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Proton magnetic resonance imaging used to investigate dewatering of green sapwood by cycling carbon dioxide between supercritical fluid and gas phase

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ABSTRACT

Proton magnetic resonance (MR) imaging at 300 MHz was used to characterise the dewatering of *Pinus radiata* sapwood. The sapwood was immersed in CO_2 that was cycled at temperatures greater than 31 °C between gas (0.1–6 MPa) and supercritical fluid (15–20 MPa) phase. A combination of FLASH and RARE pulse sequences were used to highlight differences in $T_2^*(H)$ and $T_2(H)$ relaxation. It was observed that CO_2 entered into the green sapwood via air or water vapour-filled cells in the latewood and then diffused into earlywood cells adjacent to the pith side of the latewood bands. The dissolved CO_2 reduced the surface tension of water which facilitated the expulsion of sap. As the pressure was released, and CO_2 bubbles formed and expanded, the sap flowed tangentially towards the surfaces. This accounted, in part, for the observed independence of sample size on the supercritical CO_2 dewatering process.

1. Introduction

The green sapwood of radiata pine (*Pinus radiata* D. Don) shows values for moisture content typically between 160% and 200% of the oven-dried weight of the bulk wood [1]. A patented process achieves dewatering of this sapwood by applying supercritical CO_2 to the wood, then cycling the pressure so that the state of the CO_2 alternates between the supercritical fluid and gas phases [2,3]. The moisture content is progressively lowered to an endpoint of approximately 40% of the oven-dried weight, interpreted in terms of removal of sap from cell lumens, leaving bound water in cell walls [4]. Potential applications of the dewatering process include preparation of green sapwood for impregnation by biocide formulations [2,3]. The results from bench-scale experiments were consistent with a dewatering mechanism in which CO_2 fills voids as supercritical fluid, and also becomes dissolved in sap in the lumens of cells, diffusing deeper into the wood in each cycle [4]. Releasing the pressure lowers the solubility of CO_2 in water, generating bubbles of CO_2 which expel sap from the cell lumens. In this paper, the mechanisms involved were investigated in more detail.

The dewatering process is readily scalable, in that pieces of timber with cross-sections as large as 100 mm × 50 mm have been observed to dewater [2–5] on timescales similar to those required for laboratory-scale experiments on sticks of wood not much larger than a pencil [2,3,5]. The mechanism is clearly more complex than just movement of a moisture-content profile deeper into the specimen during each successive pressure cycle.

The ready scalability is explained through supercritical CO_2 diffusing into sapwood, both at the wood specimen surface and into latewood bands [6]. The mole fraction of CO_2 in water at 20 MPa, 50 °C is 0.023 [7] corresponding to a mass increase of 5.3% in the aqueous phase, sufficient to cause a 6% volume expansion [8] of sap assuming that the supercritical CO_2 could fully access and fully dissolve in the lumen sap and possibly also in cell wall water. The mole fraction of water in supercritical CO_2 is 0.006 [7] corresponding to

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0.25% by mass of water in CO_2. There is a slight increase in density and viscosity of water containing dissolved CO_2 [9] and a significant reduction in the water interfacial tension from 70 m N m^{-1} to 55 m N m^{-1} [10,11] under the dewatering conditions. This would allow increased mixing of the supercritical CO_2 and water phases so that CO_2 dissolves in cell lumen sap and possibly in water bound in cell walls.

Imaging techniques such as computed tomography (CT) and magnetic resonance (MR) imaging have been used to study the movement of water during conventional [4,12–14] and supercritical CO_2 [15] drying processes. An integrated high-pressure cell and proton/carbon-13 (^{1}H/^{13}C) double-tuned resonator was designed and constructed so that proton MR imaging and ^{13}C nuclear magnetic resonance (NMR) could be used to study the distribution and chemistry of water and CO_2 in wood, *in situ*, during pressure cycling [16] with results for the ^{13}C MR imaging and spectroscopy reported previously [6]. This paper reports results from the proton MR experiments.

Proton MR images of plant tissues are commonly enhanced by exploiting differences in spin relaxation parameters between the different parts of the specimen [17,18]. Such parameters include the time constant $T_2(H)$ for transverse relaxation of proton magnetisation, and the time constant $T_2{}^*(H)$ for 'effective' transverse relaxation. These two parameters are related through an equation [17,18]:

$$\frac{1}{T_2*(H)} = \frac{1}{T_2(H)} + f(\Delta\chi) \quad (1)$$

here f is a function of $\Delta\chi$, *i.e.* the magnitude of local differences in magnetic susceptibility in an inhomogeneous structure. In medical applications, imaging sequences which exploit $T_2{}^*(H)$ are useful for identifying heterogeneously structured regions [19]. In characterisation of plant tissue, local differences in magnetic susceptibility are due to large differences in density. In wood, this can be caused by air bubbles in cells, or by air-filled cavities between cells [17,18]. The advantages of using $T_2{}^*(H)$-weighted imaging have been demonstrated in proton MR images of seeds [20], where vascular bundles were seen in higher contrast than in T_2-weighted images.

In MR imaging studies of wood, pulse sequences which exploit $T_2(H)$ can also be useful [21]. In the absence of spin exchange between cell walls and cell lumens, the value of $T_2(H)$ is inversely proportional to a time constant for the reorientation of a water molecule [22]. This makes it possible to distinguish between water molecules that are bound in cell walls, with $T_2(H)$ of the order of a few ms, and the relatively mobile water molecules in cells that are filled with sap, with $T_2(H)$ typically 50 to 100 ms [21]. In the presence of spin exchange, the value of $T_2(H)$ is influenced by difference in magnetic susceptibility between the cell wall and the contents of the lumen [23], in addition to the influences of molecular mobility in both environments.

In the present paper, most of the images were obtained with a pulse sequence that exploited differences in $T_2{}^*(H)$. For one specimen, the results from exploiting $T_2{}^*(H)$ or $T_2(H)$ were compared.

2. Materials and methods

2.1. Specimens

Green radiata pine (*P. radiata* D. Don) sapwood was selected from the green-chain of a local sawmill (Rotorua, New Zealand; 38°7′S, 176°15′E). Specimens intended for MR were cut to 15 mm (radial) × 15 mm (tangential) × 95 mm (longitudinal) and edge-chamfered in order to achieve a tight fit in a 20 mm internal diameter high-pressure MR cell [16].

Moisture contents (%MC) of samples were calculated as a percentage of a samples 105 °C oven-dried weight:

$$\%MC = \frac{\text{Original mass (g)} - \text{Oven-dried mass (g)}}{\text{Oven-dried mass (g)}} \times 100 \quad (2)$$

2.2. Dewatering

The schematics for the dewatering apparatus have been described in an earlier paper [16]. Supercritical CO_2 phase generation (≥31 °C and 7.4 MPa) was by liquid CO_2 delivery (99.7% pure) from a storage cylinder. Liquid CO_2 was chilled at ice-bath temperature to maintain the liquid phase entering the pump (V series, model P500V300, Williams Pumps, Warminster, PA, USA, www.williamspumps.com), which then delivered the liquid CO_2, under pressure, through a heated water-bath to establish the supercritical phase at the target pressure and temperature for the particular experiment. The target pressure was maintained for a 'hold-time,' then decreased to a value below the critical pressure, by allowing CO_2 gas to escape from the high-pressure cell.

2.3. Proton MR imaging

The proton MR experiments used a Bruker Biospec 70/30 magnetic resonance microimaging system operating at 7.05 T (300 MHz ^{1}H) with an Avance-AV console, and using ParaVision v4 software for acquisition (Bruker, Ettlingen, Germany, www.bruker.com). The high-pressure polyetheretherketone (PEEK) cell and its birdcage radiofrequency coil have been described previously [16].

Proton MR images were acquired using a FLASH (Fast Low Angle SHot) sequence [19] with a gradient echo time (TE) of 3.1 ms, a repetition time (TR) of 100 ms, and flip angle of $\alpha \approx 20°$ optimised for $T_1(H)$ of a typical specimen [24]. Images used in the present paper were taken from the fifth slice of eight, or from the third slice of four, with slice thickness = 1 mm and interslice distance = 3 mm. The field of view dimensions were 20 mm × 20 mm, with a matrix size of 128 × 128, resulting in a voxel size of 1 mm × 156 μm × 156 μm presented as a pixel of size 156 μm × 156 μm. A total of 16 signals were averaged for each phase encoding step, requiring 3 min of data averaging. Profiles across rows of pixels or up columns of pixels were processed in Prospa (Version 3.12, Magritek, Wellington, New Zealand, www.magritek.com). Because FLASH uses gradient echoes rather than spin echoes, the signal strength indicates the concentration of water molecules with $T_2{}^*(H) > TE$ [19].

The $T_2(H)$ datasets were acquired using a RARE (Rapid Acquisition with Relaxation Enhancement) sequence [25], configured with a RARE factor of 1 and with 8 echo images so that the sequence was equivalent to a multi-SE (multiple Spin Echo) sequence, with a total data acquisition time of approximately 1 h. The abbreviation MSE was avoided since it is sometimes used for Magnetic Susceptibility Enhancement, and the multi-SE sequence is designed to suppress the influence of magnetic susceptibility. The repetition time (TR) was 2 s and the echo trains used an inter-echo spacing of 9.9 ms. Signals from 80 echo trains were acquired to improve the signal-to-noise ratio. Data processing was performed using University of Würzburg in-house IDL code (Interactive Data Language, Excelis Visual Information Systems, Boulder CO, USA, www.exelisvis.com). The fit to all 8 echo images was performed with a single exponential function with time constant $T_2(H)$. Acceptance of results was based on a chi-squared test.

3. Results

3.1. Photographic image

A grey-scale photographic image of a transverse surface is shown in Fig. 1. The specimen was cut after MR imaging, at the