A review of Scion research using supercritical carbon dioxide

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Abstract

Scion has researched the application of supercritical CO_2 to remove water from timber. For CO_2 to become a supercritical fluid, a pressure of 7.4 MPa and a temperature of 31°C is required. Timber species that have been treated include a range of New Zealand softwoods and hardwoods, with radiata pine being most widely studied. Supercritical CO_2 offers advantages of being less energy intensive than thermal drying, it leaves no residue as the fluid reverts to gas below 7.4 MPa, and it can penetrate wet timber as a consequence of high pressure. Supercritical CO_2 can be used to remove water in radiata pine down to about 40% cycling from gas to supercritical fluid multiple times. At this moisture content chemicals or fluids can be added to radiata pine without water (sap) in the cell lumens to improve or add properties such as stiffness or decay resistance.

For difficult-to-dry collapse-prone hardwoods, such as eucalypts, dewatering prevents timber collapse and has the potential to increase conversion rates from green timber into product. Following the supercritical CO_2 dewatering process, a kiln drying schedule will be required to achieve a moisture content of 10–14% in the timber. However, the effect of the supercritical CO_2 dewatering process is retained and collapse will not occur on kiln drying.

Introduction

Green wood (moisture contents ~150–200% of oven dry wood mass) must be dried to about 10–14% moisture content before being converted into wooden products to prevent both distortion and decay in service (Kininmonth & Whitehouse, 1991). Traditionally, kiln drying is used to reduce the moisture content in wood. For difficult-to-dry species, air drying over six to 12 months is often required.

Scion has a patented process using supercritical CO_2 (Franich et al., 2010; 2013) to remove water (sap) from green wood down to about 40% in softwoods. This process dewaters wood by removing water from the spaces in fibres where most of the water in the green state resides.

This paper presents an overview of published Scion research using supercritical CO_2. Most of the research focussed on removal water from the softwood radiata pine (*Pinus radiata*) or the hardwood *Eucalyptus nitens*.

Anatomy of softwoods

This section introduces anatomical structures that will be important later in understanding supercritical CO_2 treatments. Softwoods and hardwoods are differentiated by their reproduction and not by their appearance. Softwoods remain green all year, and in temperate climates softwood trees produce new wood cells called earlywood in spring and summer to conduct water and support the tree as it grows more branches and foliage. Earlywood growth ring cells have thin walls and large spaces (lumens) inside them. At the end of the growing season in autumn and winter, latewood cells with thick walls and small lumens are produced.

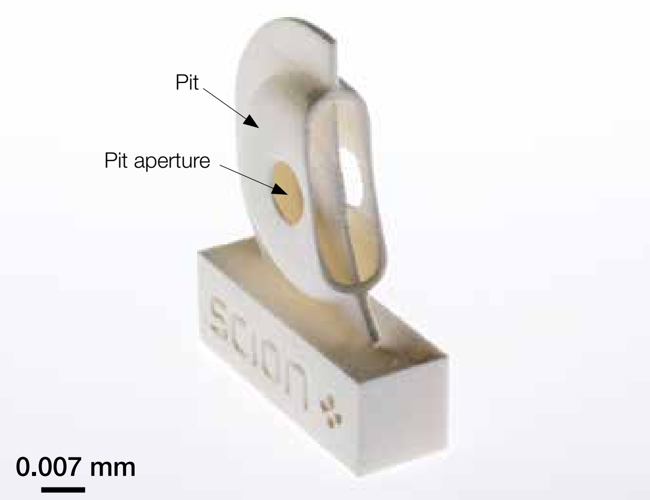
Radiata pine cells, as an example of a softwood, are dominated by tracheids (~3 mm long and 0.04 mm diameter) that are aligned longitudinally along the stem of the tree. Mechanical valve-like apertures in the tracheid walls, called pits, control water and nutrient movement both up and down the tree. Pits are relatively rigid in latewood and are not as effective as in earlywood. Pits are more abundant in the earlywood than in the latewood of softwoods and more abundant in the tangential direction than in the radial direction. This translates into low connectivity in the radial direction between latewood and earlywood, and will be shown later to determine the path of penetration of supercritical CO_2 into sapwood.

In softwood species cell lumen water is free (not bound to the cell wall), while water within the cell wall is bound. Free water can be removed by supercritical CO_2 dewatering but the bound water, which resides in very small lumen spaces (pores that are less than 2 nanometers in diameter (Telkki et al., 2013)), cannot be removed.

Models of wood anatomy can be useful aids to help visualise basic wood structure. Scion has constructed such models using 3D printing (Figure 1) (Graichen et al., 2016). Microscopic images of radiata pine have been converted to 3D computer model drawings and then 3D printed. The resulting 3D printed wood objects show the internal structure of wood.

Supercritical CO_2 treatment process

CO_2 is a gas in air at standard temperature and pressure or a solid called dry ice below –78.5°C. Above a temperature of 31.1°C and a pressure of 7.4 MPa, CO_2 becomes a supercritical fluid with gas-like liquid diffusivity and liquid-like density. Supercritical CO_2



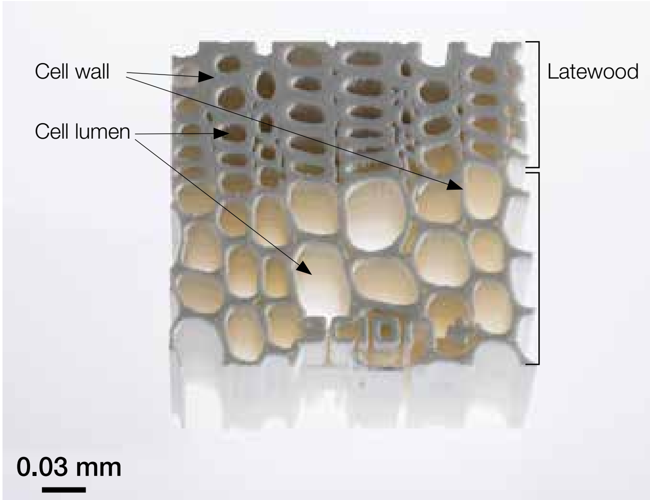


Figure 1: 3D printed objects showing anatomical structure of radiata pine. Left: Pit structure. Right: Tracheid structure. Scale bars give indicative size. Any size for 3D printed models can be selected (e.g. 50 mm)

has low toxicity and environmental impact, it does not leave residual chemicals in extracted materials such as decaffeinated coffee, and it does not result in emissions that occur on kiln drying timber.

Scion's dewatering technology demonstrates a supercritical CO_2 treatment process that removes water from wood through repeated cycling of CO_2 between supercritical fluid and gaseous phases. The supercritical dewatering process has been successfully modelled as a mechanical treatment of porous materials (e.g. wood and ceramics), in which water is expelled through gas bubble pressure and buoyancy during depressurisation of a water-filled glass capillary tube. Wood dewatering was more complex to model than other porous materials due to its anatomy, hygroscopic character, and because it binds water while porous materials do not.

A fluid dynamics model was developed to predict the behaviour of the supercritical CO_2 dewatering process (Pearson et al., 2019a; 2019b). Some of the parameters included in the model were thermodynamics, surface tension, wetting angle, pore size and bubble development. The model contributes to a fundamental understanding of dewatering behaviour and how water leaves wood during the process.

The dewatering process involves five to 10 cycles of supercritical CO_2 pressurisation to 20 MPa, holding at pressure for several minutes, followed by a depressurisation down to close to atmospheric pressure and holding at that pressure for several minutes while expelled water is drained off (Dawson et al., 2015; Franich et al., 2014) (Figure 2). The vessel jacket is maintained at 50°C. During pressurisation, the supercritical CO_2 dissolves in water present in the very small spaces in the wood cell walls. During depressurisation, CO_2 reverts to a gas, creating bubbles that push water out of the wood. Dewatering using supercritical CO_2 reduces the moisture content in green timber to its fibre saturation point (30–40%). At this point there has been no dimensional change as the wood remains in a pseudo-green state.

The process takes about an hour, is energy efficient, retains normal wood colour and reduces distortion in wood. The water (sap) collected may provide valuable extractive side streams.

Path of water movement

The saturated sapwood of radiata pine has moisture contents of 160–200% of the oven-dried mass of the bulk wood. Proton magnetic resonance imaging (^{1}H MRI) can be used to visualise water in wood of size 15 x 15 x 200 mm (Behr et al., 2014). Furthermore, only the free water in lumens can be seen since water bound to the cell wall polymers can be excluded. In ^{1}H MRI images of saturated pine sapwood at low CO_2 pressure, the latewood bands containing bound water appear blue,

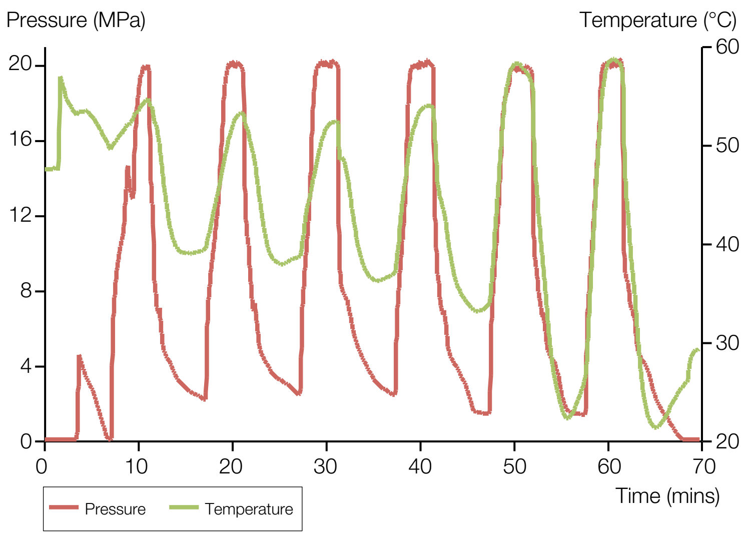


Figure 2: Supercritical CO_2 dewatering of radiata pine showing the pressure cycling. The internal temperature of the sample increasingly rises and falls with each cycle as sap is removed and more CO_2 can enter the wood. This results in an increased temperature via heat of compression of extra CO_2 and then decreased temperature due to increased decompressive cooling of the extra CO_2 as it changes into a gas. The vessel jacket was maintained at 50°C

while the earlywood bands containing free water appear green (Figure 3a; Hill et al., 2013). Saturated latewood is known to have half the moisture content of earlywood (Kininmonth & Whitehouse, 1991). The partly empty latewood lumens provide a pathway for supercritical CO_2 diffusion into the adjacent earlywood lumens.

Supercritical CO_2 diffusion into the free water increases the water volume by up to 6%. This expansion and overflow of free earlywood water fills the latewood lumens, which then appear green in ^1H MRI images (Figure 3b). On depressurisation, supercritical CO_2 reverts to the gaseous CO_2, pushing water out of the wood (Figure 3c) through rows of latewood, or from adjacent earlywood cells with water flowing tangentially through the abundant radial cell wall pit apertures towards the specimen surfaces (Newman et al., 2016). Free earlywood water is strongly reduced by cycle 5 (Figure 3d). After six cycles the wood is at its fibre saturation point with no free water remaining (Figure 3e).

Dewatering efficiency

In a study of 22 New Zealand softwood and hardwood tree species, dewatering efficiencies ranged from 4% in the hardwood red beech (*Nothofagus fusca)* to 93–94% for softwoods – radiata pine, patula pine, sugar pine (*Pinus lambertiana*) and Douglas fir (*Pseudotsuga menziesii*) (Dawson & Pearson, 2017). Several species showed medium dewatering efficiencies (50–65%). In the study, half of all the New Zealand softwoods were not suitable for dewatering since their green moisture contents were already about 40%, whereas all New Zealand hardwoods in the study had moisture contents above 60% and were suitable. The efficiency of the supercritical CO_2 dewatering process depended on the anatomy of the tree species being dewatered, as this determines the porosity of the wood and thus the permeability of supercritical CO_2 through the wood.

Permeability

The porosity of wood is the ratio of pore volume to wood volume. Dewatering with supercritical CO_2 retains the porosity of cell walls similar to that in the green state, which potentially could be useful for chemical or fluid impregnation. In green radiata pine sapwood, Grigsby et al. (2013) showed most bound water was in pores less than 50 nanometers in diameter. They also found that after supercritical CO_2 dewatering most bound water was in pore sizes less than 20 nanometers in diameter. This equates with moisture content at the fibre saturation point where only the bound water remains. In contrast, traditional kiln drying methods remove both free and bound water.

The water column in living trees is in a state of negative tensile water tension as water is dragged up the tree to the crown from the roots. Drying green timber similarly creates negative water tension (Chafe et al., 1992). Water tension and the permeability of timber are closely linked. Permeability quantifies the extent to which a gas or a liquid travels in a porous material in response to a pressure gradient.

There is a correlation between the permeability of CO_2 and the internal sample temperature during dewatering (Dawson et al., 2015). The higher the penetration of supercritical CO_2, the greater the heating effect from compression and the greater the rise in internal temperature (Figure 2). The internal temperature plot for red beech (*Nothofagus fusca)* indicates that it is impermeable to supercritical CO_2, as the temperature simply gravitates towards the vessel jacket temperature of 50°C (Figure 4). The impermeability of red beech has been reported to be due to polyphenol (Hillis & Inoue, 1967) encrustation of pits (Kininmonth, 1972).

Collapse of wood on drying

The removal of free water on supercritical CO_2 treatment prior to traditional kiln drying is important because water tension can be significantly reduced, creating a unique opportunity to avoid collapse in some collapse-prone species such as the Australian eucalypt wood species. Collapse, which occurs at high moisture content well above the fibre saturation point, is a buckling of cell walls collapsing into cell lumens. Collapse occurs perpendicular to the grain as a result of water tension forces exceeding the compressive strength of wood cell walls.

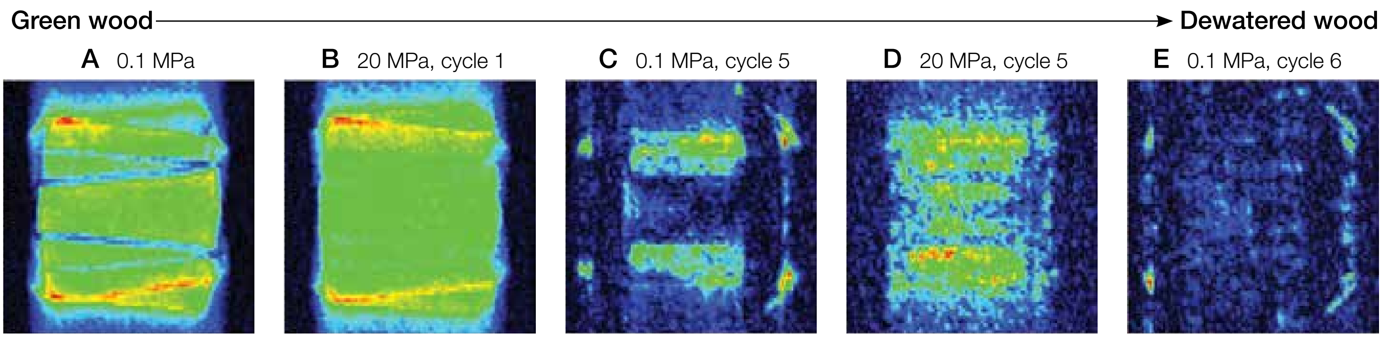


Figure 3: ^1H magnetic resonance images during supercritical CO_2 dewatering of radiata pine sapwood: a) gaseous CO_2 with latewood bands showing as blue (bound water) and earlywood bands showing as green (free water); b) supercritical CO_2 with latewood bands now green (free water) due to water movement from earlywood to latewood bands; c) gaseous CO_2 in cycle 5 corresponds to greatly increased bound water (blue); d) supercritical CO_2 mobilises both bound and free water in cycle 5; e) gaseous CO_2 with only bound water present at end of treatment

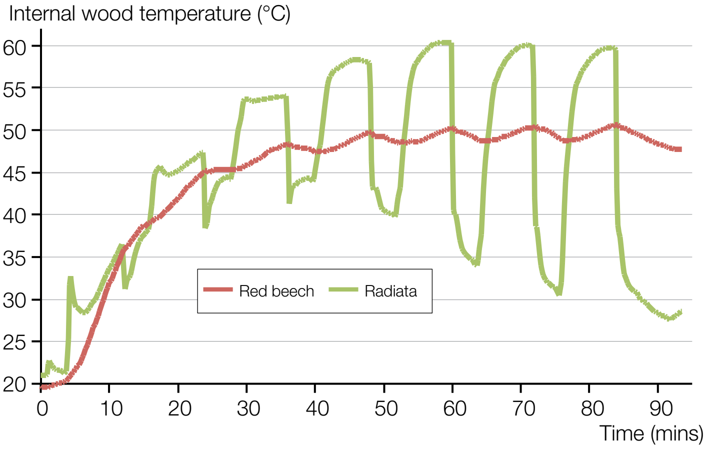


Figure 4: Supercritical CO_2 dewatering of radiata pine and red beech showing the internal temperature of the samples. The red beech gravitates to the vessel jacket temperature of 50°C, indicating there is no dewatering occurring

In the study of New Zealand softwoods and hardwoods, collapse did not occur after supercritical CO_2 dewatering of green wood (Dawson & Pearson, 2017). However, collapse was severe after only oven drying for the softwood western red cedar (*Thuja plicata*), several Australian eucalypts (*E. nitens, E. fastigata, E. delegatensis* and *E. regnans*) and red beech (*Nothofagus fusca*). For *Eucalyptus regnans*, there was a dramatic reduction in collapse if supercritical CO_2 dewatering treatment preceded oven drying (Figure 5).

Pathways to applications

Supercritical CO_2 treatments at Scion have mainly involved timber – removing water and extracting a range of biochemicals from tree-derived materials such as wood, twigs, leaves, needles and bark. Applications involving a whole of tree approach could fit well with a forest bioeconomy of the future (Graichen et al., 2016). The supercritical CO_2 dewatering technology is also applicable to a wider range of porous materials. Future applications, as yet unidentified, may reflect this.

Application opportunities:

- Using supercritical CO_2 as a carrier to treat wood with preservative chemicals (Kjellow & Henriksen, 2009), which is a process currently used in Denmark
- Treatment options for dewatered wood may include a follow-up treatment where bio-derived monomers can be introduced into empty lumens (in the case of high dewatering efficiency tree species) and polymerised to improve performance properties of the substrate. The use of a co-solvent may achieve higher extraction yields of components
- The empty lumens and porosity of dewatered cell walls could improve the accessibility of enzymes, which can reduce cellulosic biomass into small sugar molecules required for biofuel production
- Overcoming other extraction technology drawbacks when removing organic compounds. Issues include solvent use and disposal and the use of steam distillation at temperatures that thermally modify target compounds.

The group of hardwoods showing medium dewatering efficiencies become candidate species for supercritical CO_2 dewatering to reduce water tension distortions such as shrinkage, collapse and internal checking. Inclusion of a dewatering step translates into: 1) higher conversion of log into a useable product; and 2) reduction of stock in lengthy air drying (six to 12 months) due to fast dewatering (less than 24 hours). Following dewatering a kiln drying schedule is required to bring the moisture content down to service levels of around 10–14%.

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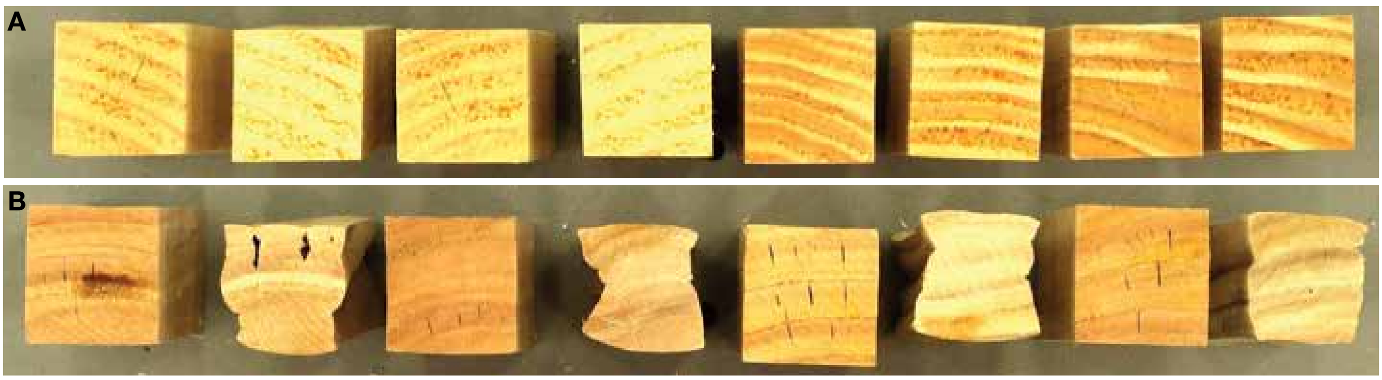

Figure 5: Four sets of duplicates showing collapse (end grain view) for: a) radiata pine; and b) *Eucalyptus regnans*. Repeating from left to right: 'dewatered and oven dried' to 'oven dried only'. Sample size was 37 x 37 x 200 mm (radial x tangential x longitudinal)

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