during SC-CO_2 pressing at 276 kPa/min.

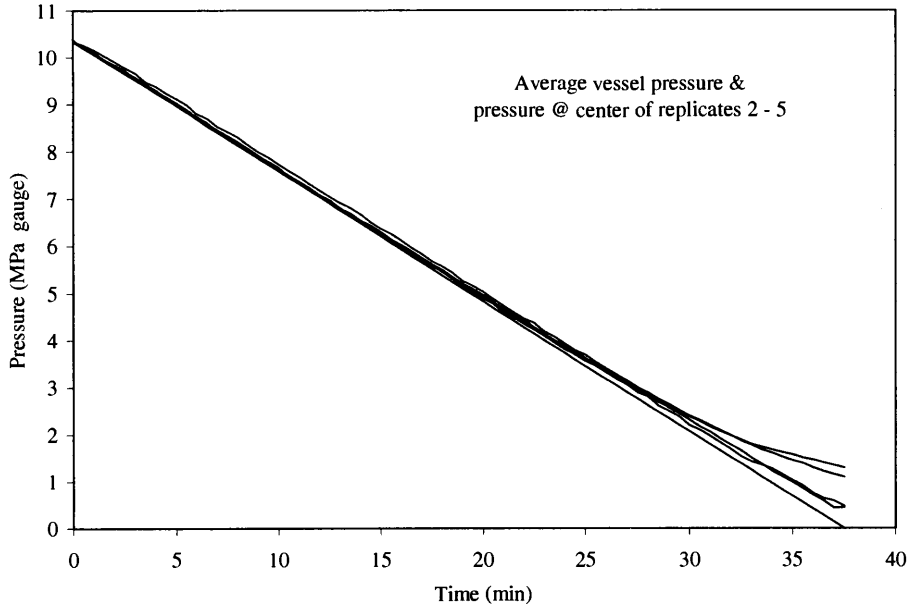


Figure 4.39 Pressure measurements at the center of sugar pine heartwood samples during venting at 276 kPa/min following SC-CO_2 treatment.

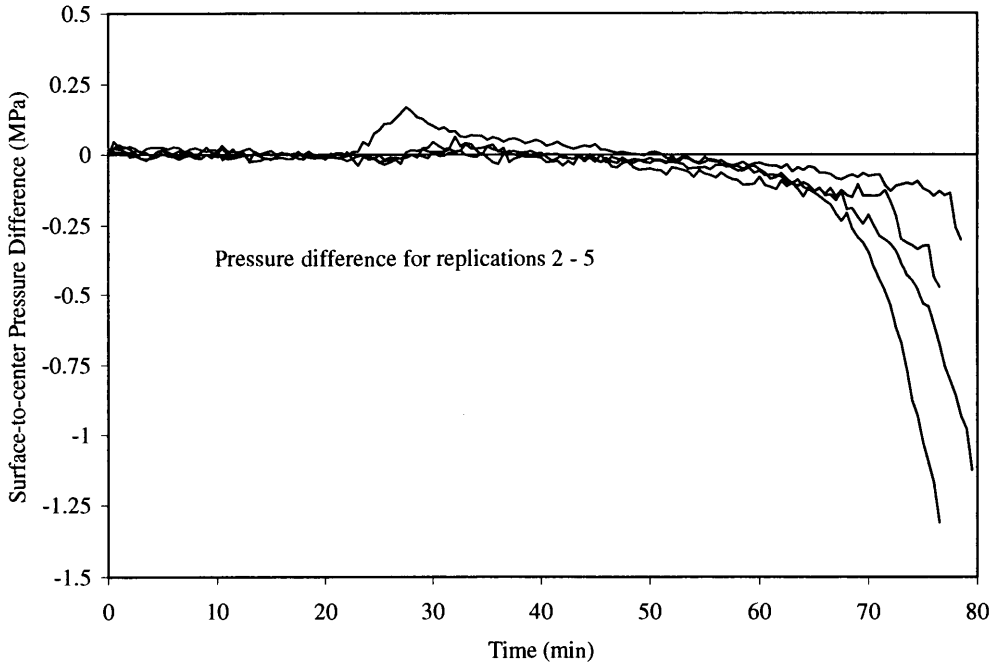


Figure 4.40 Surface-to-center pressure differences in sugar pine heartwood samples during SC-CO_2 treatment.

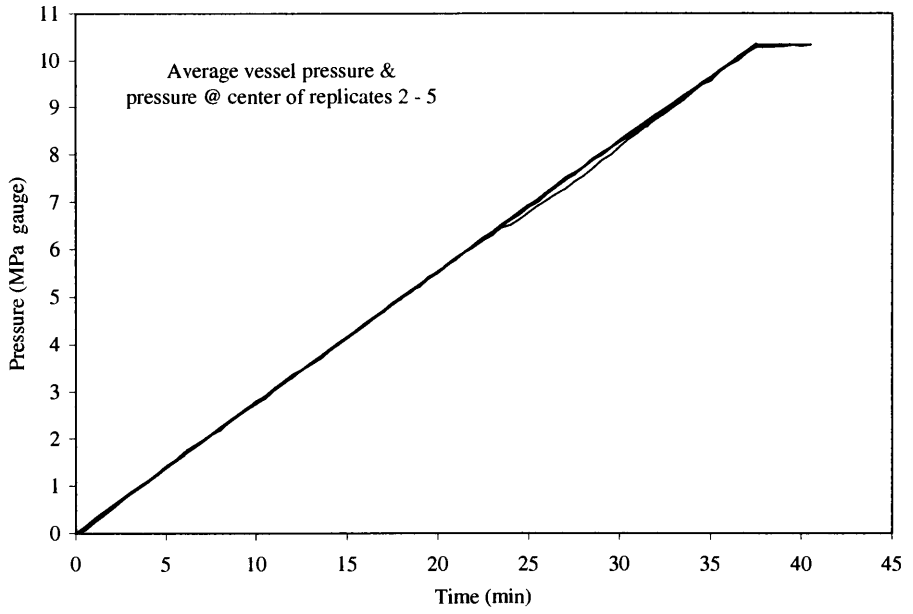


Figure 4.41 Pressure measurements at the center of lodgepole pine heartwood samples during SC-CO_2 pressing at 276 kPa/min.

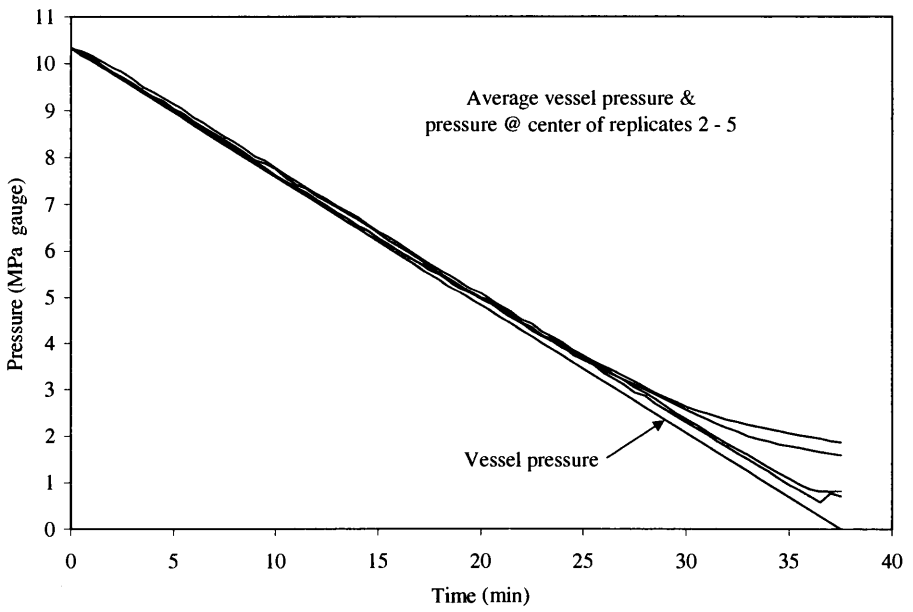


Figure 4.42 Pressure measurements at the center of lodgepole pine heartwood during venting at 276 kPa/min following SC-CO_2 treatment.

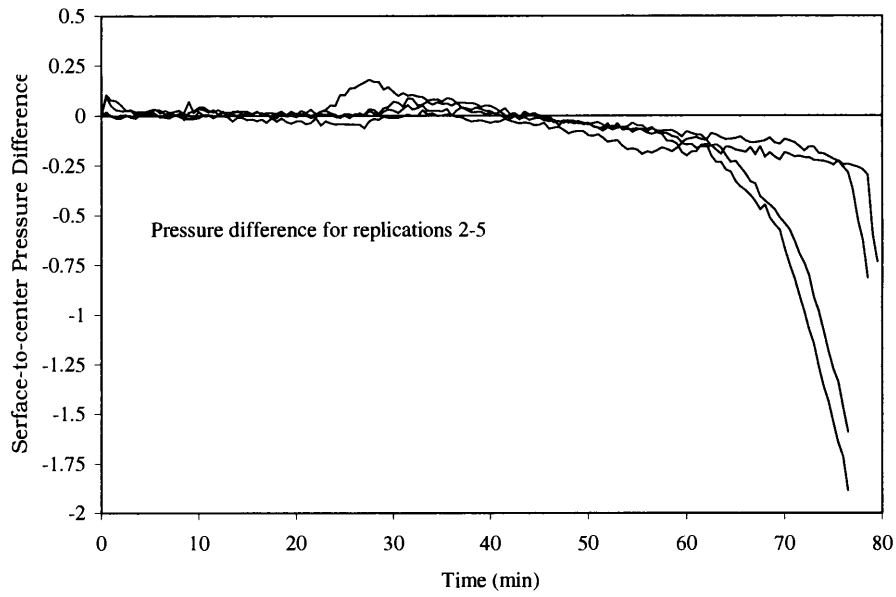


Figure 4.43 Surface-to-center pressure differences in lodgepole pine heartwood samples during SC-CO_2 treatment.

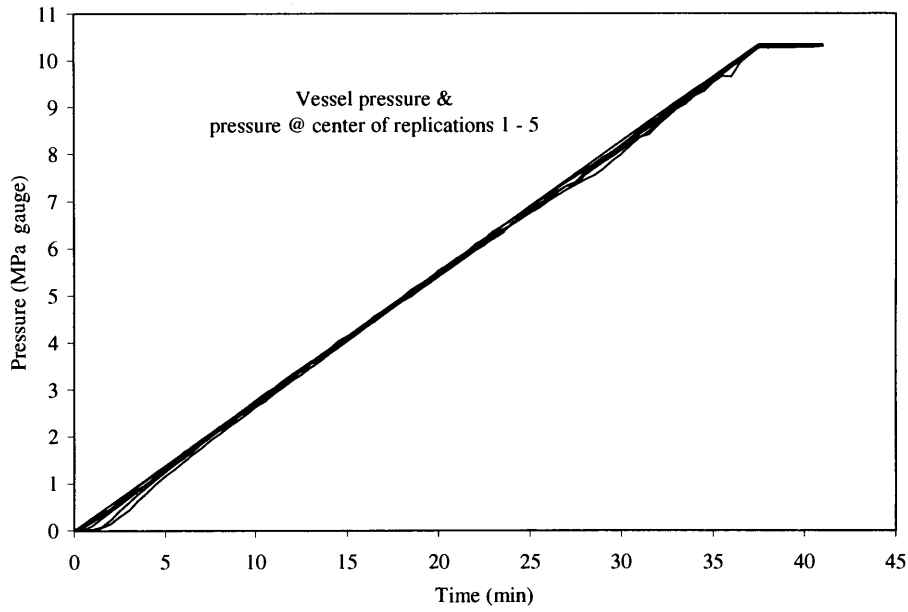


Figure 4.44 Pressure measurements at the center of ponderosa pine heartwood samples during SC-CO_2 pressing at 276 kPa/min.

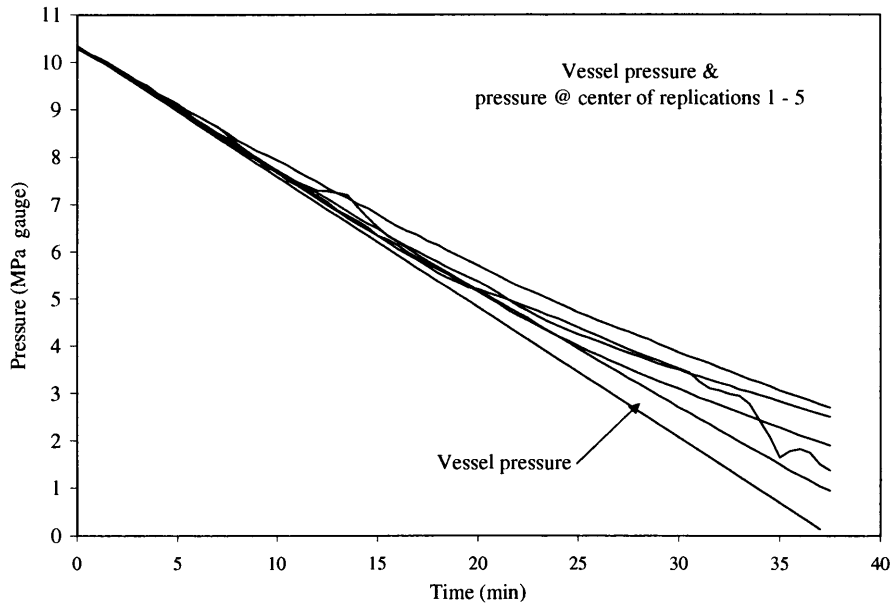


Figure 4.45 Pressure measurements at the center of ponderosa pine heartwood samples during venting at 276 kPa/min following SC-CO_2 treatment.

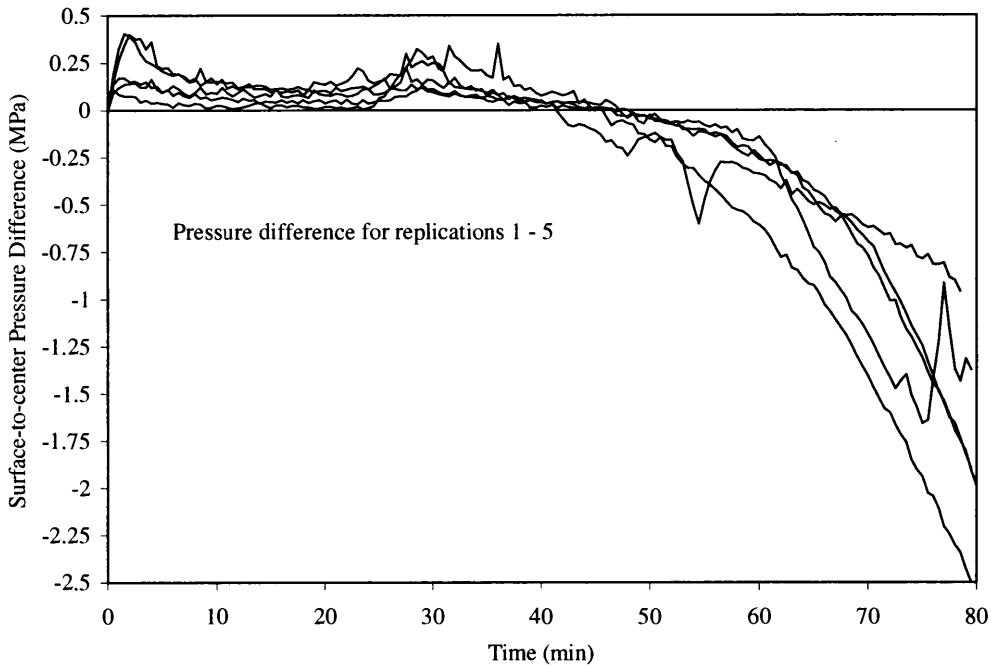


Figure 4.46 Surface-to-center pressure differences in ponderosa pine heartwood samples during SC-CO_2 treatment.

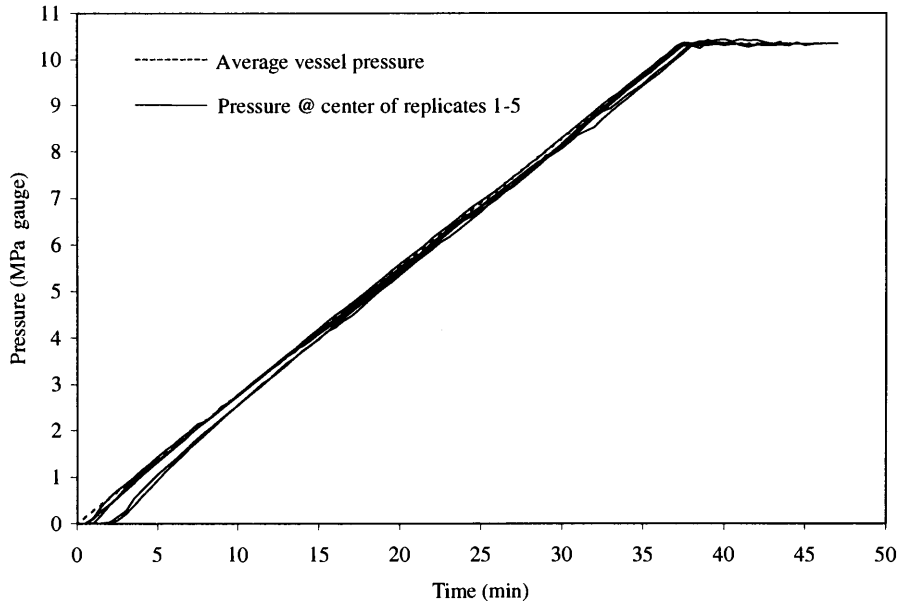


Figure 4.47 Pressure measurements at the center of Douglas-fir heartwood samples during SC-CO_2 pressing at 276 kPa/min.

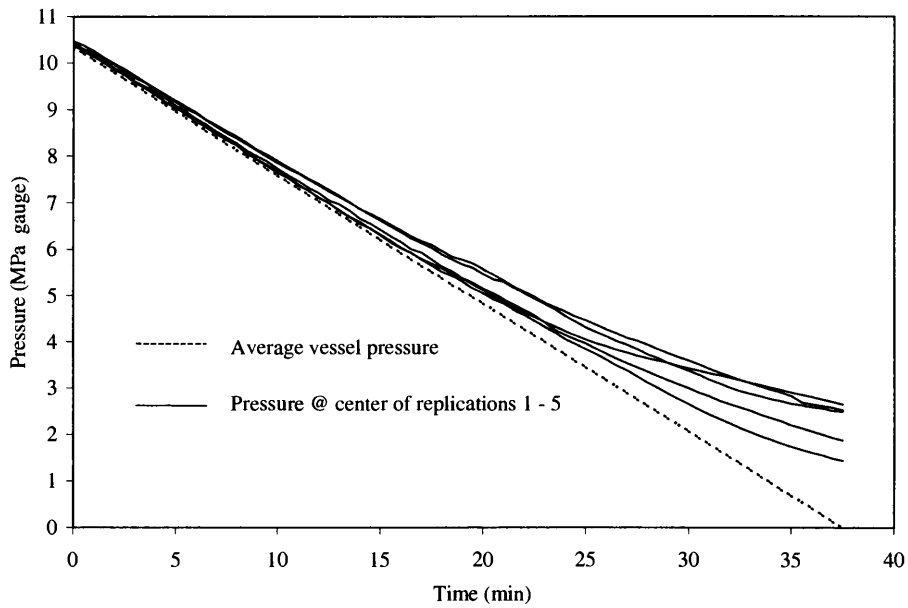


Figure 4.48 Pressure measurements at the center of Douglas-fir heartwood samples during venting at 276 kPa/min following SC-CO_2 treatment.

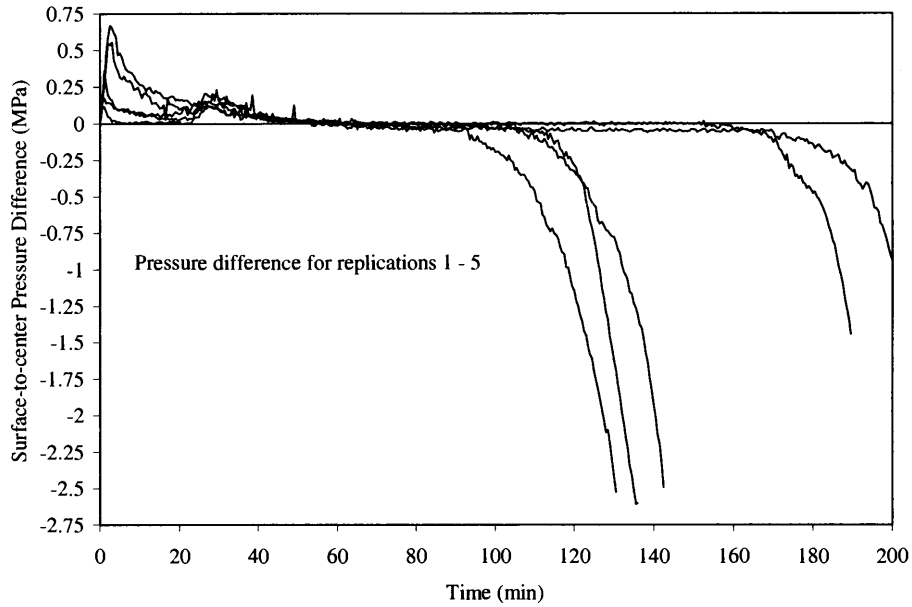


Figure 4.49 Surface-to-center pressure differences in Douglas-fir heartwood samples during SC-CO_2 treatment.

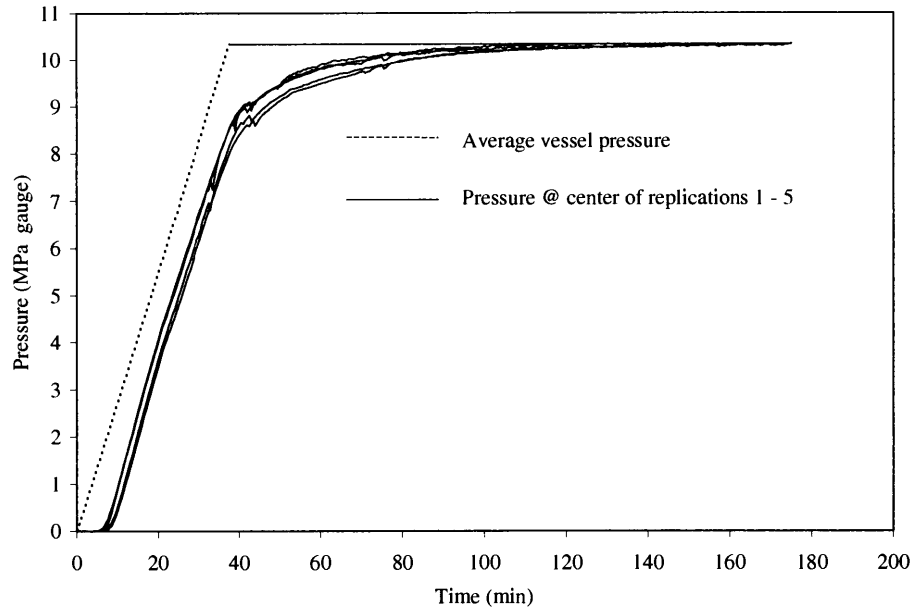


Figure 4.50 Pressure measurements at the center of white fir heartwood samples during SC-CO_2 pressing at 276 kPa/min.

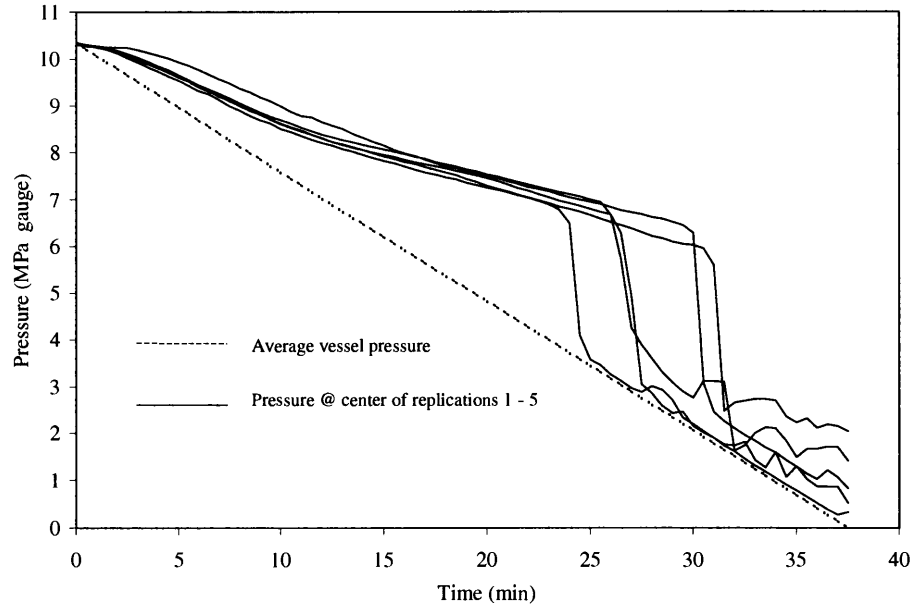


Figure 4.51 Pressure at the center of white fir heartwood samples during venting at 276 kPa/min following SC-CO_2 treatment.

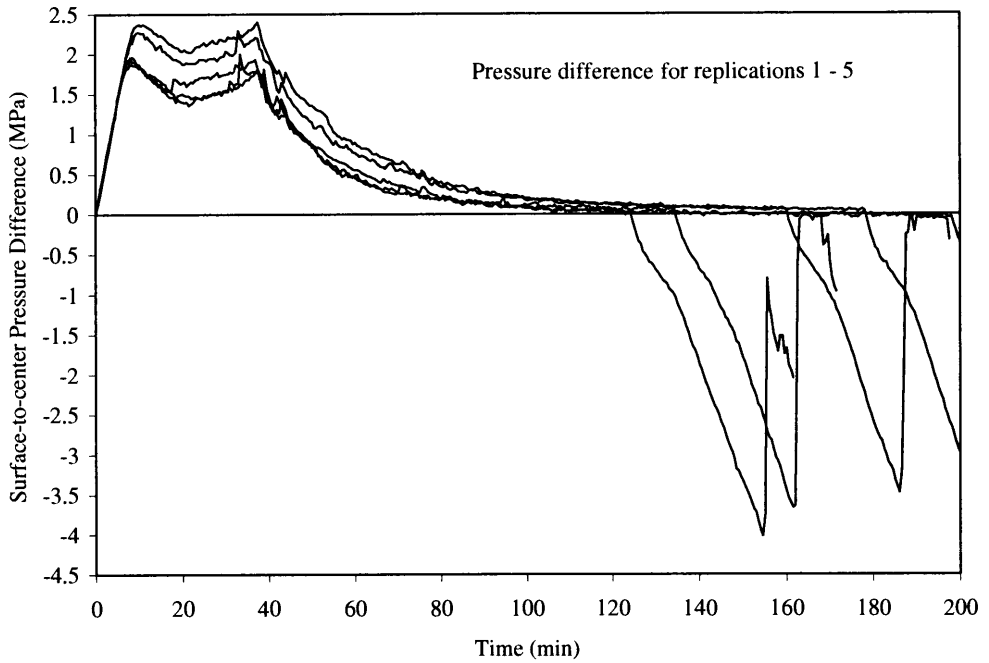


Figure 4.52 Surface-to-center pressure differences in white fir heartwood samples during SC-CO_2 treatment.

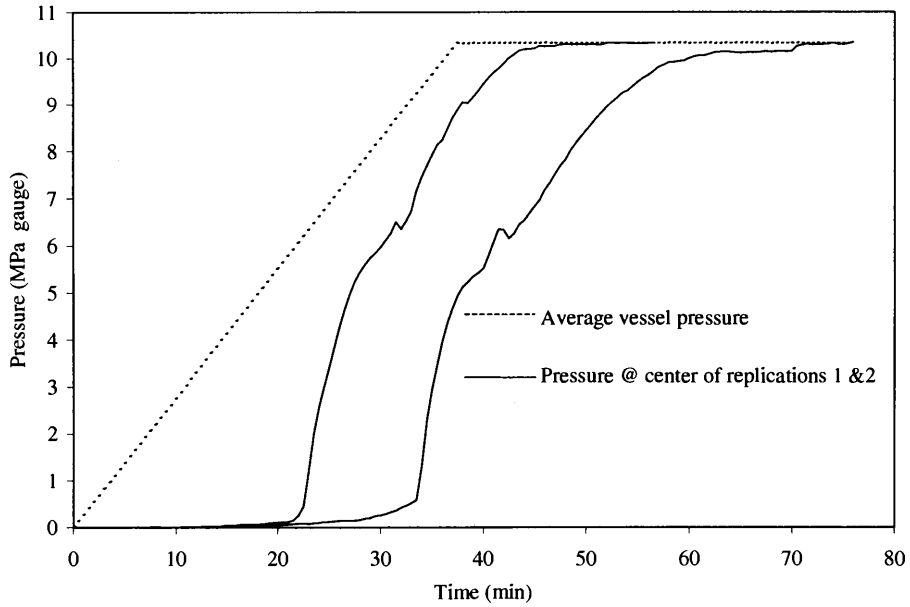


Figure 4.53 Pressure measurements at the center of Pacific silver fir heartwood samples during SC-CO_2 pressing at 276 kPa/min.

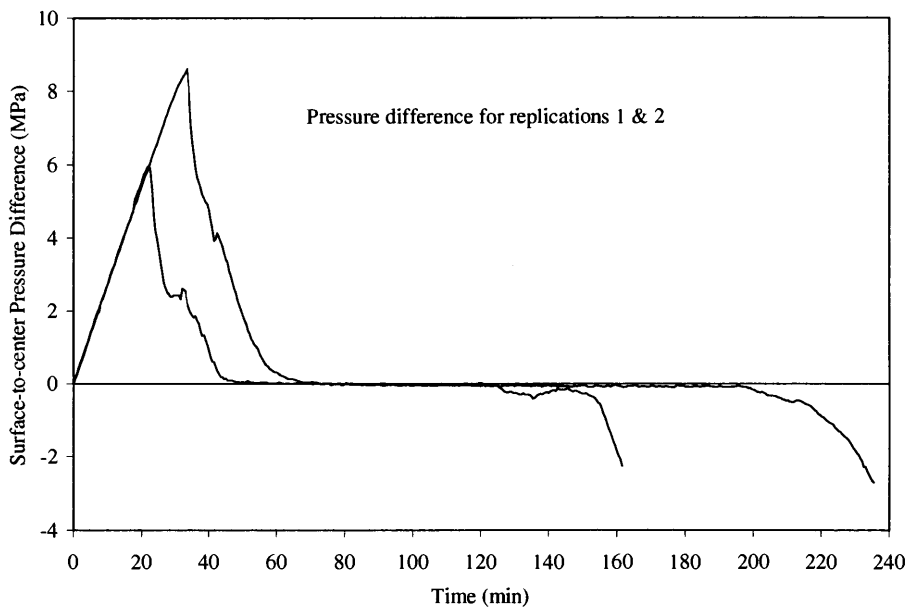


Figure 4.54 Surface-to-center pressure differences in Pacific silver fir heartwood samples during SC-CO_2 treatment.

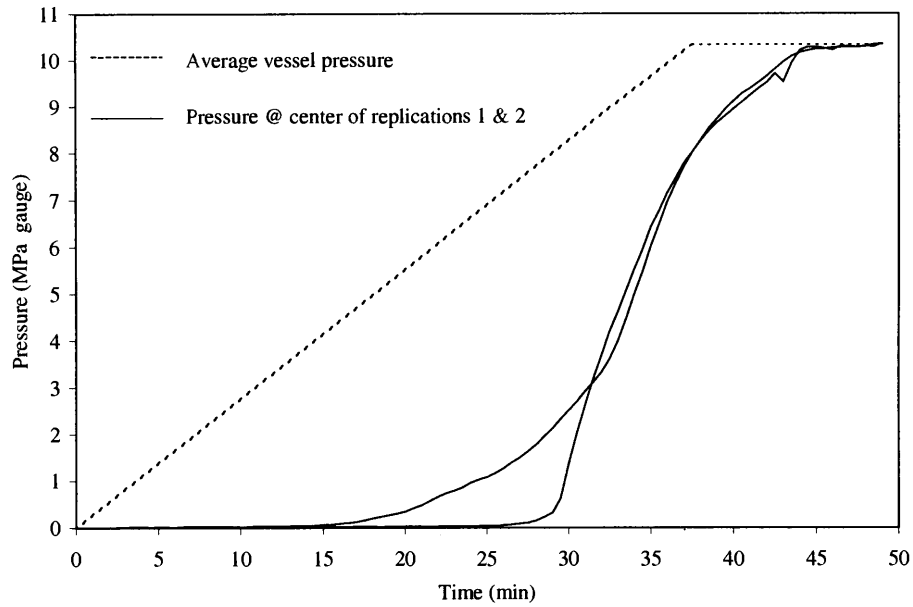


Figure 4.55 Pressure measurements at the center of Engelmann spruce heartwood samples during SC-CO_2 pressing at 276 kPa/min.

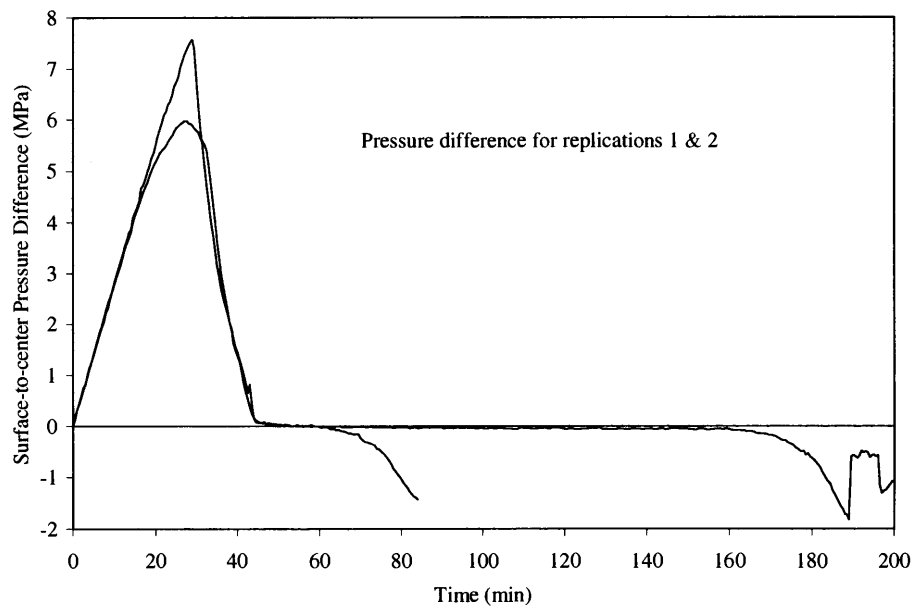


Figure 4.56 Surface-to-center pressure differences in Engelmann spruce heartwood samples during SC-CO_2 treatment.

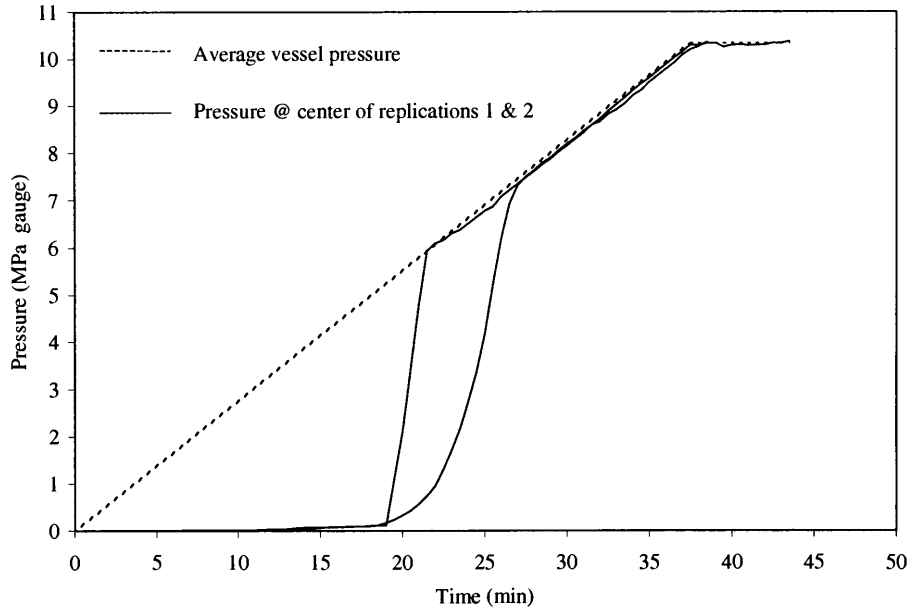


Figure 4.57 Pressure measurements at the center of western redcedar heartwood samples during SC-CO_2 pressing at 276 kPa/min.

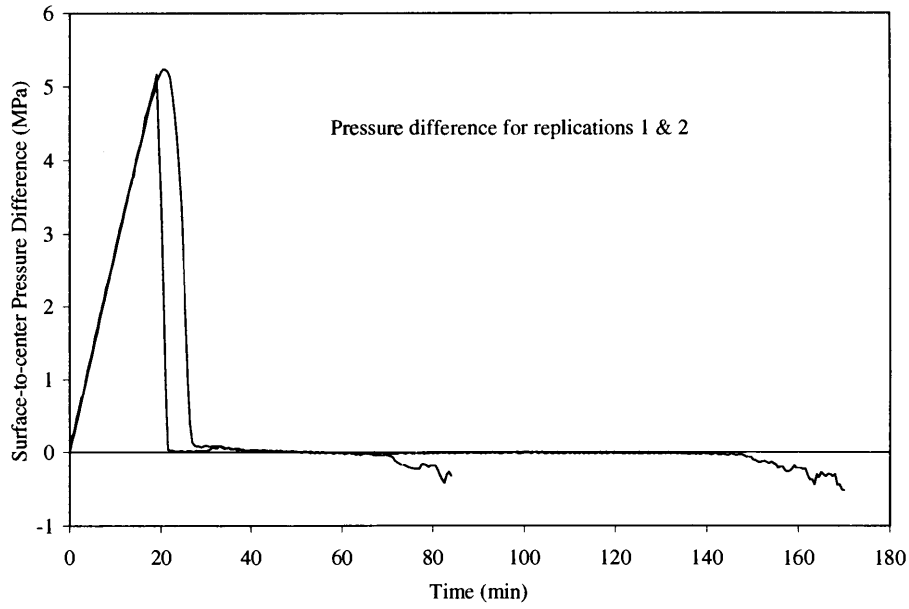


Figure 4.58 Surface-to-center pressure differences in western redcedar heartwood samples during SC-CO_2 treatment.

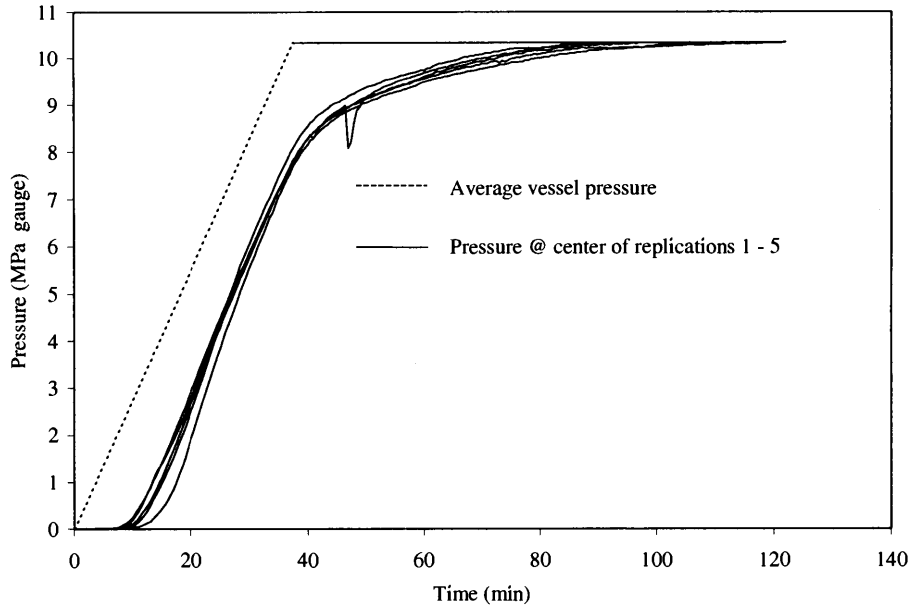


Figure 4.59 Pressure measurements at the center of yellow-poplar heartwood samples during SC-CO_2 pressing at 276 kPa/min.

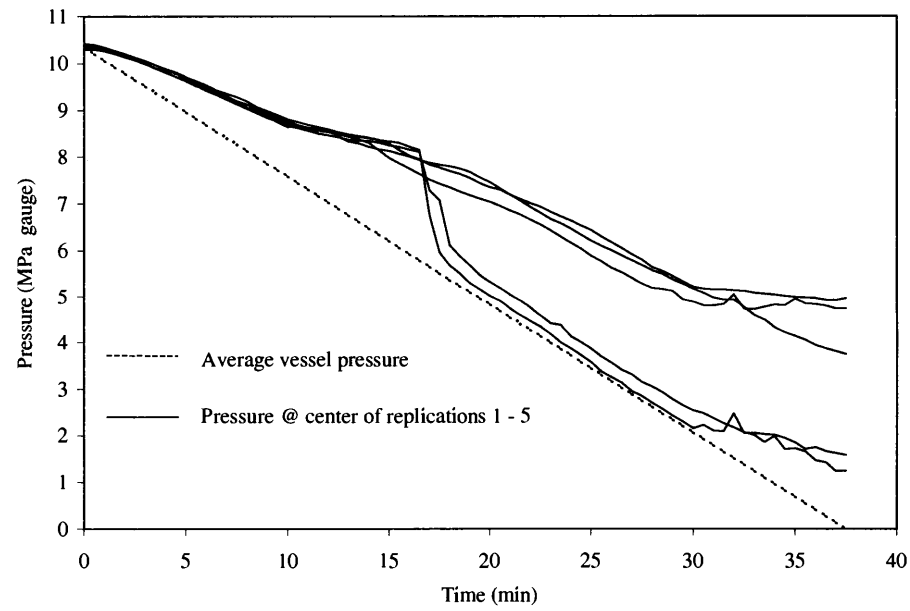


Figure 4.60 Pressure measurements at the center of yellow-poplar heartwood samples during venting at 276 kPa/min following SC-CO_2 treatment.

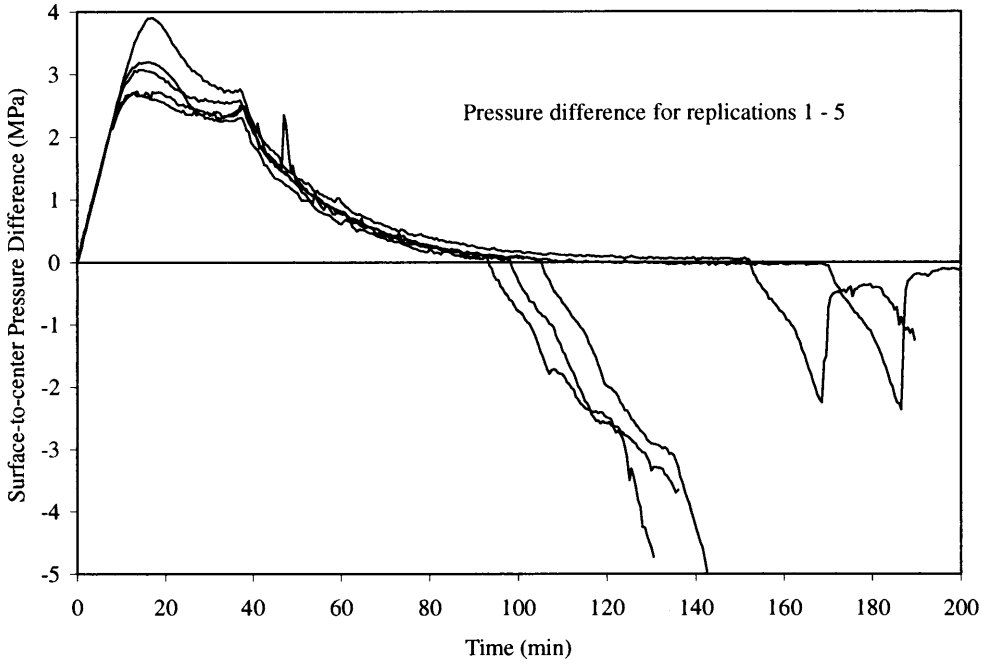


Figure 4.61 Surface-to-center pressure differences in yellow-poplar heartwood samples during SC-CO_2 treatment.

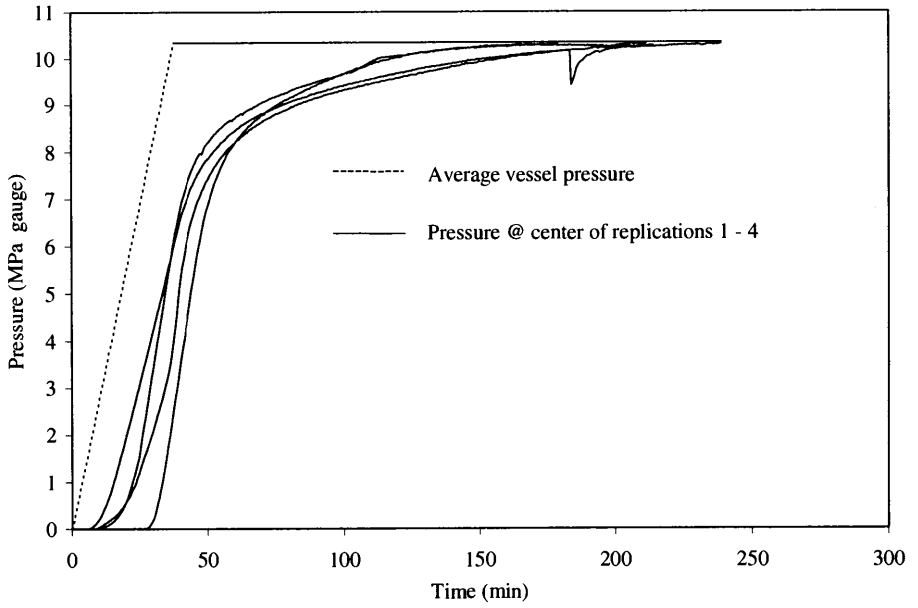


Figure 4.62 Pressure measurements at the center of black gum heartwood samples during SC-CO_2 pressing at 276 kPa/min.

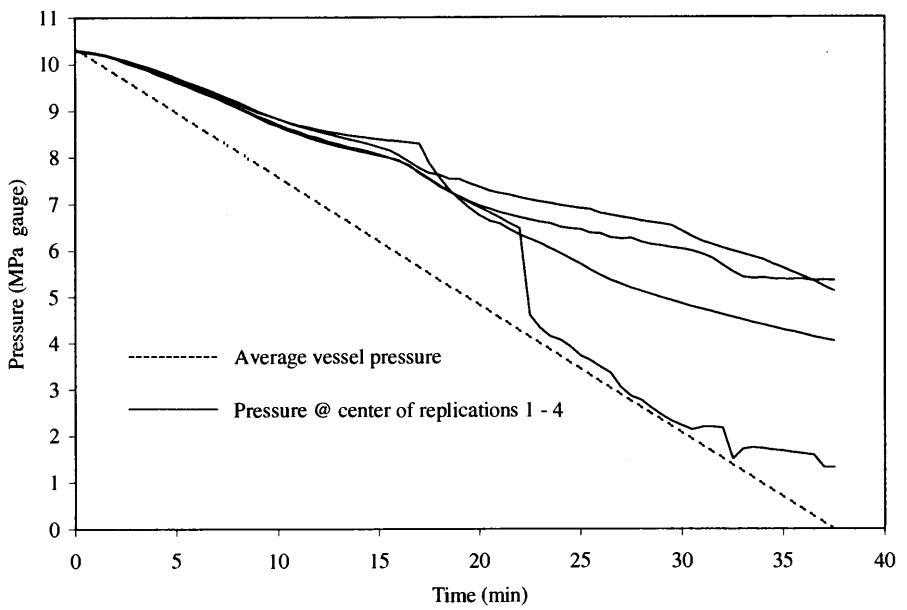


Figure 4.63 Pressure measurements at the center of black gum heartwood during venting at 276 kPa/min following SC-CO_2 treatment.

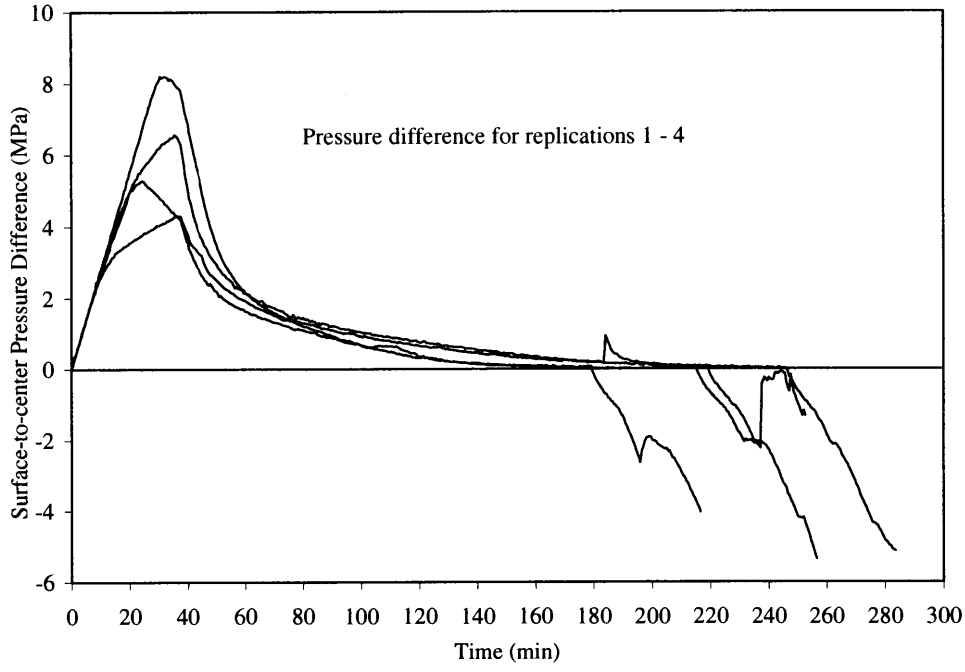


Figure 4.64 Surface-to-center pressure differences in black gum heartwood samples during SC-CO_2 treatment.

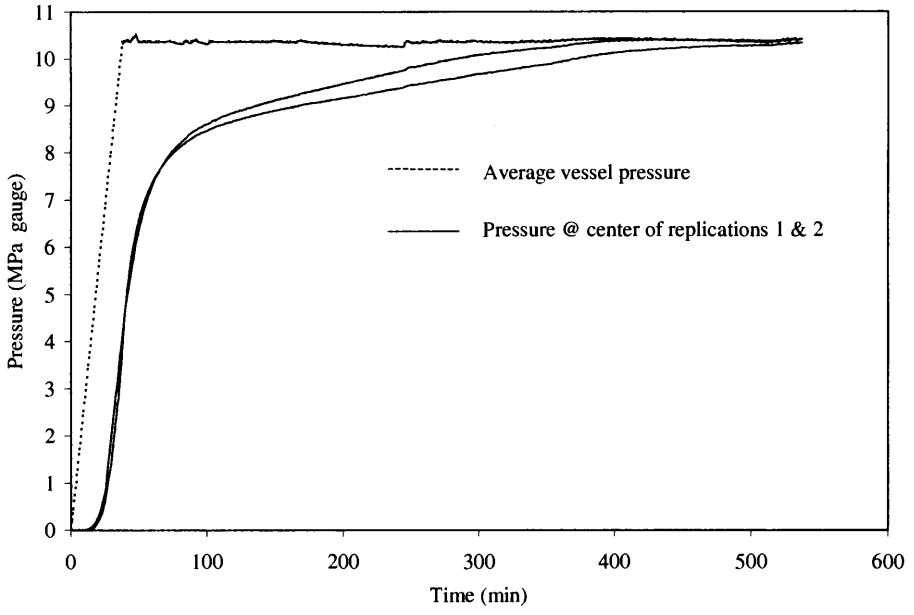


Figure 4.65 Pressure measurements at the center of red oak heartwood samples during SC-CO_2 pressing at 276 kPa/min.

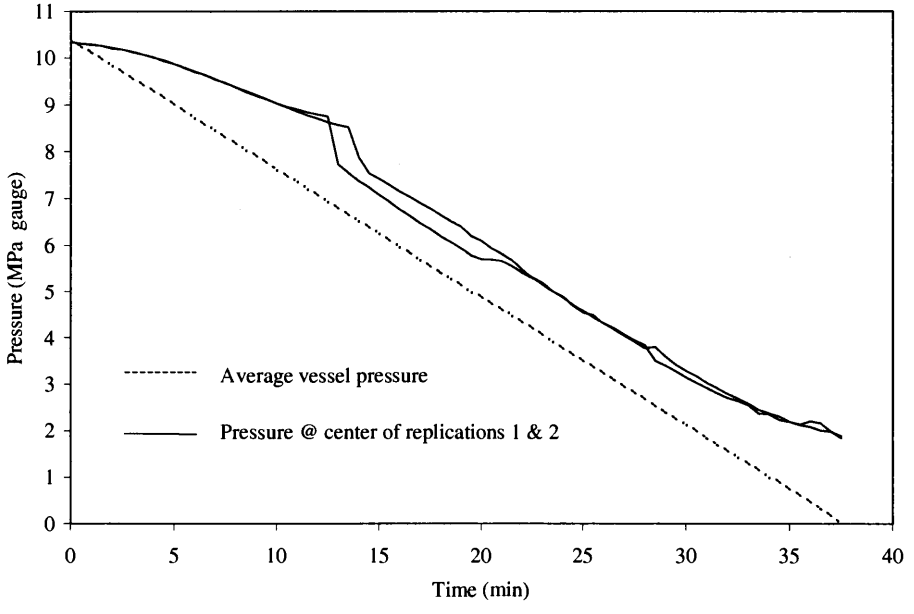


Figure 4.66 Pressure measurements at the center of red oak heartwood samples during venting at 276 kPa/min following SC-CO_2 treatment.

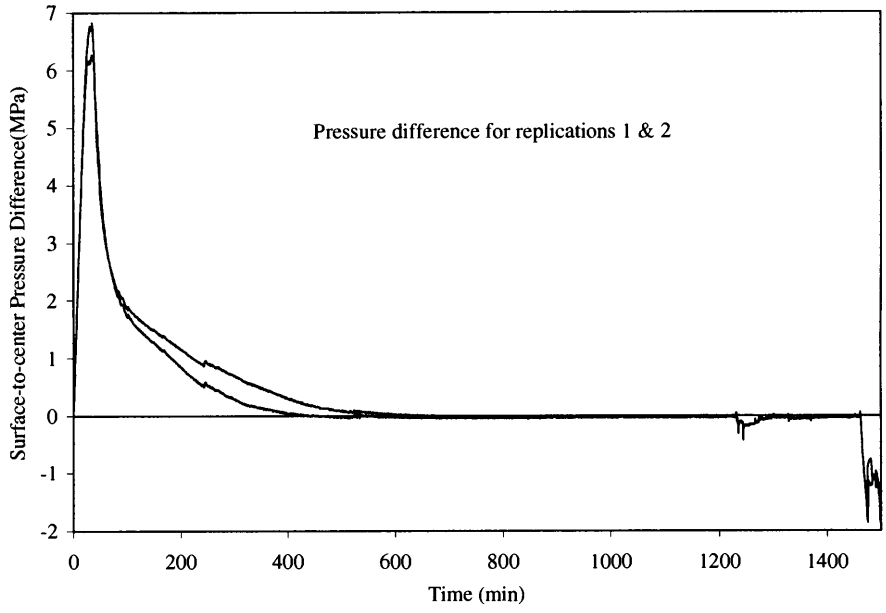


Figure 4.67 Surface-to-center pressure differences in red oak heartwood samples during SC-CO_2 treatment.

Table 4.10 Effect of wood species on time to reach 35 kPa and vessel pressure at sample center, maximum surface-to-center pressure difference, pressure difference after treatment, and wood condition during SC-CO_2 treatment by pressing at 276 kPa/min, holding at 10.3 MPa until pressure equilibrium, then venting at 276 kPa/min.

Species	Time to Reach 35kPa (min)	Time to Equilibrium after Vessel Reached Maximum Pressure (min)	Max. ΔP during Pressing (kPa gauge)	Back-pressure (kPa gauge)	Wood Condition
Sugar pine	0	0	35.0	-1,124	Good
	0	0	48.3	-1,310	Good
	0	0	62.1	-469	Good
	0	1.5	165	-303	Good
Avg. (std.)	0	0.4 (0.6)	77.6 (51.4)	-802 (425)	
Lodgepole p.	0	0	13.8	-731	Good
	0	0	96.5	-1,889	Good
	0	1.5	89.6	-1,593	Good
	0	2.0	179	-814	Good
Avg. (std.)	0	0.9 (0.9)	94.7 (58.5)	-1,257 (649)	
Ponderosa p.	0	4.5 [1]	165	-1,372	Good
	1.0	3.5 [1]	400	-958	Good
	0.5	8.5	228	-2448	Good
	1.0	5.5 [1]	408	-2,703	Good
	0.5	1.5	138	-1,896	Good
Avg. (std.)	0.6 (0.4)	4.7 (2.3)	268 (115)	-1,875 (649)	
Douglas-fir	0.5	8.5	117	-2,599	Good
	0.5	2.5	172	-1,441	Good
	2.0	3.0	669	-2,523	Good
	2.0	6.0	558	-2,496	Good
	1.0	9.5	359	-1,875	Good
Avg. (std.)	1.2 (0.7)	5.9 (2.8)	375 (214)	-2,187 (454)	

Table 4.10 (Continued)

Species	Time to Reach 35kPa (min)	Time to Equilibrium after Vessel Reached Maximum Pressure (min)	Max. ΔP during Pressing (kPa gauge)	Back-pressure (kPa gauge)	Wood Condition
White fir	6.0	80.0	1,868	-2,048 [3]	Collapsed
	6.5	85.0	1,958	-524 [3]	Good
	7.0	123	2,296	-324 [3]	Good
	6.5	96.5	1,965	-972 [3]	Good
	7.5	136	2,372	-1,407 [3]	Good
Avg. (std.)	6.7 (0.5)	104 (21.7)	2,089 (204)		
Pacific silver fir	15.0	— [2]	5,971	— [2]	Collapsed
	17.5	— [2]	8,522	— [2]	Collapsed
Avg. (std.)	16.3 (1.3)		7,247 (1276)		
Engelmann spruce	20.5	— [2]	7,577	— [2]	Collapsed
	11.0	— [2]	5,978	— [2]	Collapsed
Avg. (std.)	15.8 (4.8)		6,778 (800)		
Western redcedar	12.0	— [2]	5,171	— [2]	Collapsed
	13.5	— [2]	5,240	— [2]	Collapsed
Avg. (std.)	12.8 (0.8)		5,206 (34.5)		

Table 4.10 (Continued)

Species	Time to Reach 35kPa (min)	Time to Equilibrium after Vessel Reached Maximum Pressure (min)	Max. ΔP during Pressing (kPa gauge)	Back-pressure (kPa gauge)	Wood Condition
Black gum	28.0	174 [1]	8,198	-1,317 [3]	Collapsed
	7.5	209 [1]	4,309	-5,130	Collapsed
	10.0	182 [1]	6,564	-5,357	Collapsed
	11.5	142 [1]	5,281	-4,033	Collapsed
Avg. (std.)	14.3 (8.1)	177 (23.9)	6,088 (1457)	-4,840 (573)	
Yellow-poplar	7.5	59.0	2,730	-3,654	Good
	10.0	84.5	3,909	-1,255 [3]	Good
	9.5	55.5	3,199	-4,730	Good
	8.0	54.5	2,730	-4,971	Good
	9.0	70.5	3,082	-1,586	Good
Avg. (std.)	8.8 (0.9)	64.8 (11.4)	3,130 (432)	-4,452 (573)	
Red oak	12.5	341	6,833	-1,834 [3]	Good
	15.5	500	6,240	-1,875 [3]	Good
Avg. (std.)	14 (1.5)	421 (79.5)	6,537 (297)		

1 Samples were close to but not fully equilibrated.
2 Data not applicable due to sample failure.
3 Samples had pressure probe sealant failure during venting and were not included in the average.

Grain Orientation (Permeability): The direction of treatment media flow relative to wood grain orientation had a noticeable influence on internal pressure response during SC-CO_2 treatments. Pressure measurements with media flow restricted to the longitudinal direction were not obtainable due to the high permeability of the yellow-poplar samples. The hydraulic medium drained out of the pressure probes and could be seen on the samples' two non-coated longitudinal surfaces. Therefore, these samples did not receive SC-CO_2 treatments.

Internal pressure measurements made on yellow-poplar samples treated such that SC-CO_2 flow was restricted to ether the radial or tangential direction are shown in Figures 4.68 through 4.70 and summarized in Table 4.11. Pressure responses were more rapid in samples which had flow restricted to the tangential direction. Average time for an initial pressure response, time to pressure equalization, maximum surface-to-center pressure difference during pressing, and back-pressure for the samples having tangential were all approximately one-half the respective values for the samples with radial SC-CO_2 flow. These findings support those made in preliminary work (see Section 2.5.2), but are the opposite of expected since yellow poplar has a relatively large ray volume, and most inter-vessel pitting is in the radial direction (Panshin and de Zeeuw, 1980).

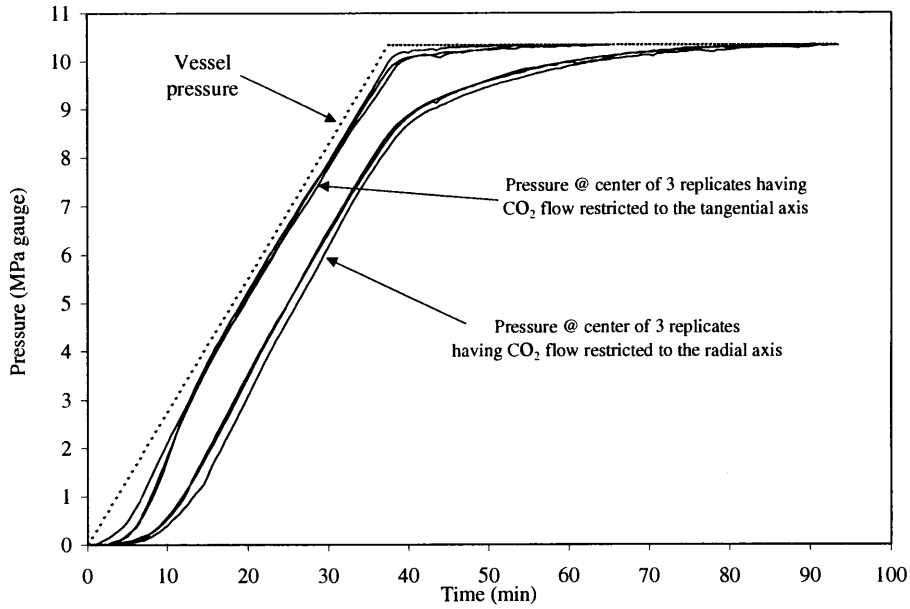


Figure 4.68 Pressure measurements at the center of yellow-poplar heartwood samples sealed to restrict flow to the radial or tangential directions during SC-CO_2 pressing at 276 kPa/min.

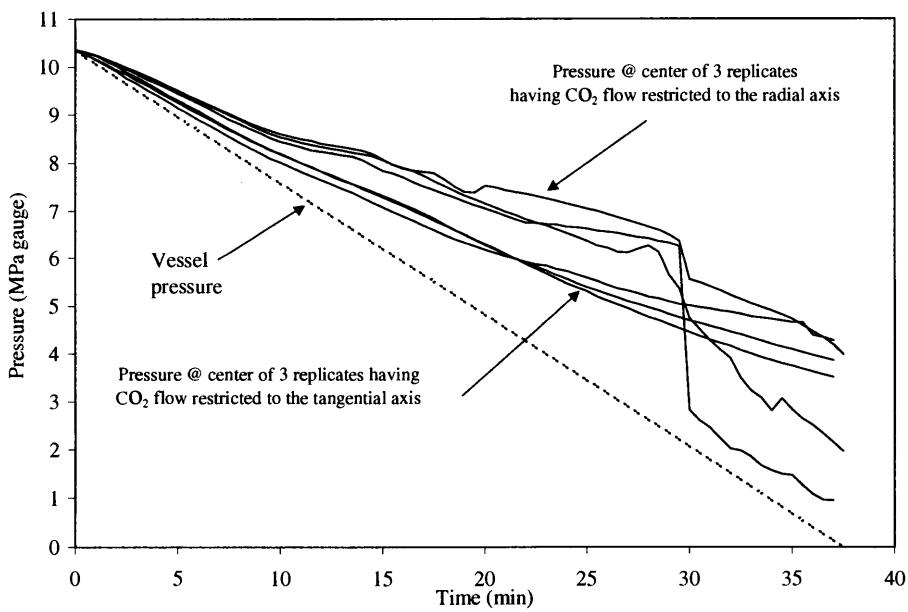


Figure 4.69 Pressure measurements at the center of yellow-poplar heartwood samples sealed to restrict flow to radial or tangential directions during venting at 276 kPa/min following SC-CO_2 treatment.

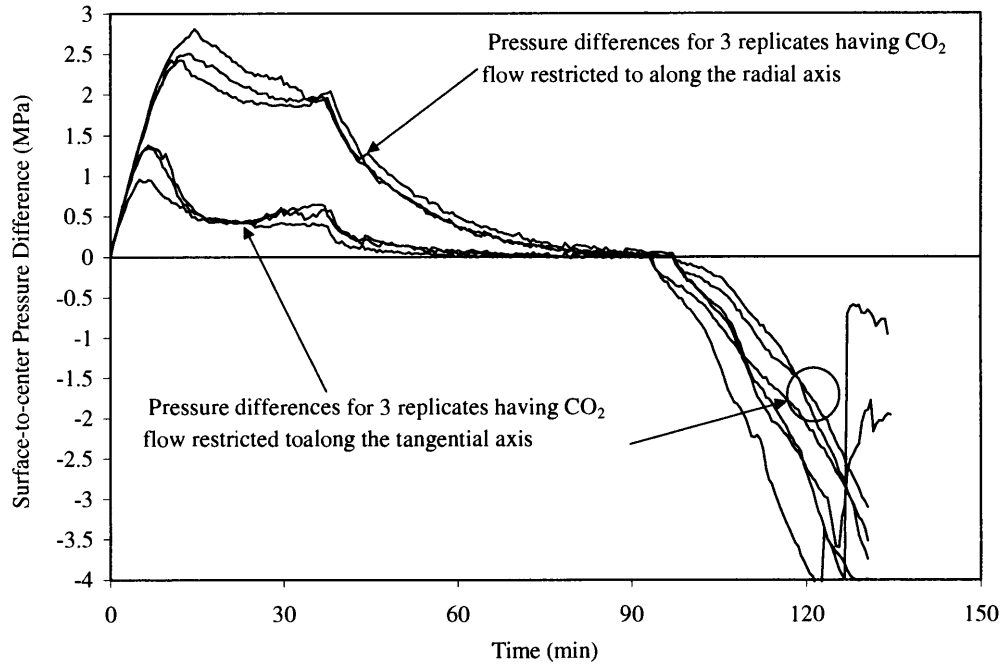


Figure 4.70 Surface-to-center pressure differences in yellow-poplar heartwood samples sealed to restrict flow to the radial or tangential directions during SC-CO_2 treatment.

Table 4.11 Effect of flow direction on time to reach 35 kPa at sample center, maximum surface-to-center pressure difference, pressure difference after treatment, and wood condition of yellow-poplar samples during SC-CO_2 treatment by pressing at 276 kPa/min, holding at 10.3 MPa until pressure equilibrium, then venting at 276 kPa/min.

Flow Direction	Time to Reach 35kPa (min)	Time to Equilibrium after Vessel Reached Maximum Pressure (min)	Max. ΔP during Pressing (kPa gauge)	Back-pressure (kPa gauge)	Wood Condition
Radial	5.0	53.0	2,510	-3,992	Good
	4.0	50.0	2,420	-806 [1]	Good
	5.0	56.5	2,806	-1,965 [1]	Good
Avg. (std.)	4.7 (0.5)	53.2 (2.7)	2,579 (165)	-2,254 (1317)	
Tangential	3.0	27.5	1,379	-3,523	Good
	1.5	18.5	951	-3,461	Good
	3.0	28.0	1,351	-3,434	Good
Avg. (std.)	2.5 (0.7)	24.5 (4.6)	1,227 (195)	-3,473 (37.3)	

[1] Samples had pressure probe sealant failure during venting and were not included in the average.

4.5 Summary

4.5.1 Pressure Measurement Techniques

Techniques for measuring pressure in wood during SC-CO_2 treatments included pressure-probe sample holders and tubing epoxied directly into a sample. The latter method proved to be the easiest and most effective during SC-CO_2 treatments.

Two coats of Gluvit epoxy provided an excellent seal for samples treated in SC-CO_2. This epoxy was inexpensive, easy to use, and cured relatively quickly. Although it softened with time, Gluvit epoxy is not likely to fail as long as treatment times are kept to less than three hours. For longer treatments, Scotch-Weld epoxy seemed to be more effective, but it too softened as seen in the 9 hr treatments of red oak sample.

Air, silicone grease, and silicone oil were investigated as pressure transfer media. Air was a poor transfer medium because of the time lag introduced as the air was compressed in the hydraulic tubing. This lag increased as wood permeability decreased and was particularly noticeable near the critical pressure. Grease was too tacky and the friction between it and the hydraulic line walls created a considerable time lag between pressure change and transducer response. Oil appeared to be the best alternative; although, differences between air and oil media decreased as sample permeability increased.

Internal pressure verification measurements using a pressure bomb showed that leaving the hydraulic lines (to the samples) empty resulted in lower than expected pressure measurements at the end of the venting phase of a treatment. The pressure bomb also showed that using oil in these lines resulted in artificially high pressure probe measurements during the same period. The results indicate that pressure measurement data during venting must be interpreted carefully.

4.5.2 Process and Wood Affects on Internal Pressure Response

Pressure changes in wood during SC-CO_2 treatment followed a typical pattern. This pattern was influenced by process and wood variables. There was an initial delay of internal pressure response at the beginning of the pressurization phase of treatments. This delay caused a pressure difference to develop between the surface and interior of the wood. This pressure difference must be controlled to avoid damaging the wood. A second delay in pressure response occurred when pressure approached the critical point and may be attributed to the densification of CO_2. After this densification, internal pressure continued to rise at a rate similar to that of the vessel. When vessel pressure was held constant, internal pressure increases slowed but eventually reached equilibrium when vessel pressure. Upon venting, internal pressure decreased at a similar rate to the vessel. Near the critical pressure, however, internal pressure decreased more slowly than vessel pressure. There was considerable residual or back-pressure in the wood at the conclusion of SC-CO_2 treatments.

Pressing and venting rates will influence the time response of internal pressure change and thus pressure differences throughout the cross section of a piece of wood. Although pressure differences resulting from the pressurization rates in this investigation were less than expected, wood having lower permeability should respond more dramatically to the applied rates of pressure change.

Internal pressure response was dependent on the rate of vessel pressure change, the distance through which CO_2 had to flow, and the permeability of the wood. Faster rates of pressure change reduced treatment times but increased surface-to-center pressure differences. Pressure responses were directly related to the length of treatment media flow. Doubling flow length resulted in a 2 to 4 fold increase in response time or surface-to-center pressure differences. Pressure response seemed to be directly correlated with wood permeability, but

conclusive data was not provided in this investigation. This relationship will be further investigated in Chapter 5. More permeable pine heartwood samples responded almost instantaneously to pressure change; while, less permeable spruce and true fir heartwood samples responded very slowly to pressure changes. Resistance to CO_2 flow in less permeable woods caused large surface-to-center pressure differences that exceeded the perpendicular crushing strength of Pacific silver fir, western redcedar, Engelmann spruce, and black gum leading to severe deformation. The influence of permeability on pressure changes was also shown when CO_2 flow was restricted to a single transverse direction. Sugar pine and Douglas-fir responded to pressure changes more quickly when flow was restricted to the radial direction; while, black gum and yellow-poplar responded more rapidly to flow in the tangential direction.

4.6 Implications

Results from the investigations presented in this chapter suggest the following:

1. The internal pressure measurement method developed in this study could be used in the development of SCF processes to impregnate wood. Specifically, by monitoring pressure in wood, treatment schedules may be developed to reduce or eliminate the collapse and fracture of wood. Knowledge of the pressure in wood can be used to determine phase and chemical composition of the treating medium. Finally, refinement of the techniques developed herein could be used to develop pressure profiles in wood during treatment. These profiles, in turn, may help explain surface-to-center retention gradients inherent to all impregnation studies thus far.

2. Wood permeability appears to be directly related to internal pressure response during SC-CO_2 treatments. Knowledge of the gas or liquid permeability of wood should therefore be useful for predicting pressure response during SCF processes.

5 CORRELATION OF INTERNAL PRESSURE RESPONSES IN WOOD DURING SUPERCRITICAL CARBON DIOXIDE TREATMENTS TO WOOD PERMEABILITY AND ANATOMICAL CHARACTERISTICS

5.1 Introduction:

Because internal pressure measurements are somewhat difficult and time consuming, it would be convenient to find more easily measured wood characteristics that, in turn, could be used to predict internal pressure response. Previous investigators have used gas permeability and various anatomical measurements in attempts to predict wood treatability with liquid media. Since the transport of these media is directly related to pressure differences in the wood, it may be possible to use these measurements to predict internal pressure response during impregnation processes.

Permeability measurements are used to assess the relative ease with which materials will flow through wood and have been studied as a means to indicate treatability. Although Arganbright and Wilcox (1969) and Venturino and Arganbright (1979) found poor correlations between air permeability and wood treatability, Miller (1961) concluded that longitudinal air permeability could be used to separate easily treated and refractory Douglas-fir. The use of air permeability to separate wood into rough treatability groups was also proposed by Cooper et al. (1974) and Erickson and Estep (1962). Several investigators have established more definitive correlations between permeability and treatability (Erickson and Estep, 1962; Koran, 1964; Siau and Shaw, 1971; Wiedenbeck et al.,1990).

The wood species used in this investigation have extractive contents ranging from 1.4 to 16.1 percent by weight (Isenberg, 1980, 1981). Extractives can prevent air flow through wood by clogging the wood voids, encrusting the pits, or aspirating pit membranes. Removing these materials using solvents such as water, ethanol, or benzene can improve wood permeability to air. Krahmer and Côté (1963) obtained 72 and 191 % increases in

permeability of Douglas-fir and western redcedar samples, respectively using an ethanol/benzene extraction. SCF extraction might be expected to produce similar improvements, although the results are somewhat more varied (Sahle-Demessie et al., 1995).

Understanding flow paths in wood may lead to methods of predicting pressure response. Behr et al. (1969), Stamm (1967), and Wardrop and Davies (1961) have shown liquid treating media inside wood structures and have speculated on flow paths during impregnation (Section 2.4.3). Although these and other investigators attribute pit membrane openings as the controlling factor in fluid flow, it may be that one or more additional anatomical characteristics are also associated with ability of fluids to flow through wood. In addition, pit membrane openings are difficult to measure; therefore, finding relationships between larger structures and the flow of treating media would be beneficial.

Specific gravity and gross anatomical features, such as percent summer wood and number of growth rings per inch, do not appear to influence treatability (Erickson and Estep, 1962 and Miller, 1961). However, wood rays, cellular dimensions, and resin canals play important roles in the transport of materials in living trees and are thought to be responsible for differences in air permeability and liquid treatability of dried wood (Erickson et al., 1937; Flynn, 1995; Krahmer and Côté, 1963; and Sebastian et al., 1965). Rays make up 5 to 12 % of the volume of softwoods and 5 to 32 % of hardwoods (Panshin and de Zeeuw, 1980). In addition, rays are the only radially oriented cells and are, therefore, likely to have an important influence on the flow of material in wood. Because of their relatively large length in comparison to inside diameter, cellular dimensions can play an important role in the flow of materials through wood. The importance of resin canals in the movement of fluids depends on their number, size, and condition. Erikson and Estep (1962) found that faster water flow resulted during longitudinal permeability measurements of Douglas-fir heartwood samples which had more resin canals in this direction. Proctor and Wagg (1947) found that the more

permeable coastal type Douglas-fir had seven times more longitudinal resin canals than did non-permeable Douglas-fir of similar age and growth rate from the Rocky Mountain region. Radial resin canals did not show this variation. Longitudinally oriented resin canals are larger than canals along the radial axis (Panshin and de Zeeuw, 1980). Decreased and sporadic flow through resin canals can be attributed to the presence of tylosoids formed during the transformation of sapwood to heartwood (Erickson and Estep, 1962 and Panshin and de Zeeuw, 1980). The influence of anatomical features on supercritical fluid treatments, however, is largely unknown.

The degree of correlation between air permeability and treatability seems to be dependent on several factors including wood species, measure of treatability, and method of analysis. Softwood permeabilities were found to have better correlations with treatability than hardwood permeabilities (Choong and Fogg, 1972 and Choong et al., 1972). In all cases, there were stronger correlations between air permeability and treatability when preservative retention versus penetration was evaluated. Stronger correlations are also possible by using a log transformation of permeability values; for example, Choong and Fogg (1972) used this procedure to improve the correlation coefficient (r) for the linear regression of air permeability on preservative retention from 0.72 to 0.85.

5.2 Objectives

The objective of this investigation was to identify easily measurable wood characteristics that can be used to explain or predict internal pressure response during pressure treatments. Specifically, the objectives of this study include:

1. To determining the air permeability of non-extracted and SC-CO_2 extracted samples from eleven species treated with SC-CO_2 in Chapter 4.
2. To measure anatomical characteristics of these eleven species.

3. To evaluate the relationships between "explanatory variables", measured in this chapter, and "pressure response quantifiers", measured in Chapter 4.

Explanatory variables include longitudinal, tangential, and radial air permeabilities of non-extracted samples; radial permeability of extracted samples; ray area; longitudinal and radial resin canal diameters, frequencies, and areas; and softwood tracheid and hardwood vessel element and fiber dimensions and cross-sectional areas. Pressure response quantifiers include time to 35 kPa, time to equilibrium, and maximum pressure difference during SC-CO_2 treatment.

5.3 Methods

5.3.1 Equipment

Permeability measurements were made using an apparatus consisting of an air pressure regulator, sample chamber, two pressure transducers, and three flow meters (Figure 5.1). Plastic tubing with friction fittings was used to connect components. The sample chamber was tapered inside to fit a No. 8 rubber stopper which held a single wood sample. Pressure was measured up- and down-stream of the sample using OMEGA PX302-200AV pressure transducers with a pressure range of 0 to 1,400 kPa ±3.4 kPa (absolute). The transducers were calibrated with a dead-weight test apparatus. Air flow leaving the sample chamber was measured in one of the three mass flow meters (MKS Instruments; Santa Clara, CA), each with an accuracy of ± 0.8 % of their full scale reading. Flow ranges for the meters were 0 - 100, 0 - 1000, and 0 - 5000 sccm. Toggle-switch valves were used to divert air flow to the appropriate meter. Soap-bubble flow meters (25 and 100 mL) were used to check electronic flow meter accuracy and measure flows that were below 50 sccm. A personal

computer and Strawberry Tree data collection system were used to monitor pressure and flow, which were then logged by hand into a lab notebook.

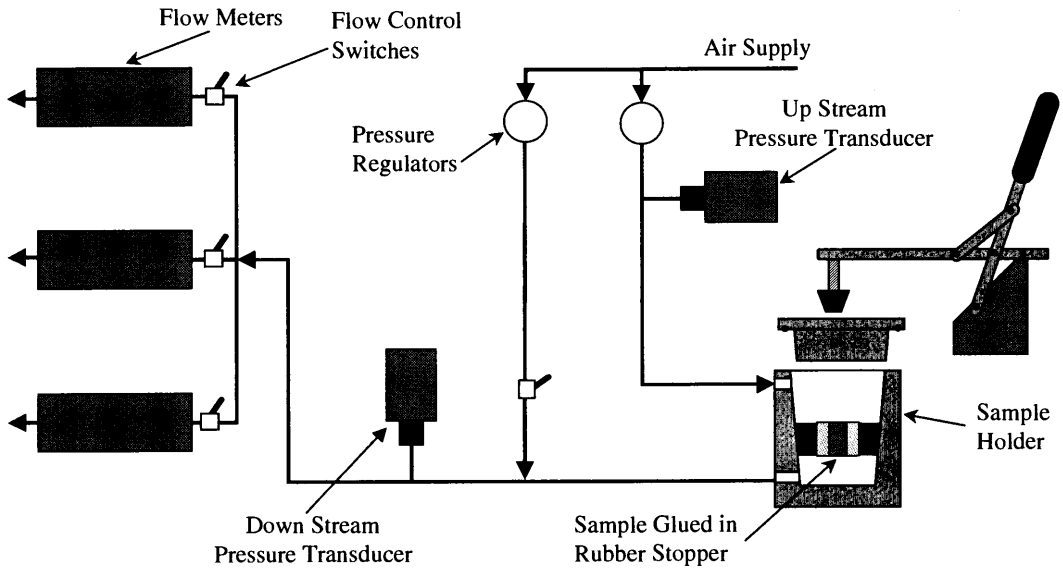


Figure 5.1 Schematic of the equipment used to measure air permeability of 12 mm diameter wood samples.

Anatomical observations were made with a Nikon compound microscope alone or coupled with a Pulnix black and white video camera. National Institute of Health (NIH) imaging software on a personal computer was used with the video camera. The microscope and camera fields were calibrated using a microscope slide scale having 0.01mm divisions.

5.3.2 Air Permeability Measurements

Sample Preparation: Wood samples (12 mm dia. x 10mm long) were cut with a plug cutter from the same kiln-dried lumber that was used in Chapter 4. Heartwood samples included sugar pine, lodgepole pine, ponderosa pine, Douglas-fir, white fir, Pacific silver fir, Engelmann spruce, western redcedar, red oak, black gum, and yellow-poplar (see Table 4.2

for scientific names and properties). 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 supercritical carbon dioxide (SC-CO_2) extraction. Three sample replicates were cut for each permeability determination, giving a total of 138 samples.

The SC-CO_2 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 a SCF treating vessel, described in Chapter 4, by pressing with CO_2 at a rate of 280 kPa/min to 10.3 MPa, holding at this pressure for 30 min, and then venting at 280 kPa/min.

Air Permeability Measurements: Air permeability was determined by measuring air flow through and pressure across individual samples at several pressures then calculating superficial gas permeability for these pressure levels. Samples were individually glued with hot-melt adhesive (Adhesives Technologies Inc.; Hampton, NH) 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). After 30 s, volumetric flow through the samples and pressures going into and exiting from them were measured. Additional measurements were made using inlet pressures of 70, 140, 210, 280, and 350 kPa. In some cases, such as when determining the longitudinal permeability of more permeable species such as red oak and black gum, inlet pressure was restricted to a range from 15 to 140 kPa.

Superficial gas permeability (k_g) (Darcy) was determined for the samples at each pressure level using the following version of Darcy's law:

$$k_g = \frac{\mu Q L P_2}{A \Delta P \bar{P}} \tag{5.1}$$

where μ is the viscosity of air (cp), **Q** is volumetric flow (cm/s), **L** is sample length (cm), P_2 is pressure after the sample (atm), **A** is the sample cross section area (cm^2), ΔP is the difference in pressure across the sample, and $\bar{P}$ is the average of pressure before and after the sample (atm) (Siau, 1984). Permeability for each sample was plotted against the reciprocal of average pressure, and a regression line was fitted to this 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 the same used by Choong et al. (1974). Finally, the average calculated air permeability of the three samples was used to compare between the different species/grain orientation groups.

5.3.3 Anatomical Measurements

Sample Preparation: Samples were prepared from the same boards used for internal pressure measurements during SC-CO_2 treatments (Section 4.4). Two 12 mm diameter by 20 mm long samples were cut from the heartwood of sugar pine, ponderosa pine, lodgepole pine, Douglas-fir, Engelmann spruce, white fir, Pacific silver fir, western redcedar, yellow-poplar, black gum, and northern red oak. One sample was taken along the longitudinal axis; the other was cut along the radial axis. All samples were exposed to a vacuum of approximately 70 cm of Hg for 30 minutes and then flooded with an ethanol/water solution (50/50 by vol.). The submerged samples were subjected to an additional 24 hr vacuum. During this time most of the ethanol volatilized. The samples were then softened by boiling for 5 hr then transferred to a fresh ethanol/water solution. Prior to sectioning, the samples were trimmed to 1cm x 1cm x

2 cm. Single sections (20-50 μm thick) were cut from each sample with a sliding microtome and mounted in glycerin.

Ray Area Determinations: Ray areas were measured on a single tangential section from each species. Five fields of view were analyzed at 100x (0.80 mm^2) for each species. The area occupied by uniseriate and fusiform rays in softwoods or uniseriate and multiseriate rays in hardwoods in each field was divided by the field area and multiplied by 100 to obtain the percent ray area.

Cellular Dimension Measurements: Radial and tangential dimensions of softwood tracheids and hardwood vessels and fibers were measured in each section. Because of the difficulty in measuring cellular lengths from sectioned samples, literature values were used for the species in this investigation. Tracheid and vessel elements in yellow-poplar and black gum were measured at a magnification of 200x. Red oak earlywood vessels were measured at 40x. Two fields of view were analyzed using a computerized image from a camera mounted on the microscope. For the softwoods, five tracheids from the first earlywood row per field were measured; for the hardwoods, ten vessel elements and ten fibers per field were measured throughout an annual growth ring. All measurements were made on a single longitudinal section.

Resin Canal Measurements: Longitudinal and radial resin canals were measured in sugar pine, ponderosa pine, lodgepole pine, Douglas-fir, and Engelmann spruce. Resin canal diameter (including the epithelial cell lining) and percent section area were determined from a single longitudinal or tangential section. Three to nineteen resin canals were measured (at a magnification of 400x) on each sample, depending on the frequency of resin canals and their condition. Percent section area covered by resin canals was based either on the entire section (approximately 70 mm^2) or on an average resin canal count from five fields of view (16.84 mm^2) per section for the longitudinal or tangential sections, respectively.

5.3.4 Relationships between Wood Properties and Pressure Response Quantifiers

Linear regression analysis was used to compare average values of a single response quantifier to average values of a single explanatory variable. Linear regression was used since polynomial or exponential curve fitting procedures did not improve prediction curves using a computer spreadsheet. In addition, log and inverse transformations of the available data did not improve correlation coefficients during linear regression analysis. Averages for explanatory variables and pressure response quantifiers were first pooled by all species for which an explanatory variable was pertinent and then pooled by wood type (i.e. softwoods or hardwoods). For each analysis, the correlation coefficient (r) and the predicted relationship (either direct or inverse) are provided in summary tables.

It is important to mention limitations of this correlation procedure. Internal pressure response quantifiers came from samples that were epoxied so that the SC-CO_2 treating media could only enter along the radial axes. Once inside samples, however, CO_2 could also flow in the longitudinal and tangential directions. It is unclear how the restricted flow altered the influence of anatomical characteristics. The low number of species groups limits the applicability of regression analysis. This is especially true when grouping data by wood type because only three hardwood species were included in the experimental design. Significance tests for correlation coefficients require at least four sample replications.

5.4 Results and Discussion

5.4.1 Air Permeability Measurements

Non-extracted Samples: Calculated air permeability values for the non-extracted samples are listed in Table 5.1. For comparison, gas permeability values from the literature for similar species are provided in Table 5.2. It is important to consider wood moisture content, type of gas, and average pressure when comparing permeability measurements from different sources. Literature values were not found for sugar pine, and in several cases, radial and tangential permeability values were not available. Permeability measurements on the wood used in this investigation were within the ranges found in previous studies.

Table 5.1 Air permeability of heartwood samples calculated at an average pressure of 125 kPa. The values are an average of three samples per species and orientation.

Species	Permeability (Darcy)		
	Longitudinal	Radial	Tangential
Sugar pine	0.611 (0.072) [1]	0.014 (0.005)	0.008 (0.004)
Ponderosa pine (sapwood)	0.191 (0.044)	0.003 (0.002)	0.001 (0.001)
Ponderosa pine (heart)	0.003 (0.001)	0.001 (0.000)	0.002 (0.002)
Lodgepole pine	0.027 (0.005)	0.005 (0.002)	0.003 (0.002)
Douglas-fir	0.074 (0.015)	0.001 (0.001)	0.004 (0.001)
Engelmann spruce	0.141 (0.022)	0.005 (0.002)	0.023 (0.010)
White fir	0.107 (0.015)	0.003 (0.002)	0.006 (0.002)
Pacific silver fir	0.037 (0.009)	0.030 (0.025)	0.006 (0.003)
Western redcedar	0.079 (0.004)	0.005 (0.003)	0.024 (0.013)
Yellow-poplar	0.339 (0.039)	0.033 (0.006)	0.008 (0.006)
Black gum	2.34 (0.138)	0.018 (0.006)	0.034 (0.010)
Northern red oak	2.75 (0.030)	0.004 (0.005)	0.002 (0.002)

[1] Values in parentheses are one standard deviation.

Table 5.2 Literature values for gas permeability of heartwood samples from species used in Chapter 4. [1]

[1] Blank spaces in the table represent values not found in a literature review.
[2] "n" Represents the number of replicates used to determine average permeability.
[3] Pressure is the average pressure inside wood during permeability measurements.
[4] Sources of information include:

1. Choong et al., 1974.
2. Choong and Fogg, 1972.
3. Choong et al., 1972.
4. Siau and Shaw, 1971.
5. Milota, 1999.
6. Wiedenbeck et al., 1990.
7. Skaar, 1959.
8. Arganbright and Wilcox, 1969.
9. Markstrom and Hann, 1972.
10. Krahmer and Côté, 1963.

Table 5.2

Species	Permeability (Darcy)						Conditions			Source [4]
	Longitudinal		Radial		Tangential		MC (%)	Medium	Average Pressure (kPa) (absolute) [3]	
	Average	n [2]	Average	n [2]	Average	n [2]				
Sugar pine										
Ponderosa pine	0.112	6	0.021	4			18	N_2	222	3
Lodgepole pine	0.014	465					13	Air	35	6
	0.038	80					0	N_2		9
Douglas-fir	0.025	4	0.015	4	0.002	4	18	N_2	222	3
	0.0041	15			0.0001	15	0	Air	172	5
	0.022	80					0	N_2		9
	0.0801	4					13	Air		10
Engelmann spruce	0.033	80					0	N_2		9
	1.430	30					9	Air	76	4
White fir	0.100	4	0.003	6	0.003	6	18	N_2	222	3
	0.387	18					12	Air	101	7
			0.0010	96	0.0007	96	0	N_2	172	8
Pacific silver fir	2.806	30					9	Air	76	4
Western redcedar	0.069	2	0.009	4	0.001	4	18	N_2	222	3
	0.035	4					13	Air		10
Yellow-poplar	1.430	35	0.0208	48	0.0083	38	20	N_2	121	1
	0.426	39	0.010	40	0.006	33	18	N_2	222	2
Black gum	7.504	17	0.0008	22	0.0005	24	20	N_2	121	1
Northern red oak	41.411	34	0.0218	44	0.0113	32	20	N_2	121	1
	5.027	36	0.0031	31	0.0019	35	20	N_2	121	1
	0.507	2	0.022	2	0.009	2	18	N_2	222	3

Air permeability differences were found both within and between species in this investigation. For a given species, the most noticeable difference was between longitudinal and either radial or tangential directions, with the exception of ponderosa pine heartwood which resulted in similar measurements for all orientations. Differences between radial and tangential permeabilities were substantial for each species, but there was little difference between radial and tangential permeabilities when averaged over all samples of all species. Longitudinal permeability differed markedly between species, up to three orders of magnitude, but radial and tangential permeability differences were less substantial, differing by a maximum of 25 times. Based on internal pressure measurements in Chapter 4, it was thought that softwoods would have greater radial versus tangential permeabilities and hardwoods would have greater tangential versus radial permeabilities. However, no consistent differences were evident between radial and tangential permeabilities when data was pooled by wood type (i.e. softwoods and hardwoods).

Permeability measurements had relatively large variations between replications. The permeability of wood can differ substantially within a tree and between trees of the same species (Panshin and de Zeeuw, 1980). Erikson and Estep (1962) and Miller (1961) have shown that Douglas-fir from the Rocky Mountain region (including eastern Oregon) has a lower permeability than wood from the western portions of Oregon and Washington. This regional difference may be attributed to different botanical varieties of this species. Wiedenbeck et al. (1990) sampled two botanical varieties of lodgepole pine (*Pinus contorta* var. latifolia and var. murrayana) and found that there was a statistical difference between the air permeabilities of these two varieties. However, she showed that for a given variety permeability did not differ between samples taken throughout its geographical range.

SC-CO_2 Extracted Samples: Calculated air permeability values for the SC-CO_2 extracted samples are listed in Table 5.3. SC-CO_2 extraction produced varying effects on air

permeability. The most striking improvement in air permeability was obtained with ponderosa pine sapwood, which produced a 10 fold increase in permeability between non-extracted and extracted samples. Only five of the eleven species experienced permeability increases. The experimental methods used may account for these mixed results. Permeability measurements were made on two separate sets of samples cut from the same boards. Effects of SC-CO_2 on permeability may have been more evident if permeability was determined before and after extraction of the same samples. However, Sahle-Demessie et al. noted similar variations and suggested that extractives may have been redistributed within the permeability samples. Resin was seen on the surface of the lodgepole pine samples after the SC-CO_2 extraction. More consistent effects may have resulted if improved extraction procedures were followed. There appeared to be no correlation between permeability and extractive content among the species.

Table 5.3 Air permeability of SC-CO_2 extracted heartwood samples calculated at an average pressure of 125 kPa. Values are an average of three samples per species.

Species	Radial Permeability (Darcy)		
	Non-extracted	Extracted	Difference (%) [1]
Ponderosa pine (sapwood)	0.003 (0.001) [2]	0.031 (0.003)	907
Ponderosa pine (heart)	0.001 (0.000)	0.007 (0.003)	458
Douglas-fir	0.001 (0.001)	0.003 (0.004)	136
Yellow-poplar	0.033 (0.006)	0.071 (0.062)	113
Engelmann spruce	0.005 (0.002)	0.007 (0.007)	60.9
Western redcedar	0.005 (0.003)	0.008 (0.001)	41.5
Sugar pine	0.014 (0.005)	0.009 (0.003)	-37.4
Lodgepole pine	0.005 (0.002)	0.003 (0.001)	-37.5
Black gum	0.018 (0.006)	0.006 (0.005)	-64.6
White fir	0.003 (0.002)	0.001 (0.000)	-71.0
Northern red oak	0.004 (0.005)	0.001 (0.001)	-93.0
Pacific silver fir	0.030 (0.025)	0.001 (0.001)	-96.7

1 Negative differences indicate extracted samples had lower permeabilities.
2 Values in parentheses are one standard deviation.

5.4.2 Anatomical Measurements

Ray Area Determinations: Average ray area measurements from a single tangential section of eight softwoods and three hardwoods are shown in Table 5.4. The softwood values were slightly greater than reported ray volumes for a given species, but the range of ray areas (5.9 to 11.3 %) was similar to the range in ray volumes for these species (Isenberg, 1980 and Panshin and de Zeeuw, 1980). Ray areas for the hardwood samples were nearly identical to ray volumes provided in the literature for each species (12.2, 16.6, and 18.8 % for yellow-poplar, black gum, and northern red oak).

Table 5.4 Ray areas of wood species treated with SC-CO_2 in Chapter 4 (Values are an average and one standard deviation based on five measurements).

Species	Ray Area (% of tangential section)
Sugar pine	8.2 (2.2) [1]
Ponderosa pine	11.3 (1.5)
Lodgepole pine	5.9 (2.1)
Douglas-fir	10.3 (1.1)
Engelmann spruce	8.9 (0.5)
White fir	9.4 (0.6)
Pacific silver fir	8.2 (0.6)
Western redcedar	6.2 (0.5)
Yellow-poplar	12.2 (1.2)
Black gum	16.5 (1.6)
Northern red oak	18.8 (9.8)

[1] Values in parentheses are one standard deviation.

Cellular Dimension Measurements: Cell dimension measurements for species used in this investigation are shown in Tables 5.5 and 5.6, respectively for softwoods and hardwoods. Dimensions were smaller than those provided by Panshin and de Zeeuw (1980)

and Isenberg (1980 and 1981); however, the relative differences between species were similar.

The softwood samples in this investigation had a similar average tangential width of approximately 30 μm, with the exception of sugar pine. According to Panshin and de Zeeuw these species would have been grouped as having medium to fine textures. Radial widths of the first earlywood cells appeared to differ among the samples with lodgepole pine, white fir, and Pacific silver fir having the smallest widths. It is likely that wood from these species came from higher elevation slower growing sites compared to the other species. Both Fleischer (1950) and Miller (1961) found that tangential and radial tracheid widths were slightly larger in wood samples that were more permeable or more easily treated with liquids under pressure. Softwood tracheid lengths are unique to a particular species, but they tend to be longer in the latewood, farther from the pith, or moving up a tree in the same growth ring.

Table 5.5 Cellular dimensions from microscopic observations of ten softwood tracheids from wood species treated with SC-CO_2 in Chapter 4 (values represent the average and one standard deviation).

Species	Tangential Width (μm)	Radial Width (μm)	Area (μm^2)	Length [2] (μm)
Sugar pine	43 (8) [1]	38 (8)	1,607 (321)	5,900
Ponderosa pine	28 (4)	33 (6)	947 (262)	3,600
Lodgepole pine	31 (3)	27 (3)	827 (108)	3,100
Douglas-fir	37 (6)	38 (5)	1,412 (322)	3,900
Engelmann spruce	31 (5)	37 (5)	1,150 (267)	3,000
White fir	31 (3)	26 (5)	794 (159)	3,400
Pacific silver fir	30 (5)	27 (3)	805 (104)	3,400
Western redcedar	30 (5)	29 (4)	874 (200)	3,500

1 Values in parentheses are one standard deviation.
2 Tracheid lengths from Isenberg (1980).

Table 5.6 Cellular dimensions from microscopic observations of twenty hardwood vessels and fibers from wood species treated with SC-CO_2 in Chapter 4 (values represent the average and one standard deviation).

Earlywood Vessel Elements				
Species	Tangential Width (μm)	Radial Width (μm)	Area (μm^2)	Length [2] (μm)
Yellow-poplar	71 (12)[1]	90 (15)	6,104 (1,626)	890
Black gum	40 (9)	52 (12)	1,680 (669)	1,330
Red oak	306 (34)	365 (39)	88,403 (16,992)	420
Fibers				
Species	Tangential Width (μm)	Radial Width (μm)	Area (μm^2)	Length [2] (μm)
Yellow-poplar	25 (6)	33 (8)	659 (283)	1,900
Black gum	20 (4)	28 (4)	439 (129)	1,800
Red oak	15 (3)	18 (4)	220 (86)	1,400

1 Values in parentheses are one standard deviation.
2 Vessel element and fiber lengths from Isenberg (1981).

Resin Canal Measurements: Average diameter, density, and area of longitudinal and radial resin canals were determined for sugar pine, ponderosa pine, lodgepole pine, Douglas-fir, and Engelmann spruce (Table 5.7). Resin canal diameters were in the ranges reported by Isenberg (1980) and Panshin and de Zeeuw (1980). Longitudinal resin canal diameters were always greater than radial resin canal diameters. Sugar pine had the largest diameter canals and Douglas-fir had the smallest for both longitudinal and radial type canals. Ponderosa and lodgepole pines had intermediate sized canals; while, the resin canals of Engelmann spruce were slightly larger than those in Douglas-fir. Longitudinal resin canals were less frequent than radial resin canals. Panshin and de Zeeuw (1980), noted that frequency of longitudinal

canals was similar for the pines and greater than in Douglas-fir or Engelmann spruce. However, the opposite was found for radial resin canals. With the exception of Douglas-fir, the percent cross section occupied by longitudinal resin canals was greater than the percent of tangential section occupied by radial canals. The area occupied by longitudinal resin canals in pines was greater than the area in Douglas-fir and Engelmann spruce, but, with the exception of sugar pine, the area occupied by radial resin canals was similar for all species.

Tylosoids were seen in all the pine samples but not in Douglas-fir or Engelmann spruce. These extensions of the resin canal epithelial cell membranes into the resin canal have been implicated in reduced flow. Erickson (1938) found that water under pressure still flowed through resin canals that were completely occluded. Although tylosoids may have hindered air permeability measurements, they did not appear to interfere with the pressure development in pine samples during supercritical carbon dioxide treatments suggesting that these obstructions may be overcome by increasing treatment pressure (Chapter 4).

5.4.3 Relationships between Wood Properties and Pressure Response Quantifiers

Air Permeability Measurements: Regression analysis was initially performed by pooling air permeability data for all species. Results (shown in Tables 5.8 – 5.10) indicated that air permeability was poorly or directly correlated with the internal pressure response quantifiers time to 35 kPa, time to pressure equilibrium, and maximum surface-to-center pressure difference. Air permeability was expected to be inversely related to pressure response since a larger permeability should indicate a greater flow of treatment media and thus a shorter time for an internal pressure response.

Table 5.7 Average resin canal diameter and percent cross section area of longitudinal or tangential sections of wood species containing resin canals. [1]

Species	Longitudinal Resin Canals			Radial Resin Canals		
	Average Diameter (μm)	Frequency (Number of Resin Canals/mm^2)	Area (% Cross Section)	Average Diameter (μm)	Frequency (Number of Resin Canals/mm^2)	Area (% Tangential Section)
Sugar pine	238 (50) [2]	0.23	1.07	99 (10)	0.36	0.27
Ponderosa pine	141 (22)	0.30	0.48	53 (1)	0.43	0.10
Lodgepole 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

1 Values based upon one field per species for each orientation.
2 Values in parentheses are one standard deviation.

When air permeability data was pooled separately for soft- and hardwoods (respectively Tables 5.11 – 5.13 and 5.14 – 5.16), correlation coefficients were generally improved but were only significant when longitudinal or radial permeabilities were regressed on hardwood pressure response quantifiers. Only radial permeability measurements on hardwood samples were significantly and inversely related to pressure response quantifiers.

The low or non-existing correlations between air permeability and pressure response quantifiers during SC-CO_2 treatments may have been due to the presence of extractives and/or tylosoids. These materials would reduce air permeability measurements, but may have been removed or redistributed during the high pressure SC-CO_2 treatments.

Ray Area Determinations: When regression analysis was performed by pooling ray area data for all species, poor or direct correlations resulted with pressure response quantifiers time to 35 kPa, time to reach equilibrium, and maximum surface-to-center pressure difference (Tables 5.8 – 5.10). Larger rays should allow more flow and thus reduce the required time for pressure change. Fleischer (1950) and Liese and Bauch (in Flynn, 1995) found larger ray volumes in more easily treated Douglas-fir and spruce heartwoods. Pooling data by wood type resulted in lower correlation coefficients for softwoods (Tables 5.11 – 5.13) and higher coefficients for hardwoods (Tables 5.14 – 5.16). Unfortunately, regression analysis still predicted direct relationships between ray area and pressure response quantifiers for hardwoods.

Differences between the correlations for soft-and hardwoods may be due to several factors. Average softwood ray area was smaller than hardwood ray area (8.6 versus 15.8 % of tangential section). Ray composition could also influence response. Pines, Douglas-fir and Engelmann spruce have ray tracheids that have small bordered pits which, although often not aspirated, can be heavily encrusted (Bains in Flynn, 1995). In addition, radial resin canals in five of the eight softwoods are more likely to explain internal pressure response variations in

softwoods. Thus, the role of ray cells in pressure transfer may be overwhelmed by other anatomical factors in softwoods.

Cellular Dimension Measurements: Tracheid dimensions were poorly or directly correlated to the pressure response quantifiers (Tables 5.11 – 5.13). This may reflect the measurements of only earlywood tracheids. Since these are in series with much smaller latewood cells, the latter could control the overall flow of gases in a radial direction. Although, previous investigators have shown that earlywood dimensions differ significantly between easily treated and refractory woods (Fleischer, 1950 and Miller, 1961).

Results from the correlation analysis between hardwood vessel element or fiber dimensions and pressure response quantifiers are shown in Tables 5.14 – 5.16. Vessel element dimensions were poorly or directly correlated to pressure response quantifiers. Although correlation coefficient for the regression of hardwood fiber dimensions on pressure response quantifiers were not significant at the 95 % level, they were fairly large and indicated an inverse relationship between these sets of variables. If more hardwood species were evaluated, it may be found that fiber dimensions account for pressure response variations. The potentially good correlation between fiber dimensions and pressure response suggested by this analysis may be explained by the fact that fibers isolate vessel elements during radial flow; although, some radial flow may occur through vessel branching in this direction (Panshin and de Zeeuw, 1980). Treatment of fibers pose a considerable challenge to conventional fluid processes, and it would appear that fibers play an equally important role in high pressure gas and supercritical fluid treatments.

Resin Canal Measurements: Results from the regression analysis of resin canal measurements on internal pressure response quantifiers are shown in Tables 5.11 – 5.13. Longitudinal and radial resin canal diameters, areas (% of cross-sectional area), and frequencies were either poorly or directly correlated with the time to 35 kPa. In addition,

longitudinal and radial resin canal frequencies were either poorly or directly correlated to the time to reach pressure equilibrium and the maximum surface-to-center pressure difference. Longitudinal resin canal diameters and areas were significantly and indirectly correlated with both the time to equilibrium and the maximum pressure difference. Radial resin canal diameters and cross-sectional areas, however, were close to but not significantly correlated with either time to equilibrium or maximum pressure difference.

These results suggests that although treatment media flow was restricted to enter and exit samples along their radial axes, longitudinal resin canals may play a significant role in the flow of treating media through wood and the subsequent internal pressure responses. Also, resin canal size may be more important than frequency. Preliminary studies with the effects of SC-CO_2 pressing rates on pressure development support this since the heartwood of sugar pine (having an average radial resin canal diameter and frequency of 99 μm and 0.36 canals /mm^2) was safely pressed at 2.1 MPa/min; whereas, ponderosa pine heartwood (having an average diameter and frequency of 53 μm and 0.43 canals/mm^2) needed to be pressed at a rate less than 0.6 MPa/min.

Table 5.8 Summary of regression analysis for air permeability and ray area against the time required to reach 35 kPa at the center of heartwood samples (3 x 3 x 6 cm long) during SC-CO_2 impregnation. This data was pooled by species for eleven species.

Explanatory Variable	Correlation Coefficient (r)	Significant Correlation Coefficient [1]		Predicted Relationship
		$\alpha = 0.05$	$\alpha = 0.01$	
Longitudinal permeability	0.389	0.602	0.735	Direct
Tangential permeability	0.555	0.602	0.735	Direct
Radial permeability	0.356	0.602	0.735	Direct
Radial permeability (extracted)	0.000	0.602	0.735	Direct
Ray area	0.325	0.602	0.735	Direct

[1] Two-tailed distribution (Wherry, 1984).

Table 5.9 Summary of regression analysis for air permeability and ray area against the time required to reach pressure equilibrium throughout heartwood samples (3 x 3 x 6 cm long) during SC-CO_2 impregnation. This data was pooled by species for eleven species.

Explanatory Variable	Correlation Coefficient (r)	Significant Correlation Coefficient [1]		Predicted Relationship
		$\alpha = 0.05$	$\alpha = 0.01$	
Longitudinal permeability	0.881	0.602	0.735	Direct
Tangential permeability	0.125	0.602	0.735	Direct
Radial permeability	0.078	0.602	0.735	Inverse
Radial permeability (extracted)	0.155	0.602	0.735	Inverse
Ray area	0.857	0.602	0.735	Direct

[1] Two-tailed distribution (Wherry, 1984).

Table 5.10 Summary of regression analysis for air permeability and ray area against the maximum surface-to-center pressure difference in heartwood samples (3 x 3 x 6 cm long) during SC-CO_2 impregnation. This data was pooled by species for eleven species.

Explanatory Variable	Correlation Coefficient (r)	Significant Correlation Coefficient [1]		Predicted Relationship
		$\alpha = 0.05$	$\alpha = 0.01$	
Longitudinal permeability	0.9074	0.602	0.735	Direct
Tangential permeability	0.5092	0.602	0.735	Direct
Radial permeability	0.3055	0.602	0.735	Direct
Radial permeability (extracted)	0.0781	0.602	0.735	Direct
Ray area	0.9139	0.602	0.735	Direct

[1] Two-tailed distribution (Wherry, 1984).

Table 5.11 Summary of regression analysis for various softwood characteristics against the time required to reach 35 kPa at the center of heartwood samples (3 x 3 x 6 cm long) during SC-CO_2 impregnation. Data pooled for eight softwood species.

Explanatory Variable	Correlation Coefficient (r)	Significant Correlation Coefficient [1]		Predicted Relationship
		$\alpha = 0.05$	$\alpha = 0.01$	
Longitudinal permeability	0.254	0.707	0.834	Inverse
Tangential permeability	0.686	0.707	0.834	Direct
Radial permeability	0.453	0.707	0.834	Direct
Radial permeability (extracted)	0.087	0.707	0.834	Inverse
Ray area	0.220	0.707	0.834	Inverse
Tracheid tangential width	0.441	0.707	0.834	Inverse
Tracheid radial width	0.250	0.707	0.834	Inverse
Tracheid area	0.389	0.707	0.834	Inverse
Tracheid length	0.462	0.707	0.834	Inverse
Longitudinal resin canal diameter	0.433	0.707	0.834	Inverse
Longitudinal resin canal frequency	0.526	0.707	0.834	Inverse
Longitudinal resin canal area	0.483	0.707	0.834	Inverse
Radial resin canal diameter	0.402	0.707	0.834	Inverse
Radial resin canal frequency	0.486	0.707	0.834	Direct
Radial resin canal area	0.341	0.707	0.834	Inverse

[1] Two-tailed distribution (Wherry, 1984).

Table 5.12 Summary of regression analysis for various softwood characteristics against the time required to reach pressure equilibrium throughout heartwood samples (3 x 3 x 6 cm long) during SC-CO_2 impregnation. Data pooled for eight softwood species.

Explanatory Variable	Correlation Coefficient (r)	Significant Correlation Coefficient [1]		Predicted Relationship
		$\alpha = 0.05$	$\alpha = 0.01$	
Longitudinal permeability	0.157	0.707	0.834	Inverse
Tangential permeability	0.223	0.707	0.834	Direct
Radial permeability	0.231	0.707	0.834	Inverse
Radial permeability (extracted)	0.659	0.707	0.834	Inverse
Ray area	0.145	0.707	0.834	Direct
Tracheid tangential width	0.296	0.707	0.834	Inverse
Tracheid radial width	0.606	0.707	0.834	Inverse
Tracheid area	0.491	0.707	0.834	Inverse
Tracheid length	0.311	0.707	0.834	Inverse
Longitudinal resin canal diameter	0.801	0.707	0.834	Inverse
Longitudinal resin canal frequency	0.364	0.707	0.834	Inverse
Longitudinal resin canal area	0.744	0.707	0.834	Inverse
Radial resin canal diameter	0.648	0.707	0.834	Inverse
Radial resin canal frequency	0.755	0.707	0.834	Direct
Radial resin canal area	0.574	0.707	0.834	Inverse

[1] Two-tailed distribution (Wherry, 1984).

Table 5.13 Summary of regression analysis for various wood characteristics against the maximum surface-to-center pressure difference in heartwood samples (3 x 3 x 6 cm long) during SC-CO_2 impregnation. Data pooled for eight softwood species.

Explanatory Variable	Correlation Coefficient (r)	Significant Correlation Coefficient [1]		Predicted Relationship
		$\alpha = 0.05$	$\alpha = 0.01$	
Longitudinal permeability	0.203	0.707	0.834	Inverse
Tangential permeability	0.195	0.707	0.834	Direct
Radial permeability	0.297	0.707	0.834	Inverse
Radial permeability (extracted)	0.681	0.707	0.834	Inverse
Ray area	0.215	0.707	0.834	Direct
Tracheid tangential width	0.310	0.707	0.834	Inverse
Tracheid radial width	0.569	0.707	0.834	Inverse
Tracheid area	0.477	0.707	0.834	Inverse
Tracheid length	0.337	0.707	0.834	Inverse
Longitudinal resin canal diameter	0.817	0.707	0.834	Inverse
Longitudinal resin canal frequency	0.484	0.707	0.834	Inverse
Longitudinal resin canal area	0.760	0.707	0.834	Inverse
Radial resin canal diameter	0.667	0.707	0.834	Inverse
Radial resin canal frequency	0.831	0.707	0.834	Direct
Radial resin canal area	0.558	0.707	0.834	Inverse

[1] Two-tailed distribution (Wherry, 1984).

Table 5.14 Summary of regression analysis for various hardwood characteristics against the time required to reach 35 kPa at the center of heartwood samples (3 x 3 x 6 cm long) during SC-CO_2 impregnation. Data pooled for three hardwood species.

Explanatory Variable	Correlation Coefficient (r)	Significant Correlation Coefficient [1]		Predicted Relationship
		$\alpha = 0.05$	$\alpha = 0.01$	
Longitudinal permeability	0.978	0.950	0.990	Direct
Tangential permeability	0.375	0.950	0.990	Direct
Radial permeability	0.856	0.950	0.990	Inverse
Radial permeability (extracted)	0.992	0.950	0.990	Inverse
Ray area	0.922	0.950	0.990	Direct
Vessel element tangential width	0.360	0.950	0.990	Direct
Vessel element radial width	0.356	0.950	0.990	Direct
Vessel element area	0.417	0.950	0.990	Direct
Vessel element length	0.030	0.950	0.990	Direct
Fiber tangential width	0.841	0.950	0.990	Inverse
Fiber radial width	0.723	0.950	0.990	Inverse
Fiber area	0.842	0.950	0.990	Inverse
Fiber length	0.617	0.950	0.990	Inverse

[1] Two-tailed distribution (Wherry, 1984).

[2] Regression analysis requires at least four sample replicates.

Table 5.15 Summary of regression analysis for various hardwood characteristics against the time required to reach pressure equilibrium throughout heartwood samples (3 x 3 x 6 cm long) during SC-CO_2 impregnation. Data pooled for three hardwood species.

Explanatory Variable	Correlation Coefficient (r)	Significant Correlation Coefficient [1]		Predicted Relationship
		$\alpha = 0.05$	$\alpha = 0.01$	
Longitudinal permeability	0.840	0.950	0.990	Direct
Tangential permeability	0.388	0.950	0.990	Inverse
Radial permeability	0.972	0.950	0.990	Inverse
Radial permeability (extracted)	0.792	0.950	0.990	Inverse
Ray area	0.927	0.950	0.990	Direct
Vessel element tangential width	0.913	0.950	0.990	Direct
Vessel element radial width	0.911	0.950	0.990	Direct
Vessel element area	0.936	0.950	0.990	Direct
Vessel element length	0.684	0.950	0.990	Inverse
Fiber tangential width	0.978	0.950	0.990	Inverse
Fiber radial width	0.999	0.950	0.990	Inverse
Fiber area	0.978	0.950	0.990	Inverse
Fiber length	0.992	0.950	0.990	Inverse

[1] Two-tailed distribution (Wherry, 1984).

[2] Regression analysis requires at least four sample replicates.

Table 5.16 Summary of regression analysis for various hardwood characteristics against the maximum surface-to-center pressure difference in heartwood samples (3 x 3 x 6 cm long) during SC-CO_2 impregnation. Data pooled for three hardwood species.

Explanatory Variable	Correlation Coefficient (r)	Significant Correlation Coefficient [1]		Predicted Relationship
		$\alpha = 0.05$	$\alpha = 0.01$	
Longitudinal permeability	0.9993	0.950	0.990	Direct
Tangential permeability	0.2122	0.950	0.990	Direct
Radial permeability	0.9308	0.950	0.990	Inverse
Radial permeability (extracted)	0.9991	0.950	0.990	Inverse
Ray area	0.9739	0.950	0.990	Direct
Vessel element tangential width	0.5127	0.950	0.990	Direct
Vessel element radial width	0.5087	0.950	0.990	Direct
Vessel element area	0.5645	0.950	0.990	Direct
Vessel element length	0.1400	0.950	0.990	Inverse
Fiber tangential width	0.9203	0.950	0.990	Inverse
Fiber radial width	0.8298	0.950	0.990	Inverse
Fiber area	0.9208	0.950	0.990	Inverse
Fiber length	0.7415	0.950	0.990	Inverse

[1] Two-tailed distribution (Wherry, 1984).
[2] Regression analysis requires at least four sample replicates.

5.5 Summary

Air permeability measurements for eleven species were in agreement with previous literature. The highest longitudinal permeability value was three orders of magnitude greater than the smallest value; whereas, the highest radial or tangential values were only 25 times greater. Pooled data for softwoods or hardwoods, showed that there were little or no permeability differences between the transverse orientations. Extraction using SC-CO_2 prior

to permeability measurement resulted in both permeability increases and decreases. Improved extraction techniques might provide more consistent improvements in air permeability, but these were beyond the scope of this project.

Anatomical measurements on wood used in this investigation were within the ranges provided in the literature. Because of the difficulty in measuring ray volumes, ray area as a percent of a tangential section were determined. When pooled into softwoods and hardwoods, average ray areas ranged from 6 to 11 % and 12 to 19 %, respectively. Cellular dimensions were slightly smaller than previously reported, but the sizes differences between species were similar. Average longitudinal and radial resin canal sizes were similar to averages provided in the literature. Longitudinal resin canals were generally larger but less frequent for a given species. The total area occupied by longitudinal resin canals was greatest for the pines followed by Engelmann spruce and Douglas-fir. With the exception of sugar pine, radial resin canal areas were similar for all species containing resin canals.

Linear regression analysis of selected measurements of wood characteristics and pressure response data from Chapter 4 showed that most of the measurements could not be used to explain pressure responses. Air permeability was poorly or directly correlated with pressure response quantifiers. Ray area measurements, tracheid dimensions, and vessel dimensions were also poorly or directly correlated with pressure response quantifiers. Results suggest that hardwood fiber dimensions may be correlated to pressure response, but more species are needed for a statistical evaluation. Longitudinal and radial resin canal diameters and percent of cross-sectional area were significantly and inversely related to two of three pressure response quantifiers. In summary, this investigation provides evidence suggesting that resin canal dimensions, in softwoods, and fiber dimensions, in hardwoods, may be useful for predicting internal pressure responses during pressure treatments.

5.6 Implications

Restricting treatment media flow to the radial axis limited the application of pressure data collected in Chapter 4 to similar situations, such as coated samples or samples having considerably longer longitudinal versus transverse dimensions. In addition, no attempt was made to representatively sample each species used and, because of lengthy and difficult treatment applications, limited sample replications were used. Despite these limitations, the following implications may be made:

1. Time to reach 35 kPa was not significantly correlated with any of the explanatory variables and thus may not be a good quantifier of internal pressure response. The poor correlation may be the result of pressure measurements being made too slowly or out of sync with incremental treatment vessel pressure increases.

2. Air permeability measurements did not have significant correlations with pressure response quantifiers. This was most likely due to the presence of extractives and tylosoids, which affected air permeability to a greater extend than pressure response during SC-CO_2 treatments. However, permeability measurements may be correlated with pressure response quantifiers if proper SCF extraction procedures are followed.

3. Longitudinal and radial resin canal dimensions seemed to explain most of the internal pressure response variation in softwoods, while fiber dimensions explained most of the pressure response variation in hardwoods. Thus, anatomical features may be more useful compared to air permeability for the prediction of pressure response in wood during SC-CO_2 treatments.

6 USE OF INTERNAL PRESSURE MEASUREMENTS TO EXPLAIN DIFFICULTIES WITH SUPERCRITICAL FLUID IMPREGNATION OF WOOD

6.1 Introduction

Supercritical fluid impregnation processes have been brought forth as one of the most promising solutions to the difficulties with treating refractory species (Sections 2.2.2 and 2.3). Descriptions of these processes in patents by Ito et al. (1984) and Kayihan (1992) and in exploratory work by Acda (1995), Smith et al. (1993a, 1993b), and Ward et al. (1990) presented nearly ideal processes in which wood was placed in one vessel and a SC-CO_2 solution containing a biocide or dimensional stabilizer was placed in another. The SCF was then passed by the wood in the first vessel, and while doing so, it was thought to be nearly instantaneously absorbed throughout the wood. The vessel containing the wood was then isolated and vented to atmospheric pressure, theoretically causing a rapid change of pressure in the wood which then lead the dissolved material to precipitate with no significant loss in the mechanical properties of the wood.

Scaled up studies with larger samples and more refractory species than were used initially indicated that the SCF impregnation process was more complex. Acda (1995), Acda et al. (in review), and Sahle-Demessie (1994) obtained large variations in biocide retention and distribution. Acda et al., Anderson (1998), and Tsunoda (1999) all found collapse or fractures in refractory samples treated by SCF processes. Internal pressure measurements in this study (Chapter 4) indicated that there can be relatively long delays in pressure response at the center of wood samples. Pressure response delays, caused by restricted fluid flow and the compressible nature of CO_2 gas and SC-CO_2, give rise to surface-to-center pressure differentials.

Measurements of surface-to-center pressure differences offer insights to difficulties encountered during the scaling up of SCF impregnation processes. For example, pressure differences within a piece of wood can be used to explain non-uniform preservative distributions or the formation of excess compressive or tensile stresses perpendicular to the grain which will cause the wood to collapse (during pressing) or fracture (during venting). Finally, measurements of surface-to-center pressure differences help to explain changes in wood dimension that occur during impregnation.

6.2 Preservative Distribution

6.2.1 The Occurrence of Retention Distributions

A nearly uniform distribution of biocide throughout the cross section of treated wood is important since interior zones are often exposed through checking, boring, or cutting. In addition, excessive preservative loadings near the surface increases product costs and can lead to exudation of the preservative causing health and environmental problems. Unfortunately, previous SCF impregnation studies have shown considerably greater retentions in the outer versus inner regions of samples (Acda, 1995; Acda et al., in review; Sahle-Demessie, 1994). Retentions in solid wood samples have been reported to range from 5 to 12 times greater in the shell versus core regions (Acda et al., in review; Sahle-Demessie, 1994), while retentions in composites have been reported to range from nearly uniform to almost 10 times greater in the shell regions (Acda, 1995).

Both process and wood variables can significantly influence the distribution of preservatives deposited in wood during SCF impregnation. Although increasing pressure or adding a co-solvent improved retentions at all depths, neither has improved preservative distributions. In fact, both Acda et al. (in review) and Sahle-Demessie (1994) have shown that

increasing pressure has increased the surface-to-core retention differences. Acda et al. showed that increasing the rate of venting after treatment from 138 to 8,274 kPa/min resulted in shell-to-core retention differences that increased from 3.3 to 10.8 times. Increasing venting rates are associated with greater surface-to-center pressure differences (Section 4.4.2). The influence of treatment time on shell-to-core retention differences seems to be dependent on the permeability of the wood. Acda et al. (in review) and Sahle-Demessie (1994) found that increasing treatment time from 30 to 60 min. reduced the shell-to-core retention differences in Douglas-fir. But, in less permeable woods, this time increase did not improve distribution. Samples that were either smaller or more permeable had more uniform preservative distributions (Sahle-Demessie, 1994). Although small samples still had shell-to-core retention differences similar to larger samples, the retentions in the inner zone were more uniform than in comparable sections of larger samples.

6.2.2 Explanations for Retention Distributions

Assuming there are no interactions between a biocide and wood constituents, possible explanations for the higher shell retentions reported above include solvating and flow problems. Both the ability to dissolve a material in a SCF and the ability to transport it into wood are dependent on pressure in the treatment vessel and in the wood. It is especially important to remember that small pressure changes have a dramatic effect on the solubility of materials in a SCF (Chapter 2).

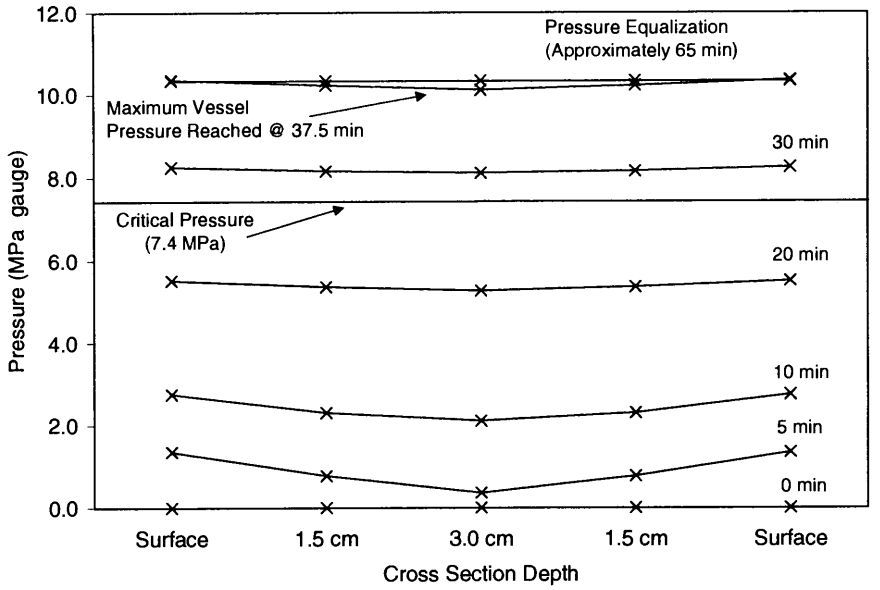
Solubilizing materials in a SCF poses little problem (Sahle-Demessie, 1994); however, pressure changes associated with the movement into wood by a biocide carrying SCF result in a sharp reduction in solvating power. Once the biocide has precipitated it may be difficult to re-dissolve particularly if a co-solvent is no longer available. If a treatment is stopped before pressure in the core region of a sample of wood has reached the level required

for the SCF to solvate sufficient quantities of a biocide, then the core region will have lower biocide levels. The potential for insufficient pressure at locations below the surface of wood was clearly shown in Chapter 4 by delays in internal pressure response. These delays are accentuated with rapid treatment pressure change, larger wood cross section, and lower wood permeability.

The influence of surface-to-center pressure differences on the flow of SCFs in wood is also likely to contribute to shell-to-core retention differences. Figure 6.1a shows pressure measurements made at depths of 1.5 and 3.0 cm from the surface of a Douglas-fir sample during the pressing phase of a SC-CO_2 treatment; Figure 6.1b shows pressure measurements during the venting phase of the same treatment. In both cases, it is assumed that pressure at the 1.5 cm depth is symmetric. During the pressing phase, pressure rose more quickly near the surface than at the center. Lagging pressure response at the center led to a 1 MPa surface-to-center pressure difference within the first 5 minutes. This pressure difference created a driving force for the flow of treating medium into the wood. As treatment progressed, vessel pressure increased, and the pressure difference declined but was not eliminated until almost 30 minutes after vessel pressure was held constant.

When the venting phase was initiated, pressure had equilibrated throughout the sample. Pressure initially decreased fairly uniformly. Just prior to reaching the critical point, pressure response at the center began to lag behind, creating a negative surface-to-center pressure difference. This negative pressure difference moved material out of the center region, just as the positive pressure difference moved it into the center before the initial pressure equalization.

(a)



(b)

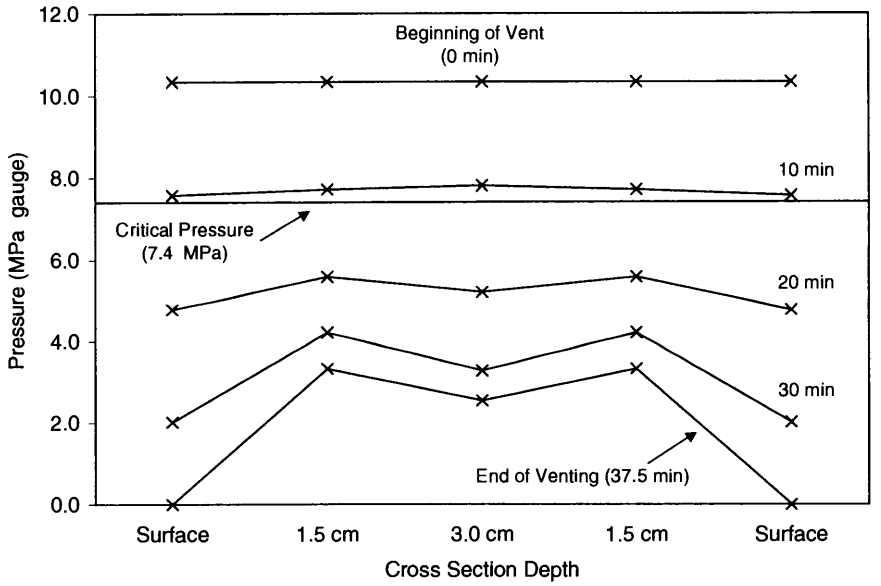


Figure 6.1 Pressure measurements in Douglas-fir heartwood (6 x 3 x 6 cm, radial x tang. x long.) during (a) the pressing and (b) venting phases of a SC-CO_2 treatment where flow was restricted to along the radial axis.

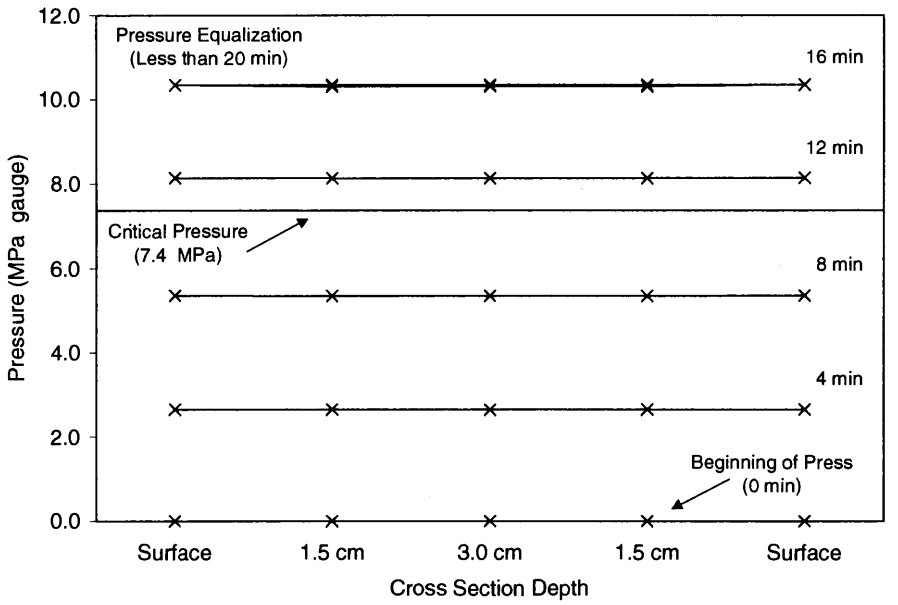
If a solute were to have been carried in the SC-CO_2, it would have begun to precipitate near the surface as pressure in that region dropped below the critical point. The negative surface-to-center pressure difference would have continued to move solute laden material outward toward an inwardly advancing critical pressure front. Eventually pressure throughout the wood dropped below the critical point. Any solute would precipitate. As a result of the negative surface-to-center pressure differences at the time of precipitation, a SCF in the core region would become depleted of solute, thus causing a shell-to-core retention difference.

Internal pressure response results in Chapter 4 indicate that slower pressing and venting rates, smaller cross section dimensions, and more permeable wood result in more uniform pressure and thus would be more likely to give rise to uniform solute deposition. This is supported by Figures 6.2a and 6.2b which show pressure measurements made at depths of 1.5 and 3.0 cm from the surface of a sugar pine sample during the pressing and venting phases of a SC-CO_2 treatment. In addition, Sahle-Demessie (1994) found that ponderosa pine sapwood samples had more uniform biocide treatment compared to Douglas-fir heartwood samples.

6.3 Collapse and Fracture

The collapse or fracture of wood is a limiting factor in the development of high pressure impregnation processes. Wood treating processes most frequently employ pressures below 1400 kPa. Occasionally, pressures above this have been used with liquid preservatives to treat refractory species (Section 2.2). Ellwood (1956), Rosen (1975), Walters (1967), and Walters and Whittington (1970), all suggest that treatment pressure level is predicated on a balance of wood permeability and strength.

(a)



(b)

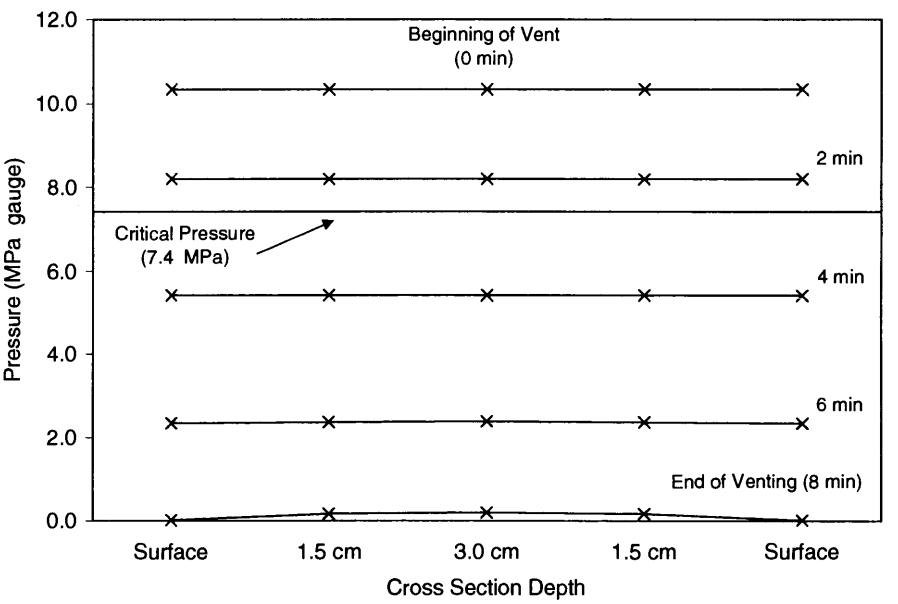


Figure 6.2 Pressure measurements in sugar pine sapwood (6 x 3 x 6 cm, radial x tang. x long.) during (a) the pressing and (b) the venting phases of a SC-CO_2 treatment where flow was restricted to along the radial axis.

For example pine, has a relatively high permeability and can withstand high pressure treatments. Eucalyptus has a lower permeability, but has a high compressive strength and therefore resists collapse. Douglas-fir also has a low permeability but is weaker than the other species and will collapse at treatment pressures below its compressive strength (Ellwood, 1956). Both collapse and fracture of wood have been noted during SCF impregnation processes (Acda et al., in review; Anderson, 1998; Kim et al., 1997; Tsunoda et al., 1999). Although the occurrence of these defects has been associated with less permeable species, no further studies have been performed to understand these failures or offer control strategies.

Excessive pressure differences in wood can be related to its failure during SCF treatments. Pressure measurements in wood during SC-CO_2 treatments (Chapter 4) have shown that the flow of a SCF into wood is not instantaneous and that substantial surface-to-center pressure differences develop because of hindered flow and the compressible nature of CO_2. Collapse occurred in all samples were the surface-to-center pressure differences exceeded the maximum compressive strengths for that species (Table 6.1). In addition, collapse occurred in a single sample of white fir and three of four black gum samples even though these samples had pressure differences below the compressive below their compressive strengths.

Excessive surface-to-center pressure differences can also result in wood fracture. Anderson (1998) noted fractures following rapid venting, and similar problems were noted in this study (Chapter 4). Pressure differences resulting during the venting phase of SC-CO_2 treatments pressure caused the fracture of several Douglas-fir heartwood samples. The surface-to-center pressure differences near the time of failure in these samples was measured to be from -2,027 to -4,240 kPa; while, the maximum tensile strength at a similar moisture content was given by Markwardt and Wilson (1935) to be -2,068 kPa. Although internal pressure measurements during the venting phase were suspected of being falsely high, a single

Douglas-fir sample treated using faster pressing and venting rates (689 versus 276 kPa/min) and then equilibrated in a pressure bomb indicated that internal pressure immediately after treatment was 2,565 kPa. Interestingly, this sample did not show signs of fracture.

Table 6.1 Incidence of collapse in various wood species (3 x 3 x 6 cm, radial x tang. x long.) during SC-CO_2 treatment (40 °C, 10.3 MPa maximum pressure with pressing and venting rates of 276 kPa/min.).

Species	Sample	Max. ΔP during Pressing (kPa gauge)	Maximum Compressive Strength [1]	Wood Condition
Black gum	1	8,198	7,929	Slight Collapse
	2	4,309	7,929	Slight Collapse
	3	6,564	7,929	Slight Collapse
	4	5,281	7,929	Slight Collapse
Engelmann spruce	1	7,577	4,413	Sever Collapse
	2	5,978	4,413	Sever Collapse
Western redcedar	1	5,171	4,206	Sever Collapse
	2	5,240	4,206	Sever Collapse
Pacific silver fir	1	5,971	3,378	Sever Collapse
	2	8,522	3,378	Sever Collapse
White fir	1	1,868	4,137	Slight Collapse
	2	1,958	4,137	No Collapse
	3	2,296	4,137	No Collapse
	4	1,965	4,137	No Collapse
	5	2,372	4,137	No Collapse

[1] Compressive stress at the proportional limit perpendicular to the grain @ 12 % mc (Markwardt and Wilson, 1935).

6.4 Dimensional Change and Recovery

When wood is placed in a vessel and pressure applied through a gas or liquid medium, stresses can develop due to pressure differences across the wood surfaces. When these stresses become great enough, the wood will deform. Two types of deformation occur simultaneously, elastic and plastic. Elastic deformation of wood is attributed to the behavior of cellulose microfibrils making up wood cell walls; plastic deformation is due to the flow of lignin (Panshin and de Zeeuw, 1980). Once pressure is released all of the elastic deformation will be recovered while the plastic deformation remains. The amount of deformation is most strongly correlated to the specific gravity of wood, but wood moisture content (in the hygroscopic range, 0 to 25 % by weight of water) and temperature (above 65 °C) also contribute to the amount of deformation an applied load will cause (Bodig and Jayne, 1982; Panshin and de Zeeuw, 1980; Walters and Huang, 1971).

Dimensional changes in wood during pressure impregnation processes are inevitable. Monitoring these changes may help determine pressure adjustments during processing that allow recovery of permanent deformation. Generally, dimensional changes are small and are completely recovered upon venting of treatment pressure or the application of a final vacuum (Richardson, 1993). Large dimensional changes are evident as collapse during high pressure and SCF treatments. Dimensional changes appear to be a direct result of surface-to-center pressure differences. Kim et al. (in review) measured the displacement of two nails placed in the face of small white spruce (*Picea glauca* [Moench.] Voss.) sample boards. The patterns of displacement during treatment were similar to those for pressure differences. There was an initial large displacement as pressure was applied; the amount of displacement decreased slightly as treatment pressure is held constant; and then, displacement was predominantly reversed during the venting phase of treatment. Faster pressing rates led to greater displacement, which corresponded to the greater surface-to-center pressure differences shown

in Chapter 4. Kim et al. showed that faster venting substantially decreased the amount of permanent deformation. Faster venting rates most likely created larger negative surface-to-center pressure differences that helped re-inflate the compressed wood. Caution must be used with this technique, however, because excessive pressure from within the wood will lead it to fracture.

6.5 Summary

Delays in the flow of CO_2 and the compressible nature it result in surface-to-center pressure differences in wood during SC-CO_2 treatments. These pressure differences can be used to help explain difficulties encountered during SCF impregnation processes. The high shell and low core retention distributions in wood samples treated with SCFs can be attributed to the lack of adequate pressure in core regions during treatment or to the outward flow of the treating medium during venting. Pressure differences in wood during pressing and venting may exceed the wood's strength, causing collapse or fracture, respectively. Wood failure during impregnation can also occur from stresses below strength values reported for a given species. These variations may reflect natural variations in wood properties or non-uniform pressure distribution. Dimensional changes of wood during SCF impregnation processes were correlated with internal pressure responses. The amount of displacement wood undergoes during SCF treatments is dependent on surface-to-center pressure differences and the elastic and plastic nature of wood. Although dimensional changes are not directly detrimental unless they become excessive, knowledge of their existence and control may help prevent or reduce mechanical damage during the treating process. All of the preceding characteristics associated with pressure differences are intensified when treatment pressures are changed rapidly or the wood has a large cross section and/or low permeability.

6.6 Implications

The relative responses to pressure application and venting during SCF treatments suggest that judicious changes in process could be used to reduce potential pressure differences in wood and the resulting physical and mechanical effects. At the same time, understanding the roles of internal pressure change provides an important opportunity to use pressure to control deposition in the wood. The results suggest that there is considerable opportunity to use internal pressure measurements to control SCF impregnation processes. Coupled with prior studies on solubility and phase behavior, these results can be used to develop more sophisticated models that would reduce the need for step-wise process testing with each new species/chemical combination. Although considerable work remains, data from this investigation help explain why initial results with SCFs have been so variable and provide insights into methods to better control impregnation processes.

7 CONCLUSIONS

A better understanding of pressure development in wood during conventional and SCF pressure impregnation processes has been achieved in this investigation through pressure measurements in wood during various treatment conditions. This goal was met using four research objectives.

To Develop a Pressure Measurement Method: Several techniques were evaluated to measure pressure in wood during conventional and SC-CO_2 treatments. Of these, the following method was the simplest and most effective. Pressure probes were made from stainless steel tubing (3.2 mm OD, 2.1 mm ID) cut to 50 mm lengths, roughed with sandpaper, cleaned with alcohol, and set into the samples with Gluvit epoxy. Holes for the probes were centered in the end-grain of wood samples and drilled to a depth of 20 mm with a 3.9 mm bit. After the epoxy cured, a 1.9 mm drill bit was used to bore through the epoxy at the bottom of the tubing creating a 10 mm long pressure chambers below the tubing. The pressure probes were then filled with silicone hydraulic oil and attached to hydraulic lines in a pressure vessel. The lines connected the samples to pressure sensors outside of the vessel.

To Quantify the Influence of Process and Wood Variables on Internal Pressure Response: The following conclusions were made form conventional pressure treatments.

1. Pressure response was faster, more complete, and less variable for Lowry versus Rüping and for Bethell versus Lowry pressure schedules.
2. Pressure response was nearly instantaneous and more complete with air versus oil treatment media and ponderosa pine sapwood versus Douglas-fir heartwood samples.
3. A greater amount of time was needed for a pressure response at a greater depth into a sample, but the rate of pressure increase at a given depth and the extent of pressure change appeared to be independent of depth.

The following conclusions were made form SC-CO_2 pressure treatments.

1. Faster pressing and venting rates provided faster internal pressure responses but longer times for pressure equalization and larger surface-to-center pressure differences. As a result, shorter treatment times were achieved at the expense of increased risk of collapsing or fracturing the wood.

2. Pressure response with increased depth into a sample was dependent on species (or more likely the permeability of a given species). Sugar pine samples showed little influence of depth on pressure response. Treatments with Douglas-fir samples showed that pressure response was delayed with increased depth.

3. More permeable species allowed faster pressure responses with lower surface-to-center pressure differences. In addition, species which were stronger were able to withstand higher pressure differences during treatment.

4. Internal pressure responses were faster and lower surface-to-center pressure differences occurred when the flow of CO_2 was restricted to tangential versus radial axes.

To Identify Easily Measurable Wood Properties That could be Used to Explain or Predict Internal Pressure Response: Regression analyses between pressure response quantifiers form SC-CO_2 treatments and air permeability or anatomical measurements showed that most of the measurements could not be used to explain or predict pressure responses. However, the following general conclusions may be made:

1. Air permeability was poorly and or directly correlated with pressure response when data was pooled for all species. Since greater flow can occur when wood has a greater permeability, an inverse relationship was expected between permeability and pressure response. Pooling data by wood type (softwoods or hardwoods) resulted in inverse relationships with larger correlation coefficients.

2. Ray area was either poorly and/or directly correlated with pressure responses even after pooling by wood type.

3. Resin canal and softwood tracheid dimensions were moderately and inversely correlated to pressure response.

4. Regression of pressure response quantifiers on vessel dimensions resulted in high correlation coefficients, but direct relationships were predicted.

5. Regression analysis of pressure response quantifiers on hardwood fiber dimensions resulted in high correlation coefficients and inverse relationships were predicted.

To Utilize Pressure Measurements to Explain Difficulties Encountered During SCF Impregnation Processes: Pressure measurements in wood showed that there typically is a delay in time between when treatment pressure is applied and when pressure within wood responds. This delay leads to surface-to-interior pressure differences. The existence of higher pressure at the center of wood as pressure is being lowered through the critical region during venting would cause the outward flow of treating media and thus could explain higher shell retentions experienced during SCF impregnation experiments. In addition, internal pressure measurements have confirmed the existence of excessive pressure differentials that cause collapse or fracture. This work suggests that by controlling pressure differences difficulties encountered during SCF impregnation processes may be reduced.

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APPENDICES

Appendix A Conventional treatments to develop pressure measurement techniques. [1]

Probe & Sealant	Pressure Process	Treating Medium	Species [2]	Wood Size [3] (cm)	Number & Condition of Pressure Probes			Treatment Date
					Blocked	Leaked	Good	
2 probes pressed in tight pre-drilled holes without epoxy	Lowry	Air	Douglas-fir	9 x 9 x 60	0	2	0	07/05/96
			Douglas-fir	9 x 9 x 60	0	2	0	07/07/96 [6]
	Rüping	Oil	Douglas-fir	9 x 9 x 60	0	2	0	07/08/96 [6]
Epoxied probe	Lowry	Air [4]	Douglas-fir	9 x 9 x 60	0	0	4	07/25/96 [6]
		Oil [3]	Douglas-fir	9 x 9 x 60	0	3	1	07/28/96
	Rüping	Air [4]	Douglas-fir	9 x 9 x 60	1	0	15	07/26-30/96 [6]
		Oil [3]	Douglas-fir	9 x 9 x 60	0	13	3	07/30-08/02/96
Single-probe holder with o-ring	Lowry	Oil	Douglas-fir	2.0 x 2.0 x 8.0	0	0	2	8/28/96
			Douglas-fir	2.5 x 2.5 x 7.6	0	2	0	09/17/96
		Air	Douglas-fir	2.5 x 2.5 x 7.6	0	1	1	08/30/96 [6]
			Douglas-fir	2.5 x 2.5 x 7.6	0	2	0	09/17/96 [6]
Single-probe holder with o-ring & 3.2 mm thick rubber gasket	Lowry	Oil	Douglas-fir	2.5 x 2.5 x 7.6	0	0	1	09/22/96
			Douglas-fir	2.5 x 2.5 x 7.6	0	4	0	09/23/96
			Douglas-fir	2.5 x 2.5 x 7.6	0	0	4	09/30/96
			Douglas-fir	2.5 x 2.5 x 7.6	0	0	4	10/18/96
			Douglas-fir	2.5 x 2.5 x 7.6	0	1	3	11/05/96
			Douglas-fir	2.5 x 2.5 x 7.6	0	0	6	11/06/96
			Douglas-fir	2.5 x 2.5 x 7.6	0	1	1	11/07/96
			Douglas-fir	2.5 x 2.5 x 7.6	0	2	1	03/12/97 [6]

Appendix A (Continued)

Probe & Sealant	Pressure Process	Treating Medium	Species [2]	Wood Size [3] (cm)	Number & Condition of Pressure Probes			Treatment Date
					Blocked	Leaked	Good	
Single-probe holder with o-ring & 3.2 mm thick rubber gasket	Lowry	Oil	D-F sapwood	2.5 x 2.5 x 7.6	0	2	0	10/01/96
			D-F sapwood	2.5 x 2.5 x 7.6	0	2	3	10/02/96
			Ponderosa pine	2.5 x 2.5 x 7.6	0	0	2	02/06/97
	Bethell	Oil	Douglas-fir	2.5 x 2.5 x 7.6	0	0	2	10/31/96 [6]
			Douglas-fir	2.5 x 2.5 x 7.6	0	0	2	11/01/96 [6]
			Douglas-fir	2.5 x 2.5 x 7.6	0	0	3	02/06/97 [6]
			Douglas-fir	2.5 x 2.5 x 7.6	2	2	0	01/30/97
			Douglas-fir	2.5 x 2.5 x 7.6	0	2	0	02/05/97
			Ponderosa pine	2.5 x 2.5 x 7.6	0	0	2	01/30/97 [6]
			Ponderosa pine	2.5 x 2.5 x 7.6	0	2	2	02/05/97 [6]
Single-probe holder with o-ring & 1.6 mm thick rubber gasket	Bethell	Oil	Douglas-fir	2.5 x 2.5 x 7.6	0	2	0	01/22/97 [6]
			Douglas-fir	2.5 x 2.5 x 7.6	1	1	0	01/23/97 [6]
			Ponderosa pine	2.5 x 2.5 x 7.6	0	2	0	01/22/97 [6]
			Ponderosa pine	2.5 x 2.5 x 7.6	0	2	0	01/23/97 [6]
Single-probe holder with 3.2 mm gasket and Si adhesive	Lowry	Oil	Douglas-fir	2.5 x 2.5 x 7.6	0	0	2	11/08/96
			Douglas-fir	2.5 x 2.5 x 7.6	0	0	2	11/10/96
Single-probe holder with 3.2 mm thick rubber gasket	Lowry	Oil	Douglas-fir	2.5 x 2.5 x 7.6	0	1	0	09/22/96
			Douglas-fir	2.5 x 2.5 x 7.6	0	2	0	04/04/97
			Douglas-fir	2.5 x 2.5 x 7.6	0	2	0	04/14/97
			Douglas-fir	2.5 x 2.5 x 7.6	2	0	0	04/16/97
			Douglas-fir	2.5 x 2.5 x 7.6	0	2	2	05/12/97 [6]

Appendix A (Continued)

Probe & Sealant	Pressure Process	Treating Medium	Species [2]	Wood Size [3] (cm)	Number & Condition of Pressure Probes			Treatment Date
					Blocked	Leaked	Good	
Single-probe holder with 3.2 mm thick rubber gasket	Lowry	Oil	Ponderosa pine	2.5 x 2.5 x 7.6	0	0	2	04/16/97
			Ponderosa pine	2.5 x 2.5 x 7.6	0	0	4	05/08/97 [6]
			Ponderosa pine	2.5 x 2.5 x 7.6	0	0	4	05/09/97 [6]
		Air	Douglas-fir	2.5 x 2.5 x 7.6	0	3	1	05/09/97 [6]
			Douglas-fir	2.5 x 2.5 x 7.6	0	1	3	05/10/97 [6]
			Douglas-fir	2.5 x 2.5 x 7.6	0	0	4	05/11/97 [6]
			Ponderosa pine	2.5 x 2.5 x 7.6	0	0	8	05/08/97 [6]
			Ponderosa pine	2.5 x 2.5 x 7.6	0	0	4	05/09/97 [6]
Two-probe holder with 3.2 mm thick rubber gasket	Lowry	Oil	Douglas-fir	5.0 x 5.0 x 7.6	0	0	1	04/09/97 [6]
			Douglas-fir	5.0 x 5.0 x 7.6	0	0	2	04/21/97 [6]
	Bethell	Oil	Douglas-fir	5.0 x 5.0 x 7.6	0	1	1	12/31/96 [6]
Three-probe holder with 3.2 mm thick rubber gasket	Lowry	Oil	Douglas-fir	5.0 x 5.0 x 7.6	0	0	3	04/29/97 [6]
	Bethell	Oil	Douglas-fir	5.0 x 5.0 x 7.6	0	0	3	01/12/97 [6]

1 Only treatments that had pressure measurements recorded during them are shown in this table.

2 Douglas-fir samples are from heartwood, ponderosa pine samples are from sapwood, unless noted in table.

3 Sample dimensions are given along the radial tangential and longitudinal axes, respectively.

4, 5 The same footnote indicates that the same samples and probes used where used for different treatments.

6 Treatments applied long enough for internal pressure to either level off below that in the treatment vessel or approach equilibrium with it.

Appendix B SC-CO_2 treatments to develop pressure measurement techniques.

Measurement Technique		Sample Preparation and Treatment Schedule				Results		
Pressure-probe Type	Sealant (Torque on sample holder nuts)	Dimensions [radial x tangential x longitudinal] (cm)	Flow Direction [1]	Rate of Pressing and/or Venting (kPa/min)	Maximum Pressure (MPa gauge)	Sealant Condition		Wood Condition
						During Pressing	During Venting	
Single-probe Sample Holders	Rubber (5.6Nm)	2.5 x 2.5 x 7.6	R & T	690/ND	6.9	Leaked	ND [2]	Cracked
	Rubber (2.8Nm)	2.5 x 2.5 x 7.6	R & T	690/ND	6.5	Ok	ND [2]	Cracked
		2.5 x 2.5 x 7.6	R & T	690/ND	6.5	Leaked	ND [2]	Cracked
	Teflon (4.5Nm)	2.5 x 2.5 x 7.6	R & T	1,400/ND	6.5	Leaked	Leaked	Cracked
	Rubber (5.6Nm)	2.5 x 2.5 x 7.6	R & T	1,400/ND	6.5	Ok	Ok	End crushed
		2.5 x 2.5 x 7.6	R & T	690/830	8.3	Ok	Ok	Good
	Teflon (9.0Nm)	2.5 x 2.5 x 7.6	R & T	690/830	8.3	Ok	Ok	End crushed
	Rubber (5.1Nm)	2.5 x 2.5 x 7.6	R & T	970/35	10.3	Ok	Ok	Good
	Si RTV	2.5 x 2.5 x 7.6	R & T	690	13.8	Ok	Leaked	Good
		2.5 x 2.5 x 7.6	R & T	690	13.8	Ok	NA [3]	Ring separated
		2.5 x 2.5 x 7.6	R & T	345	10.3	Ok	Leaked	Good
		2.5 x 2.5 x 7.6	R & T	345	10.3	Ok	Leaked	Good
		2.5 x 2.5 x 7.6	R & T	2,800	16.5	Ok	Leaked	Cracked
		2.5 x 2.5 x 7.6	R & T	2,800	16.5	Ok	Leaked	Good
		2.5 x 2.5 x 7.6	R & T	2,800	16.5	Ok	Leaked	Collapsed (D) [4]
		2.5 x 2.5 x 7.6	R & T	2,800	16.5	Ok	Leaked	Cracked (D) [4]
		2.5 x 2.5 x 7.6	R	690	13.8	Ok	NA [3]	Collapsed (D) [4]
		2.5 x 2.5 x 7.6	R	690	13.8	Ok	NA [3]	Collapsed (D) [4]
Double-probe Sample Holders	Rubber gasket	5.1 x 5.1 x 7.6	R & T	2,800	16.5	Ok	Ok	Cracked
	Si RTV	6.0 x 6.0 x 8.0	R	690	13.8	Ok	NA [3]	Collapsed (D) [4]
		6.0 x 6.0 x 8.0	R	690	13.8	Ok	Leaked	Collapsed (D) [4]
		6.0 x 6.0 x 8.0	R	172	13.8	Ok	Leaked	Good (D) [4]

Appendix B (Continued)

Measurement Technique		Sample Preparation and Treatment Schedule				Results		
Pressure-probe Type	Sealant	Dimensions [radial x tang. x long.] (cm)	Flow Direction [1]	Rate of Pressing and/or Venting (kPa/min)	Maximum Pressure (MPa gauge)	Sealant Condition		Wood Condition
						During Pressing	During Venting	
0.3cm tube	Gluvit epoxy	5.1 x 5.1 x 7.6	R & T	970/35	10.3	Ok	Ok	Good
		2.5 x 2.5 x 7.6	R & T	4,300/1,300	9.0	Ok	Ok	Good
		2.5 x 2.5 x 7.6	R & T	6,900 / Instant [5]	14.5	Ok	NA [3]	Cracked
		5.1 x 5.1 x 7.6	R & T	6,900 / Instant [5]	14.5	Ok	NA [3]	Blew up
		3.0 x 3.0 x 8.0	R & T	Instant / 600	10.3	NA [3]	NA [3]	Collapsed
		3.0 x 3.0 x 8.0	R & T	Instant / 600	10.3	NA [3]	NA [3]	Collapsed
		3.0 x 3.0 x 8.0	R & T	2,300 / Instant [5]	12.4	Ok	NA [3]	Blew up
		3.0 x 3.0 x 8.0	R	2,300 / Instant [5]	12.4	Ok	NA [3]	Collapsed
		3.0 x 3.0 x 6.0	R	138	10.3	Ok	Ok	Good
		3.0 x 3.0 x 6.0	R	138	10.3	Ok	Ok	Good
		6.0 x 3.0 x 6.0	R	138	10.3	Ok	Ok	Good
		6.0 x 3.0 x 6.0	R	276	10.3	Ok	Ok	Good
		3.0 x 3.0 x 6.0	R	276	10.3	Ok	Ok	Good
		6.0 x 3.0 x 6.0	R	276	10.3	Ok	Ok	Good
2 - 0.3cm tubes		6.0 x 6.0 x 8.0	R & T	Instant / 660 [5]	11.7	NA [3]	NA [3]	Collapsed
		6.0 x 6.0 x 8.0	R	4,600 / Instant [5]	11.7	NA [3]	NA [3]	Collapsed
		6.0 x 6.0 x 8.0	R & T	1,200 / 430	13.0	Ok	Leaked	Collapsed
		6.0 x 6.0 x 8.0	R	345	13.1	ND [2]	ND [2]	Collapsed
		6.0 x 6.0 x 8.0	R	172	10.3	Ok	NA [3]	Collapsed (D) [4]

1 The flow of CO_2 treating medium was restricted to either the radial (R) or both radial and tangential (T) axes.
2 (ND) No data collected for this value.
3 (NA) Measurement not applicable.
4 (D) Dimples in end-grain.
5 (Instant) Nearly instantaneous rate of pressure change; greater than 20,000 kPa/min.