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Department of Materials Science and Engineering

THE COMPUTATIONAL MODELING OF SUPERCRITICAL CARBON DIOXIDE FLOW IN SOLID WOOD MATERIAL

A Dissertation in
Materials

by

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ABSTRACT

The use of supercritical carbon dioxide (SC CO$_2$) as a solvent to deliver chemicals to porous media has shown promise in various industries. Recently, efforts by the wood treating industry have been made to use SC CO$_2$ as a replacement to more traditional methods of chemical preservative delivery. Previous studies have shown that the SC CO$_2$ pressure treatment process is capable of impregnating solid wood materials with chemical preservatives, but concentration gradients of preservative often develop during treatment. Widespread application of the treatment process is unlikely unless the treatment inconsistencies can be improved for greater overall treating homogeneity.

The development of a computational flow model to accurately predict the internal pressure of CO$_2$ during treatment is integral to a more consistent treatment process. While similar models that attempt to describe the flow process have been proposed by Ward (1989) and Sahle-Demessie (1994), neither have been evaluated for accuracy. The present study was an evaluation of those models. More specifically, the present study evaluated the performance of a computational flow model, which was based on the viscous flow of compressible CO$_2$ as a single phase through a porous medium at the macroscopic scale. Flow model performance was evaluated through comparisons between predicted pressures that corresponded to internal pressure development measured with inserted sensor probes during treatment of specimens. Pressure measurements were applied through a technique developed by Schneider (2000), which utilizes epoxy-sealed stainless steel tubes that are inserted into the wood as pressure
probes. Two different wood species were investigated as treating specimens, Douglas-fir and shortleaf pine.

Evaluations of the computational flow model revealed that it is sensitive to input parameters that relate to both processing conditions and material properties, particularly treating temperature and wood permeability, respectively. This sensitivity requires that the input parameters, principally permeability, be relatively accurate to evaluate the appropriateness of the phenomenological relationships of the computational flow model. Providing this stipulation, it was observed that below the region of transition from CO$_2$ gas to supercritical fluid, the computational flow model has the potential to predict flow accurately. However, above the transition region, the model does not fully account for the physics of the flow process, resulting in prediction inaccuracy.

One potential cause for the loss of prediction accuracy in the supercritical region was attributed to a dynamic change in permeability that is likely caused by an interaction between the flowing SC CO$_2$ and the wood material. Furthermore, a hysteresis was observed between the pressurization and depressurization stages of treatment, which cannot be explained by the current flow model. If greater accuracy in the computational flow model is desired, a more complex approach to the model is necessary, which would include non-constant input parameters of temperature and permeability. Furthermore, the implications of a multi-scale methodology for the flow model were explored from a qualitative standpoint.
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<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>Area (cm$^2$)</td>
</tr>
<tr>
<td>$A$</td>
<td>Coefficient matrix that contains transmissibilities</td>
</tr>
<tr>
<td>$a$</td>
<td>Specific solid surface (cm$^{-1}$)</td>
</tr>
<tr>
<td>$a_n$</td>
<td>Constant for the MBWR EOS</td>
</tr>
<tr>
<td>$B_g$</td>
<td>Gas formation volume factor</td>
</tr>
<tr>
<td>$b$</td>
<td>Empirical correction value from Bramhall (1971) for non-Darcian flow</td>
</tr>
<tr>
<td>$C$</td>
<td>Concentration (mol/cm$^3$)</td>
</tr>
<tr>
<td>$C$</td>
<td>Center transmissibility term in SIP notation (cm$^3$/s·kPa)</td>
</tr>
<tr>
<td>$c$</td>
<td>Concentration of solute in a fluid phase (mol/cm$^3$)</td>
</tr>
<tr>
<td>$c^*$</td>
<td>Equilibrium concentration of solute in the solid phase (mol/cm$^3$ solid)</td>
</tr>
<tr>
<td>$c_s$</td>
<td>Concentration of solute in the solid phase (mol/cm$^3$ solid)</td>
</tr>
<tr>
<td>$D$</td>
<td>Cumulative diffusion coefficient (cm$^2$/s)</td>
</tr>
<tr>
<td>$D_g$</td>
<td>Diffusion coefficient through a gas (cm$^2$/s)</td>
</tr>
<tr>
<td>$E$</td>
<td>East transmissibility term in SIP notation (cm$^3$/s·kPa)</td>
</tr>
<tr>
<td>$G$</td>
<td>Constant part of the transmissibility term (cm$^3$/s·kPa)</td>
</tr>
<tr>
<td>$G'$</td>
<td>Specific gravity of an oven dry wood cell wall</td>
</tr>
<tr>
<td>$G_S$</td>
<td>Specific gravity of wood as a desired moisture content</td>
</tr>
<tr>
<td>$G_W$</td>
<td>Specific gravity of water</td>
</tr>
<tr>
<td>$h$</td>
<td>Equilibrium partition coefficient (dimensionless)</td>
</tr>
<tr>
<td>$i$</td>
<td>Grid block index ($0 \leq i \leq N_x$)</td>
</tr>
<tr>
<td>$J$</td>
<td>Mass transfer coefficient (mol/cm$^2$/s)</td>
</tr>
<tr>
<td>$j$</td>
<td>Grid block index ($0 \leq j \leq N_y$)</td>
</tr>
<tr>
<td>$k$</td>
<td>Specific Permeability (cm$^2$)</td>
</tr>
<tr>
<td>$k_g$</td>
<td>Superficial gas permeability (cm$^2$)</td>
</tr>
<tr>
<td>$k_f$</td>
<td>Mass transfer coefficient related to the fluid phase (cm/s)</td>
</tr>
<tr>
<td>$L$</td>
<td>Length (cm)</td>
</tr>
<tr>
<td>$L$</td>
<td>Lower diagonal matrix of A</td>
</tr>
<tr>
<td>$l$</td>
<td>Block number</td>
</tr>
</tbody>
</table>
\( \ell \)  Depth of penetration for Bramhall (1971) (cm)

M  Moisture content (%)

\( M_w \)  Molecular weight (g)

N  North transmissibility term in SIP notation (cm\(^3\)/s·kPa)

\( N_{x} \)  Number of grid blocks in the x direction

\( N_y \)  Number of grid blocks in the y direction

\( n_k \)  Number of iteration parameters

\( P, p \)  Pressure (kPa)

\( \bar{p} \)  Average pressure in a porous material in a differential flow test (kPa)

\( Q \)  Volumetric flow rate (cm\(^3\)/s)

\( Q \)  Source transmissibility term in SIP notation ()

\( q_m \)  Mass production rate (kg/s)

\( R \)  Gas constant (cm\(^3\)·Pa/K/mol)

\( R_o \)  Radius of pit openings (μm)

\( r \)  Residuals from Stone’s SIP

\( S \)  South transmissibility term in SIP notation ()

\( S_g \)  Gas saturation (dimensionless)

\( T \)  Temperature (K)

\( t \)  Time (s)

\( t' \)  Student’s t-test statistic

\( u_z \)  Superficial velocity in the void fraction (cm/s)

\( U \)  Upper diagonal matrix of A

\( u_{x,y} \)  velocity of the flowing fluid in the respective direction (cm/s)

\( V_b \)  Bulk volume of the control volume (cm\(^3\))

\( W \)  West transmissibility term in SIP notation (cm\(^3\)/s·kPa)

\( x \)  Position in radial direction (cm)

\( y \)  Position in tangential direction (cm)

\( Z \)  Gas compressibility factor (dimensionless)

\( z \)  Axial position for Lucas (2007a) mass transfer calculation (cm)
Greek Letters

\( \alpha \) Statistical significance
\( \alpha_c \) Volumetric conversion factor
\( \beta_c \) Transmissibility conversion factor ()
\( \Delta t \) Time step (s)
\( \Delta x \) Grid block spacing in the x direction (cm)
\( \Delta y \) Grid block spacing in the y direction (cm)
\( \delta \) Improvement vector for Stone’s SIP
\( \varepsilon \) Void fraction for Lucas (2007a) calculation (dimensionless)
\( \varepsilon \) Tolerance criteria for iteration error
\( \zeta \) Flow parameter for Sahle-Demissie (1995) model
\( \zeta \) Parameter to calculate viscosity from Jossi (1962)
\( \lambda \) Mean free path of a gas (μm)
\( \mu \) Viscosity (Pa·s)
\( \rho \) Density (kg/m\(^3\))
\( \rho_g \) Density of the fluid at pressure conditions (kg/m\(^3\))
\( \rho_{gsc} \) Density of the gas at standard conditions (kg/m\(^3\))
\( T \) Transmissibility term (cm\(^3\)/s·kPa)
\( \tau \) Tortuosity (dimensionless)
\( \upsilon \) Intermediate vector for Stone’s SIP
\( \phi \) Porosity (dimensionless)
\( \chi \) Porous media factor for diffusion (dimensionless)
\( \omega \) Stone’s iteration parameter (dimensionless)

Subscript Notations

\( c \) Critical Value
\( g \) Gas phase
\( i \) Grid block i
\( j \) Grid block j
\( l \) Length of the specimen (cm)
\( \text{max} \) Maximum value
\textit{min} \quad \text{Minimum value}

\textit{R} \quad \text{Reduced value}

\textit{sc} \quad \text{Standard conditions}

\textit{w} \quad \text{Width of the specimen (cm)}

\textbf{Superscript Notations}

\(\cdot\) \quad \text{Approximation}

\(k\) \quad \text{Previous iteration step}

\(k+1\) \quad \text{Current iteration step}

\(n\) \quad \text{Previous time step}

\(n+1\) \quad \text{Current time step}
The debt of gratitude that I feel toward the people and organizations who have made this work possible is overwhelming to me. First, I’d like to thank Dr. John Janowiak, The College of Agriculture at Penn State, and Dr. Jeff Morrell and Oregon State University for their financial support and assistance of this study. To Dr. Todd Shupe and Jay Carole, I owe many thanks for their efforts in harvesting and shipping me the shortleaf pine material that I used in this study. I’d like to thank Lee Stover for his advice and help in kiln drying that material. I’d also like to thank Camille Frietag at Oregon State University for her assistance in the permeability measurements. I owe a special thanks to Milo Clausen, the real-life “MacGyver” at Oregon State University. Without his expertise, there is no possible way I could have completed the experimentation phase of my research. I also would like to thank Milo for his wonderful hospitality while I was staying in Corvallis, the introduction to real IPAs, and an aerial view that I won’t soon forget.

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Chapter 1

Introduction

1.1 Motivation

Wood materials have long been used in exterior applications because of their ease of fabrication, low cost, and good strength to weight properties compared to other materials. The shortcoming of wood, for most timber species, is that in relation to other materials it is susceptible to environmental degradation from weathering and attack from insects and fungi. To reduce the problem of biological decay, the wood is frequently treated with chemical preservatives to extend the useful in-service lifetime. These protective preservatives are typically impregnated into the wood via a pressurization treatment process, using either water or oil as a solvent.

Pressurization processes vary depending on the chemical preservative, solvent, and amount of preservative loading, but the most widely used processes have similar characteristics. A vacuum may or may not be applied to the beginning and end of the process, while applied positive pressures reach approximately 1034 kPa for several hours for successful chemical impregnation (i.e. retention level and required depth of penetration). While more advanced processing has lead to increased pressure and shorter run times, no phase changes occur. Over 100 years of wood preservation treatment technology in this regard has lead to a general understanding of the liquid flow process that allows the industry to treat wood consistently to what is required.
The wood treating industry is facing new challenges, including the desire to move away from oil-based and metal ion preservatives to organic-based biocides due to environmental and human health concerns (Evans, 2003). Furthermore, the industry is continually searching for improvements to treat wood more effectively, particularly those species of wood that are difficult to treat, known as refractory species. One option that has the potential for significant technological innovations is supercritical fluid treatment (Freeman, et al., 2003).

Supercritical fluid treatment, particularly supercritical carbon dioxide (SC CO$_2$), varies in comparison to standard treating techniques primarily by the fact that the solvent is compressible and not in a pure liquid form, resulting in a fluid that permeates the wood substrate more easily. The SC CO$_2$ treatment process is more dynamic and the guiding physicochemical phenomena much more complex in comparison to traditional liquid phase solvent delivery treatment processes. The solubility of preservative is highly dependent on temperature and pressure, particularly close to the critical point, where CO$_2$ begins to change phase from a gas to a supercritical fluid. Consequently, the fundamental understanding of the flow dynamics and the chemical deposition mechanism is limited. The lack of understanding is highlighted by fact that while wood materials have been successfully impregnated with preservatives during the SC CO$_2$ process, concentration gradients are typical. Concentration gradients are undesirable because too much preservative leads to inefficient treatment while too little preservative could lead to poor decay resistance from low or less than homogeneous biocide retention. In fact, Kjellow and Henrikson (2009) published a comprehensive review of the state of the art on the SC CO$_2$ impregnation process of wood materials. The article stated “… one of the
main future challenges for researchers within this field will be to reduce the observed concentration gradients in impregnated wood.”

The most straightforward approach to solve this problem is through computational modeling. To date, relatively limited efforts have been dedicated to modeling efforts attempting to describe the deposition of chemicals during the supercritical CO\textsubscript{2} treatment process. Sahle-Demessie (1994) and associates (1995) developed an impregnation model based on compressible viscous flow of CO\textsubscript{2}, but concentration gradients were unaccounted for in model predictions. The authors concluded that the model needed refinement, primarily because it did not include the mass transfer of chemicals from the flowing CO\textsubscript{2} to the wood substrate. Alternatively, Lucas et al. (2007a)(2007b) developed a model to predict the impregnation process that was primarily based on mass transfer. While the model was successful in predicting total retention of chemical preservative, the issue of concentration gradients was not covered. Clearly, if the issue of concentration gradients is to be resolved, further investigation is required.

The conclusions of Sahle-Demessie et al.(1995) and Lucas et al. (2007a)(2007b) suggest that the impregnation of wood materials with chemical preservatives via SC CO\textsubscript{2} occurs through multiple mechanisms, thus a more refined investigation of impregnation behavior is necessary to improve prediction performance. One aspect of modeling the impregnation process that is of critical importance is the accurate prediction of CO\textsubscript{2} pressure within the material during the treatment cycle. Both ease of flow and chemical loading are affected by pressure, since viscosity and solute, i.e. preservative, solubility are dependent on pressure. Furthermore, it is currently unclear how the movement of preservative relates to that of CO\textsubscript{2}. Once an understanding of CO\textsubscript{2} movement is
ascertained, a baseline will be established by which the movement of chemical preservatives may be compared.

The movement of SC CO$_2$ in solid wood materials has been described through the modeling efforts of Ward (1989) and Sahle-Demessie (1994). In both cases, the model was based on the viscous flow phenomena of a fluid through a porous medium. Ward proposed the theoretical principle of the model, but did not develop it computationally so it could not be used to make pressure predictions. Sahle-Demessie developed a computational pressure model which was coupled with a solubility model to predict the deposition of preservative chemicals. Although the deposition model predictions were compared to experimentally measured retentions, no attempt was made to experimentally validate the predictions of the pressure flow model. No experimental technique existed to measure the internal pressure development during supercritical treatment. Consequently, the accuracy of the pressure flow model is unknown.

A technique was developed by Schneider (2000), which successfully utilized stainless steel tubes to measure the internal pressure development during treatment at isolated locations. A computational flow model could then be evaluated through comparisons between pressure predictions of the flow model and pressures measured by inserted probes at specific locations.

1.2 Objectives

In the current field of wood treatment by supercritical carbon dioxide impregnation, a theoretical conceptualization of the flowing gas has been proposed, but
experimental verification of the theory is absent. The current study aims to verify that a flow model based on the compressible flow of a viscous fluid through a porous body is an accurate depiction of the movement of supercritical carbon dioxide in solid wood materials. The specific goals of the proposed research are as follows:

1. To verify the computational model though comparisons between the predicted pressure and the pressure measured experimentally.
2. To identify the source of potential variation between the proposed computational flow model and experimentally measured results.

Successful execution of these objectives will connect the theoretical conceptualization of the internal flow of supercritical carbon dioxide in wood materials with the experimental technique that has been developed to measure the flow phenomena. This will provide an opportunity for the scientific community to assess the applicability of the computational flow model and determine if a more rigorous model is required.

1.3 Summary of Chapters

The thesis starts with a background study in Chapter 2 that reviews the state of the art of SC CO₂ treatment of wood materials. A review of modeling internal pressure of wood materials during treatment is presented, in addition to a summary of the treatment studies performed to date. In Chapter 3, the theory of the proposed computational flow model is fully described. The model theory is similar to previous models in that it is based on the viscous flow of a compressible fluid through a porous medium, but in the
present case the model is developed through theory of the petroleum and natural gas industry, which is well established in modeling the flow of fluids through porous media (Ertekin, et al., 2001) (Aziz, 1979). In Chapter 4, a description of the experimental study in relation to the thesis objectives is provided in depth. The results of the experimentation are presented in Chapter 5, in addition to comparisons between the predicted pressure values calculated by the flow model and those values measured experimentally. Chapter 6 analyzes the performance of the computational flow model and provides insight into the disparity between the model and experimental values. In the final chapter, Chapter 7, the key findings of the study are summarized and recommendations for further study are offered.
Chapter 2

Literature Review

2.1 Introduction of Supercritical Fluids (SCFs)

SCFs can be defined as a substance that is above its critical pressure ($P_c$) and temperature ($T_c$) (Clifford, 1999). Others consider this definition inaccurate and expand the definition to any substance, the temperature and pressure of which are higher than their critical values, and which has a density close or higher than its critical density (Darr, et al., 1999). This definition is generally useful for classification purposes, but gives little insight to the physical nature of a SCF. Phase diagrams are very useful for conceptualizing what a SCF is. Figure 2-1 shows the phase diagram for carbon dioxide in two different forms. Figure 2-1A is in the standard pressure-temperature form, with a series of iso-densities included to show the wide range of densities that exist in the supercritical condition. In Figure 2-1B, the density-pressure phase diagram accentuates the dependence of temperature and pressure on density. With each isotherm, there is a region where a slight change in pressure will result in a large change in density. These drastic changes in the density and energy of the fluid occur due to complex molecular interactions that do not follow a classical understanding (Arai, et al., 2002). Because of this complexity, an extensive amount of research has been performed in order to understand the nature of SCFs so their properties can be manipulated to suit a desired application.
Figure 2-1: Phase diagrams (A) P-T and (B) Density-P for carbon dioxide. In Figure A, various densities are depicted in g/L. Figures adapted from (Mukhopadhyay, 2000) and (Dean, 1993), respectively.
2.2 Properties of Supercritical Fluids

SCFs are versatile, as properties such as density and viscosity may be adjusted radically by slight changes in temperature and pressure near the critical region (Noryori, 1999). These drastic changes can also be used to change chemical reactivity to achieve a desired rate of reaction for a process (Brennecke, et al., 1999). Overall, SCFs possess lower density, viscosity, and higher diffusivity than liquids, while possessing a higher dissolving capability than gases. In fact, research has shown that SCFs move through porous materials at rates comparable to gases (Brogle, 1982)(Filippi, 1982). The combination of properties for a SCF (SC CO\textsubscript{2}) serves to provide an exceptional solvent and an ideal fluid for a variety of applications. While the unique properties of SCFs have enabled their use in a wide variety of industrial applications, this study focuses on supercritical carbon dioxide and its modeling relative to wood materials.

Supercritical carbon dioxide (SC CO\textsubscript{2}), in particular, has gained much attention as a potential solvent that delivers a dissolved chemical or extracts a desired component of a solid matrix. SC CO\textsubscript{2} has advantages over other substances in that it is relatively inexpensive, non-toxic, and its critical parameters are relatively low, with a P\textsubscript{c} (7.39 MPa) and T\textsubscript{c} (304 K), which reduces processing difficulties over other SCFs (Wang, et al., 2003). Several investigators have written reviews on the numerous applications of SC CO\textsubscript{2} that range from chromatography, to reaction mediums and transport applications, relating to a variety of materials, such as polymers and inorganic materials (Darr, et al., 1999) (Beckman, 2004) (Kendall, et al., 1999). Investigations with SC CO\textsubscript{2} extend to
materials as far-reaching as pharmaceuticals to aquatic plants (Cui, et al., 2001) (Wang, et al., 1996), and more recently microelectronics (XiaoGang, et al., 2007).

2.3 Supercritical Carbon Dioxide Applications in Wood Products

Interest in the processing of wood products with SC CO₂ has increased significantly, primarily in the areas of chemical extraction and preservative treatment impregnation. An extensive review of the state of the art has been performed by Kjellow and Henrikson (2009), which includes the effect of the impregnation process on dimensional stability and mechanical properties on both solid wood and wood composites. Biocide deposition, retention, and deposition was also reviewed, as well as the decay resistance performance of SC CO₂-treated wood materials and modeling efforts. Because the present study focuses on understanding the flow transport process of SC CO₂, this section will highlight work on more general wood product applications. A discussion of relevant research of flow modeling in wood materials is covered separately in Section 2.5.

Because the treatment process occurs at high pressures and temperatures, physical and chemical changes to wood material during treatment were considered as a potential risk to material stability and performance. Therefore, several investigations were performed to determine the potential of such occurrences. Li and Kiran (1988) revealed that the components of the treatment fluid determine if any chemical reaction occurs between the fluid and the constituents of the wood (red spruce, sugar maple, and white pine), particularly in regard to CO₂. The results indicated that interactions with SC CO₂
were non-reactive in the case of pure CO$_2$, but mixtures of CO$_2$ and water could lead to
dissolution of primarily carbohydrate fractions of wood. The dissolution was reduced
when the mole fraction of carbon dioxide was much greater than water, suggesting that
wood moisture content could be an important consideration from an ultrastructure
perspective when treating wood materials with SC CO$_2$.

Furthermore, research has been performed to investigate the effect of the SC CO$_2$
treatment process on the dimensional stability of wood products (Kim, et al., 2000)
(Oberdorfer, et al., 2004) (Drescher, et al., 2006). Depending on the treatability of the
material (i.e. the resistance of fluid flow through the material) and the rate of pressure
change during treatment, high pressure gradients between the vessel and the internal void
space within the wood material may form, causing internal stresses. As expected,
refractory wood species are particularly susceptible to high pressure gradients since their
permeability values are lower, resulting in higher pressure gradients. If the pressure
gradients exceed the strength properties of the wood, temporary or permanent
deformation of the material may occur.

The effects of SC CO$_2$ treatment on the mechanical performance of wood
materials have also been thoroughly investigated and the results of these studies are
summarized in Table 2-1. Some agreement exists between the studies that investigated
the same wood species, where Douglas-fir and white spruce did not experience a
reduction in properties, while western red-cedar exhibited a significant loss in modulus of
elasticity (MOE) in two studies. In general, the results support the aforementioned
conclusion that processing
Table 2-1: Studies that investigated a variety of SC CO₂ processing variables and their effect on mechanical properties of several wood species in solid form.

<table>
<thead>
<tr>
<th>Study</th>
<th>Species or wood material</th>
<th>Dimension (mm)</th>
<th>T (°C)</th>
<th>Pressure Rate (MPa/min) [Max. P]</th>
<th>Treat Time (hr)</th>
<th>Test Properties*</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Smith, et al., 1993)</td>
<td>Ponderosa pine</td>
<td>2.4x2.4x54</td>
<td>80</td>
<td>13.8 [27.6]</td>
<td>2</td>
<td>None None N/A</td>
</tr>
<tr>
<td>(Smith, et al., 1993)</td>
<td>White spruce</td>
<td>2.4x2.4x54</td>
<td>80</td>
<td>13.8 [27.6]</td>
<td>2</td>
<td>None None N/A</td>
</tr>
<tr>
<td>(Kim, et al., 1997)</td>
<td>Southern pine</td>
<td>19x19x510</td>
<td>50</td>
<td>N/A [12.4-24.8]</td>
<td>0.5</td>
<td>Some N/A None</td>
</tr>
<tr>
<td>(Acda, et al., 2001)</td>
<td>Douglas-fir</td>
<td>25x25x503</td>
<td>60</td>
<td>1.24 [12.4, 24.8, 31.1]</td>
<td>0.5-1</td>
<td>None None N/A</td>
</tr>
<tr>
<td></td>
<td>White oak</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>None None N/A</td>
</tr>
<tr>
<td></td>
<td>Red alder</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>None None N/A</td>
</tr>
<tr>
<td></td>
<td>Western red-cedar</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>None None N/A</td>
</tr>
<tr>
<td></td>
<td>White spruce</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>None None N/A</td>
</tr>
<tr>
<td>(Muin, et al., 2003)</td>
<td>Japanese red pine</td>
<td>15x15x120</td>
<td>50</td>
<td>N/A [9.81]</td>
<td>0.5</td>
<td>None None N/A</td>
</tr>
<tr>
<td></td>
<td>Cryptomeria</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>None None N/A</td>
</tr>
<tr>
<td></td>
<td>Japanese Larch</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>None None N/A</td>
</tr>
<tr>
<td></td>
<td>Particleboard</td>
<td>30x210x~15</td>
<td>50</td>
<td>N/A [9.81]</td>
<td>0.5</td>
<td>None None N/A</td>
</tr>
<tr>
<td></td>
<td>OSB (oriented strand board)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>None None N/A</td>
</tr>
<tr>
<td></td>
<td>MDF (medium density fiberboard)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>None None N/A</td>
</tr>
<tr>
<td></td>
<td>Softwood plywood</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>None None N/A</td>
</tr>
<tr>
<td></td>
<td>Hardwood plywood</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>None None N/A</td>
</tr>
<tr>
<td>(Anderson, et al., 2000)</td>
<td>Douglas-fir</td>
<td>38x38x585</td>
<td>60</td>
<td>0.34, 3.44 [10.34, 20.69]</td>
<td>0.5</td>
<td>None None None</td>
</tr>
<tr>
<td></td>
<td>Yellow-poplar</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>None None None</td>
</tr>
<tr>
<td></td>
<td>Western red-cedar</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>None None None</td>
</tr>
<tr>
<td></td>
<td>Engelman spruce</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>None None None</td>
</tr>
<tr>
<td>(Acda, et al., 1997a)</td>
<td>Particleboard</td>
<td>38x150x~25.4</td>
<td>45-60</td>
<td>2.1-4.2 [12.4, 24.8, 31.0]</td>
<td>0.08, 0.25, 0.5</td>
<td>None None N/A</td>
</tr>
<tr>
<td></td>
<td>Flakeboard</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>None None N/A</td>
</tr>
<tr>
<td></td>
<td>MDF</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>None None N/A</td>
</tr>
</tbody>
</table>

* MOR = Modulus of rupture  
  MOE = Modulus of elasticity  
  WML = Work at maximum load  
  None = No change in performance with respect to tested mechanical property  
  Some = some loss of properties, but not statistically significant  
  Sig = Statistically significant change in property
conditions that produce high pressure gradients can lead to damage that is reflected by a loss of mechanical performance. These conditions are low permeability wood species and fast changes in treatment pressure, with specimens large enough that a sufficient length of materials exists to develop a pressure gradient. For tested composite materials (Muin, et al., 2003) (Muin, et al., 2004)(Muin, et al., 2003), OSB exhibited the greatest reduction in properties from treatment. The reduction was attributed to the specific orientation of the composite, where the glue lines acted as pressure barriers that could cause large pressure gradients. Temperature, absolute pressure, and treatment duration do not appear to have a significant effect on mechanical properties. As the mechanism of the pressure profile development is better understood, any deformation and subsequent deterioration of mechanical properties can be completely averted or limited so that a noticeable reduction in properties might be controlled during the treatment process.

2.3.1 Impregnation of Wood Products Using Supercritical Carbon Dioxide

The major potential application of SC CO₂ in wood is the impregnation of various chemical preservatives (biocides) and fire retardant compounds. Traditionally, this process involves a pressurization and vacuum cycle and requires a liquid solvent, typically water or a petroleum type of carrier. The sludge created from this process can be a potential health hazard and creates many problems for wood treaters; thus, alternative solvents such as SCFs are being explored. SCFs such as CO₂ eliminate the problem of traditional solvents, as the preservatives can be precipitated and recycled from the CO₂ through depressurization of the system. Furthermore, the CO₂ collected from the
process is recyclable, reducing the waste disposal issue associated with spent organic solvents.

The aforementioned properties of SCFs like CO$_2$, primarily high diffusivity in solids, make SCFs an attractive option for impregnating refractory wood species and sections of heartwood that are generally untreatable with traditional solvents. For the most part, heartwood contains aspirated, or closed, pits that prevent flow through adjacent wood cells. The flow properties of SCFs help to overcome this barrier. In addition, research has shown that SC CO$_2$ helps to dissolve some of the extractives found in wood (Sahle-Demessie, et al., 1995). These extractives can agglomerate in pits thereby clogging them. Consequently, the SC CO$_2$ helps to unclog the pits to promote flow through wood by increasing permeability.

Several patents have been established for the SC CO$_2$ impregnation process of wood materials, including the impregnation of polymers (Sunol, 1991) and biocides (Ito, et al., 1984) (Kayihan, 1992) (Qader, 2003) (Henrikson, 2003) (Henrikson, et al., 2010). Furthermore, research has shown that impregnation of preservatives with SC CO$_2$ can be highly effective. Morrell et al. (1993) investigated the impregnation of wood preservatives with SC CO$_2$ and showed that SCF impregnation can successfully treat Douglas-fir heartwood. The discovery is a significant one considering that the species is generally resistant to other fluid treatments. Later work by Acda et al. (2001) revealed that SCF impregnation could be used effectively on a variety of wood species. In the study, Douglas-fir, western red cedar, red alder, white spruce, and white oak were all impregnated with tebuconazole, a biocide, to a satisfactory level capable of deterring fungal and insect attack. Cookson et al. (2009) recently reported the successful treatment
of several species (Australian oak heartwood and Radiata pine) against termite attack using SC CO₂ treatment. Australian oak is of particular interest because it has been known to be very difficult to treat with conventional methods.

Research has also been performed to explore how processing conditions affect the amount and chemical distribution of wood preservatives delivered during SC CO₂ treatment, since these factors are paramount in the advancement of the technology for preservation purposes. The delivery of the proper amount of preservative is necessary for treating wood materials in accordance with their in-service application, but it is undesirable to overload a specimen because of the loss of resources. Furthermore, the proper distribution of preservative is necessary to ensure that the entire specimen is protected from decay, or that concentration gradients are not produced beyond a desirable level.

A summary of the studies performed to investigate these factors is presented in Table 2-2. The table highlights the complex nature of the impregnation process, as studies show little absolute agreement in trends concerning preservative distribution and retention, although with increasing time, retention generally increases and concentration gradients of preservative are reduced. Pressure and temperature conditions have mixed results throughout the studies, showing increases that resulted in both improvement and worsening in retention and distribution. While an explanation for the varied results has not been clearly defined, the variability in chemical retention has been attributed to two major issues: the lack of understanding of the solvation of the preservative at supercritical conditions, and poor understanding the flow mechanisms.
Table 2-2: Studies that investigated a variety of SC CO₂ processing variables and their effect on the amount and distribution of preservative deposited during treatment. Studies are at conditions where the CO₂ was saturated with preservative.

<table>
<thead>
<tr>
<th>Experimental Study</th>
<th>Species or wood-based composite material</th>
<th>Preservative (Biocide)</th>
<th>Dimension (mm)</th>
<th>T (°C)</th>
<th>Pressure Rate (MPa/min) [Max. P]</th>
<th>Treat Time (hr)</th>
<th>General Observations</th>
</tr>
</thead>
</table>
| (Sahle-Demessie, et al., 1995) | Douglas-fir | TCMTB* | 30x30x100 | 50 | N/A [14.0-27.0] | 0.5-1.5 | • Concentration gradients were reduced with increased time and pressure  
• Retention increased with pressure  
• Retention increased with time |
| (Acda, et al., 1997) | Plywood  
Particleboard  
Flakeboard  
MDF | Tebuconazole w/ methanol | 38x15x500  
38x13x500  
38x10x500  
38x13x500 | 45-75 | 2.1-4.2 [12.4-31.0] | 0.08–0.05 | • Retention was a maximum at mid-range pressure  
• Retention decreased with increasing temperature  
• Retention increased with time  
• Distribution was adequate for all conditions |
White oak  
Red alder  
Western red-cedar  
White spruce | Tebuconazole w/ methanol | 25x25x503 | 60 | 1.24 [12.4, 24.8, 31.1] | 0.5-1 | • Retention increased with pressure  
• Concentration gradients increased with pressure  
• Time had no effect on retention |
| (Muin, et al., 2004) | MDF  
Hardwood plywood  
Softwood plywood  
Particleboard  
OSB | Silafluofen w/ ethanol | 30x210x~15 | 35-55 | N/A [7.85-11.77] | 0.5 | • Temperature and pressure results depended on composite type  
• Composite type effected concentration gradient much more than processing conditions |

*TCMTB = 2-(Thiocyanomethylthio)benzothiazole
Table 2-2 Continued: Experimental study conditions are below the saturation of the CO$_2$ with preservative.

<table>
<thead>
<tr>
<th>Study</th>
<th>Species or wood material</th>
<th>Preservative (Biocide)</th>
<th>Dimension (mm)</th>
<th>T ($^\circ$C)</th>
<th>Pressure Rate (MPa/min) [Max. P]</th>
<th>Treat Time (hr)</th>
<th>General Observations</th>
</tr>
</thead>
</table>
| (Kang, et al., 2003) Temperature drop method | Douglas-fir | Cyproconazole w/ methanol | 20x20x100 40x40x100 90x90x100 | 40 | 0.4/min | Below $P_c$ (0.4) [10.3] | 0.5-3.0 | • Higher retention for largest sample  
• Longer treatment time did not affect retention |
| (Kang, et al., 2005) Temperature and pressure drop method | Ponderosa pine | Cyproconazole w/ methanol | 10x100x300 | 40 | 0.4/min | Pressure Drop (0.866) Temp Drop (0.086) Below $P_c$ (0.4) [10.3] | 1 | • Retention variability increased as retention increased  
• Temp Drop method increased retention  
• Temp Drop method reduced retention variability |
| (Kang, et al., 2006) Temperature drop method | Douglas-fir | Cyproconazole w/ methanol | 20x20x100 40x40x100 90x90x100 | 40 | 0.4/min | Below $P_c$ (0.4) [10.3] | 0.5-12.0 | • Higher retention for largest sample  
• Largest specimens exhibited largest gradients  
• Longest time reduced gradient |
| (Kang, et al., 2006) Temperature drop method | Ponderosa pine | Cyproconazole w/ methanol | 10x100x300 | 40, 60 | Below $P_c$ (0.4) [10.3, 20.6] | 1 | • Low temp and pressure yielded highest retention  
• Mixed results, at low pressure retention decreased with increased temp, but no change at high pressure  
• At low temp, retention decreased with increased pressure, at high temp, retention increased with pressure |
Several processing variations have been shown to improve the impregnation process. One improvement involves the transition from supercritical to subcritical conditions at the end of the treatment process. Initially, pressure was the main parameter used, but research by Kang et al. (2005) showed that reducing temperature and not pressure resulted in better impregnation. It should be noted that the reduction in temperature was not isobaric, so a subsequent loss in pressure occurred as well, but this pressure loss was slower (0.866 MPa/min) versus the slowest venting process performed by Acda (2001) at (1.2 MPa/min). Furthermore, the opposite was true for the studies that used a pressure drop, i.e. the process was not isothermal, so temperature did decrease in addition to pressure. Studies were also performed at conditions where the CO$_2$ solution was saturated and unsaturated. In general, working with sub-saturated biocide conditions resulted in a more predictable impregnation process. The reason for this occurrence is that at less than saturated conditions, the amount of preservative in solution does not change based on conditions, where at saturated conditions, the amount of preservative changes because the solubility changes with conditions (Kang, et al., 2006).

Recent work by Lucas et al. (2007a) has suggested that the impregnation and deposition of preservatives can be explained through alternative mechanisms. Instead of using a retort or immersion treatment vessel where the specimen is surrounded by the treatment fluid, Lucas devised a differential vessel that allowed for flow through the material from one end to the other. For this system, the best description is a mass transport process that involves the adsorption of preservative to the wood matrix. In this way, the process is defined by a mass transfer and partition coefficient, which describe the movement of preservative and its interaction with the wood, respectively.
SC CO$_2$ impregnation applied to wood-based composites added more difficulty in understanding the impregnation process, and generally appeared to affect impregnation more than processing parameters. The studies investigated the feasibility and applicability of several preservatives (3-iodo-2-propynyl butylcarbamate (IPBC) and silafluofen) on various types of wood-based composites, including medium density fiberboard (MDF), hardwood plywood, softwood plywood, particleboard, and oriented strand board (OSB). Results of the studies varied, depending on treatment condition and type of composite, but in most cases impregnation was successful to the point that a sufficient amount of preservative was delivered to ensure protection. The most effective conditions were reported to be around the critical point.

Overall, the results of the impregnation studies indicate that SCF impregnation may be successfully applied to a variety of wood species and wood materials, which could make it an attractive option to wood treaters. Two studies in particular, Acda et al. (2001) and Muin and Tsunoda (2004) noted that much development is needed before SC CO$_2$ impregnation is ready for industry use, considering that many inefficiencies exist, such as overloading of preservatives and high retention gradients. To resolve these issues, a variety of information is required, leading to studies such as the investigation of solubility characteristics of preservatives in SC CO$_2$ (Hassan, et al., 2001) (Cookson, et al., 2009). Solubility attributes in combination with an accurate understanding of pressure profile development would lead to much more efficient SC CO$_2$ treatment of wood materials, but this cannot be attained until fluid flow phenomena are better understood.
2.3.2 SC CO₂ Extraction of Chemicals from Wood Products

SC CO₂ has been investigated as an extraction method to remove substances from solid and liquid materials (Wai, et al., 1997). The removal technique, known as supercritical fluid extraction (SFE), involves the use of a supercritical fluid as a solvent, which dissolves an acid or other agent capable of extracting a desired compound from a solid matrix. SFE developed over the past few decades in response to environmental regulations and waste disposal costs of organic solvents (Wai, et al., 1998). This process is of noteworthy interest to the wood products industry considering new environmental regulations and health concerns regarding wood preservatives, particularly copper-chromium-arsenate (CCA). According to several researchers, the large amount of CCA-treated materials entering the waste stream is cause for concern, and methods to reduce and/or eliminate the potentially hazardous metal ions from contaminating soil and ground water have been and are being explored (Kartal, 2003) (Clausen, 2000) (Ribeiro, et al., 2000) (Burgstaller, et al., 1993).

The effectiveness of SFE using SC CO₂ on organic preservatives such as pentachlorophenol, polychlorinated dibenzo-p-dioxins, and polychlorinated dibenzofurans has been investigated by Ruddick and Cui (1995) and (Sahle-Demessie, et al., 1997), and a patent for the process exists (Levien, et al., 1994). Moreover, several investigations have been performed to measure the effectiveness of SFE as a remediation technique for CCA-treated wood products. Research by Wang et al., El-Fatah et al., and Takeshita et al. revealed successful extraction of CCA treated wood products to varying extents (Wang, et al., 2003) (El-Fatah, et al., 2004) (Takeshita, et al., 2000). Extent of
extraction for these studies depended on a number of process parameters including
temperature, pressure, and number of extractions, and type of extraction acid. In general,
copper was the easiest to extract, followed by arsenic and then chromium. A summary of
the optimal results of the studies appears in Table 2-3.

Table 2-3: Summary of SFE studies performed on CCA-treated wood products.

<table>
<thead>
<tr>
<th>Research Study</th>
<th>Extraction %</th>
<th>Cu</th>
<th>As</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Wang, et al., 2003)</td>
<td>64</td>
<td>31</td>
<td>29</td>
<td></td>
</tr>
<tr>
<td>(El-Fatah, et al., 2004)</td>
<td>80</td>
<td>20</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>(Takeshita, et al., 2000)</td>
<td>89</td>
<td>N/A</td>
<td>N/A</td>
<td></td>
</tr>
</tbody>
</table>

In addition to the aforementioned elements, SFE of manganese from wood fibers has also
been investigated to remove transition metal elements that hinder the pulping process for paper production (Al-Jabari, 2004).

Other studies have shown that SFE may be applied to extract natural components of wood, such as extractives and lignin. Ritter and Campbell revealed that SC CO₂
removes extractives from both wood and bark of southern and ponderosa pine (Ritter, et
al., 1991). Two other studies, performed by Goto et al.(1990) and Maiti and Whitmire
(1999), successfully extracted lignin from wood fibers through the SFE process.

Presently, SFE of wood materials has been limited to either sawdust or very small pieces of material. With regard to the delignification of wood, the reduction of wood to particle form is advantageous since the wood fiber is the desired raw material.
Conversely, for the other extraction processes, the reduction of wood to sawdust severely
limits their application after extraction. Processing solid wood to particle form is particularly detrimental for the CCA-treated products, as one goal of the extraction process would be to reuse the lumber in structural applications after extraction. The potential for such a process may exist, as a patent by Henrikson (2003) demonstrated that it is possible to effectively extract soluble extractive components from solid wood, such as tannins in oak. However, the extraction behavior of a fixated preservative compared to that of an extractive compound such as tannin is currently unknown, so it is uncertain if SFE of preservatives is.

2.4 Fluid Flow in Wood

From a historical perspective, the flow of fluids in wood has been a significant topic of research and discussion in the wood science community. In particular, water movement in wood influences a variety of processes ranging from the commercial drying (controlled moisture reduction) of wood products to the delivery of wood preservatives. The understanding of how water moves through wood has allowed manufacturers to optimize processing conditions for quality assurance, maximize product output, and minimize energy input. Correspondingly, once the mechanism of flow for SCFs in wood is understood, the knowledge may be applied to achieve results similar to those regarding the flow of water in wood. The mechanism of flow in wood, diffusion and dynamic flow, are dependent on environmental conditions, while the ultrastructure of the wood species can influence the speed at which flow occurs for a given set of environmental conditions.
2.4.1 Softwood Macro Structure Influences on Flow Behavior

The structure of softwoods and how it relates to fluid flow is reasonably well understood despite their complex nature. In general, softwoods are used for structural applications in temperate climates and are thereby treated with preservatives more often than hardwoods, which make them the focus of the present study.

When analyzing the structure of wood, three principal directions must be considered: longitudinal, radial, and tangential. The longitudinal direction is also the vertical (axial) direction of the tree stem. The radial direction is horizontally oriented from the pith of the tree stem to the outer bark layer, and the tangential direction is also in the horizontal plane, but oriented perpendicularly to the radial direction. The vast majority of wood material is manufactured with the length cut along the longitudinal direction, which leaves the width and thickness of the specimen oriented in the radial and tangential direction (see Figure 2-2). Because of this orientation, the tangential and radial directions are more important for fluid flow considerations relative to complete sectional treatment. The width or thickness may be oriented directly in the radial or tangential direction, but the more common case is an orientation between the two directions, as illustrated in Figure 2-2.

The structure of softwood is composed of many cellular constituents, the majority of which are hollow, tube-like cells called longitudinal tracheids. The vast remainder of cellular composition is horizontally arranged cells called ray parenchyma and tracheids and resin canal wood tissue. The primary functions of tracheids are for fluid movement
Figure 2-2: Principal directions of a representative wood stem and their typical orthogonal orientation in a cut section of wood.
and structural support, whereas parenchyma exist mainly for food storage, but flow does occur in these cells to a lesser extent. Resin canals are not supportive cells but intra-cellular tissues surrounded by epithelial cells, and are typically filled with high molecular weight substances known as extractives. Figure 2-3 depicts the typical ultrastructure relative to a softwood material, while a brief summary of wood tissue dimensions for both shortleaf pine and Douglas fir are presented in Table 2-4.

### Table 2-4: Typical dimensions of prominent wood tissue cells found in both shortleaf pine and Douglas-fir (Panshin, et al., 1980).

<table>
<thead>
<tr>
<th></th>
<th>shortleaf pine</th>
<th>Douglas-fir</th>
</tr>
</thead>
</table>
| Longitudinal tracheid tangential diameter | Max.: 60 μm  
Avg: 35-45 μm | Max.: 55 μm  
Avg: 35-45 μm |
| Longitudinal tracheid length      | 4.64 ± 0.92 mm | 3.32 ± 0.39 mm |
| Longitudinal canal diameter      | Max.:180 μm  
Avg: 90-150 μm | Max.:150 μm  
Avg: 60-90 μm |
| Transverse canal diameter       | Avg: 70 μm    | Avg: 25 μm    |

Fluid movement in softwoods occurs primarily in the longitudinal direction through the cell lumen of the tracheids. The lumen diameter of softwood tracheids is on the scale of tens of micrometers, which varies from earlywood (fast growth) and latewood (slow growth), as latewood cell walls can be much thicker in composition and have reduced lumen diameter compared to earlywood (Panshin, et al., 1980).

Flow in the horizontal directions occurs to a lesser extent through the horizontally positioned cells and inter-cellular paired openings called pits (Siau, 1984). While three types of pit pairs are present (bordered, half-bordered, and simple), the pair recognized as most influential to flow is the bordered pair (Petty, 1972). Bordered pit pairs are found
Figure 2-3: Representation of softwood cellular arrangement. The major components are longitudinal tracheids (I), rays (11, 12), and resin canals (x), and pits (radial S) (tangential H). Adapted from Siau (1984)
between adjacent tracheids. A diagram of a bordered pit pair is shown in Figure 2-4.

The most important aspect of bordered pit morphology is the pit membrane, which is composed of the torus and margo. The margo is strand-like in nature and permeable, where the torus is almost always solid and impermeable. As a result, if the pit membrane is located in the center of the pit chamber, fluid flow is possible; but a situation called pit aspiration may occur in which the membrane is stretched to contact the pit chamber, effectively aspirating (i.e. closing) the pit aperture with the margo (see Figure 2-4).

Furthermore, the pit membrane may become encrusted with other wood substances and block flow through the pit. Both pit aspiration and encrustation is more prevalent in heartwood than sapwood, which is why it is typically less permeable (Panshin, et al., 1980).

It is not fully understood what dimensions of the pit are most influential to flow, so it is typical to measure pits as having an effective diameter, which is in the range of 0.02-8 µm (Siau, 1984). The overall diameter of pits varies in earlywood or latewood, as earlywood pits are larger and more abundant than in latewood (Petty, 1972). Pits are generally in greater number and size on the radial surface, so flow between tracheids in the tangential direction is dominated by pits.

2.4.2 Diffusion Flow Through Wood Ultrastructure

Experts in the field lack a precise understanding of water diffusion in wood, but research over the past century has formulated a relatively strong understanding of the
Figure 2-4: The diagrammatic representation of an earlywood bordered pit in section transverse to the pit membrane. On the left, (A) Aspect in unaspirated situation, (B) Aspiration of a bordered pit. On the right, the microstructure of a typical earlywood bordered pit: 1) tracheid wall (secondary wall), 2) middle lamella (and primary wall), 3) margo strands, 4) torus, 5) pit aperture, and 6) pit chamber (Petty, 1970).
topic. This understanding creates a foundation through which the diffusion of SC CO$_2$ may be addressed.

According to Stamm (1964), the movement of a liquid such as water into a coarse capillary structure like wood is caused by diffusion and aided by capillary action. SC CO$_2$ will not interact with wood in a similar fashion to liquid water because there is little capillary action. Capillary action is governed by two factors, (1) the attraction of the fluid molecules to the wall of the capillary, and (2) surface tension of the fluid. In this way, the fluid is pulled into the capillary and continues to flow because of the molecular interaction caused by surface tension. Hydrogen bonding between CO$_2$ and wood, as with water and wood, establishes the issue of attraction between the fluid and the capillary. On the other hand, SC CO$_2$ has virtually no surface tension (Wilson, 2000); thus, it acts in a similar fashion to water vapor, in that the diffusion process is not assisted by capillary action.

For water movement specifically, the moisture content of the wood is of considerable importance. The water molecules bonded between cellulose chains in the cell wall are commonly referred to as “bound” water. Once the maximum amount of water is collected in the cell wall, it begins to accumulate in the cell lumens and is referred to as “free” water, which is typically in the state of water vapor. This point is known as the fiber saturation point (FSP). The FSP is a very important consideration for water movement in wood, because above the FSP, bound water molecules can be assumed to form an interconnected network for un-interrupted diffusion. Above a moisture content of 6%, the theory for the movement of bound water is considered a diffusion process driven by a moisture content gradient (Stamm, 1946). On the other
hand, if the moisture content in wood is below the fiber saturation point, then the condition of the water molecule network is uncertain and voids may exist, impeding diffusion and complicating the modeling process. Since SC CO$_2$ interacts with wood in a manner similar to water vapor, it can be speculated that the diffusion process will occur in similar fashion to water vapor as well.

If the moisture content is above the FSP, the diffusion process is a combination of bound and free water movement. The diffusion of free water (water vapor) through the capillary structure of wood is driven by a partial vapor-pressure gradient, and is based on the assumption of a gas mixture existing in the capillary tube structure (Pfalzner, 1950). An overriding issue is that the capillary structure affect diffusion considering that the dimension of the capillary is smaller than that of the mean free path of the vapor. In effect, the gas molecules may interact with the wall of the capillary more than they interact with other gas molecules. Consequently, the diffusion process of water vapor in a gas (air) would be different from diffusion in ambient air. This phenomenon is commonly known as the Knudsen diffusion (Klinkenberg, 1941). Conversely, Knudsen diffusion is not an issue when considering SC CO$_2$, since it does not apply to high pressure conditions such as the supercritical environment.

Fick’s Laws mathematically represent the process of diffusion, which can be applied to a variety of physical conditions, including the flow of liquids and gases through a porous media. Fick’s First Law in one direction expresses the simplest form of diffusion:

\[ J = -D \frac{dC}{dx} \]
where $J$ is a flux, $D$ is the diffusion coefficient or proportionality constant, and $dC/dx$ is the concentration gradient, or driving force. The equation is a phenomenological equation that represents the spontaneous movement of a substance from higher concentration to lower concentration, which is the reason for the negative sign in front of the right hand side of the equation. $D$ is a measure of the conductivity, or the measure of a material’s ability to expedite molecular flow. Fick’s first law is applicable to a steady-state condition, which can be explained as a condition where the concentration profile is independent of time or the flux is a constant. Since Fick’s law has been adapted from nonporous systems, $D$ is an effective diffusion coefficient, representing the conductivity through the solid matrix and the gas that is contained in the void space. A more specific description of $D$ can be written as follows (Ho, et al., 2006):

$$D = \chi D_g$$  \hspace{1cm} 2-2

where $D_g$ is the diffusion coefficient through the gas only and $\chi$ is a porous media factor, defined as:

$$\chi = \phi S_g \tau$$  \hspace{1cm} 2-3

where $\phi$ is porosity, $S_g$ is the gas saturation, and $\tau$ is the tortuosity which an empirical value that represents the “tortuous” path compared to a straight line value and has several correlations.

Diffusion movement in a material such as wood is an unsteady-state condition and generally only reaches steady state after long time intervals, such that Fick’s First Law no longer applies (Skaar, 1954). Impregnation and extraction processes of wood are unsteady-state problems, which are more appropriately described by Fick’s Second Law:
\[
\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}
\]

This equation again represents diffusion in one direction and \( D \) is a constant. The mathematical solution to this equation is much more cumbersome than Fick’s first law and requires various assumptions that lead to boundary and initial conditions that make solutions possible. The problem with such an approach is that the assumptions can lead to inaccurate modeling. Additionally, Eq. 2-4 assumes a constant diffusion coefficient, which is valid according to Stamm’s reporting that \( D \) is constant for non-swelling solutions, flowing through wood (Stamm, 1964).

The topic of swelling and SC CO\(_2\) is a debatable one. CO\(_2\) (in gaseous form) has been shown not to swell wood (Tarkow, et al., 1960), some controversy arises because of the polar nature of CO\(_2\) in the supercritical state. Recently, arguments have been made that SC CO\(_2\) can indeed possess some polarity (Raveendran, et al., 2005), such that SC CO\(_2\) may hydrogen bond with wood and cause a swelling action.

While the diffusion transport mechanism is not the focus of this study, it is important to note that it does play an important role in SC CO\(_2\) treatment of wood materials at certain conditions, particularly when a treatment pressure is reached (i.e. no pressure gradient) and a preservative is introduced. For this reason, Kang et al. (2006) investigated the diffusion coefficient of cyproconazole in Douglas-fir heartwood during supercritical treatment.
2.4.3 Dynamic Flow in Wood

Dynamic flow occurs when a pressure gradient is established across a medium, and the magnitude of the gradient largely determines the characteristics of flow. The other determinant of flow is the medium through which the fluid is flowing. For porous materials such as wood, the flow parameter, permeability, measures the ease at which the fluid flows. High permeability refers to large amounts of flow though the material, while the opposite is true for low permeability. In general, wood is a low permeability solid, resulting in low flow velocity. As a result, fluid flow in wood is primarily limited to the laminar, or viscous, flow regime.

Viscous dynamic flow through a porous solid can be described using Darcy’s law, which varies slightly depending on the nature of the fluid. Simply stated, Darcy’s law states that conductivity is equal to a flux divided by a pressure gradient, and is analogous to the Navier-Stokes equation. Darcy’s Law at steady state for liquids defines viscous flow applying the following relational expression:

\[ \frac{k}{\mu} = \frac{Flux}{Gradient} = \frac{Q}{A} \frac{\Delta P}{L} = \frac{QL}{A\Delta P} \]

where \( k \) is known as permeability, \( \mu \) is viscosity, \( Q \) is volumetric flow rate, \( L \) is the length of the material specimen in the flow direction, \( A \) is the cross-sectional area of the material in the flow direction, and \( \Delta P \) is the pressure differential in the direction of flow.

Compressible fluids complicate Darcy’s law since the gradient changes as pressure changes. Solution requires the use of an equation of state, such as the ideal gas law, and results in the following analogous expression:
\[
\frac{k}{\mu} = \frac{QLP}{\Lambda \Delta\bar{P}}
\]

where \( P \) is the pressure at which \( Q \) is measured and \( \bar{P} \) is the average pressure in the solid.

Eq. 2-6 applies to SCFs because they are compressible, but an adjustment is required considering that the ideal gas law does not apply to SCFs. Thus, a compressibility factor \((Z)\) is included in the solution analysis and subsequently yields:

\[
\frac{k}{\mu} = \frac{ZQLP}{\Lambda \Delta\bar{P}}
\]

While using the correct form of Darcy’s law is important for accurately modeling flow in porous solids, research has shown that both liquids and gases measure equivalent permeabilities, providing that the liquid does not swell the wood (Comstock, 1967), and permeability is sufficiently high (Klinkenberg, 1941).

Some disparity exists for the applicability of Darcy’s law to wood, especially heartwood and refractory species. Research by Bramhall (1971) suggests that Darcy’s law requires an adjustment factor as follows:

\[
\frac{k}{\mu} = \frac{QLP}{\Lambda e^{-b\ell} \Delta\bar{P}}
\]

where \((e^{-b\ell})\) is the “correction factor”, \( b \) is a term empirically calculated and varies for wood conditions, and \( \ell \) is the depth of penetration from the surface. To the contrary, others have found that Darcy’s law is valid for compressible flow through wood (Siau, 1984) (Prak, 1970).
2.5 Modeling of Wood Pressure Treatment Processes

A few distinctions should be made when classifying the modeling of flow in wood materials, which ultimately describes the wood pressure treatment process. First, models can be divided by scale, between the micro and macro. A micro-scale model includes dimensions of the wood ultrastructure, primarily cell and pit dimensions, and was the first type of flow model developed for wood. The current study does not focus on such a model, the fact of which was developed in Stamm (1946). Alternatively, a macro-scale model, as applied in this research, involves the measurement and insertion of larger scale properties into a model, such as permeability and porosity. This type of model is more prevalent because model parameters are more easily measured, and is the focus of the current study, although Comstock (1970) developed a model that correlates anatomical features to permeability, effectively linking the micro and macro-scale models. Other models have been developed for both steady and unsteady-state conditions. Since the pressure treatment process is transient, it represents unsteady state conditions and those models are the focus here. Finally, the type of fluid, whether compressible or incompressible, needs to be considered when classifying flow models, and since CO$_2$ is a compressible substance, compressible flow models are discussed in more detail later.

The prediction of the pressure response inside wood during treatment on a macroscopic scale has been performed on a limited basis for both conventional and SC CO$_2$ processes, and verification of the models is lacking in most cases, presumably because of difficulty in experimental measurement of the pressure inside the wood.
Pressure response models for both standard and supercritical conditions are similar in that they assume that dynamic flow is the dominant driving force, so viscous flow models were used in conjunction with equations of continuity to model unsteady-state conditions.

### 2.5.1 Modeling of Conventional Pressure Treatment

Several approaches to conventional pressure treatment exist, with the main differences being the rate, duration, and magnitude of pressure changes during the process. A very brief discussion of the most prominent treatment processes will be provided here. The reader is referred to more comprehensive literature by Zabel and Morrell (1992) and Goodell et al. (2003) for a more thorough and comprehensive description of commercial wood treatment. While numerous treatments exist, there are three that are most used, the full-cell (Bethel), and two empty-cell (Lowry and Reuping) methods. The main difference between the empty and full-cell treatment process is that in the beginning of the full-cell, a vacuum is applied before the preservative is introduced, where in an empty cell process no vacuum is applied and the vessel is pressurized with air. The two empty cell processes vary in the timing of the introduction of the preservative. In the Reuping process, preservative is introduced after pressurization has begun, where in the Lowry process, preservative is introduced immediately and then the vessel is pressurized. The remainder of the treatment processes are similar, where the vessel is held at a maximum treatment pressure (treatment pressure and time vary according to tree species), the system is depressurized (preservative is removed) and a vacuum is applied to remove excess preservative. Maximum typical
treatment pressures range from 345 to 1723 kPa and treatment time is generally several hours (Lebow, 2010).

Unsteady-state flow of compressible fluids in wood materials was first modeled by Resch (1967), where the evacuation of air (depressurization) in the radial direction of 20 cm diameter Douglas-fir heartwood bolts was investigated. The model basis was the one dimensional, single phase, unsteady-state flow of a compressible fluid through a solid porous media in radial coordinates, with Darcy’s Law as the governing flow equation:

\[
\frac{\partial^2 P}{\partial r^2} + \frac{1}{r} \frac{\partial P}{\partial r} = \frac{\mu \partial P}{kP \partial t}
\]

where the \(P^2\) term is a result of the equation of state used to relate the change in density at varying pressure. Through finite difference representation, the final model was determined:

\[
P_{(r, t+\Delta t)}^2 = \frac{\Delta t k P}{(\Delta r)^2 \mu \phi} \left[ \left(1 - \frac{\Delta r}{2r}\right) P_{(r-\Delta r, t)}^2 + \left(\frac{\mu \phi (\Delta r)^2}{k P \Delta t} - 2\right) P_{(r, t)}^2 + \left(1 + \frac{\Delta r}{2r}\right) P_{(r+\Delta r, t)}^2 \right]
\]

The computational flow model was tested by comparing pressure predictions to measurements made by a pressure probe that was inserted radially halfway into the specimen during a depressurization trial. In one trial, the vessel and specimen was pressurized to 1034 kPa, and then the pressure was reduced in increments of 206 kPa over a certain period of time. After the vessel reached atmospheric pressure, a vacuum of 69 kPa was drawn on the vessel for the final step. A second trial was performed that was similar to the first, but instead of a stepwise withdrawal, pressure was reduced continuously at a rate of approximately 40 kPa/min. In both trials, the model showed
good qualitative agreement with measured pressure values. In the stepwise trial, the largest disparity occurred during the initial release of pressure, with the disparity increasing as pressure decreased. In the case of the continuous trial, the model was most accurate at higher pressures and then became less so as pressure decreased. In both cases, the largest disparity between predicted and measured pressures was approximately 40 kPa.

Another study performed by Orfila and Hosli (1985) developed a computational model and verified a few predictions with experimental pressure measurements on white spruce sapwood. Pressure probes were inserted into radially cut 50 mm specimens and sealed with epoxy at varying depths (specifics as to size of probe and type of epoxy were not given). Specimens were tested at both positive and negative pressures, 500 and 3.3 kPa, respectively, which are representative pressures for the aforementioned treatment processes (Bethel, Lowry, and Reuping).

The theoretical foundation of the computational flow model was similar to that of Resch (1967), as Darcy’s Law was used as the equation to describe flow, but the effect of slip flow on permeability was incorporated into the model:

\[
\frac{1}{R} \frac{\partial}{\partial R} \left[ R \left( k + \frac{b}{P} \right) \frac{\partial P}{\partial R} \right] = \phi \frac{\partial \rho}{\partial t}
\]

where \( b \) is the Klinkenberg constant. Orfila and Hosli converted their model so that it was dimensionless:
\[
\frac{1}{R} \frac{\partial}{\partial R} \left[ R(P + \alpha) \frac{\partial P}{\partial R} \right] = \phi \frac{\partial P}{\partial \theta}
\]

where

\[
P = \frac{P}{p_o}; \quad R = \frac{r}{r_o}; \quad \theta = \frac{k_p b^2}{\phi r_o^2}; \quad \alpha = \frac{b}{k_p o}
\]

Finite difference was used to develop the explicit computational model, where it was discretized into small time steps of \( n + 1 \) and spatial segments of \( \Delta R \):

\[
\frac{P^{n+1} - P^n}{\phi_{n+1} - \phi_n} = P_1 + \alpha \left[ \frac{P_{i+1} - 2P_i + P_{i-1}}{\Delta R^2} \right] + \frac{P_i + \alpha)}{R} \left[ \frac{P_{i+1} - P_{i-1}}{2\Delta R} \right] + \left[ \frac{P_{i+1} - P_{i-1}}{2\Delta R} \right]^2
\]

where \( P^* \) stands for the value of \( P \) at the \( n + 1 \) time step and \( P_{i+1} \) and \( P_{i-1} \) refer to adjacent pressure values. A solution technique known as the Newton-Raphson method was applied to solve the series of equations.

From a qualitative perspective, the computational model performed relatively well in the case of the vacuum condition, as the model predicted the pressure within approximately 10%. While no presentation of the pressurization trial was presented, the authors reported that good agreement was achieved. With the accuracy of the model qualitatively verified, the authors used the model to examine a few theoretical trials of specimens of different thickness and permeability. Moreover, they further developed the model to show that two zones of different permeability, describing the heartwood and sapwood, could be depicted. Consequently, the computational model could be used to examine the effects of processing conditions and material properties, i.e. permeability, on the internal pressure development.


2.5.2 Modeling of Supercritical Carbon Dioxide Flow in Wood

Modeling the mass transport process of SC CO₂ into wood has been investigated on a limited basis. Ward was the first to develop a model to predict the flow of SC CO₂ combined with monomeric methyl methacrylate into wood. This research did not experimentally verify the model, which was exclusively based on a viscous dynamic flow mechanism (Ward, 1989).

More recently, the SC CO₂ flow in wood for the impregnation of biocides was modeled by Sahle-Demessie (1994). In this study, the retention of TCMTB (2-(thiocyanomethylthio) benzothiazole) was measured for the SC CO₂ impregnation of Douglas-fir heartwood samples. This equation was solved with respect to time and space (two-dimensional or 2D rectangular flow), resulting in:

$$
\frac{\partial P}{\partial t} + PZ \frac{\partial Z^{-1}}{\partial t} = \frac{\zeta}{\mu_R} \left[ \frac{\partial^2 P^2}{\partial x^2} + \frac{\partial P^2}{\partial x} \left( \frac{\partial \mu^{-1}}{\partial x} + Z \frac{\partial Z^{-1}}{\partial x} \right) + \frac{\partial^2 P^2}{\partial y^2} + \frac{\partial P^2}{\partial y} \left( \frac{\partial \mu^{-1}}{\partial y} + Z \frac{\partial Z^{-1}}{\partial y} \right) \right]
$$

2-14

where ζ is a flow parameter and μ_R is the reduced viscosity. This model assumed that the permeability was constant and maximum pressure was reached instantaneously.

Sahle-Demessie’s flow model was coupled with a solute mass balance to predict the retention of impregnated biocide, but the flow model itself was not verified. When the combined flow-mass balance was compared to experimental data, a reasonable fit was achieved from a qualitative standpoint, but no quantitative comparisons could be made because no statistical comparisons were available. Sahle-Demessie plotted experimental and predicted biocide retention versus pressure and depth of the sample. For both comparisons, the model followed a similar trend as the data, but the model accuracy
decreased as sample thickness increased. Furthermore, the measured retention close to the surface of the specimen was much greater than the retention predicted by the computational model, meaning that the model did not account for the concentration gradients that are typical of SC CO$_2$ impregnation treatment. Sahle-Demessie speculated that the disparity was a result of a lack of understanding of the preservative/wood interaction and crystallization kinetics of the preservative. Regardless, the study revealed that the model proposed to represent the process had merit.

Henderson et al. supported the work of Sahle-Demessie by proposing a flow model for supercritical fluids in porous media (Henderson, et al., 2005). The model uses a similar approach using Darcy’s Law and a continuity equation. The main difference between the two models was that Henderson used a power law to relate the porosity of the medium to permeability. This allowed Henderson to incorporate a variable permeability term in the model. To date, no attempt to verify the model has been conducted to compare flow prediction with experimental test data.

Another approach to modeling the SC CO$_2$ treatment process was taken by Lucas et al. (2007a) (2007b), who applied a model that mimicked a two phase “fixed bed” system with mass transfer between a flowing fluid and a solid, based on a mass balance of solute into the SC phase and linear equilibrium. A simplified approach was taken, in which the impregnation process of a preservative was reduced to two parameters, a mass transfer coefficient and a partition coefficient. The mass transfer coefficient depicted the mass transfer from the bulk of the fluid phase to the surface of the solid, and the partition coefficient represented the equilibrium condition by describing the maximum amount of solute that could be loaded under conditions of thermodynamic equilibrium. Lucas et al.
explored the impregnation of radiata pine with Decanal preservative was based on previous research that was developed to describe the SFE of oils from seeds (Cocero, et al., 2001). The governing equations are given as follows:

Mass balance of solute preservative in SC fluid phase:

\[
\frac{\partial c}{\partial t} = -u_z \frac{\partial c}{\partial z} - (k_f a)(c - c^*)
\]

Mass balance of solute preservative in the solid wood phase:

\[
(1 - \varepsilon) \frac{\partial c_s}{\partial t} = (k_f a)(c - c^*)
\]

Equilibrium equation:

\[
c_s = h c^*
\]

where:

- \( a \) = specific solid surface (cm\(^{-1}\)),
- \( c \) = concentration of solute in the fluid phase (mol/cm\(^3\)),
- \( c^* \) = equilibrium concentration of solute in the solid phase (mol/cm\(^3\) solid),
- \( c_s \) = concentration of solute in the solid phase (mol/cm\(^3\) solid),
- \( h \) = equilibrium partition coefficient,
- \( k_f \) = mass transfer coefficient related to the fluid phase (cm/s),
- \( t \) = time (min),
- \( u_z \) = superficial velocity in the void fraction (cm/s),
- \( z \) = axial coordinate (m), and
- \( \varepsilon \) = bed void fraction.

In the first study (Lucas, et al., 2007a), the effects of several processing conditions on the accuracy of the model prediction were explored on a pilot plant scale, including temperature, pressure, and CO\(_2\) flow rate. Model performance was evaluated through a statistical summary parameter called absolute average deviation (AAD).

The temperature values investigated were 35.0 to 46.8°C. Model predictions were most accurate in the mid range temperatures (3.66% and 3.50% AAD at 40 and 42 °C,
respectively). Some deviation occurred at very low and high concentrations at the coolest and hottest temperatures. Pressure was varied from 7.5 to 15 MPa. The effect of pressure was variable, with 10 MPa being the most accurate (AAD = 3.66%). Predictions at the other pressures were not as accurate at lower concentrations, but improved at higher concentrations. Finally, SC CO₂ flow rates were varied from 2.5 to 4.5 kg/hr, with the highest flow rate being the most accurate (AAD = 4.45%). Overall, the value for AAD did not exceed 10% for any condition explored in the study.

The second study (Lucas, et al., 2007b) investigated laboratory and pilot plant scales, and concentrations of adsorbed preservative were used for parameters to compare the theoretical model to experimental measurements: breakthrough time, saturation time, saturation capacity, and fractional bed utilization, which are all typical parameters used in describing adsorption processes. Furthermore, AAD was used to directly compare predicted and measured adsorption values. Overall, the model performed well, predicting the aforementioned parameters within 10% error for both lab scale pilot plant scales. Prediction performance was slightly better for the lab scale (7.0% AAD) in comparison to pilot scale (9.5% AAD).

---

1 Definitions for the parameters are as follows:
breakthrough time – time at which the initial adsorption of solute occurs in the solid
saturation time – time at which the concentration of adsorbed solute equals the concentration of solute in the fluid
saturation capacity - the maximum concentration of solute that a solvent can contain under specified conditions.
fractional bed utilization – percentage of the potential to actual absorption by the solid
2.5.3 Analysis of Proposed Models

The goal of Sahle-Demessie’s study was to use mathematical modeling to identify the variables and relationships that affect the impregnation process. Although he was successful in his effort, Sahle-Demessie recognized the need for further model refinement to depict the impregnation process accurately. Once an accurate, robust model is developed to describe the flow of SC CO$_2$ in wood, it may be used to describe the process in large scale applications.

As described earlier, the model developed by Sahle-Demessie was based on Darcy’s Law (Eq. 2-7), which relates the inverse of the pressure gradient in porous media flow to the permeability ($k$) of the media. Sahle-Demessie assumed that permeability was constant throughout the material, but this may not be the case. Schneider investigated how permeability and various anatomical features of wood ultrastructure affected the pressure response during the impregnation of CO$_2$ to supercritical conditions (Schneider, 2000). The pressure response was measured through three response variables, including time to pressurize to 35 kPa, time to reach equilibrium with the vessel pressure, and maximum measured pressure gradient. Schneider found that permeability (in all principal directions) could not independently predict any of the response variables over a variety of eight softwood species, while radial permeability showed some potential for predictive use for three hardwood species. Schneider also examined the effects of anatomical characteristics such as tracheid, vessel, and fiber dimensions, resin canal dimensions and frequency, and ray dimensions and frequency on the pressure response, and found that these anatomical features could not be used to predict pressure response.
with any real certainty. Schneider’s findings highlight the implication that little is known about the fundamental understanding of the SC CO$_2$-wood system. Another potential issue in Sahle-Demessie’s model is that he assumed that the permeability for the wood material did not change during treatment. Research has shown that the permeability of wood may change when exposed to SCFs. Sahle-Demessie et al. (1995) reported that wood specimens generally displayed a higher permeability after treatment with SC CO$_2$.

In reference to the work by Lucas et al. (2007a)(2007b), the model performed very accurately in predicting the total retention of the impregnation process, which is valuable in determining the level of treatment required for in-service use. Where the model is lacking, as pointed out by Kjellow and Henrikson (2009), is that it is incapable of explaining the existence of concentration gradients that occur during treatment, which is a necessary component in effective treatment.
Chapter 3

Theoretical Conceptualization and Validation of the Computational Model

Chapter 2 provided a foundation for understanding the state of the art in modeling SC CO₂ in wood materials. The current study attempts to advance the physical understanding of the process such that a simulation can be created to predict the flow of supercritical carbon dioxide in wood materials.

A useful approach to achieve this goal is to use theoretical methods employed in the petroleum and natural gas industry to describe and predict the SC CO₂ movement within semi-porous, solid wood-processed substrates. The physical nature of extracting liquids and gases from soil and rock beds has stimulated extensive research on the flow of fluids through porous matrices (Ertekin, et al., 2001). This theoretical approach to flow modeling was used for simulation predictions of oil and natural gas extraction from soil and other types of earth reservoirs. Furthermore, the coding procedure and grid configuration used in this study was purposely organized to resemble those of other published codes (Ferziger, et al., 1996), in order to make it relatively discernible for other researchers.

1 The particular code is called “LAPL2DSIN.F” and “LAPLACE.F”, and can be found at ftp.springer.de/pub/technik/peric
3.1 Definition of the System

In this study, theoretical flow simulation was to be compared to actual measurements taken from a specific set of experimental conditions that mimicked a typical treatment process. While a full explanation of that setup will be presented in Chapter 4, the important details required to develop the flow simulation are presented here.

The experimental treatment process was as follows:

- A specimen was prepared with four pressure probes inserted into the cross section of the specimen, so the pressure profile was monitored. The experimental specimen was sealed at both ends longitudinally to prevent flow in that end grain direction.

- The instrumented specimen was placed in a pressure vessel and then sealed within the retort cylinder. Carbon dioxide gas was added to the vessel at a specific pressurization rate and approximate temperature, until a maximum pressure was reached. Maximum pressure was held until the pressure equalized between the specimen and the vessel. Then the vessel was depressurized to atmospheric conditions at a controlled rate approximately equal to the rate of pressurization.

- During the retort vessel treatment process, pressure readings in the probes were taken every two seconds.
To successfully model the experiment, the conditions and geometry of the system used to create the model must appropriately correspond to the conditions of the experiment. This was a twofold process, which involved the setup of a discretized grid system and a set of initial and boundary conditions. The grid system will be explained here, while the initial and boundary conditions will be developed later.

A diagram of the grid system is shown in Figure 3-1, which is a simplified representation of the actual grid system in that the number of mesh blocks used was reduced. The reason for the simplification was to highlight the key features of the grid and how it translated to the experimental system. The actual grid system used in this study was a 30x14 system. A square mesh size of 1.59 mm was created, so that the mesh size measured the same size as the radius of the chamber used to measure the pressure in the actual sample.

First, since the flow in the wood specimens was restricted in the longitudinal direction by the epoxy coating, the majority of flow occurred in two directions; thus a two dimensional grid system was appropriate. Furthermore, the grid exploited the symmetrical nature of a rectangular specimen by taking a quadrant of the entire specimen and using it as a subsection of the entirety. The reason for the sectioning was twofold, the first being that this allowed for a more precise grid (smaller, more numerous mesh blocks), without a larger computational burden. Secondly, as explained above, the code published by Ferzinger and Peric (1996) used a symmetrical grid design, which was employed here as well to mimic that code. While the use of symmetry reduced the computation load necessary to execute the simulation, some complexity was introduced, which was handled by the boundary mesh blocks of the grid system.
Figure 3-1: Schematic of the grid system used in this study. The body centered matrix blocks are represented with the “+”, while the boundary vessel blocks are empty, and the reflection blocks are in grey. Note the figure is not to scale, and is a simplified version of the system.
For this study, a block-centered system was employed, and two different “types” of mesh blocks were used, matrix mesh blocks and vessel mesh blocks. The matrix mesh blocks were the internal mesh blocks that depict the wood material and the vessel mesh blocks depicted the conditions in the vessel. The configuration of the mesh blocks simulated the submersion of the wood in the vessel as the flow of carbon dioxide could enter the matrix material from the two directions that were not sealed with epoxy. The entry point was the boundary between the vessel mesh blocks and the matrix mesh blocks on the top and right, which represented the surface of the actual wood specimen in the experiment. The shaded matrix mesh blocks on the bottom and left represented the symmetrical internal mesh blocks that were a reflection of the values of the mesh blocks at the internal planes of symmetry.

The numbering of the system is also shown in Figure 3-1, which starts in the bottom left corner and proceeds first in the y-direction and then the x-direction. The size of the mesh blocks was determined by number of mesh blocks in which the system was discretized in both directions ($n_x, n_y$), although the vessel mesh blocks were reduced by a factor of 100 in the direction in which they contact the matrix mesh blocks. The reason for this reduction is that it limited the effect of using body centered blocks on the implemented boundary conditions, and will be explained in more detail later in the section that explains the implemented boundary conditions. Within the arrangement of matrix mesh blocks, locations were identified that corresponded to the location of the pressure probes inserted into experimental shortleaf pine and Douglas-fir specimens, allowing for the direct correlation of theoretically calculated and experimentally measured pressures.
3.2 Assumptions

The flow model was based on the following assumptions:

1. Flow will occur in two directions only, as no initial flow will occur in the longitudinal direction with the ends sealed. This includes the time after CO₂ enters the substrate from the subsequent transverse pressure development.

2. The pressurization rate is regulated so that swelling, i.e. matrix displacement, is negligible.

3. Permeability is considered relatively constant irrespective of the tangential and radial directions.

4. Porosity does not change and is independent of pressure.

5. Viscous flow is the dominant mechanism.

6. The pressure on the surface of the specimen is equivalent to the pressure of the vessel.

7. Temperature is constant during the treatment process (isothermal conditions).

8. The flowing fluid does not interact with the matrix such that matrix properties change during the treatment process.

3.3 Formulation of Computational Model

The model system developed in this study was an implicit, single-phase, single-component, two-dimensional simulation, used to describe the physical conditions of the
experiment that is outlined in the next chapter. The single-phase, single-component of carbon dioxide is a simplified description of the system. The rationale for choosing this system was as follows:

1. Previous attempts were made to model the flow of supercritical carbon dioxide in wood materials, which were based on a single-phase, single-component system, but no validation was performed (Sahle-Demessie, 1994) (Ward, 1989). This study will evaluate if such a system is valid.

2. In starting with a relatively simplified model, a baseline of understanding can be created, such that modifications to the model can be made in the future to capture the more complex interactions of the system.

3.3.1 Continuity Equations

The computational model was comprised of three continuity equations in terms of average pressure of carbon dioxide in a unit block:

1. A conservation of mass

2. An equation of state

3. A constitutive equation

The conservation of mass is based on the premise that for a differential volumetric element, the mass of fluid entering the element is equal to the mass leaving plus the net increase in mass for a specific amount of time. For a control volume in two dimensions (see Figure 3-2), mass is conserved by:
\[
- \frac{\partial}{\partial x} (\rho u_x A_x) \Delta x - \frac{\partial}{\partial y} (\rho u_y A_y) \Delta y + \frac{q_m}{\alpha_c} \frac{\partial}{\partial t} (\alpha c) = \frac{V_b}{\alpha_c} \frac{\partial}{\partial t} (\phi)
\]

where:

- \(\rho\) = density of the carbon dioxide,
- \(u_{x,y}\) = velocity of the flowing fluid in the respective direction,
- \(A_{x,y}\) = cross sectional area perpendicular to flow in the respective independent direction,
- \(q_m\) = mass production rate,
- \(\alpha_c\) = volumetric conversion factor,
- \(V_b\) = bulk volume of the control volume, and
- \(\phi\) = porosity of the control volume.

Figure 3-2: Control volume used to derive the conservation of mass.

Conceptually, Eq. 3-1 can be viewed in more simplified descriptive terms as:

\[
\left(\text{Net Flow}^{n+1}\right) \text{In & Out} + \left(\text{Source / Sink}^{n+1}\right) \text{Rate} = \left(\text{Accumulation}^{n+1}\right) \text{Rate}
\]

\[3-2\]
The convention for the source/sink \((q_m)\) is for positive values for source rates flowing into the volume and negative values for sink rates flowing out.

Once the mass balance has been established, the next steps are to incorporate the equation of state, which associates the density in terms of pressure and temperature. In this case, the formation volume factor (FVF) is used, which relates the density of the gas at conditions to those of standard conditions:

\[
\rho_g = \frac{\rho_{gsc}}{B_g \alpha_c}
\]

where:

- \(\rho_g\) = density of the gas at pressure conditions,
- \(\rho_{gsc}\) = density of the gas at standard conditions, and
- \(B_g\) = gas FVF.

Secondly, Darcy’s Law is used to describe the conditions in a generally porous material:

\[
\begin{align*}
\frac{\partial u_x}{\partial x} &= -\beta_c \frac{k_x}{\mu} \frac{\partial p}{\partial x} \\
\frac{\partial u_y}{\partial y} &= -\beta_c \frac{k_y}{\mu} \frac{\partial p}{\partial y}
\end{align*}
\]

where:

- \(\beta_c\) = transmissibility conversion factor,
- \(k_{x,y}\) = permeability in each respective direction,
- \(\mu\) = flowing fluid viscosity, and
- \(p\) = pressure.

When the equation of state (Eq. 3-3) and constitutive equation (Eq. 3-4) are substituted into the mass balance formula (Eq. 3-1), the following equation is obtained:

\[
\frac{\partial}{\partial x} \left( \beta_c \frac{A_x k_x}{\mu_s B_g} \frac{\partial p}{\partial x} \right) \Delta x + \frac{\partial}{\partial y} \left( \beta_c \frac{A_y k_y}{\mu_s B_g} \frac{\partial p}{\partial y} \right) \Delta y + q_{gsc} = \frac{V_b}{\alpha_c} \frac{\partial}{\partial t} \left( \frac{\phi}{B_g} \right)
\]
The expressional relationship given below (Eq. 3-6) for the gas FVF with its substitution
and application of the necessary assumption that porosity remains constant yields:

$$ B_g = \frac{p_{sc}TZ}{\alpha_c T_{sc} p} $$  \hspace{1cm} 3-6

$$ \frac{\partial}{\partial x} \left( \beta_e \frac{A_x k_x}{\mu_g B_g} \frac{\partial p}{\partial x} \right) \Delta x + \frac{\partial}{\partial y} \left( \beta_e \frac{A_y k_y}{\mu_g B_g} \frac{\partial p}{\partial y} \right) \Delta y + q_{gsc} = \frac{V_b \phi T_{sc}}{p_{sc} T} \frac{\partial}{\partial t} \left( \frac{p}{Z} \right) $$  \hspace{1cm} 3-7

where:

- $p_{sc}$ = pressure at standard conditions,
- $T$ = temperature,
- $T_{sc}$ = temperature at standard conditions, and
- $Z$ = gas compressibility factor.

A few assumptions made in Section 3.2 and the use of a uniform grid defined in Section
3.1 can be used to simplify Eq. 3-7.

### 3.3.2 Mathematical Model Development

Since $B_g$, $Z$, and $\mu$ all change with pressure, Eq. 3-7 is a nonlinear partial
differential equation that has no closed form algebraic solution; thus it must be estimated
numerically. The estimation is made by discretizing the specimen into smaller units, as
previously shown in Figure 3-1 and using mathematical approximations to represent the
differential equations. In this study, the approximations are made through a backward
finite difference scheme for time and dimensional space, and are written in numerical
format as per Eq. 3-8:
\[
\begin{align*}
\frac{\partial}{\partial x} \left( \beta_e A_x k_x \frac{\partial p}{\partial x} \right) \Delta x &= \left( \beta_e A_x k_x \left( \frac{P_{i+1} - 2P_i + P_{i+1}}{(\Delta x)_j^2} \right) \right) \Delta x \\
\frac{\partial}{\partial y} \left( \beta_e A_y k_y \frac{\partial p}{\partial y} \right) \Delta y &= \left( \beta_e A_y k_y \left( \frac{P_{j+1} - 2P_j + P_{j+1}}{(\Delta y)_j^2} \right) \right) \Delta y \\
\frac{\partial}{\partial t} \left( \frac{p}{Z} \right) &= \frac{P_{i,j}^{n+1} - P_{i,j}^n}{(Z_{i,j}^{n+1} - Z_{i,j}^n) \Delta t}
\end{align*}
\]

Backward difference schemes tend to be used because the size of the time increment does not affect the stability of the solution as often, as can be the case with other difference schemes (Ertekin, et al., 2001).

When the finite difference schemes are substituted into the flow equation (Eq. 3-7) and algebraically rearranged, a multidimensional system of non-linear equation terms results:

\[
\begin{align*}
\begin{bmatrix}
\beta_e A_x k_x \frac{1}{\mu_g B_g \Delta x} & \beta_e A_x k_x \frac{1}{\mu_g B_g \Delta x} \\
\beta_e A_y k_y \frac{1}{\mu_g B_g \Delta y} & \beta_e A_y k_y \frac{1}{\mu_g B_g \Delta y}
\end{bmatrix}_{i+1/2,j} \begin{bmatrix}
P_{i+1,j}^{n+1} - P_{i,j}^{n+1} \\
P_{i,j+1}^{n+1} - P_{i,j}^{n+1}
\end{bmatrix}_{i,j} &= \begin{bmatrix}
V_g \phi T_{sc} \frac{1}{\alpha_c P_{sc} \Delta t} \\
\frac{P_{i,j+1}^n}{Z_{i,j+1}^{n+1}} - \frac{P_{i,j}^n}{Z_{i,j}^{n+1}}
\end{bmatrix}_{i,j,1/2} + \begin{bmatrix}
P_{i,j}^{n+1} - P_{i,j}^{n+1} \\
P_{i,j}^{n+1} - P_{i,j}^{n+1}
\end{bmatrix}_{i-1/2,j} \\
&= \begin{bmatrix}
V_g \phi T_{sc} \frac{1}{\alpha_c P_{sc} \Delta t} \\
\frac{P_{i,j+1}^n}{Z_{i,j+1}^{n+1}} - \frac{P_{i,j}^n}{Z_{i,j}^{n+1}}
\end{bmatrix}_{i,j,1/2}
\end{align*}
\]

where the superscripts \( n \) and \( n+1 \) define the old and new time increments between pressure levels, respectively. The group of variables multiplied by the pressure terms on the left-hand side of the equation is known as the transmissibility term. It is handled in two parts, one being constant and the other being variable:
\[ T_{x_{1/2},j}^{n+1} = G_{i+1/2,j} \left( \frac{1}{\mu B_s} \right) \]

\[ T_{x_{1/2},j}^{n+1} = G_{i,1/2} \left( \frac{1}{\mu B_s} \right) \]

where the \( G \) term represents the constant part of the transmissibility. The pressure terms on the left-hand side of the equation and the transmissibility terms are written with the \( n+1 \) superscript because they are evaluated at the new time level. All pressures at the \( n+1 \) time increment are unknowns. The transmissibility terms are evaluated at the 1/2\( \Delta x \) (and \( y \)) distance because of the body centered grid configuration, as shown in Figure 3-3.

Values for the transmissibility are specified at the center of the block, but it is desired to evaluate the transmissibility at the interface between two blocks. To account for the discrepancy, the constant part of the transmissibility is evaluated via a harmonic average, and the pressure dependent part is determined by first averaging the pressure between the two blocks and then calculating the values according the average pressure.

\[ T_{x_{i-1/2},j} \]
\[ T_{x_{i+1/2},j} \]

Figure 3-3: Physical representation of the location of the transmissibility terms.

Eq. 3-8 is nonlinear because of the non-constant parts of the transmissibility terms are also a function of pressure. To find a unique and explicit solution to Eq. 3-8, it
should be linearized. Linearization can be performed by several methods (Ertekin, et al., 2001), but the current study uses a process called simple iteration. Simple iteration involves the evaluation of the non-constant part of the transmissibilities one iteration step behind the solution of the pressure terms, which can be written:

$$T_{x_{3/2},j}^{n+1} \approx T_{x_{3/2},j}^{(k)} = \left( \frac{\beta_c A_x k_x}{\mu_g B_g \Delta x} \right)_{i-1/2,j} + G_{i+1/2,j} \left( \frac{1}{\mu_g B_g} \right)_{i+3/2,j}$$

where $k$ is the old iteration level. With this new definition of the transmissibility term, Eq. 3-9 becomes:

$$\begin{align*}
\beta_c A_x k_x & \left( P_{i+1,j}^{(k+1)} - P_{i,j}^{(k+1)} \right)_{i+1/2,j} - \beta_c A_x k_y \\
& \left( P_{i,j+1}^{(k+1)} - P_{i,j}^{(k+1)} \right)_{i,j+1/2} - \beta_c A_x k_y \\
& \left( P_{i,j}^{(k+1)} - P_{i,j-1}^{(k+1)} \right)_{i,j-1/2} + \frac{V_b \phi}{\alpha_c P \Delta t} \left( \frac{P_{i+1,j}^{(k+1)}}{Z_{i+1,j}^{(k+1)}} - \frac{P_{i,j}^{(k+1)}}{Z_{i,j}^{(k+1)}} \right)_{i,j} = 0
\end{align*}$$

where $k+1$ is the new, current iteration level. It is important to note that for the simple iteration process, all pressure dependent terms are re-evaluated at every iteration.

Finally, a convention is used to organize the equation into a matrix solution notation, which makes computer coding more convenient, known as SIP notation:

$$S_{i,j}^{(k+1)} P_{i,j-1}^{(k+1)} + W_{i,j}^{(k+1)} P_{i-1,j}^{(k+1)} + C_{i,j}^{(k+1)} P_{i,j}^{(k+1)} + E_{i,j}^{(k+1)} P_{i+1,j}^{(k+1)} + N_{i,j}^{(k+1)} P_{i,j+1}^{(k+1)} = Q_{i,j}$$

where:
\[ S_{i,j}^{n+1} = \frac{\beta_i A_s k_i}{\mu g B_g \Delta y} \]
\[ E_{i,j}^{n+1} = \frac{\beta_i A_s k_i}{\mu g B_g \Delta x} \]
\[ W_{i,j}^{n+1} = \frac{\beta_i A_s k_i}{\mu g B_g \Delta x} \]
\[ N_{i,j}^{n+1} = \frac{\beta_i A_s k_i}{\mu g B_g \Delta y} \]

\[ C_{i,j}^{n+1} = \left( S_{i,j}^{n+1} + W_{i,j}^{n+1} + E_{i,j}^{n+1} + N_{i,j}^{n+1} + \Gamma_{i,j}^{n+1} \right) \]
\[ \Gamma_{i,j}^{n+1} = \left( \frac{V_h \phi T_{sc}}{\alpha_c P_{sc} T \Delta t} \right) \left( \frac{1}{Z_{i,j}^{n+1}} \right) \]
\[ Q_{i,j} = -\Gamma_{i,j}^{n} \cdot P_{i,j}^{n} \]
\[ \Gamma_{i,j}^{n} = \left( \frac{V_h \phi T_{sc}}{\alpha_c P_{sc} T \Delta t} \right) \left( \frac{1}{Z_{i,j}^{n}} \right) \]

Eq. 3-13 can then be solved using a numerical iterative procedure.

Table 3-1 summarizes the variables and associated units used in the developed flow equations.
Table 3-1: Variables used in the flow simulation.

<table>
<thead>
<tr>
<th>Inputs</th>
<th>Description</th>
<th>Parameter</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mesh Block Size</td>
<td>Δx, Δy</td>
<td>m</td>
<td></td>
</tr>
<tr>
<td>Area</td>
<td>A</td>
<td>m²</td>
<td></td>
</tr>
<tr>
<td>Specific Permeability</td>
<td>kₓ, kᵧ</td>
<td>m²</td>
<td></td>
</tr>
<tr>
<td>Viscosity</td>
<td>µ</td>
<td>Pa·s</td>
<td></td>
</tr>
<tr>
<td>Gas FVF</td>
<td>Bₓ</td>
<td>m³/std m³*</td>
<td></td>
</tr>
<tr>
<td>Gas flow rate</td>
<td>qₓ</td>
<td>m³/day</td>
<td></td>
</tr>
<tr>
<td>Compressibility Factor</td>
<td>Z</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Grid block bulk volume</td>
<td>V_b</td>
<td>m³</td>
<td></td>
</tr>
<tr>
<td>Density</td>
<td>ρ</td>
<td>kg/m³</td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>T</td>
<td>K</td>
<td></td>
</tr>
<tr>
<td>Porosity</td>
<td>φ</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Time</td>
<td>t</td>
<td>day</td>
<td></td>
</tr>
<tr>
<td>Transmissibility conversion factor</td>
<td>f_c</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

| Outputs                          | P(x, y)               | kPa       |
| Geometric position               | x, y                  | m         |

* std m³ is measured at 101 kPa and 20°C

3.3.3 Initial and Boundary Conditions

Eq. 3-7 has an unlimited number of solutions, each based on the set of imposed boundary and initial conditions. In this case, the initial conditions must be satisfied for each incremental time step from the beginning of the process (t = 0) when the vessel begins to pressurize to the end (t = t_f) when the specimen equalizes with the atmosphere after treatment. In Eq. 3-13, the pressure terms (Pⁿ and Pⁿ⁺¹) refer to the pressure at the current time step (n) to the next time unit increment (n+I). To advance from the current to next step, known values of Pⁿ are implemented into the equation and the unknown pressures Pⁿ⁺¹ are calculated, and then used as the known pressures for next step. The solution process is started by implementing a set of initial conditions at the first time step.
In this study, each experiment was started with the specimen in an unpressurized vessel, such that all $P_{i,j}$ were equal to vessel pressure which was equal to atmospheric pressure.

These initial conditions were written as follows:

$$
P_{(0, w/2), j} = P_v = P_a \\
P_{i,(0, t/2)} = P_v = P_a \\
\frac{\partial p}{\partial x} = \frac{\partial p}{\partial y} = 0 \ \forall \ P_{i,j} 
$$

From Section 3.1 and Figure 3-1, it can be determined that there were no sources or sinks present in the system, so only external boundaries existed (Vessel Mesh Blocks). The external boundaries were pressure specified, making them of the Dirichlet type (Ertekin, et al., 2001). The simplest approach to incorporate the conditions was to assign the specified boundary pressure to the grid cells at the boundary. The limitation of this approach was that, for body centered grid systems, the pressure point was at the center, or $\Delta x/2$ or $\Delta y/2$ away from the actual boundary of the system, rather than directly at the boundary. The large reduction in the size of the boundary blocks (as noted in Figure 3-1), greatly alleviated this limitation. Thus, the boundary conditions were:

$$
P_{(0, w), j} = P_v \\
P_{i,(0, t)} = P_v 
$$

The internal boundaries where the reflection blocks are located were handled by treating them as no flow boundaries or the reflection technique (Aziz, 1979), such that the flow coefficients of Eq. 3-14 in those directions were zero. This was accomplished by applying 3-17 as follows:
for all blocks that are adjacent to reflection mesh blocks.

Since the system was in an unsteady-state flow condition, the boundary conditions must be specified for every time step increment \((t \geq 0)\), meaning that they are uniquely a function of time. Because of experimental conditions that will be outlined in Chapter 4, the boundary conditions for each additional time step increment were not implemented through an equation representing the pressurization and depressurization rates, but were specified as the measured pressure in the treatment vessel at the actual experimental time of the pressure measurements.

### 3.4 Solution Technique

Once the flow model was linearized into Eq. 3-13 it could be appropriately solved by an iterative procedure, using Stone’s SIP method. A condensed summary of the procedure is presented here, but for a more in depth understanding refer to Stone (1968) or Ferziger and Peric (1996). If Eq. 3-13 is written in matrix notation, it takes the following generalized form:

\[
\begin{bmatrix} A \end{bmatrix} \bar{p} = \bar{Q} \tag{3-18}
\]

where \([A]\) is the coefficient matrix consisting of the transmissibility terms. The objective of the procedure was to take \([A]\) and replace it with an approximation \([A']\) that was a composite of two matrices \([L']\) and \([U']\), where \([L']\) and \([U']\) represented the lower and
upper diagonals of $[A']$. The equation was then iterated until $[A']$ was an adequate estimation of $[A]$ thru Stone’s iterative equation:

$$
[A']^{(k+1)} = [A']^{(k)} - \omega \left[ AP - Q \right]
$$

where $\omega$ was an iteration parameter to be defined later and the values for $[A']$ were estimated according to the set of equations found in Appendix A.

First, the residual from an iterative step can be defined:

$$
\tilde{r}^{(k)} = \tilde{Q} - [AP]^{(k)}
$$

Next, a vector was defined as the improvement vector from one iteration to the next,

$$
\tilde{\delta}^{(k)} = \tilde{P}^{(k+1)} - \tilde{P}^{(k)}
$$

When Eq. 3-20 and Eq. 3-21 were substituted into 3-19, a new conversion equation was attained:

$$
[A'] \tilde{\delta}^{(k+1)} = \omega \tilde{r}^{(k)}
$$

so as $\tilde{\delta}^{(k)}$ approached zero, convergence was attained. When the component matrices $([L']$ and $[U']$) were substituted into Eq. 3-22, we obtain:

$$
[L'] [U'] \tilde{\delta}^{(k+1)} = \omega \tilde{r}^{(k)}
$$

This two part algorithm was derived from the incorporation of an intermediate vector:

$$
U^{(k+1)} = U' \tilde{\delta}^{(k+1)}
$$
such that the forward solution was:

\[
[L]u^{(k+1)} = \omega r^{(k)}
\]

and the backward solution was Eq. 3-24. The forward solution was solved by sweeping in the positive indices direction, i.e. starting from \(i, j = 1, 1\) to \(i, j = N_x, N_y\), the maximum number of indices in each direction. The backward solution was performed in the opposite direction, starting from \(i, j = N_x, N_y\) to \(i, j = 1, 1\).

Convergence of the iterative process was attained when the maximum value of all \(\delta^{(s+1)}_{i,j}\) was less than a desired tolerance (\(\varepsilon\)). If the value defined was greater than the tolerance, all values of the matrices were updated accordingly and the iterative process was repeated.

The iteration parameter (\(\omega\)) was an integral aspect of the solution process. The parameter was in actuality a set of values. Stone (1968) recommended that the number of iteration parameters (\(n_k\)) be at least four. First, the maximum value for the iteration parameter was determined. The maximum iteration parameter was the most essential value in the set. If the value of \(\omega_{max}\) was too large, then the iterative process became unstable and diverged. Conversely, if the value was too small, a very large number of iterations were required to achieve a solution. While the value of \(\omega_{max}\) can be adjusted to optimize the iteration process, a first estimate can be determined from the following expressional relationship:
The iteration parameters $\omega^{(k)}$ were then determined by cycling between zero and $\omega_{\text{max}}$ geometrically applying:

$$1 - \omega^k = (1 - \omega_{\text{max}})^{k-1} \quad 3-27$$

If the number of iterations required for convergence was greater than $n_k$, the cycle was repeated.

### 3.5 Computational Procedure

An implicit, two-dimensional single phase flow simulator was developed in the previous sections to investigate the flow of supercritical carbon dioxide within wood material. The flow simulator was used to explore the applicability of the theoretical physical predictions to experimental measurements performed on southern pine and Douglas-fir specimens.

A description of the computer program outlines the procedure used to execute the model solution. The program consisted of three major organizational sections:

1. Wood matrix properties in the form of data files were initialized into arrays and the computation of the constant part of the transmissibilities was performed.

2. The iterative procedure was executed, which included the following steps...
a. Time dependant parameters were initialized and the pressure sensitive parameters were computed.

b. The iteration parameters $\omega_k$ were determined.

c. The values for the approximation of the coefficient matrix were determined, and the forward and backward solutions to Stone’s SIP method were computed.

d. Convergence was evaluated by $|\tilde{\delta}_{i,j}^{(k+1)}| \leq \varepsilon$. Based on the outcome, the pressure values were updated and the iterative process was repeated, or the time step was advanced.

3. Material balances were evaluated and data was stored to a data file.

The computer program (named “CO2MODEL”), which was written in FORTRAN (Version 95) language, was based on the procedure outlined above, is explained in more detail below. The program copy can be found in Appendix B.

3.5.1 Conversion of Two-Dimensional Grid

In Section 3.1, the proposed mesh as a grid system for the “CO2MODEL” simulation was illustrated in two dimensions for the sake of understanding how the grid properties related to the respective x and y coordinates in a Cartesian system. While this practice provides a clear conceptual basis for the simulation, it is not a computationally sound approach, which is outlined by Ferziger and Peric (1996). Thus, the two dimensional grid was “reduced”, or converted to a one dimensional vector through the
alterations of grid location directionals as coefficient values according to Table 3-2. The convention used here followed the block ordering outlined in Figure 3-1. Accordingly, the simulation was written with one index in the notation, such that Eq. 3-13 was modified to:

\[
S_i^{n+1} P_{j-1}^{n+1} + W_i^{n+1} P_{j-N_j}^{n+1} + C_i^{n+1} P_l^{n+1} + E_{i,j}^{n+1} P_{j+N_j}^{n+1} + N_{i,j}^{n+1} P_{j+1}^{n+1} = Q_l
\]

where \( l \) was the block number.

<table>
<thead>
<tr>
<th>Grid Location</th>
<th>Coefficient Direction</th>
<th>Block Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>( i, j )</td>
<td>( C )</td>
<td>( l = (i-1)N_j + j )</td>
</tr>
<tr>
<td>( i-l, j )</td>
<td>( E )</td>
<td>( l + N_j )</td>
</tr>
<tr>
<td>( i+1, j )</td>
<td>( W )</td>
<td>( l - N_j )</td>
</tr>
<tr>
<td>( i, j-l )</td>
<td>( S )</td>
<td>( l - 1 )</td>
</tr>
<tr>
<td>( i, j+l )</td>
<td>( N )</td>
<td>( l + 1 )</td>
</tr>
</tbody>
</table>

**3.5.2 Main Program**

The function of the main program format was to open data files that contained the properties of the matrix, perform the major calculations specific to the simulation, and call upon the appropriate set of subroutines that:

1. Initialized the experimental data file and load the values to be used in the “CO2MODEL” simulation,
2. Determined the pressure dependent parameters.

The main program also allocated a timer that controlled the advancement of the time steps, such that the program proceeded in a temporal manner that was analogous to the experimental trials performed in Section 4.3.
3.5.3 Subroutine DENSITY

This subroutine was adapted from the model developed by Sahle-Demessie (1994) and used an iterative process to determine the density of carbon dioxide at a specified pressure and temperature, and then calculated the compressibility factor $Z$ along with $B_g$, the gas FVF, term. All of these calculations were initiated in one parametric subroutine because the main program required these input properties in many of the same algorithm locations, which limited the calls to subroutines and thereby sped up the calculation time.

The modified Benedict-Webb-Rubin (MBWR) Equation of State (EOS) was used to calculate the density of carbon dioxide (Ely, 1986):

\[
Z(T, \rho) = \frac{1}{RT} \left[ \sum_{n=1}^{9} a_n(T) \rho^{n-1} + e^{-3\rho T} \sum_{n=10}^{15} a_n(T) \rho^{2n-18} \right]
\]

where:

$R =$ the gas constant,
$\rho =$ is density, and
$\{a_n\} =$ a series of constants (See Appendix C)

An estimation for the density was used to start the subroutine, and Newton’s method was subsequently used to iterate until the density was determined within an acceptable tolerance. Once density was determined, a second function, as a simple variation of the ideal gas law, was used to determine the compressibility factor according to the expression:

\[
Z = \frac{P}{\rho RT}
\]
The value for $B_g$ was computed applying the previously given formula (Eq. 3-6) for the gas formation volume factor.

### 3.5.4 Subroutine VISCOSITY

This subroutine was adapted from the model developed by Sahle-Demessie (1994) and calculated the viscosity of carbon dioxide based on specified temperature and density values. The viscosity ($\mu$) was calculated for a low pressure and higher pressure condition (Jossi, et al., 1962). For lower pressures the following relation was used:

$$
\mu \xi = 4.610 T_R^{0.618} - 2.04 e^{-0.449 T_R} + 1.94 e^{-4.058 T_R} + 0.1
$$

$$
\xi = \left( T_C^{1/6} \right) \left( M_w^{1/2} \right) \left( P_C^{-2/3} \right)
$$

where:

$T_R$ = reduced temperature,

$T_C$ = critical temperature,

$P_C$ = critical pressure, and

$M_w$ = molecular weight.

For higher pressures the following relation was used:

$$
\left[ (\mu - \mu_o) \xi + 1 \right]^{0.25} = 1.0230 + 0.23364 \rho_R + 0.58533 \rho_R^2 - 0.40758 \rho_R^3 + 0.093324 \rho
$$

Low and high pressures were defined by the reduced density ($\rho_R$). Low pressure was any pressure at which the reduced density was less than 0.1. Higher pressures were designated as pressures that resulted in a reduced density of 0.1 to 3.0, since any pressure that resulted in a $\rho_R$ of 3.0 was outside the bounds of applicability set by Jossi et al. (1962).
3.5.5 Subroutine LOAD TABLE

This subroutine took a data file in tabular form and returned a dummy array that was used to load a vector of properties or the input values into the main program.

3.5.6 Subroutine TABLE LOOK

This subroutine was a table look-up that used a binary search to identify values in a data file. If a “look-up” quantity was between two values in the data file, linear interpolation was used to estimate the value.

3.6 Convergence Criteria

Proper convergence criteria are an essential component in determining the exact solution to a flow simulation. If the criteria are not established appropriately, the proposed solution might not accurately portray the exact solution. To avoid such an occurrence, convergence criteria were based on a tolerance check and a material balance. The tolerance check determined if the magnitude of the change in the unknown calculated parameter during an iteration was negligible. Then, the material balance was considered to ensure that the solution did not include losses to the system.

Convergence was first considered by the tolerance check:

$$\left| \delta_{i,j}^{(k+1)} \right| \leq \varepsilon = 1 \times 10^{-5} \text{ (kPa)}$$

Then, the material balance was then considered by the following:
The material balance was examined in two ways, through an incremental procedure and a cumulative one, to ensure that mass was conserved at convergence of the simulation process and overall. The incremental material balance ($IMB$) and cumulative material balance ($CMB$), respectively, were calculated by:

\[
IMB = \sum_{i=1}^{n_i} \sum_{j=1}^{n_j} V_{b,i} \phi \left( \frac{1}{B_{g,i}^0} + \frac{1}{\Delta B_{g,i,j}} \right)_i \]

\[
CMB = \sum_{i=1}^{n_i} \sum_{j=1}^{n_j} V_{b,i} \phi \left( \frac{1}{B_{g,i}^{n+1}} + \frac{1}{\Delta B_{g,i,j}} \right)_i \]

If at this point the computational material balances were not satisfied, the iteration process was reevaluated to achieve a more resolute and precise tolerance.

### 3.7 Optimization

Several steps were made to optimize the implemented code to minimize execution time. The first set of optimization steps occurred within the software compiler. The compiler package used to execute the FORTRAN programs was an open source software called G95 (WishesWebPages.com, 2001). G95 contains an optional optimizer, which adds function inlining to the program execution. There also was the option in G95 that
allows the programmer to specify the architecture of the PC being used, which improves the efficiency of the way the computer processor executes commands. Finally, a command was used that unrolls the “DO” loops used in the computer code.

Several steps within the code were performed to optimize the results. The first step involved the way in which the matrices were solved in the program. By alternating the order of the \((i,j)\) indices from every other iteration, speed of convergence was increased. The alternation introduced other diagonal entries into the calculation and prevented any non-standard diagonals from dominating the solution (Stone, 1968). Also, the maximum iteration parameter \((\omega_{\text{max}})\) in Eq. 3-26 was tuned by a trial and error to minimize the number of iterations in the solution.

### 3.8 Validation

A vital step in producing a reliable simulation was validating the calculated values by comparing them to already published model predictions. In this case, the proposed simulation was set up to solve the same problem derived by Resch (1967). As described in Chapter 2, Resch predicted the internal pressure of air at one location for a round specimen of Douglas-fir. The conditions of the experiment, which determined many model parameters, are presented in Table 3-3.
Table 3-3: Geometry and fluid properties for the Resch (1967) case. Values are in units as presented by Resch.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial Pressure (psig)</td>
<td>150, 30</td>
</tr>
<tr>
<td>Air viscosity (cp)</td>
<td>0.018</td>
</tr>
<tr>
<td>Wood Porosity</td>
<td>0.61</td>
</tr>
<tr>
<td>Wood Permeability (cm(^2))</td>
<td>5x10(^{-12})</td>
</tr>
<tr>
<td>Radius, r (in)</td>
<td>4</td>
</tr>
<tr>
<td>Grid Mesh size (in)</td>
<td>r/10 = 0.4</td>
</tr>
<tr>
<td>Location of probe (in)</td>
<td>r/2 = 2</td>
</tr>
</tbody>
</table>

Resch performed three particular experimental tests, measuring the pressure response at the half radius of the specimen during a depressurization cycle. In two of the tests, the initial pressure was set to 150 psig and the system depressurized. In the first test, the pressure was dropped in a stepwise manner in 30 psi increments, and in the other, the pressure was dropped continuously at a rate of approximately 5 psi/min. In the last test, the initial pressure was set to 30 psig and then immediately reduced to zero.

While Resch used a similar approach with regard to the governing equations used to develop the flow model, less specifics were given in terms of solution technique, mesh, and treatment of boundary conditions. The main difference between the model used by Resch and the proposed model was geometry. Resch used cylindrical coordinates in his model, while the current one used Cartesian coordinates. While this dissimilarity may cause a difference in predicted pressure values, it can be minimized through the setup of the grid (Figure 3-4). While a more refined grid size would have made for a more accurate representation of the geometrical difference, it was more important to keep the mesh size consistent with that of Resch’s model to allow proper comparisons between the two models.
The comparison between the proposed model predictions and those of Resch are presented in Figure 3-5 to Figure 3-7. One point to note is that Resch measured and predicted negative pressures (vacuum conditions) in his model, while the current model was not designed to handle such a condition; therefore, values were not computed at those pressures. The proposed model matched very well with those predictions of Resch for depressurization from 150 psig, although some disparity is seen in the case of depressurization from 30 to 0 psig (Figure 3-7). It is uncertain why the two models agreed in two cases and not the third, but the difference was relatively small at approximately 5 psig. Furthermore, any uncertainty created by the disparity between the two models was relatively inconsequential in terms of the current study, considering that pressures at or below 30 psig are not important in the scope of supercritical carbon

### Figure 3-4: Grid system used in the setup of the Resch case.

<table>
<thead>
<tr>
<th>y = 0</th>
<th>y = 4 in</th>
</tr>
</thead>
<tbody>
<tr>
<td>x = 0</td>
<td>x = 4 in</td>
</tr>
<tr>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>+</td>
<td>+</td>
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<td>+</td>
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<td>+</td>
<td>+</td>
</tr>
<tr>
<td>1</td>
<td>7</td>
</tr>
<tr>
<td>2</td>
<td>14</td>
</tr>
<tr>
<td>3</td>
<td>21</td>
</tr>
<tr>
<td>4</td>
<td>28</td>
</tr>
<tr>
<td>5</td>
<td>35</td>
</tr>
<tr>
<td>6</td>
<td>42</td>
</tr>
</tbody>
</table>

- Boundary of the proposed model
- Hypothetical surface of the specimen
- Location of measured pressure
Figure 3-5: Pressure predictions by Resch (A) and the proposed flow model (B) for the continuous depressurization case.
Figure 3-6: Pressure predictions by Resch (A) and the proposed flow model (B) for the stepwise depressurization case.
Figure 3-7: Pressure predictions by Resch (A) and the proposed flow model (B) for the stepwise depressurization case.
dioxide treatment. The most critical case was considered to be the first (Figure 3-5), because it most accurately represented the conditions of the current study with a continuous depressurization rate. In this case, the two models appeared to be in relative agreement and only varied slightly in their prediction of the pressure. Therefore, it was concluded that the computational flow model was free of calculation errors and made the proper prediction of pressure based on the mathematical theory.
Chapter 4

Materials and Methods

The primary objective of this research methodology was to experimentally measure the flow parameters of carbon dioxide in wood into the supercritical condition, and use these parameters to develop a computational model that depicted the flow process. In this chapter, the experimental procedure used to evaluate the model developed in Chapter 3 was introduced and described relative to wood specimen preparation and characterization. Furthermore, the statistical techniques used to evaluate the measured values and comparisons to theoretical results were explained in detail.

4.1 Materials

The two wood species used in this study, shortleaf pine (Pinus echinata) and Douglas-fir (Pseudotsuga menziesii), were chosen because they are two highly used species in the lumber industry, and represent a broad spectrum of treatability, with the southern yellow pine being regarded as an easy to treat material and Douglas-fir (D-F) more a refractory wood species. Shortleaf was chosen in particular because of the availability of permeability values (Choong, et al., 1972). The dimensions of the samples were selected to replicate an industry standard 2x4 (1.5 x 3.5 in actual cross section) nominal piece of dimensional lumber.
4.1.1 Wood Preparation

The shortleaf pine material for this study was obtained through cooperation with Dr. Todd Shupe, Louisiana State University (LSU, Baton Rouge, LA). A shortleaf tree was harvested (approximately 35-year age class) from the LSU experimental forest, quarter sawn to 8/4 thickness and shipped in the green condition to the Forest Resources Laboratory (FRL, Pennsylvania State University, University Park, PA). Accordingly, this harvested material was a representation of the geographic location of the southern pine utilized in an earlier shortleaf permeability study (Choong, et al., 1972). Upon arrival to FRL, the material was placed in a small volume laboratory kiln for drying to correspond to industrial moisture reduction. Kiln drying was performed applying the recommended moisture content according to schedule T12-C5 from Dry Kiln Operator’s Manual – USDA Agricultural Handbook AH-188 (Simpson, 1991). The schedule is typical a moisture reduction for higher grade 8/4 southern pine for approximately 19% core (15% average) moisture content (MC). After kiln-drying, the samples were milled to a final dimension of approximately 38 mm x 89 mm and stored in an environmental chamber (65% relative humidity, 21°C) to condition to an equilibrium moisture content of approximately 12%. The material was a mixture of heartwood and sapwood (Figure 4-1A). Because the material was radially sawn, the thickness was primarily in the tangential direction (radial plane) and the width was in the radial direction (tangential plane).
Figure 4-1: Grain orientation of shortleaf pine (A) and Douglas-fir (B) used in this study. Note that images are not to scale.

D-F samples were taken from one stem from a forest located in the Corvallis, Oregon region, air seasoned, and cut to dimensions similar to the shortleaf pine. The material contained slightly more heartwood volume (Figure 4-1B). Differences in heartwood to sapwood content between the two timber species were unavoidable due to the older age class of the D-F material. Despite being radially sawn, the experimental materials recovered were not oriented perfectly to purely radial and tangential surface directions. This meant that a range of radial and tangential directions occurred depending on the location along the width and thickness. Samples were placed in a climate chamber and were conditioned as previously noted to approximately 12% equilibrium moisture.
content (EMC). Wood EMC was subsequently maintained throughout the experimental research.

4.1.1.1 Pressure Treatment Specimens

Previous work by (Schneider, 2000) revealed that the pressure development of supercritical carbon dioxide in wood could be successfully monitored by using stainless steel tubing as pressure probes that were epoxy-sealed into the specimen. The probes are connected to pressure transducers through a series of compression fittings so pressure readings could be made.

Pressure treatment specimens were isolated from the kiln dried lumber by cutting the material to 120mm lengths. Pressure probes were made by cutting stainless steel tubing (3.2 mm OD, 2.1 mm ID, McMaster-Carr, Princeton, NJ). Tubing was roughed with sandpaper and inserted into the end grain of the specimen by drilling pilot holes with a 3.3 mm diameter drill bit and filling the hole with wet two-part Gluvit epoxy (ITW Philadelphia Resins; Montgomeryville, PA), and then cured for 48 hours. This epoxy was chosen because it was shown to perform best during the supercritical carbon dioxide treating process (Schneider, 2000). A 1.6 mm diameter drill bit was used to remove cured epoxy from inside the steel tube, and a pressure chamber was created by drilling 10mm past the end of the steel tube and into the wood. Figure 4-2 provides a schematic illustration of the epoxied installation within the material section used for experimentation of applied carbon dioxide with the measurement of temperature via type-T thermocouple wire. After drilling, both end-grain (longitudinal) surfaces were sealed
Figure 4-2: Schematic cutaway view of pressure probe configuration used to measure the pressure development during the SC CO\textsubscript{2} treatment process. Note that figure is not entirely to scale.
With two coats of Gluvit epoxy to limit flow to the width and thickness of the specimens.

After a 48 hour curing process, the samples were placed back in the environmental
chamber to equilibrate back to approximately 12% MC.

The arrangement of the pressure probes in the wood specimens appears in Figure 4-3. The configuration of the probes made use of two planes of symmetry in the cross-
section that divided the specimen into four equal quadrants, which reduces the number of
probes needed to measure the flow profile accurately. This assumption was verified by
placing “mirror” probes in equivalent locations of other quadrants and comparing the
corresponding pressure values. The number of probes was limited by the apparatus (as
described in Section 4.2), as only four ports were available for pressure lines into the
treatment vessel. Moreover, the compression fittings used to connect the specimen to the
lines prevented the probes from being placed too closely together. For this reason, the
probes were placed approximately equidistant from each other. The probes were inserted
at staggered depths, so as to not impede the flow of pressure. The outermost probe was
inserted at a depth of 20 mm, and each probe increased in depth by 10 mm, such that the
center probe was inserted at a depth of 50 mm.
Figure 4-3: Schematic configuration of pressure probes to measure the pressure profile development.

<table>
<thead>
<tr>
<th>w</th>
<th>t</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11</td>
</tr>
<tr>
<td>2</td>
<td>22</td>
</tr>
<tr>
<td>3</td>
<td>33</td>
</tr>
<tr>
<td>4</td>
<td>44.5</td>
</tr>
</tbody>
</table>
4.1.1.2 Permeability Samples

During the cutting of the pressure treatment specimens, short lengths of matched material approximately 50 mm long were also cut to assess wood permeability. All samples were cut from the same region of the specimen where the probes were inserted. Samples were bored from the 50 mm samples using a plug cutter so the final approximate dimensions of the plugs were 12 mm diameter ($D$) and 10 mm in length ($l$).

Figure 4-4 depicts how the permeability samples were cut for shortleaf pine. Attention was paid to the sapwood-heartwood interface, so that each primarily consisted of one or the other. After cutting, all samples were sprayed with compressed air to remove any particles and conditioned to 12% moisture content until the permeability test was performed on each specimen.

![Extracted plugs (12 mm $D$, 10 mm $l$)](image)

Figure 4-4: Example of how permeability samples were cut from available wood material in relation to the probe locations (numbered 1 to 4). Note that figure is not to scale.
4.1.2 Wood Material Characterization

Several characteristics of the wood samples were used as parameters in the theoretical model. The following section explains how each of the parameters was determined in terms of critical measurement of not just species permeability (width and thickness) values but also discrete physical determination of wood density collected as the specific gravity property.

4.1.2.1 Permeability

One of the main parameters in the mathematical prediction model for supercritical CO$_2$ that was developed in Chapter 3 was the empirical property input of liquid permeability. Permeability is described as the ease by which a fluid can move through a porous material under a pressure gradient. The value for the permeability of a porous body is defined using Darcy’s Law and solving for permeability ($k$) according to the following relational expression:

\[
\frac{k}{\mu} = \frac{QLP}{A\Delta P} \quad 4-1
\]

At lower pressures, a phenomenon known as slip flow occurs when gases are used to measure permeability. Klinkenberg derived a correlation to consider slip flow (Klinkenberg, 1941):

\[
k_s = k \left(1 + \frac{3.8\lambda}{R_s}\right) \quad 4-2
\]
where $\lambda$ is the mean free path of the flowing gas and $R$ is the radius of the pit openings of the wood matrix Eq. 4-2 can be rewritten as:

$$k_g = k\left(1 + \frac{b}{P}\right)$$  \hspace{1cm} 4-3

where $b$ is the Klinkenberg factor and can be estimated by the following empirical relation derived by Heid et al. (1950):

$$b = \left(3.98 \times 10^{-5}\right) k^{-0.39}$$  \hspace{1cm} 4-4

where $b$ is in atmospheres and $k$ is in cm$^2$.

For the measurement of the permeability for the two experimental wood species, a differential pressure test was performed in collaboration with Oregon State University. The experimental test apparatus used to perform the measurements is shown schematically in Figure 4-5. The flowing gas used was air at ambient conditions. Pressure upstream was measured using the pressure gauge readout, and the pressure downstream was open to the atmosphere. Upstream pressure was recorded for each specimen after approximately 30s. Flow rate was measured using a Gilian Gliberator bubble flow meter (Sensidyne, Clearwater, FL). Specimens were placed snugly in a Number 8 rubber stopper, which was then placed in the sample chamber. Care was taken to avoid damaging the specimen surfaces when being fit into the stopper, which could restrict flow. Section 4.4 for further details on the various conditions under which permeability values were explored and replication of those tests.
4.1.2.2 Specific Gravity and Porosity

Since the permeability samples were fairly regular in shape and were representative of the material being modeled, they were used to determine specific gravity after permeability was measured. Specific gravity was determined by ASTM D 2395, Method A- Volume by Measurement (ASTM, 2002). Weights were measured...
using a digital scale (Digiweigh) with precision to 0.01 gram. Measurements were taken using calipers with a precision of 0.03 mm.

Once the specific gravity ($G$) was determined, porosity ($\phi$) was determined from the following relation (Siau, 1984):

$$\phi = 1 - G_S \left( \frac{1}{G_0} + 0.01 \frac{M}{G_W} \right)$$

where:

- $G_S$ = the specific gravity at 12% moisture content
- $G_0$ = the specific gravity of the oven dry cell-wall, taken as 1.46 (Stamm, et al., 1937)
- $G_W$ = the specific gravity of absorbed water
- $M$ = the moisture content of the sample (%)

### 4.2 Supercritical Carbon Dioxide Treatment Apparatus

The supercritical CO$_2$ treatment system used in this experimental study to investigate the pressure development inside a wood specimen is shown schematically in Figure 4-6. Carbon dioxide of standard technical grade 99% pure (Industrial Welding Supply, Inc.) from a cylinder with a double dip tube configuration was used for flow to a single diaphragm high pressure compressor (Fluitron, Model A1-400) with a capacity of approximately 30 MPa. The compressor moved the carbon dioxide into the high pressure storage vessel, where pressure was controlled by a back-pressure regulator (Tescom, Model 26-1722-24). The flow of carbon dioxide from the high pressure storage vessel into the treatment vessel was regulated using low and high flow metering valves (flow coefficients of 0.04 and 0.37, respectively) to manually to regulate the flow rate into the treatment vessel during CO$_2$ impregnation and then back out of vessel during venting.
Figure 4-6: Schematic of the experimental system for supercritical carbon dioxide treatment of the 38 mm x 89 mm x 160 mm specimens with installed pressure and temperature probe measurement sensors.
The original dimensions of the storage and treatment vessel were 15 cm diameter by 100 cm length and 10 cm diameter by 60 cm length, respectively. A steel slug was placed in the bottom of the treatment vessel to reduce the effective length to 35 cm, reducing the gas volume load required in the treatment vessel. The lines used to connect into the treatment vessel were 12.7 mm stainless tubing. All fittings and vessel edges were tested with liquid leak detector (Snoop, Swaglok) to ensure that no leaks existed in the system.

Temperature of the vessel walls was controlled by jacketing the vessels with conducting sleeves, and was regulated by a master (West Model 3100) and slave (West Model 2072) controller, which monitored the vessel surface and wall temperatures, respectively. The lines connecting the vessels were also heated by wrapping them with heating tape to help maintain the desired temperature during treatment. The temperature of the atmosphere inside the treatment vessels was monitored with a Type K thermocouple of gauge 24 wire (OMEGA), with a precision of approximately ±2.2°C. Temperature measurements were taken as milli-volt readings using a Campbell 21x real time acquisition logger and then stored to subsequent data files on a computer.

Temperature inside the pressure probe arrangement (Figure 4-2) was monitored with 20 gauge type T thermocouple wire (Omega, TT-T-20) with copper positive and constantan negative leads that were insulated with a neoflon protective coating film. The accuracy of the thermocouple was ±1°C in the range of use in the study. These thermocouples were connected in series to the Campbell Data Logger in a similar fashion to those measuring the temperature of the pressure vessel.
Pressure measurements were collected with several OMEGA pressure transducers. Three transducers were of the type PX 420-5K GI with a range of 0 to 34.5 MPa with an estimated error of 0.5% at full scale reading. Two PX 4100-3KGV series transducers with a measurement range of 0 to 20.7 MPa, and an accuracy of 0.25% were also used. The PX4100 transducers were factory calibrated, so the remaining transducers were calibrated against them by pressurizing the vessel and normalizing the readings. All transducers had a maximum output of 40 mV, so a precision resistor was placed in series with each sensor. The Campbell 21x data logger was used to measure the voltage across the resistor. Furthermore, an analog to digital converter was placed in series with each Vessel’s pressure transducer, and was used as the control display of simultaneous pressure reading on the cabinet display during treatment.

Connection of the instrumented pressure treatment samples within the CO₂ treatment apparatus required special precautions to ensure that proper pressure readings were taken during the process. Because of the high treatment pressures and limited space, the pressure transducers were located outside the treatment vessel. A series of compression fittings and a welded union were constructed to connect the pressure line to the sample with impregnated pressure probes (Figure 4-7).

Each pressure probe in the sample was connected to the treatment system at the T-union compression fitting. The compression joints for the pressure lines consisted of two-part front and back brass ferrules. The thermocouple line was sealed by making a solid ferrule out of Teflon which was drilled with a 1mm pilot hole through which the thermocouple was guided. A silver solder union was made to connect the 3.2 mm line to the 1.5 mm line. This reduction was performed because the 1.5 mm tubing was flexible
Figure 4-7: Schematic representation of the complete connection of the pressure sample to the treatment vessel apparatus. One of the four lines is shown here, but all lines are identical.
and allowed for movement of the pressure lines so that all the compression fittings could be secured. This allowed placement of the connected sensor configuration properly within the inside of the treatment vessel. The smaller diameter tubing also reduced the volume of gas flowing to the pressure transducer, such that any lag in response time was negligible (Sinclair, et al., 1952). More compression fittings were used to transmit the pressure and thermocouple lines through the top and side ports of the treatment vessel. The lines were plugged at the end and inserted into the pressure vessel to ensure that all the pressure lines had no leaks. The vessel was then rapidly pressurized to maximum pressure to create a large pressure gradient in the lines and the system was observed for any elevation in pressure. All compression fittings were adjusted and the process was repeated several times until no pressure elevation was observed in any test measurement line. This series of pressure elevation checks was much more rigorous than that would be used during actual testing, ensuring that the line connections to the specimen were satisfactorily isolated from the surrounding pressurized environment of the treating vessel. Furthermore, the lines were plugged and retested every five specimens to ensure the integrity of the systematic pressurization of specimens during the loading and unloading of the CO₂ treatment cycle.

4.3 Supercritical Carbon Dioxide Treatment Procedure

The procedure used to treat the pressure specimens followed a standard pressurization, equalization, depressurization process (Figure 4-8). Pressurization and depressurization rates were always consistent for a specific test. The duration of the hold
period at maximum pressure (equalization) was dependent on the time it would take for all for probes to reach maximum pressure. Once the last probe reached maximum pressure, the depressurization process began until the CO$_2$ pressure inside the matrix probes was equalized at ambient atmospheric pressure. For those samples that were treated twice, the process was repeated in the exact same manner as the prior treatment.

The experimental conditions for treatment are summarized in Table 4-1.

<table>
<thead>
<tr>
<th>Treatment Parameters</th>
<th>Targeted Test Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>40°C</td>
</tr>
<tr>
<td>Maximum Pressure</td>
<td>10.3 MPa</td>
</tr>
<tr>
<td>Pressurization Rate</td>
<td>550, 825, 1240 kPa/min</td>
</tr>
<tr>
<td>Depressurization Rate</td>
<td>-550, -825, -1240 kPa/min</td>
</tr>
<tr>
<td>Equalization time</td>
<td>Variable dependent on specimen</td>
</tr>
</tbody>
</table>
Figure 4-8: Depiction of the treatment process with a pressurization and depressurization rate of 550 kPa/min.
4.4 Experimental Design

Table 4-2 summarizes the test conditions and replication of samples used to evaluate the mathematical model derived in Chapter 3.

Table 4-2: Specimen and test conditions used for measuring the pressure response in wood materials.

<table>
<thead>
<tr>
<th>Species Specimen</th>
<th># of Test Specimens</th>
<th>Flow Rate (kPa/min)</th>
<th># of Specimen Treatments</th>
</tr>
</thead>
<tbody>
<tr>
<td>shortleaf pine</td>
<td>5</td>
<td>1240</td>
<td>1</td>
</tr>
<tr>
<td>shortleaf pine</td>
<td>5</td>
<td>1240</td>
<td>2</td>
</tr>
<tr>
<td>shortleaf pine</td>
<td>5</td>
<td>825</td>
<td>1</td>
</tr>
<tr>
<td>shortleaf pine</td>
<td>5</td>
<td>825</td>
<td>2</td>
</tr>
<tr>
<td>Douglas-fir</td>
<td>5</td>
<td>550</td>
<td>1</td>
</tr>
<tr>
<td>Douglas-fir</td>
<td>5</td>
<td>550</td>
<td>2</td>
</tr>
<tr>
<td>Douglas-fir</td>
<td>5</td>
<td>825</td>
<td>1</td>
</tr>
<tr>
<td>Douglas-fir</td>
<td>5</td>
<td>825</td>
<td>2</td>
</tr>
</tbody>
</table>

To evaluate the appropriateness of the model developed in Chapter 3, one of the treatment parameters needed to be varied from one test to another. Of the two possible parameters, temperature and pressurization rate, pressurization rate was chosen, because temperature was very difficult to control in the vessel once the pressure in the vessel changed. Pressurization rate is an effective parameter to vary because the pressure gradient increases with the magnitude of the pressurization rate for a given porous material. Referring back to derived flow model (Eq. 3-7):

\[
\frac{\partial}{\partial x} \left( \beta_x \frac{A_x k_x \frac{\partial p}{\partial x}}{\mu_x B_g \frac{\partial}{\partial x}} \Delta x + \frac{\partial}{\partial y} \left( \beta_y \frac{A_y k_y \frac{\partial p}{\partial y}}{\mu_y B_g \frac{\partial}{\partial y}} \right) \Delta y + q_{gsc} = \frac{V_b \phi T_{sc}}{p_{sc} T} \frac{\partial}{\partial t} \left( \frac{p}{Z} \right) \right]

it can be recognized that the flow model is dependent on the pressure gradient \((\frac{\partial p}{\partial x})\) and \((\frac{\partial p}{\partial y})\), so any change in the pressure gradient will create a corresponding change
in the pressure throughout the matrix of the material. The baseline pressurization rate of 825 kPa/min was chosen according to prior work by (Schneider, 2000), meaning that both Douglas-fir and shortleaf pine specimens were treated at this rate. The second pressurization rates for the Douglas-fir and shortleaf pine specimens was 80 kPa/min and 1240 kPa/min, respectively. In this way, a common flow was used between the two species and could be used for a basis of comparison. The higher flow rate for the shortleaf pine and lower for the Douglas-fir were used because shortleaf pine tends to be more permeable in comparison to Douglas-fir.

Half of the samples were treated only once, with the remainder being retreated directly after the first treatment. The retreatment allowed for the exploration of the effect of two treatments on the wood matrix. Secondly, since the process conditions were practically identical for one specimen, the retreatment provided an opportunity to identify how any changes in the wood matrix (e.g. extractive treatment migration) might affect the prediction performance of the model.

The values collected from permeability measurements were used as inputs for the permeability parameter in the flow model, according the type of wood and orientation (Table 4-3). Non-treated specimens provided background wood permeability values. Additional permeability samples were subjected to one or two pressure treatments in the vessel during the treatment of a pressure specimen. The permeability specimens were placed in a loose nylon bag during the treatment of the pressure samples to hold the specimens in place without impeding CO₂ flow.
Table 4-3: Test conditions used to measure wood permeability of shortleaf pine and Douglas-fir specimens.

<table>
<thead>
<tr>
<th>Species Specimen</th>
<th># of Test Specimens</th>
<th>Orientation</th>
<th># of Pressure Treatments</th>
<th>Flow Rate (kPa/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>shortleaf pine</td>
<td>4</td>
<td>Width</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>shortleaf pine</td>
<td>4</td>
<td>Width</td>
<td>1</td>
<td>2 @ 825</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2 @ 1240</td>
</tr>
<tr>
<td>shortleaf pine</td>
<td>4</td>
<td>Width</td>
<td>2</td>
<td>2 @ 825</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2 @ 1240</td>
</tr>
<tr>
<td>shortleaf pine</td>
<td>4</td>
<td>Thickness</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>shortleaf pine</td>
<td>4</td>
<td>Thickness</td>
<td>1</td>
<td>2 @ 825</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2 @ 1240</td>
</tr>
<tr>
<td>shortleaf pine</td>
<td>4</td>
<td>Thickness</td>
<td>2</td>
<td>2 @ 825</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2 @ 1240</td>
</tr>
<tr>
<td>Douglas-fir</td>
<td>4</td>
<td>Width</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>Douglas-fir</td>
<td>4</td>
<td>Width</td>
<td>1</td>
<td>2 @ 550</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2 @ 825</td>
</tr>
<tr>
<td>Douglas-fir</td>
<td>4</td>
<td>Width</td>
<td>2</td>
<td>2 @ 550</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2 @ 825</td>
</tr>
<tr>
<td>Douglas-fir</td>
<td>3</td>
<td>Thickness</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>Douglas-fir</td>
<td>3</td>
<td>Thickness</td>
<td>1</td>
<td>2 @ 550</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1 @ 825</td>
</tr>
<tr>
<td>Douglas-fir</td>
<td>3</td>
<td>Thickness</td>
<td>2</td>
<td>2 @ 550</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1 @ 825</td>
</tr>
</tbody>
</table>
Chapter 5

Modeling and Experimental Results and Evaluation

This chapter presents the results of the experiments performed in this study. The chapter is divided into three sections. The first section summarizes the results of experiments that measured the model parameters. The second section presents the results of the pressure measurements and compares them to the mathematical model predictions. The final section presents results regarding particular assumptions applied relative to experimental development with verification of the critical CO$_2$ flow prediction model described in Chapter 3.

5.1 Model Parameters (Porosity and Permeability)

The two model parameters that were experimentally measured in this study were porosity and permeability. These measurements were used as input values for the computational model. In the following sections, the term “treated” refers to samples that were placed in the pressure vessel during an experimental trial as described by Section 4.3. Accordingly, the term “untreated” refers to those samples not placed in the pressure vessel.
5.1.1 Permeability Results

Observed permeability values from the test measurements outlined in Section 4.1.2.1 are shown in Table 5-1 to Table 5-3. Measured permeability values for shortleaf pine are presented along with those published in previous research, for the direction of the measured permeability value most closely related to that of the literature value (Table 5-1 and Table 5-2). The minimum, maximum, and mean values for radial permeability were between the two tree stem specimens (10 and 50 years old) studied by Choong and Fogg (1972). Values measured by Tesoro et al. (1966) were a mixture of the radial and tangential directions, but are still useful for comparative purposes. Radial permeability values measured in the current study closely corresponded to those of the mean test measure for southern pine sapwood evaluated in the Tesoro et al. (1966). Values for tangential permeability were higher by approximately an order of magnitude when compared to Choong and Fogg, but compared relatively closely to the mean sapwood values measured by Tesoro. Permeability after treatment in the current study was similar to that of the untreated samples.

Douglas-fir permeability results are summarized in Table 5-3 for untreated and treated samples, using only the mean value of the measurements for comparison to previous research. Untreated radial values ranged from approximately equivalent to those from Choong et al. (1972) to one and a half orders of magnitude higher when compared to Smith (1963). Tangential values ranged from 1.5 to 5 times higher (Smith, 1963) (Milota, 1998). Similar trends were seen when treated permeability values were compared to those in the literature.
Table 5-1: Summary of permeability measurements of untreated shortleaf pine (12% MC) in comparison to previously reported values expressed in µm$^2$ units of measure.

<table>
<thead>
<tr>
<th>Source</th>
<th>Age</th>
<th>Direction</th>
<th>Wood Type</th>
<th>Min.</th>
<th>Max.</th>
<th>Mean</th>
<th>St. Dev.</th>
<th># samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current Study</td>
<td>~40 yr</td>
<td>Radial</td>
<td>Heartwood</td>
<td>0.01</td>
<td>0.07</td>
<td>0.04</td>
<td>0.02</td>
<td>4</td>
</tr>
<tr>
<td>Current Study</td>
<td>~40 yr</td>
<td>Radial</td>
<td>Sapwood</td>
<td>0.02</td>
<td>0.10</td>
<td>0.07</td>
<td>0.03</td>
<td>6</td>
</tr>
<tr>
<td>Current Study</td>
<td>~40 yr</td>
<td>Radial</td>
<td>Both</td>
<td>0.01</td>
<td>0.10</td>
<td>0.06</td>
<td>0.03</td>
<td>10</td>
</tr>
<tr>
<td>Choong &amp; Fogg (1972)</td>
<td>10 yr</td>
<td>Radial</td>
<td>Both</td>
<td>0.036</td>
<td>0.343</td>
<td>0.176</td>
<td>n/a</td>
<td>13</td>
</tr>
<tr>
<td>Choong &amp; Fogg (1972)</td>
<td>50 yr</td>
<td>Radial</td>
<td>Both</td>
<td>0.006</td>
<td>0.056</td>
<td>0.028</td>
<td>n/a</td>
<td>80</td>
</tr>
<tr>
<td>Tesoro et al.(1966)*</td>
<td>n/a</td>
<td>Both</td>
<td>Sapwood</td>
<td>n/a</td>
<td>n/a</td>
<td>0.0753</td>
<td>n/a</td>
<td>4</td>
</tr>
<tr>
<td>Tesoro et al.(1966)*</td>
<td>n/a</td>
<td>Both</td>
<td>Heartwood</td>
<td>n/a</td>
<td>n/a</td>
<td>0.0146</td>
<td>n/a</td>
<td>4</td>
</tr>
<tr>
<td>Current Study</td>
<td>~40 yr</td>
<td>Tangential</td>
<td>Heartwood</td>
<td>0.02</td>
<td>0.25</td>
<td>0.09</td>
<td>0.09</td>
<td>5</td>
</tr>
<tr>
<td>Current Study</td>
<td>~40 yr</td>
<td>Tangential</td>
<td>Sapwood</td>
<td>0.08</td>
<td>0.30</td>
<td>0.17</td>
<td>0.09</td>
<td>5</td>
</tr>
<tr>
<td>Current Study</td>
<td>~40 yr</td>
<td>Tangential</td>
<td>Both</td>
<td>0.02</td>
<td>0.30</td>
<td>0.13</td>
<td>0.10</td>
<td>10</td>
</tr>
<tr>
<td>Choong &amp; Fogg (1972)</td>
<td>10 yr</td>
<td>Tangential</td>
<td>Both</td>
<td>0.005</td>
<td>0.026</td>
<td>0.009</td>
<td>n/a</td>
<td>14</td>
</tr>
<tr>
<td>Choong &amp; Fogg (1972)</td>
<td>50 yr</td>
<td>Tangential</td>
<td>Both</td>
<td>0.003</td>
<td>0.027</td>
<td>0.009</td>
<td>n/a</td>
<td>65</td>
</tr>
<tr>
<td>Tesoro et al.(1966)*</td>
<td>n/a</td>
<td>Both</td>
<td>Sapwood</td>
<td>n/a</td>
<td>n/a</td>
<td>0.0753</td>
<td>n/a</td>
<td>4</td>
</tr>
<tr>
<td>Tesoro et al.(1966)*</td>
<td>n/a</td>
<td>Both</td>
<td>Heartwood</td>
<td>n/a</td>
<td>n/a</td>
<td>0.0146</td>
<td>n/a</td>
<td>4</td>
</tr>
</tbody>
</table>

* Value reported in cm$^3$/sec·cm·atm. Conversion to µm$^2$ based on the assumption of viscosity of air at standard conditions (17.8x10$^{-6}$ Pa·s)
Table 5-2: Summary of permeability measurements (µm²) of treated shortleaf pine (12% MC) from the current study.

<table>
<thead>
<tr>
<th>Age</th>
<th>Direction</th>
<th>Wood Type</th>
<th>Min.</th>
<th>Max.</th>
<th>Mean</th>
<th>St. Dev.</th>
<th># samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>~40 yr Radial</td>
<td>Heartwood</td>
<td>0.01</td>
<td>0.07</td>
<td>0.03</td>
<td>0.02</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>~40 yr Radial</td>
<td>Sapwood</td>
<td>0.02</td>
<td>0.10</td>
<td>0.05</td>
<td>0.03</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td>~40 yr Radial</td>
<td>Mixed</td>
<td>0.01</td>
<td>0.10</td>
<td>0.04</td>
<td>0.02</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>~40 yr Tangential</td>
<td>Heartwood</td>
<td>0.01</td>
<td>0.25</td>
<td>0.06</td>
<td>0.06</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>~40 yr Tangential</td>
<td>Sapwood</td>
<td>0.06</td>
<td>0.30</td>
<td>0.11</td>
<td>0.07</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>~40 yr Tangential</td>
<td>Mixed</td>
<td>0.01</td>
<td>0.30</td>
<td>0.08</td>
<td>0.05</td>
<td>28</td>
<td></td>
</tr>
</tbody>
</table>
Table 5-3: Summary of permeability measurements of treated and untreated Douglas-fir heartwood (12% MC) in comparison to previously reported values expressed in \( \mu m^2 \) units of measure.

<table>
<thead>
<tr>
<th>Source</th>
<th>Treated (+)</th>
<th>Untreated (-)</th>
<th>Direction</th>
<th>Min.</th>
<th>Max.</th>
<th>Mean</th>
<th>St. Dev.</th>
<th># samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current Study</td>
<td>(-)</td>
<td>-</td>
<td>Radial</td>
<td>0.002</td>
<td>0.03</td>
<td>0.015</td>
<td>0.011</td>
<td>6</td>
</tr>
<tr>
<td>Schneider (2000)</td>
<td>(-)</td>
<td>-</td>
<td>Radial</td>
<td>n/a</td>
<td>n/a</td>
<td>0.001</td>
<td>0.001</td>
<td>3</td>
</tr>
<tr>
<td>Smith (1963)</td>
<td>(-)</td>
<td>-</td>
<td>Radial</td>
<td>n/a</td>
<td>n/a</td>
<td>0.00054E-4</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>Choong et al. (1972)</td>
<td>(-)</td>
<td>-</td>
<td>Radial</td>
<td>n/a</td>
<td>n/a</td>
<td>0.015</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
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<td>(-)</td>
<td>-</td>
<td>Tangential</td>
<td>0.010</td>
<td>0.18</td>
<td>0.06</td>
<td>0.06</td>
<td>8</td>
</tr>
<tr>
<td>Schneider (2000)</td>
<td>(-)</td>
<td>-</td>
<td>Tangential</td>
<td>n/a</td>
<td>n/a</td>
<td>0.003</td>
<td>0.004</td>
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<td>Smith (1963)</td>
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<td>-</td>
<td>Tangential</td>
<td>n/a</td>
<td>n/a</td>
<td>0.015E-4</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Choong et al. (1972)</td>
<td>(-)</td>
<td>-</td>
<td>Tangential</td>
<td>n/a</td>
<td>n/a</td>
<td>0.002</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>Milota (1998)</td>
<td>(-)</td>
<td>-</td>
<td>Tangential</td>
<td>n/a</td>
<td>n/a</td>
<td>0.0001</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>Current Study</td>
<td>(+)</td>
<td>-</td>
<td>Radial</td>
<td>0.002</td>
<td>0.04</td>
<td>0.015</td>
<td>0.012</td>
<td>20</td>
</tr>
<tr>
<td>Schneider (2000)</td>
<td>(+)</td>
<td>-</td>
<td>Radial</td>
<td>n/a</td>
<td>n/a</td>
<td>0.001</td>
<td>0.001</td>
<td>3</td>
</tr>
<tr>
<td>Current Study</td>
<td>(+)</td>
<td>-</td>
<td>Tangential</td>
<td>0.01</td>
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</tr>
<tr>
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<td>(+)</td>
<td>-</td>
<td>Tangential</td>
<td>n/a</td>
<td>n/a</td>
<td>0.004</td>
<td>0.001</td>
<td>3</td>
</tr>
</tbody>
</table>
A student’s two sample t-test was used to make comparisons between the sample groups. Statistical comparisons for differences between radial and tangential wood permeability, are presented in Table 5-4. Permeability was significantly higher in the tangential direction for untreated and treated shortleaf pine samples. This trend was in contrast to prior research, indicating that the permeability was greater in the radial direction than the tangential direction among the Southern yellow pine species, including shortleaf pine (Comstock, 1970)(Erickson, 1970). Radial permeability was significantly higher in the tangential, untreated Douglas-fir samples. There were no significant differences between the wood flow directions for treated Douglas-fir. The flow trend in directional permeability for Douglas-fir was less clear, (see Table 5-3). All sample groups of similar direction and wood type were also compared (Table 5-5). In all cases, the differences between the treated and untreated samples were not significant. Conversely, Sahle-Demessie et al. (1995) investigated the effects of supercritical carbon dioxide treatment on permeability and found that treatment typically improved permeability. Despite this trend, SC CO$_2$ treatment in this test did not significantly alter permeability, nor was the change consistent in terms of direction.

In summary, the permeability values measured in this study were poorly correlated with previous measurements. Permeability values were larger in almost every case except for the radial shortleaf pine values. Furthermore, the trends in directional permeability for the shortleaf pine used in this research were the opposite of those found previously.
Table 5-4: t-test comparisons between the directional permeabilities (µm²) for treated and untreated samples (α=0.05).

<table>
<thead>
<tr>
<th>Wood Type</th>
<th>Direction</th>
<th>Radial Mean (S.D.)*</th>
<th>Tangential Mean (S.D.)*</th>
<th>t-value</th>
<th>t*</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>Radial</td>
<td>0.06 (0.03)</td>
<td>0.13 (0.10)</td>
<td>-2.39</td>
<td>2.23</td>
<td>0.038</td>
</tr>
<tr>
<td>shortleaf pine</td>
<td>Tangential</td>
<td>0.08 (0.05)</td>
<td>0.06 (0.06)</td>
<td>-3.03</td>
<td>2.07</td>
<td>0.005</td>
</tr>
<tr>
<td>Treated</td>
<td>Radial</td>
<td>0.04 (0.03)</td>
<td>0.08 (0.10)</td>
<td>-2.23</td>
<td>2.37</td>
<td>0.061</td>
</tr>
<tr>
<td>shortleaf pine</td>
<td>Tangential</td>
<td>0.04 (0.05)</td>
<td>0.06 (0.06)</td>
<td>-2.69</td>
<td>2.13</td>
<td>0.017</td>
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</tbody>
</table>

Table 5-5: t-test comparisons between the permeabilities (µm²) of treated and untreated samples (α=0.05).

<table>
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<tr>
<th>Wood Type</th>
<th>Direction</th>
<th>Untreated Mean (S.D.)*</th>
<th>Treated Mean (S.D.)*</th>
<th>t-value</th>
<th>t*</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>shortleaf pine</td>
<td>Radial</td>
<td>0.06 (0.03)</td>
<td>0.04 (0.03)</td>
<td>1.65</td>
<td>2.12</td>
<td>0.12</td>
</tr>
<tr>
<td>shortleaf pine</td>
<td>Tangential</td>
<td>0.13 (0.10)</td>
<td>0.08 (0.05)</td>
<td>1.58</td>
<td>2.20</td>
<td>0.14</td>
</tr>
<tr>
<td>Douglas-fir</td>
<td>Radial</td>
<td>0.015 (0.011)</td>
<td>0.015 (0.012)</td>
<td>-0.06</td>
<td>2.26</td>
<td>0.95</td>
</tr>
<tr>
<td>Douglas-fir</td>
<td>Tangential</td>
<td>0.06 (0.06)</td>
<td>0.04 (0.04)</td>
<td>0.82</td>
<td>2.23</td>
<td>0.43</td>
</tr>
</tbody>
</table>

*S.D. equals test population standard deviation
5.1.2 Porosity Results

The results of the porosity measurements are summarized in Table 5-6.

Porosity is directly related to specific gravity (SG) (Eq. 4-5). A SG value of 0.55 is at the upper end of the typical range for Douglas-fir from Western Oregon, where the average SG value is reported to be 0.45 (Bowyer, 2003). SG values of sampled shortleaf pine wood material were above published values for shortleaf pine with a value of 0.75 compared to 0.51 (U.S. Forest Products Laboratory, 1999). The values could potentially be higher because the wood contained more latewood, i.e. higher density material, than would normally constitute a sample of tested material. In the case of the pine specimens, which were segregated between heartwood and sapwood, no significant differences in specific gravity were observed. The values for both species of wood had a COV of 10 which was comparable to other results (U.S. Forest Products Laboratory, 1999).

Table 5-6: Porosity measurements of Douglas-fir and shortleaf pine samples tested, at 12% MC.

<table>
<thead>
<tr>
<th></th>
<th># of Samples</th>
<th>Specific Gravity</th>
<th>Porosity</th>
<th>Descriptive Statistics*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Douglas fir</td>
<td>12</td>
<td>0.55 (0.06)</td>
<td>0.62 (0.04)</td>
<td>mean (S.D.) [COV]</td>
</tr>
<tr>
<td>shortleaf pine</td>
<td>12</td>
<td>0.75 (0.07)</td>
<td>0.49 (0.05)</td>
<td>mean (S.D.) [COV]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[9]</td>
<td>[10]</td>
<td></td>
</tr>
</tbody>
</table>

* S.D. equals observed test population standard deviation with also computed coefficient of variation (COV).
5.2 Pressure Measurement Results

According to the experimental design described in Section 4.4, pressure treatment trials were performed on 20 Douglas-fir (DF) and 20 shortleaf pine (SLP) specimens. Half of each type of wood was treated twice, so that 30 trials were performed on each type of wood. Overall, a total of 57 trials were performed, including 27 DF trials and 30 SLP. Three trials with DF samples were lost due to material or probe failures. In the following sections, the designations P1 to P4 refer to the probes that were located and arbitrarily numbered one through four in Figure 4-3.

The results from these trials are summarized in Table 5-7 and Table 5-8. Any specimen designated with DFx-2 or SLPx-2 signifies the second measurement of the double treatment. The results were summarized by choosing several pressure values for both the pressurization and depressurization cycles, including the average difference in pressure between the vessel and the probe. Secondly, the maximum pressure difference between the vessel and probe during each stage of the cycle was tabulated. Vessel pressure was assumed to represent the pressure at the surface of the specimen. Finally, the time required for each of the probes to reach equilibrium with the vessel at maximum pressure was tabulated. These values provided a generalized indication of the transient rate of movement of the SC CO₂ through the sample.
Table 5-7: Summary of experimental SC CO\textsubscript{2} pressure trials for Douglas-fir samples.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Avg. ΔP During Pressing</th>
<th>Max. ΔP During Pressing</th>
<th>Time to Max. P after vessel reaches Max. P</th>
<th>Avg. ΔP During Venting</th>
<th>Max. ΔP During Venting</th>
</tr>
</thead>
<tbody>
<tr>
<td>DF1</td>
<td>402</td>
<td>2007</td>
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<td>-171</td>
<td>-1985</td>
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<tr>
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<td>4071</td>
<td>13.4</td>
<td>-340</td>
<td>-2056</td>
</tr>
<tr>
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<td>3474</td>
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<td>-211</td>
<td>-2893</td>
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<tr>
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<td>-3402</td>
</tr>
<tr>
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<td>3337</td>
<td>14.7</td>
<td>-344</td>
<td>-2584</td>
</tr>
<tr>
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<td>0.5</td>
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<td>-531</td>
</tr>
<tr>
<td>P1</td>
<td>499</td>
<td>1176</td>
<td>0.2</td>
<td>-128</td>
<td>-318</td>
</tr>
<tr>
<td>P2</td>
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<td>0.0</td>
<td>-33</td>
<td>-134</td>
</tr>
<tr>
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<td>118</td>
<td>498</td>
<td>0.1</td>
<td>-266</td>
<td>-659</td>
</tr>
<tr>
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<td>0.2</td>
<td>-172</td>
<td>-411</td>
</tr>
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</tr>
<tr>
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<td>-342</td>
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</table>

* Pressure Values represented in kPa and time in minutes.
ΔP represents the difference between the CO\textsubscript{2} pressure-controlled vessel and wood inserted probe pressure measurements.
### Table 5-7: cont.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Avg. ΔP During Pressing</th>
<th>Max. ΔP During Pressing</th>
<th>Time to Max. P after vessel reaches Max. P</th>
<th>Avg. ΔP During Venting</th>
<th>Max. ΔP During Venting</th>
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* Pressure Values represented in kPa and time in minutes.  
ΔP represents the difference between the CO₂ pressure-controlled vessel and wood inserted probe pressure measurements.
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*Pressure Values represented in kPa and time in minutes.

ΔP represents the difference between the CO$_2$ pressure-controlled vessel and wood inserted probe pressure measurements.
Table 5-8: Summary of the experimental SC CO$_2$ pressure trials for shortleaf pine samples

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* Pressure Values represented in kPa and time in minutes.

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* Pressure Values represented in kPa and time in minutes. 
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</table>

* Pressure Values represented in kPa and time in minutes.
ΔP represents the difference between the CO₂ pressure-controlled vessel and wood inserted probe pressure measurements.
In Table 5-9 and Table 5-10, the data were tabulated in a similar manner to the aforementioned Tables with only the average of all probes presented. The specimens for each wood species exhibited variable pressure values. Values for Douglas-fir had COVs of 38 for the *Max. ΔP Pressing*, 99 for *Max. ΔP Venting* at the low pressurization rate, 54 for the *Max. ΔP Pressing*, and 96 for *Equilibrium Time* at the high pressurization rate. For shortleaf pine, values ranged from 64 for *Max. ΔP Pressing* to 111 for *Equilibrium Time* at the low pressurization rate and 48 for *Max. ΔP Pressing* to 236 for *Equilibrium Time* at the high pressurization rate.

A new value was introduced to the final columns of Table 5-9 and Table 5-10 in attempt to classify the variability observed in the pressure profile behavior, which was given the generic name of “Gradient”. This quantity was a normalization of the other values in the table and was calculated empirically as follows:

\[
Weighted\ Gradient = Average\left(\frac{\Delta P\ PRESS}{1000},\frac{Max\ \Delta P\ PRESS}{2000},\frac{\Delta P\ VENT}{1000},\frac{Max\ \Delta P\ VENT}{2000},\frac{EQUILLIBRIUM\ TIME}{2000}\right)
\]

In Eq.5-1, the \(\Delta P\) and *Max. ΔP* values were divided by 1000 and 2000, respectively, in order to give all the values approximate equal weight, so that one category was not overemphasized in comparison to another. The calculation resulted in an intuitive relationship, where samples with a low gradient value exhibited discretely low pressure gradients and shorter equilibrium times, while the converse held for higher observed gradient values. Consequently, the gradient value was
Table 5-9: Summary of pressure measured during SC CO$_2$ treatment trials for Douglas-fir.

### Low Pressurization Rate (550 kPa/min)

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Avg. ΔP Pressing</th>
<th>Max. ΔP Pressing</th>
<th>Equilibrium Time</th>
<th>Avg. ΔP Venting</th>
<th>Max. ΔP Venting</th>
<th>Gradient</th>
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### High Pressurization Rate (825 kPa/min)

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<th>Max. ΔP Pressing</th>
<th>Equilibrium Time</th>
<th>Avg. ΔP Venting</th>
<th>Max. ΔP Venting</th>
<th>Gradient</th>
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* Pressure Values represented in kPa and time in minutes.

ΔP represents the difference between the CO$_2$ pressure-controlled vessel and wood inserted probe pressure measurements.
Table 5-10: Summary of pressure measured during SC CO₂ treatment trials for shortleaf pine.

### Low Pressurization Rate (825 kPa/min)

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<th>Specimen</th>
<th>Avg. ΔP Pressing</th>
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<th>Equilibrium Time</th>
<th>Avg. ΔP Venting</th>
<th>Max. ΔP Venting</th>
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### High Pressurization Rate (1240 kPa/min)

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<th>Max. ΔP Pressing</th>
<th>Equilibrium Time</th>
<th>Avg. ΔP Venting</th>
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<tr>
<td>COV</td>
<td>76</td>
<td>48</td>
<td>236</td>
<td>57</td>
<td>50</td>
<td>118</td>
</tr>
</tbody>
</table>

* Pressure Values represented in kPa and time in minutes.

ΔP represents the difference between the CO₂ pressure-controlled vessel and wood inserted probe pressure measurements.
similar to transmissibility (Eq. 3-10) in that it was a measure of fluid propagation (flow movement).

The samples in Table 5-9 and Table 5-10 are arranged in ascending order of gradient magnitude to help delineate the highly permeable samples from the less permeable samples. The gradient value was used to classify data into groups of less and more easily treated samples. The gradient value was the average of several averaged values, so using it as response variable to make distinct inferences could be misleading. The gradient value was used to delineate observations and to classify the data into groups of less easily and more easily treated samples, while a more in depth evaluation will be provided in forthcoming sections. The gradient values were used to divide each wood type at a particular pressurization rate into fast flow (low gradient) and slow flow (high gradient) groups at the median of each population. This provided each subset with sufficient replication for analyses. A reduction in COV of at least 24% was achieved by classifying the wood species into subgroups according to gradient value (Table 5-11).

In Figure 5-1 and Figure 5-2, representative treatment plots for each wood species at a high and low gradient value are presented. A noticeable difference existed between the pressures at each probe location for the representative high gradient sample for both wood species. These differences were much smaller in the representative
Table 5-11: Comparison of the average weighted gradient values when they are divided into low and high subgroups.

<table>
<thead>
<tr>
<th>Specimen Grouping</th>
<th>Gradient Average</th>
<th>Gradient St. Dev.</th>
<th>Gradient COV</th>
<th>% Reduction in COV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Douglas-fir at Low Pressurization Rate (550 kPa/min)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>All</td>
<td>1.23</td>
<td>0.78</td>
<td>0.63</td>
<td>-</td>
</tr>
<tr>
<td>Low Gradient</td>
<td>0.57</td>
<td>0.27</td>
<td>0.46</td>
<td>27</td>
</tr>
<tr>
<td>High Gradient</td>
<td>1.80</td>
<td>0.61</td>
<td>0.34</td>
<td>30</td>
</tr>
<tr>
<td>Douglas-fir at High Pressurization Rate (825 kPa/min)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>All</td>
<td>1.42</td>
<td>1.15</td>
<td>0.81</td>
<td>-</td>
</tr>
<tr>
<td>Low Gradient</td>
<td>0.64</td>
<td>0.26</td>
<td>0.41</td>
<td>49</td>
</tr>
<tr>
<td>High Gradient</td>
<td>2.20</td>
<td>1.17</td>
<td>0.53</td>
<td>35</td>
</tr>
<tr>
<td>shortleaf pine at Low Pressurization Rate (825 kPa/min)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>All</td>
<td>0.46</td>
<td>0.40</td>
<td>0.87</td>
<td>-</td>
</tr>
<tr>
<td>Low Gradient</td>
<td>0.12</td>
<td>0.05</td>
<td>0.41</td>
<td>53</td>
</tr>
<tr>
<td>High Gradient</td>
<td>0.76</td>
<td>0.32</td>
<td>0.43</td>
<td>51</td>
</tr>
<tr>
<td>shortleaf pine at High Pressurization Rate (1240 kPa/min)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>All</td>
<td>0.50</td>
<td>0.59</td>
<td>1.18</td>
<td>-</td>
</tr>
<tr>
<td>Low Gradient</td>
<td>0.17</td>
<td>0.05</td>
<td>0.28</td>
<td>76</td>
</tr>
<tr>
<td>High Gradient</td>
<td>0.79</td>
<td>0.71</td>
<td>0.90</td>
<td>24</td>
</tr>
</tbody>
</table>

low gradient samples. The pressure gradient increased noticeably for both species close to the critical pressure (7.4 MPa) during the pressurization and depressurization stages of treatment. Appendix D contains plots of every sample in this study.

Samples within a wood species generally showed larger gradients at faster pressurization rates in comparison to slower rates of applied CO₂ pressurization. The average gradient value at the lower pressurization rate of 550 kPa/min for Douglas-fir samples was 1.23 compared to that of the higher pressurization rate of 825 kPa/min at 1.42. The difference between the two gradient values was not substantial, which was affected by a higher number of low gradient samples occurring in the high pressurization rate population. The distribution of the low pressurization gradient values was skewed slightly to the high end, with a mean of 1.23 compared to a median
Figure 5-1: Typical treatment cycle plot of CO$_2$ pressure measurements made from the inserted probes (P1 to P4), with respect to a low gradient Douglas-fir sample DF20 (A) compared to a high gradient sample DF4-1 (B).
Figure 5-2: Typical treatment cycle plot of CO$_2$ pressure measurements made from the inserted probes (P1 to P4), with respect to a low gradient shortleaf pine sample SLP8 (A) compared to a high gradient sample SLP10 (B).
of 1.09. Conversely, the high pressurization gradient values were skewed to the low end, with a mean of 1.42 compared to an estimated median of 1.07. For shortleaf pine, the values were relatively close between low and high applied pressurization rates of 825 and 1240 kPa/min, at 0.46 and 0.50, respectively. The two pressurization rates did not differ considerably to cause a large disparity in the pressure profile gradient. A comparison of the two wood species at a similar pressurization rate (825 kPa/min) indicated that the Douglas-fir samples exhibited a higher gradient value in comparison to the shortleaf pine samples (1.42 compared to 0.46).

5.2.1 Modeling Results

The CO$_2$ pressure at each individual pressure probe location (Figure 4-3) was compared to the pressure predicted by the computational flow model to evaluate the accuracy of the computational flow model and summarized in Table 5-12 and Table 5-13. The tables include pressure values that are similar to Table 5-7 and Table 5-8, only in this case the differences are between the experimental pressure measured by the inserted pressure probe and the pressure predicted by the computational flow model. Thus the model can be characterized as being more accurate when the differences are smaller and less accurate when the differences are larger. Negative differences in the tables indicate that measured pressure was greater than the predicted pressure.

The pressure values depict a consistent response in prediction accuracy for both wood species, where a large magnitude of the \textit{Max. AP Pressing} and \textit{Venting}...
Table 5-12: Summary of the comparisons between the experimental SC CO₂ pressure measured by the inserted pressure location probes (P1-P4) and the pressure predicted by the computational flow model for the Douglas-fir (DF) samples.

**Low Pressurization Rate (550 kPa/min)**

<table>
<thead>
<tr>
<th>Probe Location</th>
<th>Avg. ΔP During Pressing</th>
<th>Max. ΔP During Pressing</th>
<th>Avg. ΔP During Venting</th>
<th>Max. ΔP During Venting</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1 AVERAGE</td>
<td>293</td>
<td>1015</td>
<td>-164</td>
<td>-750</td>
</tr>
<tr>
<td>S. D.</td>
<td>143</td>
<td>389</td>
<td>186</td>
<td>1024</td>
</tr>
<tr>
<td>COV</td>
<td>49</td>
<td>38</td>
<td>113</td>
<td>137</td>
</tr>
<tr>
<td>P2 AVERAGE</td>
<td>1006</td>
<td>2162</td>
<td>-432</td>
<td>-1604</td>
</tr>
<tr>
<td>S. D.</td>
<td>531</td>
<td>926</td>
<td>286</td>
<td>1539</td>
</tr>
<tr>
<td>COV</td>
<td>53</td>
<td>43</td>
<td>18</td>
<td>96</td>
</tr>
<tr>
<td>P3 AVERAGE</td>
<td>796</td>
<td>1688</td>
<td>-363</td>
<td>-1309</td>
</tr>
<tr>
<td>S. D.</td>
<td>453</td>
<td>848</td>
<td>255</td>
<td>1531</td>
</tr>
<tr>
<td>COV</td>
<td>57</td>
<td>50</td>
<td>70</td>
<td>117</td>
</tr>
<tr>
<td>P4 AVERAGE</td>
<td>852</td>
<td>1840</td>
<td>-582</td>
<td>-1489</td>
</tr>
<tr>
<td>S. D.</td>
<td>419</td>
<td>802</td>
<td>369</td>
<td>1293</td>
</tr>
<tr>
<td>COV</td>
<td>49</td>
<td>44</td>
<td>63</td>
<td>87</td>
</tr>
</tbody>
</table>

**High Pressurization Rate (825 kPa/min)**

<table>
<thead>
<tr>
<th>Probe Location</th>
<th>Avg. ΔP During Pressing</th>
<th>Max. ΔP During Pressing</th>
<th>Avg. ΔP During Venting</th>
<th>Max. ΔP During Venting</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1 AVERAGE</td>
<td>309</td>
<td>1176</td>
<td>-115</td>
<td>-772</td>
</tr>
<tr>
<td>S. D.</td>
<td>265</td>
<td>756</td>
<td>87</td>
<td>532</td>
</tr>
<tr>
<td>COV</td>
<td>86</td>
<td>64</td>
<td>76</td>
<td>69</td>
</tr>
<tr>
<td>P2 AVERAGE</td>
<td>940</td>
<td>2342</td>
<td>-294</td>
<td>-1164</td>
</tr>
<tr>
<td>S. D.</td>
<td>593</td>
<td>1155</td>
<td>300</td>
<td>822</td>
</tr>
<tr>
<td>COV</td>
<td>63</td>
<td>49</td>
<td>102</td>
<td>71</td>
</tr>
<tr>
<td>P3 AVERAGE</td>
<td>626</td>
<td>1581</td>
<td>-254</td>
<td>-1162</td>
</tr>
<tr>
<td>S. D.</td>
<td>458</td>
<td>1111</td>
<td>224</td>
<td>912</td>
</tr>
<tr>
<td>COV</td>
<td>73</td>
<td>70</td>
<td>88</td>
<td>79</td>
</tr>
<tr>
<td>P4 AVERAGE</td>
<td>709</td>
<td>1773</td>
<td>-411</td>
<td>-1355</td>
</tr>
<tr>
<td>S. D.</td>
<td>434</td>
<td>1167</td>
<td>190</td>
<td>822</td>
</tr>
<tr>
<td>COV</td>
<td>61</td>
<td>66</td>
<td>46</td>
<td>61</td>
</tr>
</tbody>
</table>

* Pressure Values represented in kPa

ΔP represents the difference between the CO₂ pressure-predicted by the flow model and the inserted measurement sensor probe.
Table 5-13: Summary of the comparisons between the experimental SC CO₂ pressure measured by the inserted pressure location probes (P1-P4) and the pressure predicted by the computational flow model for the shortleaf pine (SLP) samples.

**Low Pressurization Rate (825 kPa/min)**

<table>
<thead>
<tr>
<th>Probe Location</th>
<th>Avg. AP During Pressing</th>
<th>Max. ΔP During Pressing</th>
<th>Avg. AP During Venting</th>
<th>Max. ΔP During Venting</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1 AVERAGE</td>
<td>17</td>
<td>216</td>
<td>-21</td>
<td>-180</td>
</tr>
<tr>
<td>S. D.</td>
<td>12</td>
<td>67</td>
<td>20</td>
<td>48</td>
</tr>
<tr>
<td>COV</td>
<td>73</td>
<td>31</td>
<td>93</td>
<td>27</td>
</tr>
<tr>
<td>P2 AVERAGE</td>
<td>108</td>
<td>491</td>
<td>-120</td>
<td>-618</td>
</tr>
<tr>
<td>S. D.</td>
<td>140</td>
<td>436</td>
<td>146</td>
<td>751</td>
</tr>
<tr>
<td>COV</td>
<td>129</td>
<td>89</td>
<td>121</td>
<td>122</td>
</tr>
<tr>
<td>P3 AVERAGE</td>
<td>398</td>
<td>1028</td>
<td>-379</td>
<td>-1346</td>
</tr>
<tr>
<td>S. D.</td>
<td>538</td>
<td>947</td>
<td>334</td>
<td>1261</td>
</tr>
<tr>
<td>COV</td>
<td>135</td>
<td>92</td>
<td>88</td>
<td>94</td>
</tr>
<tr>
<td>P4 AVERAGE</td>
<td>572</td>
<td>1413</td>
<td>-525</td>
<td>-1928</td>
</tr>
<tr>
<td>S. D.</td>
<td>561</td>
<td>940</td>
<td>336</td>
<td>1423</td>
</tr>
<tr>
<td>COV</td>
<td>98</td>
<td>66</td>
<td>64</td>
<td>74</td>
</tr>
</tbody>
</table>

**High Pressurization Rate (1240 kPa/min)**

<table>
<thead>
<tr>
<th>Probe Location</th>
<th>Avg. AP During Pressing</th>
<th>Max. ΔP During Pressing</th>
<th>Avg. AP During Venting</th>
<th>Max. ΔP During Venting</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1 AVERAGE</td>
<td>37</td>
<td>253</td>
<td>-35</td>
<td>-235</td>
</tr>
<tr>
<td>S. D.</td>
<td>26</td>
<td>71</td>
<td>34</td>
<td>86</td>
</tr>
<tr>
<td>COV</td>
<td>69</td>
<td>28</td>
<td>98</td>
<td>36</td>
</tr>
<tr>
<td>P2 AVERAGE</td>
<td>95</td>
<td>389</td>
<td>-112</td>
<td>-478</td>
</tr>
<tr>
<td>S. D.</td>
<td>116</td>
<td>296</td>
<td>152</td>
<td>562</td>
</tr>
<tr>
<td>COV</td>
<td>123</td>
<td>76</td>
<td>136</td>
<td>117</td>
</tr>
<tr>
<td>P3 AVERAGE</td>
<td>325</td>
<td>835</td>
<td>-267</td>
<td>-964</td>
</tr>
<tr>
<td>S. D.</td>
<td>501</td>
<td>858</td>
<td>315</td>
<td>1079</td>
</tr>
<tr>
<td>COV</td>
<td>154</td>
<td>103</td>
<td>118</td>
<td>112</td>
</tr>
<tr>
<td>P4 AVERAGE</td>
<td>627</td>
<td>1573</td>
<td>-603</td>
<td>-1964</td>
</tr>
<tr>
<td>S. D.</td>
<td>401</td>
<td>716</td>
<td>374</td>
<td>1303</td>
</tr>
<tr>
<td>COV</td>
<td>64</td>
<td>45</td>
<td>62</td>
<td>66</td>
</tr>
</tbody>
</table>

* Pressure Values represented in kPa
ΔP represents the difference between the CO₂ pressure-predicted by the flow model and the inserted measurement sensor probe.
corresponded to a large \textit{Avg. \( \Delta P \) Pressing} and \textit{Venting} and vice versa. This indicates that model inaccuracy was primarily caused by a consistent error rather than a deviation at a specific point during the treatment process. The consistency between average and maximum values permits the use of only \textit{Avg. \( \Delta P \) Pressing} and \textit{Venting} to make comparisons from this point forward.

Model accuracy was generally lower for DF specimens in comparison to SLP specimens. \textit{Avg. \( \Delta P \) Pressing} values for DF specimens ranged from 293 to 1006 kPa at the low pressurization rate, and 309 to 940 kPa at the high pressurization rate. Values for SLP ranged from 17 to 572 kPa at the low pressurization rate and 37 to 627 for the high pressurization rate. For both wood species, the smallest differences were observed in the most shallow probe (P1 at 12-mm diagonal depth location). The largest differences in DF specimens were observed in the next probe (P2 at 24-mm diagonal depth location), while the deepest probe (P4 at 48-mm diagonal depth location) exhibited the largest inaccuracy for SLP specimens. Inaccuracy increased as probe depth increased in every case except for Probe #2 in the DF specimens.

\textit{Avg. \( \Delta P \) Venting} values exhibited a slightly different trend compared to \textit{Avg. \( \Delta P \) Pressing}, where DF specimens varied by -164 to -582 kPa and -115 to -411 kPa for low and high pressurization rates, respectively. Values for SLP specimens at low and high pressurization rates varied from -21 to -525 kPa and -35 to -603 kPa, respectively. The differences were typically greater for DF specimens compared to SLP specimens, except for high pressurization rate specimens, where the difference was greater for SLP specimens. Furthermore, the magnitude of \textit{Avg. \( \Delta P \) Venting} was smaller compared to \textit{Avg. \( \Delta P \) Pressing} for DF specimens, but the values for SLP
specimens was relatively similar. *Avg. ΔP Venting* values were lowest at the most shallow probe (P1 at 12-mm diagonal depth location) and highest at the deepest probe (P4 48 mm diagonal depth). Prediction accuracy declined with increasing depth in every case except for the case Probe #2 (12-mm diagonal depth location) to Probe #3 (36-mm diagonal depth location) for DF specimens.

Differences were observed between pressurization rates for both DF and SLP specimens. Average disparities between predicted and measured pressures ranged from approximately 25 to 200 kPa and 20 to 350 kPa for DF and SLP specimens, respectively. No consistent trend was recognized for either wood species, as the pressure differences were smaller at higher pressure rates in some cases while the converse occurred in others.

Table 5-14 and Table 5-15 summarize the prediction performance of the computational flow model, with the results divided into subgroups of high and low gradient value for each wood species. *Avg. ΔP Pressing* increased from low to high gradient values for both DF and SLP specimens. DF Values ranged respectively from 241 to 633 kPa and 355 to 1316 kPa and SLP values ranged from 23 to 245 kPa and 31 to 932 kPa from low to high gradient groups. *Avg. ΔP Venting* values generally exhibited a similar trend. DF specimens ranged from -123 to -373 kPa in the low gradient group and increased in range from -159 to -625 kPa in the high gradient group. SLP specimens ranged from -42 to -313 kPa in the low gradient group and -16 to -801 kPa in the high gradient group, increasing in magnitude in every case except the low end range.
Table 5-14: Summary of the comparisons between the experimental SC CO₂ pressure measured by the inserted pressure location probes (P1-P4) and the pressure predicted by the computational flow model for the Douglas-fir (DF) samples divided in gradient groups.

<table>
<thead>
<tr>
<th>Probe Location</th>
<th>Low Gradient</th>
<th></th>
<th></th>
<th>High Gradient</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Avg. ΔP</td>
<td>Max. ΔP</td>
<td>Avg. ΔP</td>
<td>Max. ΔP</td>
<td></td>
</tr>
<tr>
<td></td>
<td>During Pressing</td>
<td>During Pressing</td>
<td>During Venting</td>
<td>During Venting</td>
<td></td>
</tr>
<tr>
<td>P1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AVERAGE</td>
<td>241</td>
<td>904</td>
<td>-123</td>
<td>-508</td>
<td></td>
</tr>
<tr>
<td>S. D.</td>
<td>111</td>
<td>376</td>
<td>81</td>
<td>235</td>
<td></td>
</tr>
<tr>
<td>COV</td>
<td>46</td>
<td>42</td>
<td>66</td>
<td>46</td>
<td></td>
</tr>
<tr>
<td>P2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AVERAGE</td>
<td>633</td>
<td>1587</td>
<td>-333</td>
<td>-1070</td>
<td></td>
</tr>
<tr>
<td>S. D.</td>
<td>251</td>
<td>599</td>
<td>261</td>
<td>706</td>
<td></td>
</tr>
<tr>
<td>COV</td>
<td>40</td>
<td>38</td>
<td>78</td>
<td>66</td>
<td></td>
</tr>
<tr>
<td>P3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AVERAGE</td>
<td>411</td>
<td>978</td>
<td>-190</td>
<td>-600</td>
<td></td>
</tr>
<tr>
<td>S. D.</td>
<td>412</td>
<td>762</td>
<td>186</td>
<td>449</td>
<td></td>
</tr>
<tr>
<td>COV</td>
<td>100</td>
<td>78</td>
<td>98</td>
<td>75</td>
<td></td>
</tr>
<tr>
<td>P4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AVERAGE</td>
<td>529</td>
<td>1207</td>
<td>-373</td>
<td>-955</td>
<td></td>
</tr>
<tr>
<td>S. D.</td>
<td>309</td>
<td>642</td>
<td>181</td>
<td>346</td>
<td></td>
</tr>
<tr>
<td>COV</td>
<td>58</td>
<td>53</td>
<td>49</td>
<td>36</td>
<td></td>
</tr>
</tbody>
</table>

* Pressure Values represented in kPa

ΔP represents the difference between the CO₂ pressure-predicted by the flow model and the inserted measurement sensor probe.
Table 5-15: Summary of the comparisons between the experimental SC CO₂ pressure measured by the inserted pressure location probes (P1-P4) and the pressure predicted by the computational flow model for the shortleaf pine (SLP) samples divided in gradient groups.

### Low Gradient

<table>
<thead>
<tr>
<th>Probe Location</th>
<th>Avg. ΔP During Pressing</th>
<th>Max. ΔP During Pressing</th>
<th>Avg. ΔP During Venting</th>
<th>Max. ΔP During Venting</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1 AVERAGE</td>
<td>23</td>
<td>211</td>
<td>-42</td>
<td>-197</td>
</tr>
<tr>
<td>S. D.</td>
<td>20</td>
<td>64</td>
<td>26</td>
<td>73</td>
</tr>
<tr>
<td>COV</td>
<td>87</td>
<td>30</td>
<td>62</td>
<td>37</td>
</tr>
<tr>
<td>P2 AVERAGE</td>
<td>53</td>
<td>267</td>
<td>-51</td>
<td>-232</td>
</tr>
<tr>
<td>S. D.</td>
<td>61</td>
<td>133</td>
<td>65</td>
<td>118</td>
</tr>
<tr>
<td>COV</td>
<td>116</td>
<td>50</td>
<td>126</td>
<td>51</td>
</tr>
<tr>
<td>P3 AVERAGE</td>
<td>52</td>
<td>284</td>
<td>-84</td>
<td>-327</td>
</tr>
<tr>
<td>S. D.</td>
<td>86</td>
<td>197</td>
<td>86</td>
<td>190</td>
</tr>
<tr>
<td>COV</td>
<td>165</td>
<td>69</td>
<td>103</td>
<td>58</td>
</tr>
<tr>
<td>P4 AVERAGE</td>
<td>245</td>
<td>852</td>
<td>-313</td>
<td>-1178</td>
</tr>
<tr>
<td>S. D.</td>
<td>128</td>
<td>316</td>
<td>169</td>
<td>708</td>
</tr>
<tr>
<td>COV</td>
<td>52</td>
<td>37</td>
<td>54</td>
<td>60</td>
</tr>
</tbody>
</table>

### High Gradient

<table>
<thead>
<tr>
<th>Probe Location</th>
<th>Avg. ΔP During Pressing</th>
<th>Max. ΔP During Pressing</th>
<th>Avg. ΔP During Venting</th>
<th>Max. ΔP During Venting</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1 AVERAGE</td>
<td>31</td>
<td>255</td>
<td>-16</td>
<td>-218</td>
</tr>
<tr>
<td>S. D.</td>
<td>24</td>
<td>71</td>
<td>25</td>
<td>76</td>
</tr>
<tr>
<td>COV</td>
<td>80</td>
<td>28</td>
<td>156</td>
<td>35</td>
</tr>
<tr>
<td>P2 AVERAGE</td>
<td>144</td>
<td>592</td>
<td>-173</td>
<td>-825</td>
</tr>
<tr>
<td>S. D.</td>
<td>153</td>
<td>443</td>
<td>174</td>
<td>802</td>
</tr>
<tr>
<td>COV</td>
<td>107</td>
<td>75</td>
<td>101</td>
<td>97</td>
</tr>
<tr>
<td>P3 AVERAGE</td>
<td>632</td>
<td>1499</td>
<td>-532</td>
<td>-1879</td>
</tr>
<tr>
<td>S. D.</td>
<td>577</td>
<td>880</td>
<td>311</td>
<td>1189</td>
</tr>
<tr>
<td>COV</td>
<td>91</td>
<td>59</td>
<td>58</td>
<td>63</td>
</tr>
<tr>
<td>P4 AVERAGE</td>
<td>932</td>
<td>2096</td>
<td>-801</td>
<td>-2664</td>
</tr>
<tr>
<td>S. D.</td>
<td>427</td>
<td>627</td>
<td>311</td>
<td>1375</td>
</tr>
<tr>
<td>COV</td>
<td>46</td>
<td>30</td>
<td>39</td>
<td>52</td>
</tr>
</tbody>
</table>

*Pressure Values represented in kPa

ΔP represents the difference between the CO₂ pressure-predicted by the flow model and the inserted measurement sensor probe.
Several trends were observed when the specimens were organized by gradient that were similar to the previous case (Table 5-12 and Table 5-13). The largest inaccuracy during pressing was observed at Probe #2 for DF specimens and Probe #4 for SLP specimens in both gradient groups, with inaccuracy generally increasing with depth, except for Probe #2 for DF specimens. Inaccuracy increased with increasing depth during venting of both species, with the largest inaccuracy occurring at the deepest probe (P4). The magnitude of the difference during venting was noticeably smaller compared to pressing for DF specimens, but mixed results were observed for SLP specimens.

The one distinction between the two cases is that when the specimens are divided into gradient groups, model accuracy does not generally decrease from SLP to DF specimens. Avg. $\Delta P$ Pressing and Avg. $\Delta P$ Venting both increased in several cases when the low gradient DF group is compared to the high gradient SLP group. Avg. $\Delta P$ Pressing values for the low gradient DF groups did not exceed 633 kPa, while values for the high gradient DF group ranged to 932 kPa, and Avg. $\Delta P$ Venting values peaked to -373 and -801 kPa respectively.

A graphic representation of the model predictions compared to the experimentally measured pressures is shown in Figure 5-3 to Figure 5-6. The specimens depicted in these figures were the same as the specimens that were shown in Figure 5-1 and Figure 5-2 to provide a more comprehensive examination of a particular specimen at each gradient level for a particular wood species. Table 5-16 serves as a reference so that each specimen may be compared.
Figure 5-3: Individual comparisons between experimentally measured and flow model predicted CO$_2$ pressures for the varying probe locations for the low gradient Douglas-fir sample (DF20).
Figure 5-4: Individual comparisons between experimentally measured and flow model predicted CO$_2$ pressures for the varying probe locations for the high gradient Douglas-fir sample (DF4-1).
Figure 5-5: Individual comparisons between experimentally measured and flow model predicted CO\textsubscript{2} pressures for the varying probe locations for the low gradient shortleaf pine sample (SLP8).
Figure 5-6: Individual comparisons between experimentally measured and flow model predicted CO\textsubscript{2} pressures for the varying probe locations for the low gradient shortleaf pine sample (SLP10).
Table 5-16: Organization of the representative specimens that were presented in this section.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Grouping</th>
<th>Pressure Profile Figure</th>
<th>Model Comparison Figure</th>
</tr>
</thead>
<tbody>
<tr>
<td>DF20</td>
<td>Low Gradient</td>
<td>Figure 5-1(A)</td>
<td>Figure 5-3</td>
</tr>
<tr>
<td>DF6</td>
<td>High Gradient</td>
<td>Figure 5-1(B)</td>
<td>Figure 5-4</td>
</tr>
<tr>
<td>SLP8</td>
<td>Low Gradient</td>
<td>Figure 5-2(A)</td>
<td>Figure 5-5</td>
</tr>
<tr>
<td>SLP10</td>
<td>High Gradient</td>
<td>Figure 5-2(B)</td>
<td>Figure 5-6</td>
</tr>
</tbody>
</table>

The figures present visual evidence that model accuracy declined for a specimen in the high gradient group for each wood species. The model appeared to predict pressure more consistently at lower pressures in the subcritical region during pressurization, but disparity between the predicted and measured pressure increased when the pressure approached the critical point and maximized in this region. Model accuracy then improved above the critical region. During depressurization, model accuracy again declined and the maximized as the pressure approached and then reached the critical point. Model accuracy improved below the critical point in the subcritical region.

5.3 Validation of Model Assumptions

Measurements were conducted to investigate the validity of certain assumptions made in the computational model. Because the pressure vessel apparatus used in the study was limited to four pressure transducers as sensors to measure internal pressure, the measurement of the pressure profile development was confined to one diagonal location in the material section (see Figure 4-3). A preliminary assumption taken was that the pressure profile in the wood would develop symmetrically. To test this hypothesis, measurement probes were inserted into the material at “mirror” sites located at equivalent
depths from the surface during treatment. Secondly, the model assumed isothermal conditions within the vessel and the wood material during treatment. This assumption was investigated through the use of thermocouples placed within the pressure probes (see Figure 4-2) which monitored temperature during treatment. Lastly, an assumption made that the flowing fluid did not interact with the wood matrix such that the transmissibility of the wood was changed. This assumption was tested by treating a specimen and then retreating it and comparing the pressure profiles to see if a change occurred.

5.3.1 Verification of Symmetry Assumption

Because the experimental apparatus instrumentation used limited the number of pressure probes to four, an assumption of symmetry was made so that all four probes could be used to monitor the pressure gradient in one segment of the specimen as a representative unit of the entire specimen section (see Figure 4-3). The assumption was verified by measuring the pressure at an equivalent distance of a specific probe in another segment section of the specimen. Because of time limitations during the experimentation procedure, the measurements were taken for the three probe locations (Probes 1, 2, and 3) once for both DF and SLP samples (Figure 5-7 and Figure 5-8). The experimental parameters of the trials were intended to reflect those of the actual pressurization experiments, with an approximate pressurization and depressurization rate of 600 kPa/min and temperature of 40°C. While this depressurization rate was attainable, some difficulty was experienced during several trials to pressurize the vessel at the target rate because of technical difficulties in the apparatus.
Overall, the agreement between the measured probe pressure and mirror pressure was relatively high. The largest disparity between the probe and mirror pressure for the DF trials tended to exist at the beginning of the test and around the critical pressure (7.4 MPa) during the pressurization and depressurization phases. While these maxima existed, the largest differences between the probe and mirror location did not exceed 0.25 MPa (250 kPa). The specimen that exhibited the largest difference corresponded to the pressure measurement of probe location three. A similar trend was observed for the shortleaf pine trials, with the location of the largest differences occurring at the beginning and around the critical point. The largest differences occurred in trials measuring probes two and three, but the largest observed pressure difference was approximately 0.15 MPa (150 kPa) for shortleaf pine. The results of the mirror experiments above suggested that pressure development did not occur in a precisely symmetrical manner, although the degree to which the disparity occurred was not drastic enough to negate the assumption of symmetry.
Figure 5-7: Plots of the symmetry experiments for Douglas-fir for probes 1, 2, and 3. Each plot shows the pressure measured at the specific probe location and the corresponding mirror location.
Figure 5-8: Plots of the symmetry experiments for shortleaf pine for probes 1, 2, and 3. Each plot shows the pressure measured at the specific probe location and the corresponding mirror location.
5.3.2 Validation of Constant Temperature Assumption

The flow models described in Sections 2.5.2 and 2.5.3 include the most sophisticated description of the physics of supercritical carbon dioxide flow in solid wood materials. Modeling efforts have assumed isothermal conditions during the treatment process and this was an assumption of the current proposed flow model. Temperature is a critical parameter because the pressure of a compressible substance like carbon dioxide gas is directly related to temperature. Chemical solubility is highly dependent on temperature. Hence, temperature of gas inside the pressure probes was monitored to verify if it remained constant.

It is important to note that the temperature measurements in this study were only intended for qualitative purposes. As described in Section 4.2, the thermocouples used in this study were fine flexible filament wire that was inserted down through the tubing coupling. Thus it was impossible to ensure that the thermocouple was inserted entirely into the pressure chamber. Moreover, the possibility existed that the thermocouple was in direct contact with the stainless steel tubing, which would tend to more readily transfer heat than the surrounding wood. Both of these occurrences could introduce potential artifacts in temperature measurements.

Figure 5-9 and Figure 5-10 are plots of a typical treatment process for each type of wood and the corresponding temperature measurements taken at each pressure reading. The temperature inside the specimen at the probe locations was not constant for either species and varied by approximately 20-25°C. The temperature inside the specimen also changed fairly drastically in relation to the vessel temperature (Figure 5-11). These
Figure 5-9: Plot of a typical pressure treatment of shortleaf pine and corresponding temperature readings.
Figure 5-10: Plot of a typical pressure treatment of Douglas-fir and corresponding temperature readings.
Figure 5-11: Plot of the temperature differences between the vessel and probe locations for (A) Southern Pine in Figure 5-9 and (B) Douglas-fir in Figure 5-10.
changes revealed that the heat transfer and thermodynamics within the specimen were different than those in the vessel, causing the non-constant increase in \( \Delta T \) during pressurization and for both wood species close to the critical point. These inconsistent changes in temperature could be the result of the Joule-Thomson effect acting in conjunction with the densification of the gas (Civan, 2011). The Joule-Thomson effect causes cooling when the CO\(_2\) passes from higher to lower pressure while heat transfer improves upon densification.

The evidence of non-isothermal conditions observed in the specimens during treatment voided the assumption of constant temperature. The effect of non-isothermal conditions on the predictive capability of the model is further elaborated in Chapter 6.

### 5.3.3 Validation of Fluid/Matrix Interaction Assumption

Research by Sahle-Demessie(1995) indicated that SC CO\(_2\) treatment of Douglas-fir improved permeability significantly. The extent of this effect was investigated by comparing the pressure profiles of the same specimen over two successive and essentially identical treatments. The flow properties of the fluid should remain relatively constant from one treatment to the next, and any discrepancy in the pressure profile response could be attributed to a dynamic change in the flow properties of the wood material during treatment.

The specimens that were treated twice are summarized in Table 5-17 and Table 5-18. For each specimen, the values were an average of all four pressure probe locations. Consistent trends existed for DF specimens. In every case, the second treatment
decreased the gradient value, indicating an increase in flow through the specimen. Furthermore, the magnitudes of the differences were larger for the pressurization stage than the depressurization stage for every specimen except DF3-1, DF3-2, and DF19-1, indicating that the flow improved more on the pressurization side from first to second treatment. In all cases, equilibrium time decreased from first to second treatment. The results confirm the findings by Sahle-Demissie (1995), that flow properties are noticeably improved through potential supercritical fluid extraction of the pore structure of the wood material.
Table 5-17: Comparisons to evaluate the effect of a second treatment on the pressure profile development Douglas-fir specimens.

### Low Pressurization Rate (550 kPa/min)

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Avg. ΔP Pressing</th>
<th>Max. ΔP Pressing</th>
<th>Equilibrium Time</th>
<th>Avg. ΔP Venting</th>
<th>Max. ΔP Venting</th>
<th>Gradient</th>
</tr>
</thead>
<tbody>
<tr>
<td>DF3-1</td>
<td>356</td>
<td>1012</td>
<td>2.0</td>
<td>-439</td>
<td>-899</td>
<td>0.75</td>
</tr>
<tr>
<td>DF3-2</td>
<td>284</td>
<td>741</td>
<td>1.5</td>
<td>-411</td>
<td>-974</td>
<td>0.61</td>
</tr>
<tr>
<td>DF4-1</td>
<td>1236</td>
<td>2665</td>
<td>9.0</td>
<td>-630</td>
<td>-1706</td>
<td>2.61</td>
</tr>
<tr>
<td>DF4-2</td>
<td>829</td>
<td>2040</td>
<td>7.1</td>
<td>-312</td>
<td>-675</td>
<td>1.92</td>
</tr>
<tr>
<td>DF9-1</td>
<td>1120</td>
<td>2632</td>
<td>9.4</td>
<td>-423</td>
<td>-1955</td>
<td>2.65</td>
</tr>
<tr>
<td>DF9-2</td>
<td>871</td>
<td>1910</td>
<td>4.3</td>
<td>-177</td>
<td>-558</td>
<td>1.32</td>
</tr>
</tbody>
</table>

### High Pressurization Rate (825 kPa/min)

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Avg. ΔP Pressing</th>
<th>Max. ΔP Pressing</th>
<th>Equilibrium Time</th>
<th>Avg. ΔP Venting</th>
<th>Max. ΔP Venting</th>
<th>Gradient</th>
</tr>
</thead>
<tbody>
<tr>
<td>DF12-1</td>
<td>1110</td>
<td>2501</td>
<td>5.9</td>
<td>-317</td>
<td>-1577</td>
<td>1.87</td>
</tr>
<tr>
<td>DF12-2</td>
<td>909</td>
<td>2061</td>
<td>3.5</td>
<td>-226</td>
<td>-770</td>
<td>1.21</td>
</tr>
<tr>
<td>DF17-1</td>
<td>777</td>
<td>1730</td>
<td>4.0</td>
<td>-479</td>
<td>-1417</td>
<td>1.37</td>
</tr>
<tr>
<td>DF17-2</td>
<td>569</td>
<td>1517</td>
<td>2.4</td>
<td>-329</td>
<td>-1096</td>
<td>0.92</td>
</tr>
<tr>
<td>DF19-1</td>
<td>326</td>
<td>933</td>
<td>5.2</td>
<td>-379</td>
<td>-991</td>
<td>1.37</td>
</tr>
<tr>
<td>DF19-2</td>
<td>346</td>
<td>791</td>
<td>2.9</td>
<td>-256</td>
<td>-978</td>
<td>0.88</td>
</tr>
<tr>
<td>DF20-1</td>
<td>395</td>
<td>915</td>
<td>0.7</td>
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<td>-662</td>
<td>0.40</td>
</tr>
<tr>
<td>DF20-2</td>
<td>372</td>
<td>844</td>
<td>0.4</td>
<td>-188</td>
<td>-629</td>
<td>0.34</td>
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</tbody>
</table>

*Pressure Values represented in kPa and time in minutes. ΔP represents the difference between the CO₂ pressure-controlled vessel and wood inserted probe sensor pressure measurements.
Table 5-18: Comparisons to evaluate the effect of a second treatment on the pressure profile development shortleaf pine specimens.

### Low Pressurization Rate (825 kPa/min)

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Avg. ΔP Pressing</th>
<th>Max. ΔP Pressing</th>
<th>Equilibrium Time</th>
<th>Avg. ΔP Venting</th>
<th>Max. ΔP Venting</th>
<th>Gradient</th>
</tr>
</thead>
<tbody>
<tr>
<td>SLP8-1</td>
<td>59</td>
<td>323</td>
<td>0.5</td>
<td>-105</td>
<td>-414</td>
<td>0.21</td>
</tr>
<tr>
<td>SLP8-2</td>
<td>46</td>
<td>313</td>
<td>0</td>
<td>-78</td>
<td>-390</td>
<td>0.10</td>
</tr>
<tr>
<td>SLP10-1</td>
<td>669</td>
<td>1421</td>
<td>2.4</td>
<td>-610</td>
<td>-1929</td>
<td>1.07</td>
</tr>
<tr>
<td>SLP10-2</td>
<td>543</td>
<td>1247</td>
<td>1.3</td>
<td>-543</td>
<td>-2054</td>
<td>0.81</td>
</tr>
<tr>
<td>SLP13-1</td>
<td>294</td>
<td>1059</td>
<td>2.1</td>
<td>-287</td>
<td>-1332</td>
<td>0.78</td>
</tr>
<tr>
<td>SLP13-2</td>
<td>322</td>
<td>1009</td>
<td>1.4</td>
<td>-496</td>
<td>-1451</td>
<td>0.69</td>
</tr>
<tr>
<td>SLP17-1</td>
<td>70</td>
<td>434</td>
<td>0</td>
<td>-111</td>
<td>-407</td>
<td>0.12</td>
</tr>
<tr>
<td>SLP17-2</td>
<td>78</td>
<td>332</td>
<td>0</td>
<td>-110</td>
<td>-434</td>
<td>0.11</td>
</tr>
<tr>
<td>SLP19-1</td>
<td>34</td>
<td>264</td>
<td>0</td>
<td>-72</td>
<td>-233</td>
<td>0.07</td>
</tr>
<tr>
<td>SLP19-2</td>
<td>57</td>
<td>309</td>
<td>0</td>
<td>-54</td>
<td>-303</td>
<td>0.08</td>
</tr>
</tbody>
</table>

### High Pressurization Rate (1240 kPa/min)

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Avg. ΔP Pressing</th>
<th>Max. ΔP Pressing</th>
<th>Equilibrium Time</th>
<th>Avg. ΔP Venting</th>
<th>Max. ΔP Venting</th>
<th>Gradient</th>
</tr>
</thead>
<tbody>
<tr>
<td>SLP4-1</td>
<td>360</td>
<td>928</td>
<td>1.6</td>
<td>-290</td>
<td>-1014</td>
<td>0.64</td>
</tr>
<tr>
<td>SLP4-2</td>
<td>129</td>
<td>755</td>
<td>0.2</td>
<td>-212</td>
<td>-967</td>
<td>0.28</td>
</tr>
<tr>
<td>SLP6-1</td>
<td>111</td>
<td>407</td>
<td>0.3</td>
<td>-106</td>
<td>-438</td>
<td>0.19</td>
</tr>
<tr>
<td>SLP6-2</td>
<td>133</td>
<td>430</td>
<td>0</td>
<td>-75</td>
<td>-515</td>
<td>0.14</td>
</tr>
<tr>
<td>SLP11-1</td>
<td>270</td>
<td>766</td>
<td>0.1</td>
<td>-242</td>
<td>-546</td>
<td>0.25</td>
</tr>
<tr>
<td>SLP11-2</td>
<td>294</td>
<td>657</td>
<td>0.3</td>
<td>-182</td>
<td>-582</td>
<td>0.28</td>
</tr>
<tr>
<td>SLP14-1</td>
<td>244</td>
<td>775</td>
<td>1.3</td>
<td>-421</td>
<td>-1536</td>
<td>0.62</td>
</tr>
<tr>
<td>SLP14-2</td>
<td>448</td>
<td>1107</td>
<td>10.2</td>
<td>-496</td>
<td>-1451</td>
<td>2.48</td>
</tr>
<tr>
<td>SLP18-1</td>
<td>147</td>
<td>505</td>
<td>0.1</td>
<td>-105</td>
<td>-691</td>
<td>0.19</td>
</tr>
<tr>
<td>SLP18-2</td>
<td>110</td>
<td>498</td>
<td>0</td>
<td>-208</td>
<td>-745</td>
<td>0.19</td>
</tr>
</tbody>
</table>

* Pressure Values represented in kPa and time in minutes.
ΔP represents the difference between the CO₂ pressure-controlled vessel and wood inserted probe sensor pressure measurements.
Less definitive conclusions can be made for the SLP specimens. The gradient value decreased from the first to second treatment for half of the specimens, while the gradient value either remained constant or increased for the other half of the samples. For those specimens that decreased in gradient, pressure differences tended to decrease from the first treatment to the second, and treatment times decreased as well. Furthermore, the improvement in flow was less dramatic for SLP compared to DF specimens. No clear trend was observed between the pressurization and depressurization values of the same specimen. These results suggested that supercritical fluid extraction does notably occur in shortleaf pine, but not in the same consistent manner as with Douglas-fir.
Chapter 6
Discussion of Results

The previous chapter presented the results of the experimental measurements and compared to the results of the computation flow model, including measurements taken to analyze certain assumptions made on inputs and environmental conditions of the flow model. The results showed that model predictive performance was better for SLP than DF samples and decreased as the gradient, or transmissibility, decreased. In addition, the results indicated that some of the initial assumptions applied to the development of the computational flow model were less than appropriate with regard to the physical phenomena of the system.

In this chapter, a rationale for the discrepancy between the computational flow model and the experimental measurements are explored, and the effective influence of the model parameters are also examined. Furthermore, a conceptual foundation examines how the “spatial scale” of the present model limited its ability to describe the flow phenomena, and how subsequent reduction in scale may enhance model applicability.

6.1 Analysis of Model Performance

In Section 5.2.1, the results indicated that the computational flow model was limited in accuracy to describe the SC CO₂ behavior. The limited prediction performance suggested that the model did not completely describe the flow process of the system.
Model performance decreased with increased gradient value, i.e. the model was more accurate with samples where flow was faster and less accurate with samples where flow was slower. The flow model also limited in predictive ability to accurately depict a characteristic change in flow close to the critical point that was prevalent in high gradient samples. Moreover, model inaccuracy tended to increase as probe depth increased for SLP specimens. The same general trend was observed in DF specimens with one anomaly, as the second deepest probe (P2) was the most inaccurate, followed by P4, P3, and then P1. Pressurization rate had a much smaller effect on model performance, suggesting that the difference between the pressurization rate was not large enough to differentiate the flow change caused by variability in the transmissibility of the wood.

A loss in model performance could result from two sources. First, the phenomenological expression used to describe the flow process could be incorrect or only applicable within a certain boundary of the system. Decreased model performance with increasing depth, as observed here, implies that Darcy’s Law may be inadequate so another flow relationship such as Navier-Stokes might be advantageous, or it may need to be augmented empirically to account for depth effects (Bramhall, 1971).

Another possibility for the limitation of model prediction performance was that the model parameters, such as porosity, permeability, and temperature, were imprecise. The most obvious parameter to explore was permeability, because it directly relates to the ease of flow of a fluid through a porous material. As stated earlier, the model performance was worse for low flow samples, suggesting that the permeability parameter values used to predict the flow for these specimens deviated from those values previously published in the scientific literature, particularly all those specimens classified as high
gradient (Table 5-9 and Table 5-10). The measured permeability values in this study (Table 5-3) were well above those found in the literature. Accordingly, an analysis of the permeability measurement methodology was warranted.

Since the permeability specimens were cut from material in close proximity to the pressure specimens themselves, it was expected that the observed variability in the pressure profiles would be reflected in the variability in the permeability samples, but this was not the case. While the low gradient (high flow) treatment specimens were relatively well predicted by the model, the high gradient (low flow) treatment specimens were not, and it is unlikely that the wood material of the permeability samples was vastly different than the pressure samples. As noted in Section 5.1.1, the measured permeability values in this study were higher than those in prior research. This disparity could explain why the model was less accurate for the cases of low SC CO$_2$ flow. It is difficult to postulate the cause of the disparity, as a comprehensive review of the test procedure was discussed with researchers at Oregon State University and no systematic error in experimentation was determined. The disparity could be a result of a lack of a standardized method to test permeability, particularly concerning wood material characterization. Variations in moisture content, growth ring content, wood extractives concentration, and sample size could all contribute to changes in permeability from one study to another.

A possible cause for miscalculation of the permeability parameter pertains to the issue of scale. While the pressure probes measured pressure on a 1.6 mm diameter chamber, the specimen used to measure permeability was 10 mm. Consequently, the permeability value could have been too coarse to properly identify the actual permeability on the size scale of the of the pressure measurements. Research by Prak (1970) has
shown that the permeability of wood can be represented on a larger scale by dividing a larger volume of wood into two zones of higher and lower permeability, hence the permeability measurements on a large scale may not accurately describe the permeability on a smaller scale. Prak did not elaborate on the potential source of the permeability differences, but some potential sources are variations in wood density (i.e. growth rings) anatomical variation like pit size and number.

The predominant outcome of the permeability consideration was that enough ambiguity existed in the predictive capability of the computational model, warranting further examination in terms of how the model responds to various input parameter values.

6.2 Sensitivity Analysis

The results presented in Chapter 5 revealed that some disparities existed between the predicted and actual measure of the internal CO$_2$ pressure. A sensitivity analysis was performed to better understand the influence of the input parameters on behavior of the derived computational flow model. A sensitivity analysis provides useful insights into what input parameters most influence the variation of the output of a model by changing the magnitude of the input parameter and measuring the response of the output parameter. Several approaches exist as to how to perform a sensitivity analysis (Frey, et al., 2002). In this study, the magnitude of the individual input parameters was changed from extreme high and low values for an entire flow prediction simulation, and the resulting pressure
profiles were compared. The values of the parameters were held constant the sensitivity analysis trials.

In the present case, permeability, temperature, and porosity were assessed (Table 6-1). For permeability, the ranges of values selected represented the highest and lowest values found in the literature. The high values for both species were the untreated mean values measured in this study (Table 5-1 for Douglas-fir and Table 5-3 for shortleaf pine). The low values for Douglas-fir were those measured by Smith (1963), while values from Choong and Fogg (1972) were used for shortleaf pine. Porosity values evaluated were those exclusively measured in this study because of their relative accuracy to publish values. The high and low ends of the values represented one standard deviation plus and minus the observed statistical mean (Table 5-6). While porosity values were evaluated, it was determined that within the range of variability, an inconsequential difference (10 kPa) in the pressure profile was produced. Therefore, the results are not discussed further.

Table 6-1: High and low end values for temperature (T), permeability (k), and porosity (ϕ) used in the sensitivity analysis.

<table>
<thead>
<tr>
<th>Sensitivity Analysis Parameter</th>
<th>Douglas-fir</th>
<th>Shortleaf pine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low k (µm²)</td>
<td>Radial – 0.0005x10⁻⁴</td>
<td>Radial – 0.003</td>
</tr>
<tr>
<td></td>
<td>Tangential – 0.015x10⁻⁴</td>
<td>Tangential – 0.006</td>
</tr>
<tr>
<td>High k (µm²)</td>
<td>Radial – 0.015</td>
<td>Radial – 0.04</td>
</tr>
<tr>
<td></td>
<td>Tangential – 0.06</td>
<td>Tangential – 0.09</td>
</tr>
<tr>
<td>Low T (°C)</td>
<td>32</td>
<td>32</td>
</tr>
<tr>
<td>High T (°C)</td>
<td>45</td>
<td>45</td>
</tr>
<tr>
<td>Low ϕ</td>
<td>0.58</td>
<td>0.44</td>
</tr>
<tr>
<td>High ϕ</td>
<td>0.66</td>
<td>0.54</td>
</tr>
</tbody>
</table>
The temperature range selected represented a physical boundary that was relevant to this study. The high end value (45°C) corresponded to the highest temperature measured during treatment, while the low end value (32°C) was just above the critical temperature of 31.1°C. While temperatures below the critical temperature were measured, none were measured when the pressure was above the critical pressure. Thus, it is believed that the flow movement of CO₂ always remained in the critical region above the critical temperature, without a phase change between liquid and gas.

Overall, lower permeability and temperature values were expected to lead to greater pressure profile gradients. As stated in Section 3.3.2, the ease of flow is quantified in the computational flow model through transmissibility (see Eq. 3-11). Transmissibility is directly related to permeability, so it will change accordingly with changes in permeability. Temperature is related to transmissibility through viscosity, which is inversely related to transmissibility. Lower temperatures result in higher viscosity, thus as temperature decreased the transmissibility also decreased.

The results of the sensitivity analysis conducted for shortleaf pine (Figure 6-1 and Figure 6-2) showed that the parameters had a limited effect on the prediction of the computational flow model, even for low temperature and permeability input values. The only disparity between the two sets of parameter values existed at the beginning and end of the trial, and in a very short portion around the critical region.

Results for the Douglas-fir sensitivity analysis are presented in Figure 6-3 to Figure 6-5. Since the high permeability values are close to those of shortleaf pine and revealed only a small effect on the pressure profile, a similar trend to Figure 6-1 was
Figure 6-1: Response profiles generated by the computational flow model at (A) high and (B) low input values of temperature (T) and permeability (k) (Table 6-1) for a shortleaf pine specimen.
Figure 6-2: Individual comparisons of predicted pressure between low and high temperature and permeability input values for shortleaf pine. Locations P1 to P4 are the same corresponding pressure measurement locations as those shown in Figure 4-3.
Figure 6-3: Response profiles generated from the computational flow model at (A) high temperature (T) and permeability (k) and (B) High T and low k values (Table 6-1), for a Douglas-fir specimen.
Figure 6-4: Response profiles generated from the computational flow model at (A) high temperature (T) and permeability (k) and (B) low T and low k values (Table 6-1), for a Douglas-fir specimen.
Figure 6-5: Individual comparisons of predicted pressure between low and high temperature (T) at high permeability (k) input values for Douglas fir. Locations P1 to P4 are the same corresponding pressure measurement locations as those shown in Figure 4-3.
observed. For this reason the analysis was not included from the performed sensitivity analysis. Figure 6-3 shows the effects of the low value of the permeability on the predicted pressure profiles at varying temperatures. The appreciably lower permeability values for Douglas-fir resulted in much greater variance between the pressure responses at varying locations. Furthermore, the pressures at all four locations do not reach equilibrium with the vessel under the allotted time of the actual trial.

Temperature variation affects flow at the lower permeability value in several ways. Figure 6-5 highlights the effect of temperature on probe depth location relative to measured pressure. As the depth of the probe increases, the disparity between the predicted pressures at each temperature increases. Furthermore, the behavior of the pressure profile around the critical point changes dramatically between the two temperatures. At the elevated temperature, the characteristic increase in pressure gradient that typically occurs is eliminated, whereas at the lower temperature, the gradient effect is magnified. This phenomena suggests that at these specific conditions, fluid viscosity may have an important effect on the flow process. Viscosity decreases with increasing temperature, which would cause faster CO₂ flow and result in a smaller pressure gradient in the sample. Furthermore, the converse is observed, as temperature decreased, CO₂ viscosity increased, resulting in a larger pressure gradient in the specimen. Figure 6-5 also highlighted that viscosity does not appreciably change with temperature below the critical point, as the profiles were essentially the same during pressurization in the subcritical region.


### 6.3 History Match

In certain cases of computational simulation, the input parameters of the model are not well known or easily defined. In cases such as these, a history match is a useful technique to improve the adequacy of the model’s predictive capability (Ertekin, et al., 2001). Typically, a history match is performed such that the input parameters are manipulated within realistic values until the computational model is optimized for accuracy. This process is sometimes called the “inverse problem” or “reverse engineering” the input parameters.

In the present case, the goal of the history match is not to optimize accuracy but to highlight certain phenomena that can be identified by the computational model. For this reason, only one specimen from each wood species was evaluated and the matched input parameters were selected to highlight the variation that occurred between the computational flow model and experimental measurements. Regardless, history matches were analyzed in a similar fashion to the original model results presented in Section 5.2.1 so that the prediction performance could be evaluated.

As the sensitivity analysis revealed, temperature effects were more prevalent at lower permeability values. Furthermore, the specimens that exhibited pressure profiles characterized by low permeability exhibited the largest disparity between model predicted pressure and experimentally measured pressure, which represents the most extreme case for model improvement. Accordingly, the specimens that were selected for evaluation were on the higher end of the gradient values derived in Section 5.2. As with the sensitivity analysis, the two input parameters investigated were permeability and
temperature. For the purpose of continuity, the matched parameters were identical for each species:

- Temperature = 35°C
- Permeability = 5x10^{-4} \mu m^2

The temperature of 35°C represented an approximate average of the temperature experienced over the duration of a treatment schedule within the supercritical realm (greater than 7.38 MPa). The value for the permeability (5x10^{-4} \mu m^2) was within the range of values of the sensitivity analysis for Douglas-fir in both radial and tangential directions. This value was approximately one order of magnitude smaller than any published value for shortleaf pine indicated that the sensitivity analysis for pine, the smallest reported values for shortleaf pine were not sufficient to create a substantial pressure gradient. For the purpose of analysis, the history match for shortleaf pine is presented in this section, and rationale for the lack of an appropriate value will be elucidated later.

The history match for DF4-1 and SLP10-1 are depicted Figure 6-6 to Figure 6-7 and Figure 6-8 to Figure 6-9, respectively. From a qualitative standpoint, an improvement is recognized in the history matched predictions versus those of the original model (see Figure 5-4 and Figure 5-6 for original model comparisons). The predicted pressure profile at lower pressure was much closer in relation to measured pressure. Furthermore, an improvement in prediction performance at higher pressures was observed as the general shape of the experimental pressure profile is now reflected in the computational predicted profile. This assertion was supported by the comparisons made in Table 6-2 and Table 6-3.
Figure 6-6: Comparison between (A) the predicted CO$_2$ flow model pressure with “history matched” input parameters and (B) the experimentally measured pressure. (Sample DF4-1)
Figure 6-7: History match for DF4-1, comparing the measured and predicted CO₂ pressures for each probe location. Locations P1 to P4 are the same corresponding pressure measurement locations as those shown in Figure 4-3.
Figure 6-8: Comparison between (A) the predicted CO$_2$ flow model pressure with “history matched” input parameters and (B) the experimentally measured pressure. (Sample SLP10-1)
Figure 6-9: History match for SLP10-1, comparing the measured and predicted CO\textsubscript{2} pressures for each probe location. Locations P1 to P4 are the same corresponding pressure measurement locations as those shown in Figure 4-3.
Table 6-2: Comparisons between the experimental SC CO\textsubscript{2} pressure measured by the inserted pressure location probes (P1-P4) and the pressure predicted by the original and history-matched computational flow models for specimen DF4-1.

<table>
<thead>
<tr>
<th>Probe Location</th>
<th>Avg. ΔP During Pressing</th>
<th>Max. ΔP During Pressing</th>
<th>Avg. ΔP During Venting</th>
<th>Max. ΔP During Venting</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>625</td>
<td>1730</td>
<td>-101</td>
<td>-1191</td>
</tr>
<tr>
<td>P2</td>
<td>1477</td>
<td>3180</td>
<td>-460</td>
<td>-1842</td>
</tr>
<tr>
<td>P3</td>
<td>1440</td>
<td>2952</td>
<td>-771</td>
<td>-1655</td>
</tr>
<tr>
<td>P4</td>
<td>1363</td>
<td>2755</td>
<td>-1138</td>
<td>-2092</td>
</tr>
<tr>
<td><strong>AVERAGE</strong></td>
<td><strong>1226</strong></td>
<td><strong>2654</strong></td>
<td><strong>-618</strong></td>
<td><strong>-1695</strong></td>
</tr>
<tr>
<td>S.D.</td>
<td>404</td>
<td>640</td>
<td>442</td>
<td>381</td>
</tr>
<tr>
<td>COV</td>
<td>33</td>
<td>24</td>
<td>72</td>
<td>22</td>
</tr>
</tbody>
</table>

|                |                          |                          |                        |                        |
| **History-Matched Model** |                          |                          |                        |                        |
| P1             | 415                      | 1102                     | 269                    | 719                    |
| P2             | 931                      | 1898                     | 337                    | 872                    |
| P3             | 626                      | 1491                     | 331                    | 1961                   |
| P4             | 429                      | 1233                     | 45                     | 1139                   |
| **AVERAGE**    | **600**                  | **1431**                 | **246**                | **1173**               |
| S.D.           | 241                      | 351                      | 137                    | 553                    |
| COV            | 40                       | 25                       | 56                     | 47                     |

* Pressure Values represented in kPa

ΔP represents the difference between the CO\textsubscript{2} pressure predicted by the flow model and the inserted measurement sensor probe.
Table 6-3: Comparisons between the experimental SC CO\textsubscript{2} pressure measured by the inserted pressure location probes (P1-P4) and the pressure predicted by the original and history-matched computational flow models for specimen SLP10-1.

<table>
<thead>
<tr>
<th>Probe Location</th>
<th>Avg. ΔP During Pressing</th>
<th>Max. ΔP During Pressing</th>
<th>Avg. ΔP During Venting</th>
<th>Max. ΔP During Venting</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Base Model</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P1</td>
<td>30</td>
<td>308</td>
<td>-6</td>
<td>-215</td>
</tr>
<tr>
<td>P2</td>
<td>377</td>
<td>972</td>
<td>-390</td>
<td>-1277</td>
</tr>
<tr>
<td>P3</td>
<td>919</td>
<td>1751</td>
<td>-988</td>
<td>-2844</td>
</tr>
<tr>
<td>P4</td>
<td>1313</td>
<td>2618</td>
<td>-1117</td>
<td>-3321</td>
</tr>
<tr>
<td>AVERAGE</td>
<td>660</td>
<td>1412</td>
<td>-625</td>
<td>-1914</td>
</tr>
<tr>
<td>S.D.</td>
<td>569</td>
<td>997</td>
<td>520</td>
<td>1430</td>
</tr>
<tr>
<td>COV</td>
<td>86</td>
<td>71</td>
<td>-83</td>
<td>-75</td>
</tr>
<tr>
<td><strong>History-Matched Model</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P1</td>
<td>-301</td>
<td>-647</td>
<td>460</td>
<td>948</td>
</tr>
<tr>
<td>P2</td>
<td>-482</td>
<td>-1431</td>
<td>522</td>
<td>1494</td>
</tr>
<tr>
<td>P3</td>
<td>-445</td>
<td>-1582</td>
<td>265</td>
<td>1404</td>
</tr>
<tr>
<td>P4</td>
<td>-562</td>
<td>-1979</td>
<td>165</td>
<td>1118</td>
</tr>
<tr>
<td>AVERAGE</td>
<td>-448</td>
<td>-1410</td>
<td>353</td>
<td>1241</td>
</tr>
<tr>
<td>S.D.</td>
<td>109</td>
<td>559</td>
<td>166</td>
<td>253</td>
</tr>
<tr>
<td>COV</td>
<td>24</td>
<td>40</td>
<td>47</td>
<td>20</td>
</tr>
</tbody>
</table>

* Pressure Values represented in kPa
ΔP represents the difference between the CO\textsubscript{2} pressure-predicted by the flow model and the inserted measurement sensor probe.
When the average of all pressure probe locations are considered, an increase in model accuracy was observed for both Douglas-fir and shortleaf pine for pressure values (Avg. $\Delta P$ and Max. $\Delta P$) during pressing and venting. For example, Douglas-fir Avg. $\Delta P$ decreased from 1226 to 600 kPa and -618 to 246 kPa for the pressing and venting stages, respectively. The change in sign from negative to positive indicates that the original model over-estimated the pressure, while the history-matched model under-estimated the pressure change. For shortleaf pine, Avg. $\Delta P$ decreased from 660 to -440 kPa and -625 to 353 kPa for pressing and venting stages, respectively. In this case, the original model over-predicted the pressure during pressing while the history-matched model under-predicted the pressure. During venting, the converse occurred. Despite the overall improvement in prediction capability, a closer look at the model prediction revealed that the improvement was not consistent for all probe depths. Model performance improved for three of the four probe locations for DF4-1, except for the outermost Probe #1. For SLP10-1, model performance improved for the inner two Probes #3 and #4, but generally did not for the outer two Probes #1 and #2.

For both “history matched” specimens, the difference between predicted and measured pressure no longer increases with increasing probe depth, implying that Darcy’s Law was an appropriate description of the system in terms of describing the flow process throughout the dimensions of the material.

From Section 5.3.3, it was determined that in the flow properties of the wood material changed during treatment. A hysteresis phenomena depicted in Figure 6-10 between the predicted pressure and experimentally measured pressure can be used to explore the change in flow properties in greater detail. For DF4-1, the model consistently
over-predicted the pressure during pressurization process in the subcritical region, but
over-predicted the pressure much less appreciably during the depressurization process so
that it is relatively equivalent to the measured pressure. For SLP10-1, the trend switches
where the model consistently under-predicts the measured pressure during pressurization
in the subcritical region to being relatively equivalent to the measured pressure during
venting in the subcritical region. An evaluation of the other probe locations in this
manner is summarized in Table 6-4, which highlighted that the wood material was
undergoing a noticeable change during the treatment process.

Table 6-4: Evaluation of the prediction of the computational CO₂ model in
relation to the pressurization and depression stage in the sub-critical
region.

<table>
<thead>
<tr>
<th>Probe Location</th>
<th>Pressurization Prediction</th>
<th>Depressurization Prediction</th>
<th>Potential Implication</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DF4-1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P1</td>
<td>Over</td>
<td>Under</td>
<td>Increasing Permeability</td>
</tr>
<tr>
<td>P2</td>
<td>Over</td>
<td>Under</td>
<td>Increasing Permeability</td>
</tr>
<tr>
<td>P3</td>
<td>Over</td>
<td>Under</td>
<td>Increasing Permeability</td>
</tr>
<tr>
<td>P4</td>
<td>Over</td>
<td>Equivalent</td>
<td>Increasing Permeability</td>
</tr>
<tr>
<td>SLP10-1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P1</td>
<td>Under</td>
<td>Under (+)</td>
<td>Decreasing Permeability</td>
</tr>
<tr>
<td>P2</td>
<td>Under</td>
<td>Under (+)</td>
<td>Decreasing Permeability</td>
</tr>
<tr>
<td>P3</td>
<td>Under</td>
<td>Equivalent</td>
<td>Increasing Permeability</td>
</tr>
<tr>
<td>P4</td>
<td>Under</td>
<td>Equivalent</td>
<td>Increasing Permeability</td>
</tr>
</tbody>
</table>

+ indicates that the prediction error increased in magnitude

In the case of the two samples evaluated, the change in pressure profile from over-
prediction to under-prediction or equivalence for the Douglas-fir sample could be the
result of an increase in permeability. A similar reasoning could be used for the probe
locations for the shortleaf pine sample, where prediction under-estimated pressure during
pressurization and equivalence was observed during depressurization. The converse
would be true for the probe locations where the model under-estimated the pressure profile to a greater extent from pressurization to depressurization, suggesting that permeability decreased during the treatment process. This same trend was observed in Section 5.3.3, where permeability improved during consecutive treatments for Douglas-fir while shortleaf pine exhibited an inconsistent behavior.

The reason that shortleaf pine could react differently to the SC CO₂ treatment process in comparison to Douglas-fir is that shortleaf pine contains larger amounts of high molecular weight substances (extractives) that tend to agglomerate in flow paths for pine wood (Olsson, et al., 2001). In large amounts, the extractives could not be fully removed or only slightly dissolved in the flowing SC CO₂, and what was dissolved or not removed could be redeposited in the flow pathways to negatively affect flow. These areas of heavy concentration of extractives can restrict flow at a localized scale, which could explain why the permeability of the history match was below that of reported values.

When the transitions to and from the supercritical condition were considered for the pressure profiles in Figure 6-10, a distinct deviation between the predicted and measured pressure occurs. The deviation on the pressurization side (depicted by the dotted circled region) differed between the species. For Douglas-fir, pressure prediction was initially over-estimated in the subcritical region, then began to converge with measured pressure in the supercritical region, and then steadily diverged, again with the model over-estimating pressure. For shortleaf pine, the reverse occurred. The model initially underestimated the measured pressure in the subcritical region then began to converge before the critical pressure was reached. Once the critical pressure was
reached, the predicted pressure diverged from the measured pressure, again under-
estimating the measured pressure. The deviation is particularly relevant for the
depressurization stage (depicted by the dotted boxed region), since the subcritical
regions appeared to be fairly equivalent in pressure response, while the supercritical
regions clearly were not. For Douglas-fir, it appeared that the predicted decrease in flow
rate was much more pronounced than the actual case, and that the predicted decrease in
flow rate occurred at a higher pressure in comparison to the actual measured flow rate
decrease. Similarly, for shortleaf-pine, the predicted increase in pressure gradient was at a
higher pressure compared to the actual pressure, but the magnitude of the gradient was
approximately the same. The rationale for these disparities was difficult to conceptualize,
because the potential dynamic changes of the system could result in changes in the
parameters that influence the pressure profile development. For ex-
ample, in the case of
the shortleaf pine specimen, the pathways for flow, i.e. pits, could be relatively clear
above the critical point, and then become blocked by chemical constituents once they
precipitate out of solution from the phase change to CO$_2$ gas. The implication of this
event would mean that permeability would be higher in the supercritical region compared
to the subcritical region, resulting in a pressure profile that would be shifted to lower
pressures in comparison to the model. For the case of the Douglas-fir specimen, it is
uncertain as to why the increased pressure gradient is notably reduced to where it is
almost non-existent, while there is good agreement between the model and the predicted
values over the remaining portion of the depressurization stage. This event emphasizes
that the model does not completely describe the physics of the system, disparities in
prediction can occur.
Figure 6-10: Predicted CO₂ pressure response for the “history matched” flow model compared to experimentally measured pressure at probe location #4. Circled and boxed regions emphasize the dynamic response regions where (A) corresponds to specimen DF4-1 and (B) to SLP10-1.
6.4 Discussion of Dimensional Scale

To this point, a discussion of the model performance has been presented, including rationale for disparity between the computational flow model and measured values, an analysis of the sensitivity of the flow model to critical input values, and a history match that depicts how the computational model can more accurately predict the super and subcritical pressure profile development. For example, Section 6.3 presented evidence of how the permeability of the wood matrix changes from the treatment process as a dynamic physical property. Currently, the model does not possess the capability of accurately handling how this phenomena occurs or to what extent it changes the magnitude of the permeability input value. Effects on permeability are a key focus because of the results of the sensitivity analysis in Section 6.2, which highlighted the large effect permeability had on the prediction of computational flow model.

In this section, various spatial scales are presented to explore how the model may be revised to further improve its predictive capabilities. Previous research has shown that a multi-scale approach can be applied to successfully identify flow mechanisms of water in wood that were previously unrecognizable. While the flow phenomenon of liquid water is different in relation to SC CO$_2$, it sets a reliable precedent that flow prediction can be enhanced by a multi-scale analysis. Zillig (2009) determined that moisture movement can be modeled more accurately through the use of refined microscopic unit cell approach over a larger macroscopic view that was limited to seasonal growth variation. Research by Auman and Ford (2005) revealed that numerous measurements of the microscopic properties of wood can be used in a model that translate to macroscopic
flow properties, and used the macroscopic predictions to highlight differences between coastal and inland varieties of Douglas-fir.

The proceeding discussion presents an overview of the scales of the present model and revisits the approach taken to represent the model at these scales. Then the discussion evaluates the model at millimeter, micrometer, and nanometer scales. While the nature of the discussion is highly computational, the goal of this section is to introduce the concepts that could be of significance to flow at various scales; therefore the mathematics is withheld because it is beyond the scope of the present discussion.

Figure 6-11 gives a visual representation of the scales in relation to wood microstructure, with the nanometer scale omitted. The discussion is limited to factors relevant to softwood ultra-structure and single-phase flow because they are the focus of the current study. Furthermore, the discussion is restricted to clear wood material, i.e. no anomalies are considered, such as knots, bark inclusions, pitch pockets frequently found within a gross section or potential ultrastructure of a generalized piece of wood material. Figure 6-12 is a summary of the primary factors under consideration at each respective scale. Considerations at each scale are divided into two categories, ultrastructure and phenomenological. Ultrastructure considerations encompass the physical input parameters of the computational model, where phenomenological considerations are the conceptual relations of the physics of the system.
Figure 6-11: Visual representation of the spatial scales that exist in softwood. Millimeter and Micrometer images adapted from (Koch, 1972).
Figure 6-12: Summary of how spatial scale can change the scope of what determines the guiding principles for the computational flow model. Solid arrows represent a continuation of the property to the next scale, where dashed arrows represent the applicability of the physics from smaller to larger scale.
The list of considerations in Figure 6-12 is not thought of as exhaustive, but highlights what is believed to be the most prevalent influences. From the wood ultrastructure perspective, the arrows point in the direction of decreasing scale because the property distinctions at a larger scale are applicable to smaller scales. For instance, the tangential direction can still be considered at the micro-scale, but cell size cannot be at the centimeter scale. For the case of phenomenological considerations, the arrows are pointing in the direction of increasing scale, because as scale increases, the equations that control the computational model can be simplified to be equivalent, but the converse is not true. It should be noted that since the computational flow model is solved numerically, the method used to relate scales can have a significant effect on the solution. Specifically, a term known as “upscaling” refers to how the properties at a small scale are related to a larger scale. This section explores upscaling from a conceptual basis only, and does not consider the numerical methodology. Other studies have been performed that are entirely dedicated to upscaling properties for porous media flow simulation (Jenny, et al., 2003).

6.4.1 The Centimeter and Millimeter Scales

The present computational flow model, which was developed at length in Chapter 3, was a multi-scale approach comprised of the centimeter and millimeter scales. The multi-scale approach was used because it most accurately matched the physical conditions of the experiment. The phenomenological scale of the flow model, which is related to the mesh size, was set at the millimeter scale to match the size of the pressure
probe chamber of the actual experimental measurement of pressure (see Section 4.2). At the millimeter scale, Darcy’s Law is used to describe the flow phenomenon, which is also directly applicable at the centimeter scale. The primary structural parameter that governs Darcy’s Law is permeability.

Permeability was measured on samples with a diameter of approximately 1 cm, so the ultrastructure parameters were considered on this scale. At the centimeter scale, permeability varies for each principle orthogonal direction (radial and tangential), and for varying wood type (heartwood and sapwood). Permeability was measured on plugs from various locations for both principle directions, and these values were averaged and used as the permeability parameters in the flow model for the x and y directions, respectively. Furthermore, porosity was measured from the same samples and the values applied in a similar fashion as permeability. The Douglas-fir samples consisted entirely of heartwood, while the Southern pine samples were a minor mix of heartwood and sapwood. The Southern pine flow model could be developed at the centimeter scale to reflect both wood types with the inclusion of a variable permeability value that changes in locations that correspond to heartwood and sapwood, but in the case of the present study, no significant difference was measured between the two wood types, so no distinction was possible. When permeability is considered at the millimeter scale, a new anatomy consideration must be made to account for variations in seasonal growth rates between earlywood and latewood material. Permeability can potentially vary between earlywood and latewood, thus it could be an important consideration in the computational flow model. In general, earlywood is more permeable than latewood, which could cause preferential pathways for flow. In addition, earlywood is significantly less dense than
latewood, which could cause a significant enough change in porosity that it will become an important consideration for the computational flow model.

### 6.4.2 The Micrometer Scale

At the micrometer scale, more complexity arises from both phenomenological and ultrastructure perspectives. The governing equation for flow through a porous media at the micro-scale has been theorized and evaluated from several perspectives, including the Navier-Stokes equation and the Lattice Boltzmann method. The Navier-Stokes equation differs from the Darcy equation primarily in that it accounts for a boundary drag force that occurs when a flowing fluid is in very close proximity to the internal cavity of a porous body. Therefore, the structure and shape of the pore structure influence flow, which can be quantified by a value known as pore conductance. Narsilio et al. (2009) determined that Navier-Stokes reduces to the Darcy equation when it is upscaled, the difference is the value of permeability is determined based on the pore structure instead of a larger scale measurement. Another method that has been explored is the Lattice Boltzmann method.

The Lattice Boltzmann method is similar to Navier-Stokes in that it defines the flow of fluid in small void spaces, but goes a step further in that it also considers flow through smaller voids within the solid matrix. Basically, the lattice Boltzmann method uses a kinetic equation on a lattice framework, where the movement of molecules is considered between hindered and free paths. This approach could be of great interest considering that it could potentially handle fluid interaction with pits. Spaid and Phelan
(1997) used the Lattice Boltzmann approach to successfully simulate the flow of a fluid during a process known as liquid composite molding, which produces porous heterogeneous bodies potentially similar in nature to wood.

A relatively new multi-scale approach has been proposed and evaluated that is called thermodynamically constrained averaging theory (TCAT) (Miller, et al., 2005) (Gray, et al., 2006). The method was developed specifically to relate the physical phenomena occurring at the larger macro-scale so that it is thermodynamically consistent with phenomena at the micro-scale. The novel part of the approach is that it accounts for entropy changes and handles them consistently from the micro to the macro-scale. From that point, mass, momentum, and energy conservation equations are formulated at a desired scale based upon averages of micro-scale quantities, along with thermodynamic relationships. TCAT could solve a particular deficiency in the current approach since it is capable of handing non-isothermal conditions, which has been identified in this system.

From the ultrastructure perspective, the micro-scale reveals numerous venues of complexity that can be explored because the cell structure of wood exists at the micrometer scale. Examples of such parameters are size, number and dimensions of cells like tracheids and resin canals, and the size, shape, and number of bordered pits, but numerous other options have been explored. In fact, Auman and Ford (2005) explored 17 different microstructural attributes in their research. From Section 5.3.3 it has been shown that during the course of treatment, a change is occurring in the system that is resulting in a change in the pressure profile response. It has been theorized that this change is a result of the clearing of agglomerated or aspirated pits by the flowing SC CO₂
(Sahle-Demessie, et al., 1995). At the micro-scale, it would be possible to investigate this theory further.

Schneider et al. (2006) investigated the effect of wood ultrastructure characteristics on the pressure response during SC CO₂ treatment. The authors found that a limited number of anatomical properties were useful in characterizing the pressure response, including longitudinal resin canals for softwoods, and radial gas permeability or fiber dimensions for hardwoods. Consequently, it is unclear if a computational model that includes wood ultrastructure properties would yield a more accurate model.

6.4.3 The Nanometer Scale

At the nanometer scale, new phenomena must be explored from a phenomenological perspective, such as diffusion of the flowing fluid through the solid cell wall (shown in Figure 6-13), as explained by Fick’s Law. In the case of handling voids that may be encountered within the cellular structure, the Lattice Boltzmann method has been shown to be a potentially useful method to describe the flow of fluids through porous media at the nano-scale (Suga, et al., 2010). Additionally, the concept of molecular dynamics has been used to describe flow on the nano-scale (Vrabec, et al., 2010). This approach, the time dependent interaction between fluid-fluid and fluid-matrix particles is described by a relation such as the Lennard Jones potential (Lennard-Jones, 1924). From a structural perspective, at the nanometer scale the main consideration is the makeup of the cell wall. Within the cell wall, several layers
Figure 6-13: Schematic drawing of the components of the wood cell wall. Adapted from (Dinwoodie, 1989)
exist that vary in chemical composition and morphology. Of particular interest could be the makeup of microfibrils within the cell wall. These crystalline-like regions of the cell wall might influence flow differently in comparison to the amorphous regions.

Other phenomena otherwise not considered may occur at the nano-scale. One such instance is the concept of directional flow properties, such as permeability changing with the direction of flow. Research by Firouzi et al. (2006) investigated the effect of pore geometry on flow characteristics of SC CO₂ and SC CO₂/SC CH₄ mixtures. In the study, they determined that permeability changed based on the inlet and outlet direction of a pore. Considerations such as this could give insight into the hysteresis phenomena observed in the present study, where the flow that occurred during the pressurization phase of treatment (inward) was observed to be different from the depressurization phase (outward).

6.5 Implications

The analysis of the proposed computational CO₂ flow model is summarized in Figure 6-14. From the predictions made by the computational flow model using the initial input parameter values, it was determined that the flow model performed better for low gradient materials compared to high gradient ones. Another important observation was the observed trend of increased inaccuracy with increasing probe depth. At that juncture, it was not possible to determine if the inaccuracy was due to inaccurate parameter values or an incorrect phenomenological description of the system.
Figure 6-14: Schematic flow chart to outline the resulting implications of the study analysis for the computational flow model experimentation.
Consequently, a parameter analysis was performed in the form of a sensitivity analysis and history match, where values from the body of literature were examined to acquire appropriate input parameters for the computational model that resulted in more accurate pressure predictions in relation to the experimentally measured pressures. The result of the comparisons between “history-matched” pressure predictions measured pressures revealed that when relatively accurate input parameters are employed in the model, it performs noticeably better in terms of describing the flow process in the subcritical region. Conversely, in the supercritical region, the model does not capture the entire dynamics of the system. Furthermore, the current state of the computation model fails to account for the observed hysteresis, suggesting that it does not capture a physical phenomena that that occurs between pressurization and depressurization stages.

The discussion of dimensional scale presented potential avenues by which the computational flow model could be enhanced to more accurately describe the CO₂ flow process. However, to fully understand the flow process at smaller scales, a subsequent enhancement in experimental sophistication is required to evaluate the theoretical conjectures. Permeability measurements on the mili-scale are required so that measured values for input parameters of the computational model directly relate to the scale of the pressure measurements made during SC CO₂ treatment. On the micro-scale and below, a larger hurdle exists. Presently, no technique has been used to measure the flow of SC CO₂ movement below the mili-scale, thus a new technique is required.

A potential imaging technique to monitor the flow of SC CO₂ in wood is nuclear magnetic resonance (NMR). NMR has been used to successfully by Harel et al. (2006) to visualize the flow of a multi-component gas in a porous structure. The authors found that
NMR can be used to resolve gas particle flow in and around the pore structure of a solid on a nano-scale (2-50 nm) and above, as well as discern the movement between the various components of the gas. This second aspect could be advantageous in future work, if a system of SC CO$_2$ solvent/biocide solute is explored.

More specifically, NMR has been used as a technique to visualize the flow of supercritical fluids in porous structures (Dvoyashkin, et al., 2007). In this study, the flow of subcritical and supercritical n-pentane in and around a porous glass (6 nm pore size) was measured through the determination of diffusion coefficients. By monitoring the fluid inside the porous medium and outside, the investigators were able to contrast the two conditions. This lead to the observation that the confined gas (inside the porous glass) achieved criticality at a lower temperature in comparison to the gas outside of the solid. Insights such at this highlight the potential of new experimentation techniques to discover and understand phenomena that occurs during SC CO$_2$ treatment of wood materials that is currently unrecognized.
Chapter 7

Conclusions and Recommendations

7.1 Conclusions

In this study, a computational flow model was developed to investigate the movement of supercritical carbon dioxide in solid wood materials. The pressure values generated by the model were used as predictions that were compared to pressure experimental pressure measurements. The applicability of the model was investigated through the pursuit of two primary objectives:

1. **To verify the computational model through comparisons between the predicted pressure and the pressure measured experimentally.**

The computational model was fully developed from theory and a computer program was generated in FORTRAN. The program has the capability of investigating the SC CO₂ treatment process of solid wood materials as a compressible fluid flowing through a porous body. Input system parameters such as temperature and wood properties of permeability and porosity are held constant. These parameters can be adjusted to prescribe to various conditions of the system. Accordingly, the computational flow model properly represents the principles established by prior proposed models of Sahle-Demessie (1994) and Ward (1989). To verify the computational model, a series of experiments were conducted, where the pressure profile was measured in four locations.
of Douglas-fir and shortleaf pine wood specimens and these pressures were compared to pressures predicted by the computational flow model. From these comparisons, it was determined that accurate input parameters are necessary to properly evaluate the computational flow model. Once these parameters are attained, the proposed computational CO$_2$ flow model can be characterized for both Douglas-fir and shortleaf pine as follows:

- Below supercritical conditions, the computational model has the potential to predict the flow of CO$_2$ relatively accurately.
- Close to the supercritical condition and above, the computational model does not perform as well as the subcritical condition, although it is capable of describing the flow phenomena to some extent.

Once the overall performance of the computational flow model was characterized, a second object was investigated:

2. **To identify the source of potential variation between the proposed computational SC CO$_2$ flow model and experimentally measured results.**

Several analyses were performed to determine the source of discrepancy between the pressure predicted by computational flow model and the pressure measured experimentally, including a sensitivity analysis and a history match. From these efforts, the following observations were made:
• Over the range of applicable values, the flow model accuracy is particularly sensitive to permeability, and somewhat sensitive to temperature. Porosity is not a major factor that affects model accuracy.

• A distinct dynamic change occurs during CO\textsubscript{2} flow through the wood material when the fluid reaches the supercritical condition. This phenomena potentially changes the permeability such that the computational model accuracy is reduced.

• Another source of inaccuracy is an observed hysteresis that occurs between the pressurization depressurization stages of treatment in certain specimens, which is currently unexplained by the computational flow model.

This study applied the current state of the art in terms of experimentation and theoretical understanding of the flow of SC CO\textsubscript{2} in solid wood materials. If a more accurate prediction of the flow process is desired, more sophistication is required from both theoretical and experimental perspectives.

7.2 Recommendations

From this study, several recommendations can be made to further progress the understanding of the flow of SC CO\textsubscript{2} in solid wood materials. From an experimentation standpoint:
● The effect of the SC CO₂ treatment process on permeability of solid wood materials is not well understood. A dedicated study that experimentally measures how permeability changes under supercritical conditions would greatly improve the performance of a computational model.

From a theoretical standpoint:

● Complexity can be added to the computational flow model in several ways to possibly enhance prediction performance. The most straightforward option is to include non constant parameters such as temperature and permeability.

● A multi-scale approach to the model, particularly down the micrometer lever, could potentially improve the performance of the computational model. This would require an increase in complexity of the mathematical correlations used to develop the computational flow model.
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Appendix A

Estimation of Coefficient Matrix using Stone’s Method

The solution technique developed by Stone (1968) requires that the coefficient matrix \([A]\) be estimated by \([A']\). In the current study, the equation to be solved is:

\[
S^{(k+1)}_i P^{(k+1)}_{l-1} + W^{(k+1)}_{i-N_y} + C^{(k+1)}_i P^{(k+1)}_{l} + E^{(k+1)}_{i,j} P^{(k+1)}_{i+N_y} + N^{(k+1)}_{i,j} P^{(k+1)}_{j+1} = Q_i
\]

where \(S, W, C, E, N\) comprise the set of coefficients that need to be estimated. The follow series of equations are used to determine the proper estimation:

\[
\begin{align*}
    b_i &= S_i - \omega H_i \\
    c_i &= W_i - \omega G_i \\
    d_i + b_i f_{i-1} + c_i e_i &= C_i + \omega H_i + \omega G_i \\
    d_i e_i &= E_i - \omega H_i \\
    d_i f_i &= N_i - \omega G_i
\end{align*}
\]

where

\[
\begin{align*}
    H_i &= b_i e_{i-1}, \\
    G_i &= c_i f_{i-N_y}.
\end{align*}
\]

In the previous relations, \(\omega\) is the iteration parameter determined by Eq. 3-26 and Eq. 3-27, and \(N_y\) is the number of grid blocks in the \(y\) direction.
Appendix B

Computer Simulation Code “CO2MODEL”

!***********************************************************************!
! CO2 IN WOOD SIMULATOR
!***********************************************************************

PROGRAM CO2MODEL
IMPLICIT NONE

!define matrix arrays and values*********************************************
CHARACTER*9 SPECFILE
CHARACTER*10 DELXFILE, DELEYFILE, XPERMFILE, YPERMFILE, PORFILE,
INDEXFILE
CHARACTER*20 DATALIST(6)
CHARACTER*9 OUTFILE1
DOUBLE PRECISION,ALLOCATABLE :: DELX(:), DELEY(:), XPERM(:), YPERM(:), POR(:)
DOUBLE PRECISION,ALLOCATABLE :: AX(:), AY(:), VB(:)
DOUBLE PRECISION,ALLOCATABLE :: MUCD(:), ROCD(:), B(:), ZCD(:)
INTEGER, ALLOCATABLE :: VESLT(:)
DOUBLE PRECISION,ALLOCATABLE :: PCD(:),PPCD(:),VESLP(:),POUT(:)
DOUBLE PRECISION,ALLOCATABLE :: INDEX (:)
DOUBLE PRECISION WIDTH, THICK
INTEGER XNUM, YNUM
DOUBLE PRECISION P_AVG
DOUBLE PRECISION FDIF, PDIF, A
INTEGER MAXLOK (1), MAXLOKR(1)

!define transmissibility arrays****************************************************
DOUBLE PRECISION,ALLOCATABLE :: SCD(:),WCD(:),ECD(:),NCD(:),CCD(:),QCD(:)
DOUBLE PRECISION,ALLOCATABLE ::
CON_SCD(:),CON_ECD(:),CON_WCD(:),CON_NCD(:)
DOUBLE PRECISION,ALLOCATABLE ::
NON_SCD(:),NON_WCD(:),NON_ECD(:),NON_NCD(:),GAM(:)

!define material balance variables and arrays****************************************
DOUBLE PRECISION,ALLOCATABLE ::  NN(:),OO(:),DELIB(:),DELC(:),NNPLUS(:)
DOUBLE PRECISION,ALLOCATABLE ::  DELPCD(:),TDELPCD(:)
DOUBLE PRECISION,ALLOCATABLE ::  DELIC(:), LUCKH(:), DELIA(:), DELI(:)
DOUBLE PRECISION NN_SUM, OO_SUM, DELI_SUM, DELC_SUM, NNPLUS_SUM,
LUCK_SUM
DOUBLE PRECISION IMB, CMB

!define test markers and inputs*****************************************************
CHARACTER*9 DATAFILE!char for data file setup
CHARACTER*10 :: FNAMES(27)
CHARACTER :: UNI_BLOCK, PRINT_MATRIX, DEFAULT!test char for yes no questions
INTEGER :: SETUP = 0!test for setup completion
DOUBLE PRECISION :: DUMMY (2, 1000000) !dummy array for load_table subroutine
INTEGER :: N ! # of rows in file from load_table
INTEGER :: ALLOKATE = 0 ! gate for array allocation
INTEGER :: LOOP! gate for SIP algorithm
INTEGER :: I,J,K,L,M! variables for loops
DOUBLE PRECISION :: ITOD(7) = [1,2,3,4,5,6,7]! array used to convert integers to doubles
INTEGER :: ALPHAGATE = 0
INTEGER :: FNAMETRACKER = 1
INTEGER :: ITER
INTEGER :: FILEGATE = 0
INTEGER :: VESLTPOS = 1
DOUBLE PRECISION :: WRITECHECK

! define SIP algorithm variables
DOUBLE PRECISION, ALLOCATABLE ::
LOWER_B(:,), LOWER_C(:,), LOWER_D(:,), LOWER_E(:,), LOWER_F(:,), LP(:,)
DOUBLE PRECISION :: P1, P2
DOUBLE PRECISION, ALLOCATABLE :: ALPHAMINX(:,), ALPHAMINY(:,)
DOUBLE PRECISION :: ALMINX, ALMINY, ALPHAMIN, ALPHAMAX, ALPHA(5)
DOUBLE PRECISION, ALLOCATABLE :: V(:,), R(:,), RA(:,), DELTA(:,), DELTAA(:,), OLPD(:,)
DOUBLE PRECISION :: MAXDELTA, RMAX
INTEGER :: ALPHAPOS

! define constants and initials
DOUBLE PRECISION :: PO ! initial pressure
DOUBLE PRECISION :: VSLP, H ! vessel pressure
DOUBLE PRECISION :: T = 318.15! Temperature (K)
INTEGER :: TIME = 0! Time (sec)
integer :: timep = 0
DOUBLE PRECISION :: DEL_T = 2! time change (Day)
DOUBLE PRECISION :: BETA = 1E-9
DOUBLE PRECISION :: OUTDATA(8)
CHARACTER*20 DATE
INTEGER :: IJ, NIJ
INTEGER, ALLOCATABLE :: ORDER(:,), ONED(:,)
DOUBLE PRECISION, ALLOCATABLE :: PRYNT(:,)

! set values for initial setup

CALL fdate(DATE)
PRINT*, DATE

PRINT*, " WHAT SPECIMEN DATA FILE ARE YOU SIMULATING" READ*, SPECFILE
OUTFILE1 = 'XXXX1.DAT'
OUTFILE1(1:4) = SPECFILE(1:4)

CALL load_table(SPECFILE, DUMMY, N)
ALLOCATE (VESLP(N), VESLT(N))
VESLT(1:N) = DUMMY(1,1:N)
VESLP(1:N) = DUMMY(2,1:N)

! Default properties
WIDTH = 0.04445! 1.75 in to m
THICK = 0.01905!0.75 in to m
XNUM = 30
YNUM = 14
NIJ=XNUM*YNUM

! Convert 2D grid to 1D
ALLOCATE (ONED(XNUM),ORDER(NIJ),PRYNT(XNUM))

DO I=1,XNUM
   ONED(I)=(I-1)*YNUM
END DO

! Set grid parameter values******************************
***************************
ALLOCATE (DELX(NIJ),DELY(NIJ),XPERM(NIJ), &
YPERM(NIJ),POR(NIJ),INDX(NIJ))

OPEN (4,FILE='INDEXCF.DAT',STATUS='OLD')
READ(4,*) INDX
CLOSE(4)

DO I = 1,XNUM
   DO J = 1,YNUM
      IJ = ONED(I) + J
      ORDER(IJ) = IJ
      IF (INDX(IJ) == 0) THEN
         POR(IJ) = 0.61
         XPERM(IJ) = 0.00054E-4
         YPERM(IJ) = 0.015E-4
      ELSE
         POR(IJ) = 1
         XPERM(IJ) = 1000
         YPERM(IJ) = 1000
      END IF
   END DO
END DO

OPEN (4,FILE='FNAMED.DAT',STATUS='OLD')
READ(4,*) FNAMES
CLOSE(4)

OPEN (11, FILE = OUTFILE1, POSITION = 'APPEND', FORM = 'FORMATTED', STATUS = 'OLD') !, ACCESS = 'APPEND'
WRITE (11,12) "Variable values for Douglas fir simulation"
12 FORMAT (A50)
WRITE (11,13) "TEMP = ",T
13 FORMAT (A8,F5.1)
WRITE (11,14) "  KX = ",XPERM(16),"KY = ",YPERM(16)
14 FORMAT (A8,ES8.2,A8,ES8.2)

DO J = 2,YNUM
   DO I = 2,XNUM
      IJ = ONED(I) + J
      IF (I==XNUM) THEN !INDX(IJ+1)==1 .OR. INDX(IJ)==1
DELX(IJ) = DELX(16)/100!
ELSE
DELX(IJ) = WIDTH/(XNUM-2)
END IF

IF(J==YNUM) THEN !INDX(IJ+YNUM)==1 .OR. INDX(IJ)==1
DELY(IJ) = DELY(16)/100!
ELSE
DELY(IJ) = THICK/(YNUM-2)
END IF
END DO
END DO

!Constant part of transmisibilities coefficients************************
!Coefficients are determined via harmonic average

IF (ALLOCATE == 0) THEN
ALLOCATE ( AX(NIJ), AY(NIJ), VB(NIJ), CON_SCD(NIJ), &
      CON_WCD(NIJ), CON_ECD(NIJ), CON_NCD(NIJ))
CON_SCD = 0
CON_WCD = 0
CON_ECD = 0
CON_NCD = 0
ELSE
END IF

DO I = 1,XNUM
DO J = 1,YNUM
IJ = ONED(I) + J
AY(IJ) = DELX(IJ)
AX(IJ) = DELY(IJ)
VB(IJ) = DELX(IJ)*DELY(IJ)
END DO
END DO

DO J = 2,YNUM-1
DO I = 2,XNUM-1
IJ = ONED(I) + J
!solve S coefficient
CON_SCD(IJ) = BETA*(1/(0.5*((1/(AY(IJ)*YPERM(IJ)/DELY(IJ)) &
                      + (1/(AY(IJ-1)*YPERM(IJ-1)/DELY(IJ-I)))))))

!solve W coefficient
CON_WCD(IJ) = BETA*(1/(0.5*((1/(AX(IJ)*XPERM(IJ)/DELX(IJ)) &
                      + (1/(AX(IJ+YNUM)*XPERM(IJ+YNUM)/DELX(IJ+YNUM)))))))

!solve E coefficient
CON_ECD(IJ) = BETA*(1/(0.5*((1/(AX(IJ)*XPERM(IJ)/DELX(IJ)) &
                      + (1/(AX(IJ+YNUM)*XPERM(IJ+YNUM)/DELX(IJ+YNUM)))))))

!solve N coefficient
CON_NCD(IJ) = BETA*(1/(0.5*((1/(AY(IJ)*YPERM(IJ)/DELY(IJ)) &
                      + (1/(AY(IJ-1)*YPERM(IJ-1)/DELY(IJ-1)))))))
\[ + \frac{1}{(AY(IJ+1)*YPERM(IJ+1)/DELY(IJ+1))} \]

END DO
END DO

DO I = 2,XNUM-1
J=2
IJ = ONED(I) + J
!solve S coefficient
CON_SCD(IJ) = 0
END DO

DO J = 2,YNUM-1
I=2
IJ = ONED(I) + J
!solve W coefficient
CON_WCD(IJ) = 0
END DO

! Start pressure simulation

IF (ALLOKATE == 0) THEN
ALLOCATE (PCD(NIJ), PPCD(NIJ), &
ROCD(NIJ), MUCD(NIJ), B(NIJ), &
ZCD(NIJ), POUT(NIJ), &
DELP(CD(NIJ), TDELP(CD(NIJ), &
NN(NIJ), OO(NIJ), DELIB(NIJ), DELC(NIJ), &
NNPLUS(NIJ), DELIC(NIJ), LUCKH(NIJ), &
DELIA(NIJ), DELI(NIJ))

DELP(CD) = 0
TDELP(CD) = 0
NN = 0
OO = 0
DELIB = 0
DELC = 0
NNPLUS = 0
PPCD = 0
PCD = 0
ELSE
END IF

Determine vessel pressure

vslp = veslp(vesltpos)
VSLP = VSLP*6.89475729316836!Convert pressure to kPa

IF (TIME == 0) THEN
DO I = 1,XNUM
DO J = 1,YNUM
IJ = ONED(I) + J
PCD = VSLP
PPCD = VSLP
NN = 0
OO = 0
DELIB = 0
DELC = 0
NNPLUS = 0
END DO
END DO

ELSE
END IF

LOOP = 1
ALPHAPOS = 5
ITER = 1

DO WHILE (LOOP == 1) ! SIP iteration

DO I = 2,XNUM
PPCD(ONED(I)+YNUM) = VSLP
END DO

DO J = 2,YNUM
PPCD(ONED(XNUM)+J) = VSLP
END DO

IF (ALLOKATE == 0) THEN
ALLOCATE(NON_SCD(NIJ),NON_WCD(NIJ), &
NON_ECD(NIJ),NON_NCD(NIJ))
ELSE
END IF

DO J = 2,YNUM-1
DO I = 2,XNUM-1
IJ = ONED(I) + J
P_AVG = (PPCD(IJ)+PPCD(IJ-1))/2
CALL DENSITY (T,P_AVG,ROCD(IJ),ZCD(IJ),B(IJ))
CALL VISCOSITY(T,ROCD(IJ),MUCD(IJ))
NON_SCD(IJ) = 1/(MUCD(IJ)*B(IJ))

P_AVG = (PPCD(IJ)+PPCD(IJ-YNUM))/2
CALL DENSITY (T,P_AVG,ROCD(IJ),ZCD(IJ),B(IJ))
CALL VISCOSITY(T,ROCD(IJ),MUCD(IJ))
NON_WCD(IJ) = 1/(MUCD(IJ)*B(IJ))

P_AVG = (PPCD(IJ)+PPCD(IJ+YNUM))/2
CALL DENSITY (T,P_AVG,ROCD(IJ),ZCD(IJ),B(IJ))
CALL VISCOSITY(T,ROCD(IJ),MUCD(IJ))
NON_ECD(IJ) = 1/(MUCD(IJ)*B(IJ))

P_AVG = (PPCD(IJ)+PPCD(IJ+1))/2
CALL DENSITY (T,P_AVG,ROCD(IJ),ZCD(IJ),B(IJ))
CALL VISCOSITY(T,ROCD(IJ),MUCD(IJ))
NON_NCD(IJ) = 1/(MUCD(IJ)*B(IJ))

END DO
END DO

! SIP coefficients*****************************************************************************

IF (ALLOKATE == 0) THEN
ALLOCATE (SCD(NIJ), WCD(NIJ),
       ECD(NIJ), NCD(NIJ),
       CCD(NIJ), GAM(NIJ), &
       QCD(NIJ))
ELSE
END IF

DO J = 2, YNUM-1
DO I = 2,XNUM-1

IJ = ONED(I) + J

NCD(IJ) = CON_NCD(IJ)*NON_NCD(IJ)
WCD(IJ) = CON_WCD(IJ)*NON_WCD(IJ)
ECD(IJ) = CON_ECD(IJ)*NON_ECD(IJ)
SCD(IJ) = CON_SCD(IJ)*NON_SCD(IJ)

IF (TIME == 0) THEN
DEL_T = 0.0001
ELSE
END IF

GAM(IJ) = (VB(IJ)*POR(IJ)*288.15)/(101.35*T*DEL_T)

! Solve C coefficient
P_AVG = PPCD(IJ)
CALL DENSITY (T,P_AVG,ROCD(IJ),ZCD(IJ),B(IJ))
CCD(IJ) = -(SCD(IJ) + WCD(IJ) + ECD(IJ) + NCD(IJ) + GAM(IJ)*(1/ZCD(IJ)))

! Solve Q coefficient
P_AVG = PCD(IJ)
CALL DENSITY (T,P_AVG,ROCD(IJ),ZCD(IJ),B(IJ))
QCD(IJ) = -GAM(IJ)*(1/ZCD(IJ))*PCD(IJ)

END DO
END DO

! Calculate Alpha*****************************************************************************
IF (ALLOKATE == 0) THEN
ALLOCATE (ALPHAMINX(NIJ), ALPHAMINY(NIJ))
ELSE
END IF

IF (ALPHAGATE == 0) THEN
DO J = 1,YNUM
DO I = 1,XNUM
IJ = ONED(I) + J
IF (I == 1 .OR. J <= 2 .OR. I >= XNUM-1 .OR. J == YNUM) THEN
ALPHAMINX(IJ) = 100000
ALPHAMINY(IJ) = 100000
ELSE
ALPHAMINX(IJ) = (3.141592653559**2)/(2*XNUM**2*(1+(SCD(IJ)/ECD(IJ))))
ALPHAMINY(IJ) = (3.141592653559**2)/(2*YNUM**2*(1+(ECD(IJ)/SCD(IJ))))
END IF
END DO
END DO
ALMINX = MINVAL(ALPHAMINX)
ALMINY = MINVAL(ALPHAMINY)

IF (ALMINX - ALMINY > 0) THEN
ALPHAMIN = ALMINY
ELSE
ALPHAMIN = ALMINX
END IF
ALPHAMAX = 1 - ALPHAMIN
ELSE
END IF

ALPHA(1) = 0.001
DO K = 2,5
ALPHA(K) = 1 - (1-ALPHAMAX)**((ITOD(K-1))/4)
END DO

! Calculate lowercase coefficients**************************

IF (ALLOKATE == 0) THEN
ALLOCATE (LOWER_B(NIJ), LOWER_C(NIJ), LOWER_D(NIJ), & LOWER_E(NIJ), LOWER_F(NIJ), LP(NIJ))
ELSE
END IF

IF (ALLOKATE == 0) THEN
ALLOCATE (DELTA(NIJ), DELTAA(NIJ), RA(NIJ))
ELSE
END IF

IF (MOD(ITER,2) > 0) THEN
DO I = 2,XNUM-1
DO J = 2, YNUM-1
IJ = ONED(I) + J

LOWER_B(IJ) = SCD(IJ)/(1+ALPHA(ALPHAPOS)*LOWER_E(IJ-1))
LOWER_C(IJ) = WCD(IJ)/(1+ALPHA(ALPHAPOS)*LOWER_F(IJ-YNUM))
P1 = ALPHA(ALPHAPOS)*LOWER_C(IJ)*LOWER_F(IJ-YNUM)
P2 = ALPHA(ALPHAPOS)*LOWER_B(IJ)*LOWER_E(IJ-1)
LOWER_D(IJ) = 1/(CCD(IJ) + P1 + P2 - LOWER_C(IJ)*LOWER_E(IJ-YNUM) - LOWER_B(IJ)*LOWER_F(IJ-1))
LOWER_E(IJ) = (ECD(IJ) - P2)*LOWER_D(IJ)
LOWER_F(IJ) = (NCD(IJ) - P1)*LOWER_D(IJ)
END DO
END DO
ELSE
DO J = 2, YNUM-1
DO I = 2, XNUM-1
IJ = ONED(I) + J

LOWER_B(IJ) = SCD(IJ)/(1+ALPHA(ALPHAPOS)*LOWER_E(IJ-1))
LOWER_C(IJ) = WCD(IJ)/(1+ALPHA(ALPHAPOS)*LOWER_F(IJ-YNUM))
P1 = ALPHA(ALPHAPOS)*LOWER_C(IJ)*LOWER_F(IJ-YNUM)
P2 = ALPHA(ALPHAPOS)*LOWER_B(IJ)*LOWER_E(IJ-1)
LOWER_D(IJ) = 1/(CCD(IJ) + P1 + P2 - LOWER_C(IJ)*LOWER_E(IJ-YNUM) - LOWER_B(IJ)*LOWER_F(IJ-1))
LOWER_E(IJ) = (ECD(IJ) - P2)*LOWER_D(IJ)
LOWER_F(IJ) = (NCD(IJ) - P1)*LOWER_D(IJ)
END DO
END DO
END IF

Calculate algorithm***************************************************************************
IF (MOD(ITER,2) > 0) THEN

DO J = 2, YNUM-1
DO I = 2, XNUM-1
IJ = ONED(I) + J

DELTA(IJ) = QCD(IJ) - SCD(IJ)*PPCD(IJ-1) - WCD(IJ)*PPCD(IJ-YNUM) - ECD(IJ)*PPCD(IJ+YNUM) & - NCD(IJ)*PPCD(IJ+1) - CCD(IJ)*PPCD(IJ)
RA(IJ) = ABS(DELTA(IJ))
DELTA(IJ) = (DELTA(IJ) - LOWER_B(IJ)*DELTA(IJ-1) - LOWER_C(IJ)*DELTA(IJ-YNUM))*LOWER_D(IJ)
END DO
END DO

DO J = YNUM-1,2,-1
DO I = XNUM-1,2,-1

IJ = ONED(I) + J

DELTA(IJ) = DELTA(IJ) - LOWER_E(IJ)*DELTA(IJ+YNUM) - LOWER_F(IJ)*DELTA(IJ+1)
DELTAA(IJ) = ABS(DELTA(IJ))

END DO
END DO
ELSE

DO I = 2,XNUM-1
DO J = 2,YNUM-1

IJ = ONED(I) + J

DELTA(IJ) = QCD(IJ) - SCD(IJ)*PPCD(IJ-1) - WCD(IJ)*PPCD(IJ-YNUM) - ECD(IJ)*PPCD(IJ+YNUM) &
- NCD(IJ)*PPCD(IJ+1) - CCD(IJ)*PPCD(IJ)
RA(IJ) = ABS(DELTA(IJ))
DELTA(IJ) = (DELTA(IJ) - LOWER_B(IJ)*DELTA(IJ-1) - LOWER_C(IJ)*DELTA(IJ-YNUM))*LOWER_D(IJ)

END DO
END DO

DO I = XNUM-1,2,-1
DO J = YNUM-1,2,-1

IJ = ONED(I) + J

DELTA(IJ) = DELTA(IJ) - LOWER_E(IJ)*DELTA(IJ+YNUM) - LOWER_F(IJ)*DELTA(IJ+1)
DELTAA(IJ) = ABS(DELTA(IJ))

END DO
END DO
END IF

DO J = 2,YNUM-1
DO I = 2,XNUM-1
IJ = ONED(I) + J

P_AVG = PPCD(IJ)
CALL DENSITY (T,P_AVG,ROCD(IJ),ZCD(IJ),B(IJ))
DELIB(IJ) = VB(IJ)*(POR(IJ)/B(IJ))
IF (ITER > 40 .and. ITER < 99) THEN !
    DELTA(ij) = DELTA(ij)/2
    ALPHA = .01
ELSE IF (ITER > 100) THEN
    DELTA(ij) = DELTA(ij)/4
    ALPHAMAX = .92
END IF

PPCD(IJ) = PPCD(IJ) + DELTA(IJ)

P_AVG = PPCD(IJ)
CALL DENSITY (T,P_AVG,ROCD(IJ),ZCD(IJ),B(IJ))
DELIA(IJ) = VB(IJ)*(POR(IJ)/B(IJ))

DELIC(IJ) = DELIA(IJ) - DELIB(IJ)
DELI(IJ) = DELI(IJ) + DELIC(IJ)

END DO
END DO

MAXDELTA = MAXVAL(DELTAA)
MAXLOK = MAXLOC(DELTAA)
RMAX = MAXVAL(RA)
MAXLOKR = MAXLOC(RA)

IF (MAXDELTA > 1E-3) THEN
    LOOP = 1
ELSE IF (MOD(ITER,2) > 0) THEN
    IF (ITER == 1) THEN
        ELSE
            IF (ALPHAPOS == 1) THEN
                ALPHAPOS = 5
            ELSE
                ALPHAPOS = ALPHAPOS - 1
            END IF
        END IF
    END IF
    ELSE
        LOOP = 2
    END IF

ALLOKATE = 1
ALPHAGATE = 1
ITER = ITER + 1

END DO !SIP iteration (LOOP=1)
DO J = 2, YNUM-1
DO I = 2, XNUM-1

IJ = ONED(I) + J
IF (TIME == 0) THEN
P_AVG = VSLP
CALL DENSITY (T, P_AVG, ROCD(IJ), ZCD(IJ), B(IJ))
OO(IJ) = VB(IJ)*((POR(IJ)/B(IJ))
ELSE
END IF

P_AVG = PCD(IJ)
CALL DENSITY (T, P_AVG, ROCD(IJ), ZCD(IJ), B(IJ))
NN(IJ) = VB(IJ)*((POR(IJ)/B(IJ))

P_AVG = PPCD(IJ)
CALL DENSITY (T, P_AVG, ROCD(IJ), ZCD(IJ), B(IJ))
NNPLUS(IJ) = VB(IJ)*((POR(IJ)/B(IJ))

DELC(IJ) = DELC(IJ) + DELI(IJ)
END DO
END DO

NN_SUM = SUM(NN)
DELI_SUM = SUM(DELI)
NNPLUS_SUM = SUM(NNPLUS)
OO_SUM = SUM(OO)
DELC_SUM = SUM(DELC)

IMB = (NN_SUM + DELI_SUM)/NNPLUS_SUM
CMB = (OO_SUM + DELC_SUM)/NNPLUS_SUM

WRITECHECK = TIME - VESLT(VESLTPOS)
VESLTPOS = VESLTPOS + 1

OUTDATA = [POUT(420), POUT(319), POUT(218), POUT(117),
POUT(16), IMB, CMB, RMAX]
FNAMETRACKER = FNAMETRACKER+1
END IF

IF (TIME == 0) THEN
WRITE (11,997) TIME, OUTDATA, FNAMES(FNAMETRACKER)
FNAMETRACKER = FNAMETRACKER+1
ELSE
WRITE (11,998) TIME, OUTDATA
END IF
IF (TIME > 8000 ) THEN
    GOTO 99
ELSE
    IF (TIME == 0) THEN
        DEL_T = 2
    ELSE
        END IF
    END IF

TIME = vesl(vesltpos)
PCD = PPCD
DELI = 0
ALPHAGATE = 0
ALPHAPOS = 5
GOTO 50
END IF

CONTINUE

END

!! SUBROUTINES

SUBROUTINE DENSITY (TEMP,PRES,RHO,ZEE,BEE)
!!
DOUBLE PRECISION TEMP, PRES, RHO, ZEE, BEE
DOUBLE PRECISION B(32), A(15)
DOUBLE PRECISION SUM1, SUM2, SUM3, SUM4, SUM5
DOUBLE PRECISION TERM1, TERM2, TERM3, TERM4, TERM5
DOUBLE PRECISION FOFX, FOXDX, ROP1, ERROR

TCR = 304.1282
PCR = 73.773
R = 0.08314
ESP1 = 0.000001
NITER1 = 100
NC1 = 0

RHO = 1
PRES = PRES/100 !Convert pressure from kpa to bar
!TEMP = TEMP + 273.15 ! Convert temperature from C to K
!....PARAMETERS AND COEFFICIENTS

B(1) = -0.9818510658E-2
B(2) = 0.9950622673E+0
B(3) = -0.2283801603E+2
B(4) = 0.2818276345E+4
B(5) = -0.3470012627E+6
B(6) = 0.3947067091E-3
B(7) = -0.3255500001E+0
B(8) = 0.4843200831E+1
B(9) = -0.3521815430E+6
B(10) = -0.3240536033E-4
B(11) = 0.4685966847E-1
B(12) = -0.7545470121E+1
B(13) = -0.3818943540E-4
B(14) = -0.4421929339E-1
B(15) = 0.5169251681E+2
B(16) = 0.2124509852E-2
B(17) = -0.2610994748E-4
B(18) = -0.888533890E-1
B(19) = 0.1552261794E-2
B(20) = 0.4150910049E+6
B(21) = -0.1101739675E+8
B(22) = 0.2919905833E+4
B(23) = 0.1432546065E+8
B(24) = 0.1085742075E+2
B(25) = -0.2477996570E+3
B(26) = 0.1992935908E-1
B(27) = 0.1027499081E+3
B(28) = 0.3776188652E-4
B(29) = -0.3322765123E-2
B(30) = 0.1791967071E-7
B(31) = 0.9450766278E-5
B(32) = -0.1234009431E-2
GAMA = 0.8899964400E-2

A(1) = R*TEMP
A(2) = B(1)*TEMP + B(2)*TEMP**0.5 + B(3) + B(4)/TEMP + B(5)/TEMP**2
A(3) = B(6)*TEMP + B(7) + B(8)/TEMP + B(9)/TEMP**2
A(4) = B(10)*TEMP + B(11) + B(12)/TEMP
A(5) = B(13)
A(6) = B(14)/TEMP + B(15)/TEMP**2
A(7) = B(16)/TEMP
A(8) = B(17)/TEMP + B(18)/TEMP**2
A(9) = B(19)/TEMP**2
A(10) = B(20)/TEMP**2 + B(21)/TEMP**3
A(11) = B(22)/TEMP**2 + B(23)/TEMP**4
A(12) = B(24)/TEMP**2 + B(25)/TEMP**3
A(13) = B(26)/TEMP**2 + B(27)/TEMP**4
A(14) = B(28)/TEMP**2 + B(29)/TEMP**3
A(15) = B(30)/TEMP**2 + B(31)/TEMP**3 + B(32)/TEMP**4

NC1 = NC1 + 1
SUM1 = 0.0
SUM2 = 0.0
SUM3 = 0.0
SUM5 = 0.0

DO 100 I = 1,9
TERM1 = A(I)*RHO**I
TERM2 = A(I)**I*RHO**(I-1)
SUM1 = SUM1 + TERM1
SUM2 = SUM2 + TERM2
100 CONTINUE
DO 110 I = 10,15
TERM3 = A(I)*RHO**(2.*I-17.)
TERM5 = A(I)*(2.*I-17.)*(RHO**(2.*I-18.))
SUM3  = SUM3 + TERM3
SUM5  = SUM5 + TERM5
110 CONTINUE
SUM3 = EXP(-GAMA*RHO**2.)*SUM3
SUM4 = 2.*RHO*GAMA*SUM3
SUM5 = EXP(-GAMA*RHO**2.)*SUM5

FOFX = PRES - SUM1 - SUM3
FOFDX = -SUM2 + SUM4 - SUM5
ROP1 = RHO - FOFX/FOFDX
ERROR = ROP1 - RHO

!PRINT*,"ERROR",ERROR

IF (ABS(ERROR) > ESP1 .AND. NC1 < NITER1) THEN
RHO = ROP1
GOTO 5
ELSE
GOTO 120
END IF

120 NC = 0
ZEE = PRES/(RHO*R*TEMP)

RHO = RHO*44.009! Convert density from mol/l to kg/m3
PRES = PRES*100! Convert pressure back to kPa

! This subroutine calculates the B value that relates fluid values at standard conditions to ! different conditions. Standard conditions are 288.15 K and 101.35 kPa
BEE = (101.35*TEMP*ZEE)/(288.15*PRES)

RETURN
END

SUBROUTINE VISCOSITY (TEMP, RHO, MUU)
DOUBLE PRECISION TEMP, RHO, MUU
DOUBLE PRECISION MUU0, MUUC, MUUE, TEMPR, MUOSUM, CROSS
DOUBLE PRECISION SCDATA(2,1060)
DOUBLE PRECISION, ALLOCATABLE :: SCDATX(:,), SCDATY(:,)
CHARACTER*10 SCFILE
CHARACTER*9 FILLER
INTEGER NUM, TABS, TABE,GATE
INTEGER TABLOC(3,16)
DOUBLE PRECISION TABTEMP(16)

IF (TEMP >= 502 .AND. TEMP < 309.75 .AND. RHO > 300 .AND. RHO < 600) THEN
  GOTO 500
ELSE
  GOTO 501
END IF

500  GATE = 0
     I = 1
     DO WHILE (GATE == 0)
       IF (I == 16) THEN
         GATE = 1
       ELSE IF (TEMP >= TABTEMP(I) .AND. TEMP < TABTEMP(I+1)) THEN
         GATE = 1
       ELSE
         GATE = 0
       END IF
       I = I+1
     END DO
     GOTO 502

!ZERO DENSITY CALCULATION
501  TEMPR = TEMP*(1/251.196)
     MUOSUM = 0.235156*(LOG(TEMPR))**0-0.491266*(LOG(TEMPR))**1+(5.211155E-2)*(LOG(TEMPR))**2 &
          +(5.347906E-2)*(LOG(TEMPR))**3-(1.537102E-2)*(LOG(TEMPR))**4
     CROSS = EXP(MUOSUM)
     MUUO = 1.00697*TEMP**0.5/CROSS

!EXCESS CALCULATION
     MUUE = (0.4071119E-2)*RHO + (0.7198037E-4)*RHO**2 + ((0.2411697E-16)*RHO**6)/TEMPR**3 &
          + (0.2971072E-22)*RHO**8 - ((0.1627888E-22)*RHO**8)/TEMPR
     MUU = MUUO + MUUE

502  CONTINUE

     MUU = MUU/1000000 ! convert micro Pa*s to Pa*s

RETURN
END

!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!
!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!

SUBROUTINE LOAD_TABLE(DATFILE,DATAVS,NUM)
!
This subroutine takes a datafile in tabular form and returns a dummy array that can be used
! to load vector properties in the main program.

CHARACTER*9 DATFILE
INTEGER NUM
DOUBLE PRECISION DATAVS(2,1000000)
NUM = 1
DO WHILE (.TRUE.)
OPEN (UNIT=250, FILE=DATFILE, ERR=302, STATUS='OLD')
READ(250, *, END=311) DATAVS(:, NUM)
NUM = NUM + 1
END DO
NUM = NUM - 1
CLOSE (250)
GOTO 301
PRINT *, " ERROR LOADING DATAFILE (TABLE_LOAD)", DATFILE
CONTINUE
RETURN
END

SUBROUTINE TABLE_LOOK (TABLE_NAME, X, Y, N, XX, YY)
! This subroutine is a table look-up that uses a binary search
! Linear interpolation is used between table values
INTEGER X(N), XX
DOUBLE PRECISION Y(N), YY
CHARACTER*9 TABLE_NAME
IF (XX < X(1)) GOTO 499
IF (XX > X(N)) GOTO 498
N1 = 1
N2 = N

400 NDIF = N2 - N1
IF (NDIF == 1) GOTO 420
NH = NDIF/2 + N1
IF (XX < X(NH)) GOTO 410
N1 = NH
GOTO 400

410 N2 = NH
GOTO 400

420 YY = Y(N1) + (Y(N2) - Y(N1))*(XX - X(N1))/(X(N2) - X(N1))
RETURN

499 YY = Y(1)
WRITE (6, 489) TABLE_NAME, XX
RETURN

489 FORMAT (‘ARGUMENT OUT OF TABLE: ’, A10, ’ ... XX =’, F12.5)
498 YY = Y(N)
WRITE (6, 489) XX
SUBROUTINE LOAD_FILE(XDIR, YDIR, DATAVALS)
!
! This program takes a datafile and loads the data into a variable array and also
! fills the array for a homogeneous matrix.
! If the file is read incorrectly or an error is experienced, an error message is displayed.
!
CHARACTER DATFILE*9, Q*1
INTEGER XDIR, YDIR, XD, YD
DOUBLE PRECISION DATAVALS(XDIR, YDIR)
DOUBLE PRECISION PROPERTY

XD = XDIR - 1
YD = YDIR - 1
DATAVALS = 0
PRINT*, "IS THIS PROPERTY HOMOGENEOUS/CONSTANT? (Y OR N)?"
READ*, Q

IF (Q == 'Y' .OR. Q == 'y') THEN
PRINT*, "WHAT IS THE VALUE OF THE PROPERTY?"
READ*, PROPERTY

DO I = 2, XD, 1
DO J = 2, YD, 1
DATAVALS(I,J) = PROPERTY
END DO
END DO
GOTO 503
END IF

500 PRINT*, "WHAT IS THE FILE NAME FOR THE DATA?"
READ*, DATFILE
OPEN (UNIT=550, FILE=DATFILE, ERR=502, STATUS=OLD)
READ(550,*, END=501) DATAVALS

501 GOTO 503
502 PRINT *, "ERROR LOADING DATAFILE ", DATFILE, " :RELOADING"
GOTO 500

503 CONTINUE
RETURN
END
Appendix C

Constants for the Modified Benedict Webb Rubin Equation

The Modified Benedict Webb Rubin Equation of State, requires a series of 32 constants \((a_n)\) to relate density\((\rho)\), temperature\((T)\), and the compressibility factor \((Z)\) of a substance:

\[
Z(T, \rho) = \frac{1}{RT} \left[ \sum_{n=1}^{9} a_n (T) \rho^{n-1} + e^{-\gamma \rho^2} \sum_{n=10}^{15} a_n (T) \rho^{2n-18} \right]
\]

The series of constants are as follows:

\[
\begin{align*}
a_1 &= -0.9818510658E-2 & a_{17} &= -0.2610094748E-4 \\
a_2 &= 0.9950622673E+0 & a_{18} &= -0.8885333890E-1 \\
a_3 &= -0.2283801603E+2 & a_{19} &= 0.1552261794E-2 \\
a_4 &= 0.2818276345E+4 & a_{20} &= 0.4150910049E+6 \\
a_5 &= -0.3470012627E+6 & a_{21} &= -0.1101739675E+8 \\
a_6 &= 0.3947067091E-3 & a_{22} &= 0.2919905833E+4 \\
a_7 &= -0.3255500001E+0 & a_{23} &= 0.1432546065E+8 \\
a_8 &= 0.4843200831E+1 & a_{24} &= 0.1085742075E+2 \\
a_9 &= -0.3521815430E+6 & a_{25} &= -0.2477996570E+3 \\
a_{10} &= -0.3240536033E-4 & a_{26} &= 0.1992935908E-1 \\
a_{11} &= 0.4685966847E-1 & a_{27} &= 0.1027499081E+3 \\
a_{12} &= -0.7545470121E+1 & a_{28} &= 0.3776188652E-4 \\
a_{13} &= -0.3818943540E-4 & a_{29} &= -0.3322765123E-2 \\
a_{14} &= -0.4421929339E-1 & a_{30} &= 0.1791967071E-7 \\
a_{15} &= 0.5169251681E+2 & a_{31} &= 0.9450766278E-5 \\
a_{16} &= 0.2124509852E-2 & a_{32} &= -0.1234099431E-2
\end{align*}
\]
Appendix D

Pressure Profile Plots

The following plots are a collection of every specimen in this study, depicting the pressure measurements taken during the treatment process. They are similar to plots shown in Figure 5-1 and Figure 5-2. In each plot, the vessel pressure is plotted along with the pressure that was measured at each pressure probe location. The pressure probe locations correspond to those depicted in Figure 4-3. The specimen ID is shown in brackets in each plot, and the pressurization rate (in kPa/min) in parenthesis. The plots are sorted by wood species and pressurization rate.
[DF18]
[DF19-1] (825)

[DF19-2] (825)
[SLP7] (825)

[SLP9] (825)
[SLP17-1] (825)

[SLP17-2] (825)
[SLP19-1] (825)

[SLP19-2] (825)
[SLP15] (825)
[SLP4-1] (1240)

[SLP4-2] (1240)
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