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Dewatering green sapwood using carbon dioxide cycled between supercritical fluid and gas phase

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ABSTRACT

Green radiata pine sapwood was dewatered through exposure to CO_2, cyclically alternated between supercritical fluid and gas phase. Plots of moisture content against cycle number showed sigmoidal shapes, with the maximum slope showing a linear dependence on the maximum pressure applied in each cycle, over the range 8–20 MPa. The initial slope varied as the square root of the hold time at 40 MPa, as expected for diffusion of CO_2 through water into the wood. The temperature of the vessel showed no influence on the dewatering rate over the range 38–58 °C. Dissection of partly-dewatered specimens showed strong moisture gradients in green wood, changing to a relatively uniform distribution through a cross-section as the moisture content decreased to an end-point of 40% of the oven-dry weight. This end-point was attributed to moisture remaining in cell walls, after the lumens had been emptied.

1. Introduction

Wood in its green state, when freshly-sawn from the log, usually has a high moisture content. The moisture content and distribution differs between tree species. That of green radiata pine sapwood is typically 100–200% of the oven-dry weight of the bulk wood material, the majority of the moisture being resident within the cell lumens [1]. In routine modelling, it is often assumed that moisture in cell walls accounts for 30% of the oven-dry weight of wood [2]. During kiln drying, water molecules undergo diffusion from within the wood material towards the surface, where, from an evaporation layer, there is a phase change from liquid to gas [3,4]. The moisture gradient can be so large that cell walls can lose most of their moisture if they are located close to the evaporation layer, while lumens retain much of their moisture if they are located further within the wood. Removal of water from the cell walls when green wood is dried can cause irreversible changes in cell-wall structure [5] and permeability [6] depending on the drying severity. These changes can impede subsequent wood processing steps, particularly if those steps involve ingress of aqueous solutions of chemicals such as those used to enhance the physical or biological durability of the wood.

In the present study, supercritical CO_2 was used to extract water from green wood in order to test the selectivity of the dewatering process in removing moisture from lumens, rather than from cell walls.

In the supercritical phase, CO_2 is known to exhibit solvent properties similar to those of hexane, and this property has been widely-exploited for the extraction of natural products from dried wood [7] and for delivery of biocides into dried wood [8,9]. Use of CO_2 as the working fluid, in these processes, can be seen as environmentally friendly in that the treated wood does not release residual traces of potentially harmful solvents or co-solvents while in storage or in use. While wood drying techniques using CO_2 critical point drying [10] are known, and are used to advantage for wood artefact conservation work, these require initially a gradual replacement of the specimen moisture with an aqueous-compatible solvent, such as methanol or acetone, which is subsequently extracted using supercritical CO_2 to afford a dry specimen with dimensional and conformational aspects preserved. Critical point drying is clearly too expensive to use in commercial timber production.

A patented process dewaters green sapwood by cycling the vessel pressure so that the CO_2 is cycled between supercritical fluid and gaseous phases [11,12]. According to the patents, potential applications include preparation of green sapwood for impregnation by aqueous biocide formulations. In one of the examples presented in the patents, specimens of nominal dimensions 100 mm × 50 mm × 1.5 m were partly dewatered and then impregnated with a solution of boric acid, achieving 0.4% by weight retention of boric acid. Success was attributed to removal of water

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from cell lumens, without removal from cell walls, so that the cell wall structure remained receptive to chemicals.

Bench-scale versions of the patented process were used in the experiments described in this paper. The experiments were designed to provide a better understanding of the physical processes that result in dewatering. Pressure and temperature have been identified as influencing the flow of supercritical CO_2 through dry wood [13,14]. In this paper, those same two parameters were tested for their influence on the rate of dewatering of wood from the green state, and to test for possible influences on the end-point moisture content of the wood. Partly-dewatered specimens were also dissected to test for uniformity of the moisture content when mapped over cross-sections.

2. Materials and methods

2.1. Green wood material

Green radiata pine (*Pinus radiata* D. Don) sapwood specimens for experimental work were freshly-cut from commercially-produced wood selected from the green-chain of a local sawmill (Rotorua, New Zealand; S 38°7′ E 176°15′). Wood specimens were therefore obtained shortly after sawing from the log. The elapsed time from tree felling to sawing was unknown, but likely to be less than 10 days. Longitudinal specimens were cut to dimensions of 18 mm × 18 mm × 100 mm for dewatering at maximum pressures up to 20 MPa, or 8 mm × 8 mm × 140 mm for 40 MPa, since the cell used at the higher pressure had smaller internal dimensions. The specimens were kept at 4 °C and returned to ambient prior to running the experiments.

2.2. Dewatering rates

For experiments in the pressure range 8–20 MPa, specimens of dimensions 18 mm × 18 mm × 100 mm were inserted into a 100 cm^3 high-pressure stainless steel vessel which was fitted with inlet and outlet ports in the top section. The bottom section of the vessel sat within a heated mantle and the temperature within the vessel was measured using a thermocouple contained within a probe. The temperature of the vessel was controlled, during the hold time at maximum pressure, to within ±2 °C of 38, 47 or 58 °C for experiments in this apparatus. Supercritical CO_2 phase generation was by liquid CO_2 delivery (99.7% pure) from a storage vessel. The liquid CO_2 was pumped using a Dionex SFE-703 (Supercritical Fluid Extractor) pump which delivered the CO_2 into the vessel at a target maximum pressure.

The apparatus used for experiments at 40 MPa was similar, but a 24 cm^3 vessel was completely enclosed in the oven of the Dionex Supercritical Fluid Extractor, which was set at 50 °C. Specimens were cut to 8 mm × 8 mm × 140 mm for this apparatus.

For all of the above experiments, green wood specimens were weighed to ±1 mg, and held in contact with supercritical CO_2, at a target maximum pressure, for a hold time of up to 16 min. These hold times were nominal values, since the time taken to open and close valves added approximately 10 s to each value. Pumping was sustained for the duration of each hold time, in order to keep the pressure close to the target value while the wood absorbed CO_2. The pressure was then decreased to atmospheric pressure, 0.1 MPa, by allowing CO_2 gas to escape through the outlet valve. The specimen was removed from the vessel, weighed after cessation of CO_2 emission, and returned to the vessel. The process was repeated as alternating pressure cycles effecting dewatering until the specimen weight approached a constant value. Specimens cut to 18 mm × 18 mm × 100 mm were dried at 105 °C to constant weight. Those cut to 8 mm × 8 mm × 140 mm were dried in a controlled-environment room (65% relative humidity at 20 °C) to a moisture content of approximately 12% of oven-dried weight. In both cases, the final weight was then used to calculate the moisture content, as percent of oven-dried weight, at the end of each cycle.

Six of the specimens that were cut to 8 mm × 8 mm × 140 mm were measured in both transverse and longitudinal directions, in the green state, after supercritical CO_2 dewatering, and after further drying in air, in order to test for dimensional changes associated with dewatering and drying.

2.3. Specimen dissection for moisture profiles

The apparatus used for these experiments had a vessel volume of 500 cm^3 in order to hold multiple specimens of dimensions 18 mm × 18 mm × 100 mm. The vessel had top and bottom outlets. The top opening had two valves: (1) a CO_2 inlet connected to a Haskel DSTV-122 air-driven pump and a CO_2 pre-heating water bath which was controlled at the target temperature, (2) a CO_2 outlet, connected directly to the CO_2 recovery cylinder as long as the pressure was above 7 MPa, and the flow re-routed through the pump into the top-end of the CO_2 recovery cylinder when the pressure was between 7 and 4 MPa. The bottom outlet had one valve which was used to drain wood sap and gaseous CO_2 at the end of each cycle.

Six green radiata pine sapwood specimens were selected, all consisting predominantly of earlywood as determined by visual inspection. One specimen was left in the green state, while the other five were arranged together in the pressure vessel and dewatered for up to five cycles, with one specimen removed at the end of each cycle. A maximum pressure of 20 MPa was held for 2 min in each cycle. The specimen was then carefully dissected into 25 matchsticks, first using a fine bandsaw to produce five veneers and then using a sharp razor blade to cut each veneer into five equal sections. The location of each matchstick in the original specimen was recorded, and then the matchstick was promptly weighed to minimise weight loss by evaporation. Finally, each matchstick was dried at 105 °C to allow calculation of the moisture content as it had been in the partly-dewatered state.

2.4. Specimen shrinkage

Shrinkage was determined by using digital callipers to measure the distances between pairs of radial, tangential and longitudinal faces, before and after part-drying. For these measurements, a single position was marked at the midpoint of each face. The transverse and longitudinal dimensions were each averaged for six specimens.

3. Results and discussion

3.1. Influence of pressure and time

The influence of the maximum pressure on the dewatering rate was investigated over the range 8–20 MPa. The temperature of the vessel was 47 °C during a hold time of 2 min at maximum pressure, in all of these experiments. Plots of moisture content against the number of cycles gave sigmoidal curves (Fig. 1a) , and the moisture expulsion process became inefficient at moisture contents approaching 40%. This value is higher than the fibre-saturation point, which for plant material in general is approximately 30% moisture content [2], but is consistent with removal of moisture from lumens, while leaving the cell wall biopolymers fully hydrated.

The maximum dewatering rate was defined as the change in moisture content for the most productive cycle of each dewatering curve, i.e., the steepest line joining two consecutive data points in