Specialty Wood Products Research Partnership

UNIVERSITY OF CANTERBURY
Te Whare Wānanga o Waitaha
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Measuring Strain in Wet Eucalyptus Wood by NIR

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Date: June 2017

Publication No: SWP-T026

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INTRODUCTION

The theory behind this work has been reviewed (Guo and Altaner, 2016) and a feasibility study investigating the technology on dry radiata pine wood has been reported (Guo and Altaner, 2017). The previous report found that in air-dry radiata pine, NIR signals at 6286 cm^{-1} and 6465 cm^{-1} in the second derivative spectra shifted to higher wavenumbers with increased levels of strain. The good correlation between the shift of the 6286 cm^{-1} band and the level of strain indicated that it might be possible to predict strain or stress in wood using NIR spectroscopy.

NIR spectra are dominated by overtones and combinations of bonds involving hydrogen, like O-H and C-H, due to their small reduced mass (Osborne et al., 1993). Therefore, NIR spectra are sensitive to moisture.

Growth-strain should be measured in green logs or *in situ* on standing trees. Therefore any observation of NIR band shifts in relation to molecular strain need to be observable at high moisture contents. It is believed that the band shift at around 6286 cm^{-1} is caused by molecular deformation of crystalline cellulose structures. Considering crystalline cellulose is inaccessible to water, it is possible that the band shifts are still detectable in green wood. However, the strong and often overlapping signals from water might interfere.

These experiments investigated whether band shifts in the NIR caused by strain can be observed in fully water saturated eucalyptus wood samples. Air-dry samples with minor changes in moisture content helped to understand the effect of strain on NIR spectra. Fully water saturated samples without tensile stress illustrated spectral changes due to drying. Whether band shifts of green wood caused by stress were detectable was revealed by NIR spectroscopy of fully water saturated samples under tensile loads.

METHODS

Eucalyptus regnans wood strips with a width (roughly tangentially) of 16 mm were cut from an air-dried board. Six samples of 85 mm in length were cut from the strips before they were sanded to a thickness (radial) of about 0.7 mm. Strain gauges were glued onto the samples with an adhesive (Loctite 454, Australia) and connected to a strain-meter (TC-31K, Tokyo Sokki Kenkyujo, Japan).

Three of the samples were put in a sealed box with saturated K_2CO_3 solution (relative humidity of 43%) until they reached constant weight. The other three samples were immersed in water for a few days to mimic full saturation. The weights of the samples were recorded before and after collecting NIR spectra.

NIR spectra were collected as the samples were under different levels of tensile stress. Tensile tests were conducted using the device described in the previous report (Guo and Altaner, 2017). Samples were stretched to 8 strain levels (0 to 7) by driving the screw of the test device. “Strain 0” represented no applied tensile force, while “Strain 7” was at the greatest tensile force. Collection of each NIR spectrum took about 80 s. With the increase of strain levels, 8 spectra were collected in sequence. Then the sample was returned to the relaxed state and the procedure was repeated to obtain another 8 spectra for the same sample. The strain values at each measurement were recorded using the strain-meter. The humidity in the lab was about 40% and the mass loss during the measurement of the air-dry samples was less than 0.1%.

For the fully water saturated samples, NIR spectra under 8 strain levels (0 to 7) were collected using the same procedure as with the air-dry samples. Fully water saturated samples kept losing moisture during the process with mass losses ranging from 17% to 30%. Therefore, the spectral changes were caused by both drying and mechanical stress. To isolate the effect of drying on NIR spectra, the same samples were immersed in water a second time to full saturation before collecting NIR spectra in the relaxed state (Strain 0). These spectra were collected at similar time intervals as the previous tests under strain.

RESULTS

Effect of moisture content on NIR spectra

The effect of moisture on NIR spectra in a fully water saturated wood sample compared to air-dry conditions can be seen in Figure 1. The strong signal from free water dominated the spectra and water signals were overlapping with signals from cellulose and other wood composites. As a consequence fewer distinct bands were observed. The most conspicuous change was the increase in the intensity of the water band at 5000 to 5300 cm^{-1}, which was assigned to the combination bands of OH stretching and OH bending of water (Workman and Weyer, 2008).
The broad peak from 6100 to 7200 cm^{-1} was dominated by the first overtone of OH stretching vibrations from water, cellulose and hemicelluloses. Stronger OH groups from free water resonate at higher wavenumbers (6954-6974 cm^{-1}), while weaker OH groups involved in strong hydrogen bonds from crystalline cellulose are found at lower wavenumbers (Schwanninger et al., 2011). As expected, compared to the air-dry sample, the fully water saturated sample showed higher intensity at higher wavenumbers in this region, greatly reducing the shoulder peak at around 6600 cm^{-1}.

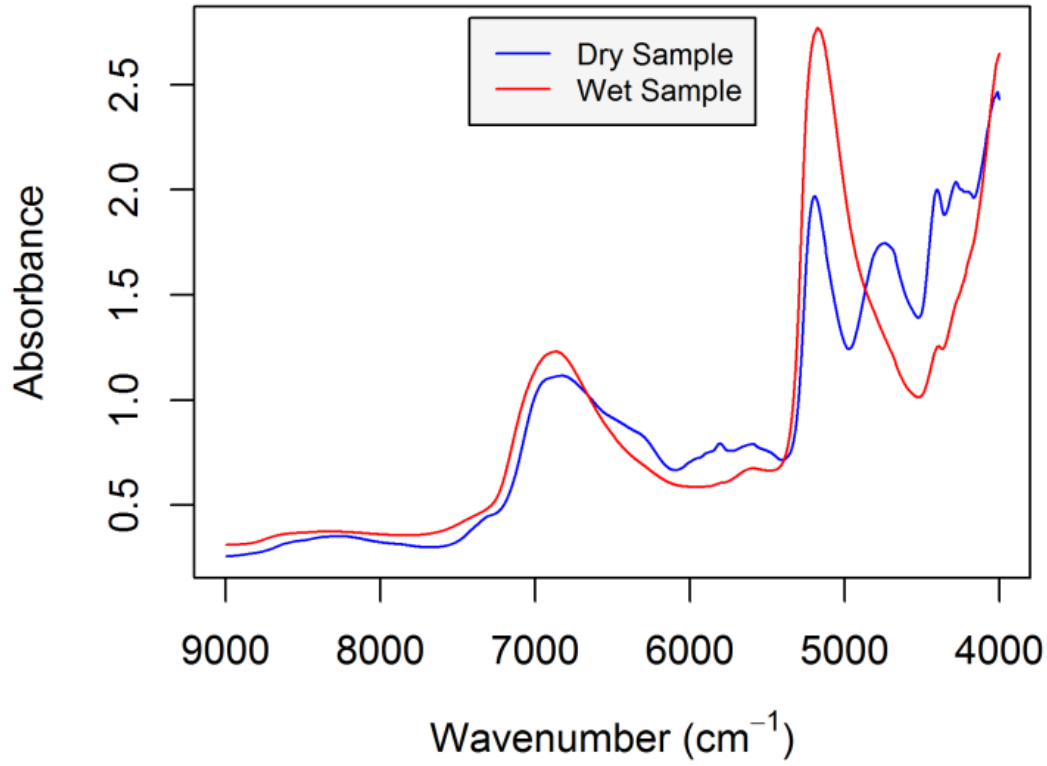

Figure 1: NIR spectra of air-dry and full water saturated eucalypts samples.

The effect of drying on NIR spectra was visualised by calculating the rate of signal intensity change (Figure 2). The negative peak at 5150 cm^{-1} revealed the dominating drying effect, a decrease in intensity of this water band. Only minor changes were observed in the region of 5700 to 6080 cm^{-1}, which was assigned to the C-H stretching vibration from lignin (Schwanninger et al., 2011).

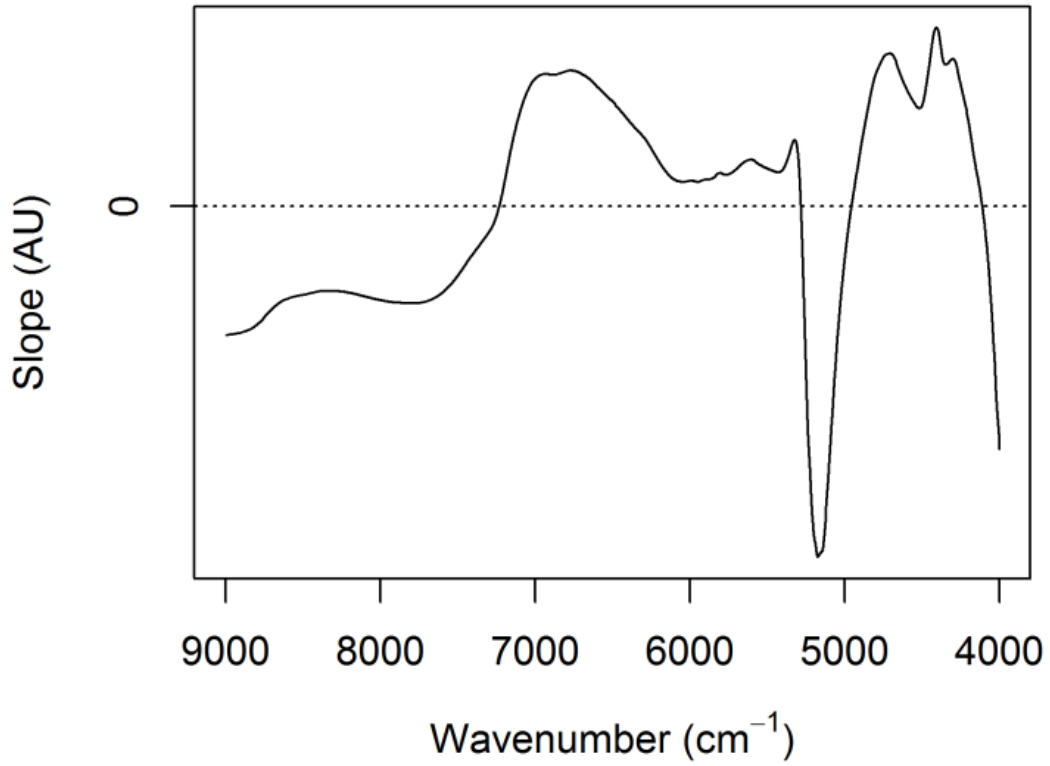

Figure 2: Slope spectra of a fully water saturated eucalypts sample during air drying for ~10 min.

Effect of strain and moisture changes on normalized NIR spectra of eucalyptus wood

We previously reported a way to visualise effects of molecular strain on NIR spectra of air-dry radiata pine by normalization of the spectra in the range from 6100 to 7200 cm^{-1}. Similar results were found for air-dry eucalypts samples (Figure 3A). The observed change around 6400 cm^{-1} could be explained by the elongation of hydrogen bonds resulting in shifts of the vibrational frequency of the associated OH groups to higher wavenumbers (Altaner et al., 2014).

Figure 3B shows the normalized spectra of a fully water saturated sample during air-drying. With the decrease of moisture content, the relative intensity at around 6500 cm^{-1} increased gradually. This apparent increase in intensity is in fact caused by a decrease in the intensity of the free water band centred ~6900 cm^{-1}, to which spectra were normalised. Therefore, drying and mechanical strain have opposite effects on the relative signal intensity at around 6500 cm^{-1}.

The combined effect of air-drying and strain for fully water saturated samples is shown in Figure 3C. The decrease in moisture content dominated the spectral changes with an increase in relative intensity in the normalised spectra around 6500 cm^{-1}. The effect of mechanical stretching was masked in the normalized spectra.

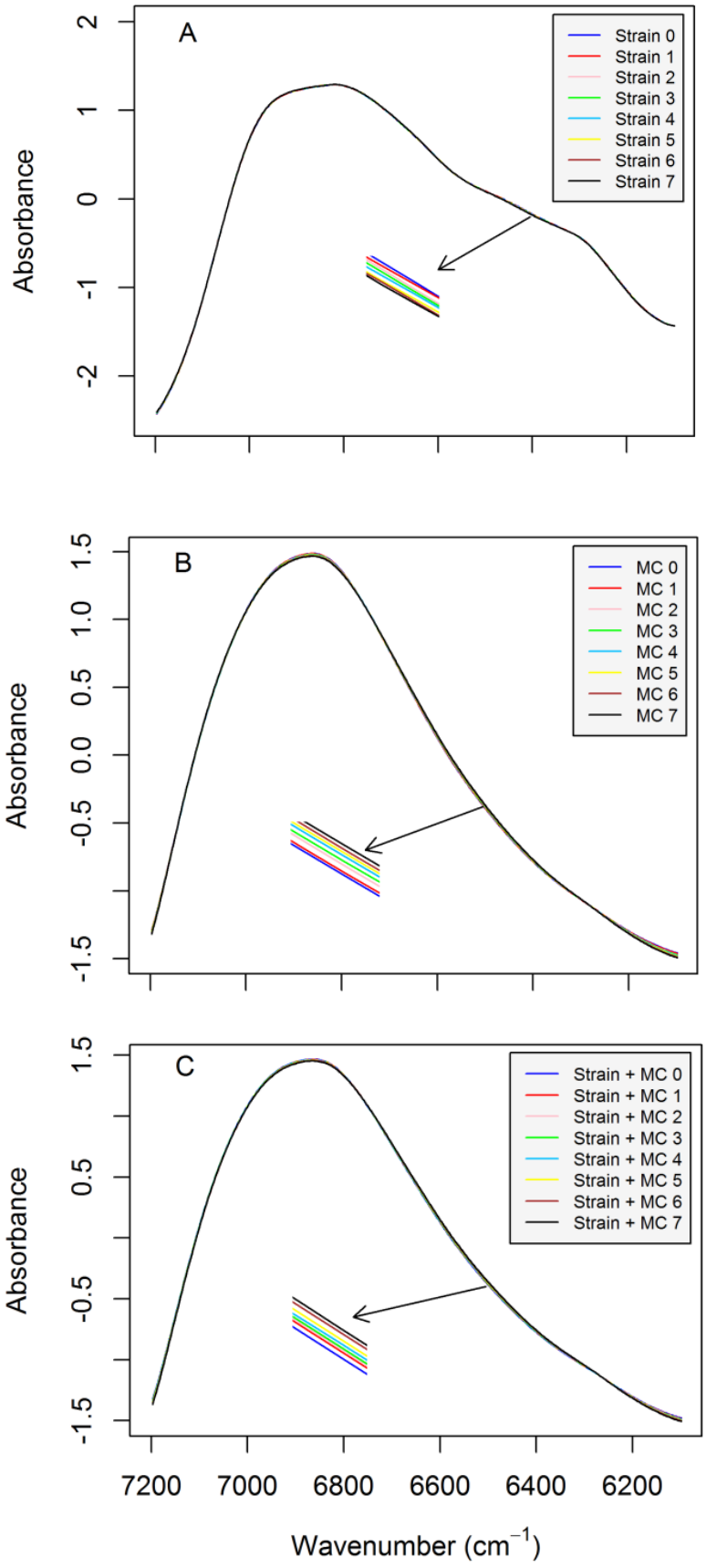

Figure 3: Normalized spectra of air-dry eucalyptus wood under strain (A), fully water saturated samples during air-drying (B) and under strain while drying (C).

Second derivative spectra of hydrogen bonded OH groups

A better way than using normalised spectra to quantify band shifts in NIR of air-dry radiata pine under tensile strain was by analysing the 2nd derivative spectra (Guo and Altaner, 2017). A strong linear relationship was found between strain levels and the shift of the 6286 cm^{-1} band. This was confirmed for air-dry eucalyptus samples (Figure 4A). The signal at around 6290 cm^{-1} shifted to higher frequency with increasing strain. The band positions correlated well with the strain level. It is worth noting that the peak position for eucalypts was at slightly higher wavenumbers than that for radiata. This might have been caused by the different chemical composition of hardwood and softwood.

The 2nd derivative spectra of fully water saturated samples were of similar shape but lower intensity in the 6200 to 6400 cm^{-1} region as that of the air-dry samples (Figure 4B). Consistent with this observation the band became more intense as the samples lost moisture. Furthermore, compared to air-dry samples, the band positions were at lower frequencies for fully water saturated samples. It is possible that the strong signal from water caused baseline offset and 'deformed' the signal. Although changes in moisture content above fibre saturation point can influence the observed band position, the shifts due to drying during the ~10 min acquisition period appeared to be small.

When fully water saturated samples were put under tensile strain the band shifted to higher wavenumbers with increasing strain (Figure 4C). The drying effect was not pronounced. However, the differences in the minima positions for air-dry and fully saturated samples indicated that, moisture content did influence the observed band position. This is more likely an effect of baseline distortion rather than molecular strain. To predict strain levels in fully saturated samples, moisture contents need to be taken into account. The dependence of band position on moisture content and strain levels needs to be quantified.

Quantifying band shifts

Similar to radiata pine, the band position of the 6290 cm^{-1} correlated well (r^2 = 0.78) with strain for the air-dry eucalyptus samples (Figure 5). The slope for the linear model was 0.94 $\times 10^{-3}$ $cm^{-1}/\mu\varepsilon$, stating that 1000 με strain can cause a band shift of 0.94 cm^{-1}. This agreed well with the value for radiata pine wood, which was previously reported to be 1.04 $\times 10^{-3}$ $cm^{-1}/\mu\varepsilon$. Considering measurement accuracy, the band shift rate is likely to be consistent between wood species.

When fully water saturated eucalypts samples were losing moisture by air-drying a tendency of a shift to higher frequencies of the 6290 cm^{-1} band was observed (Figure 6). During this time period, the samples lost 17 to 30% of their mass. The correlation between moisture loss and peak position was weak (r^2 = 0.28) and the rate of band shift was 0.09 cm^{-1}/acquired spectra. Or in other words, 0.7 cm^{-1} during the duration of the tensile strain experiment (spectra acquired for 8 strain levels).

The band position of the 6290 cm^{-1} band dependent on tensile strain in the fully water saturated eucalyptus samples were plotted in Figure 7. Moisture content decreased gradually due to air-drying. A linear relationship (r^2 = 0.75) was found between band shifts and strain in fully water saturated samples. The band shift rate for fully water saturated samples (1.25×10^{-3} $cm^{-1}/\mu\varepsilon$) was higher compared to air-dry samples (0.94×10^{-3} $cm^{-1}/\mu\varepsilon$). At a strain level of 2200 με, the total band shift was 2.75 cm^{-1} for the fully water saturated samples. The contribution of air-drying during this experiment would have been 0.70 cm^{-1}. Therefore the band shift due to strain was 2.05 cm^{-1}, which was almost identical to that calculated using the air-dry eucalyptus band shift rate (2.07 cm^{-1}). This suggested that in this experiment moisture loss accounted for ~25% of the band shifts, while the rest was explained by the molecular stretching.

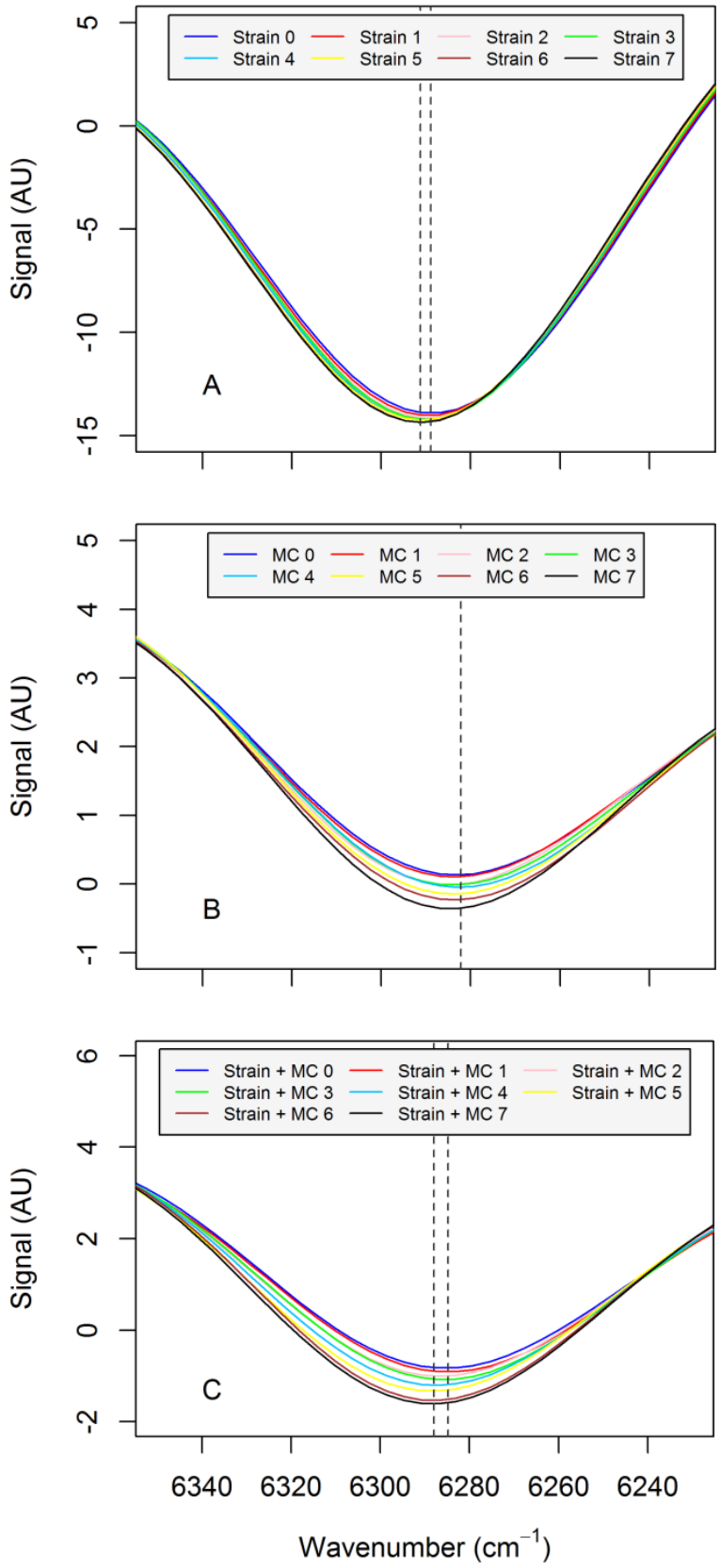

Figure 4: 2nd derivative spectra of dry samples under strain (A), fully water saturated samples during drying (B) and under strain while drying (C). The minima positions of the lowest and highest strain levels were labelled by dashed lines in A and C.

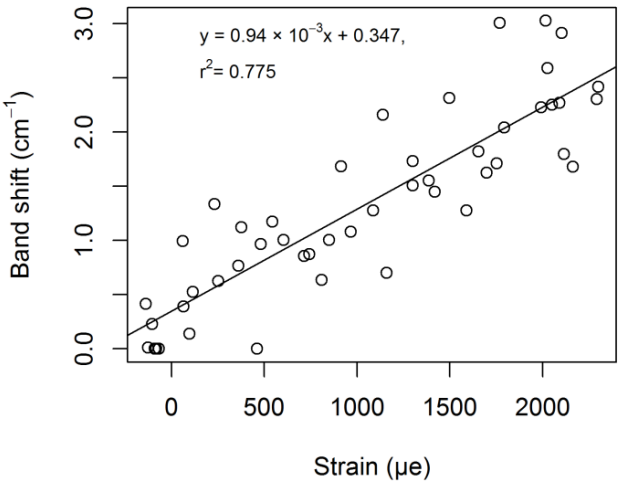

Figure 5: Band position of the 6290 cm^{-1} signal dependent on tensile strain for 3 air-dry eucalypts samples (duplicate measurements).

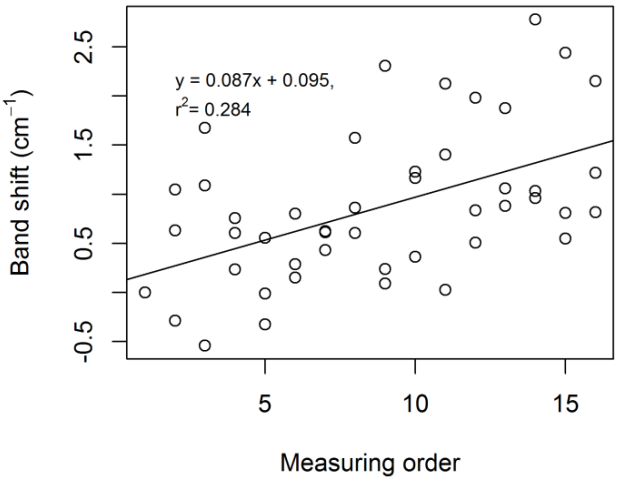

Figure 6: Effect of ~20 min air-drying on the position of the 6290 cm^{-1} band for 3 fully water saturated samples. Moisture content was decreasing with measuring order.

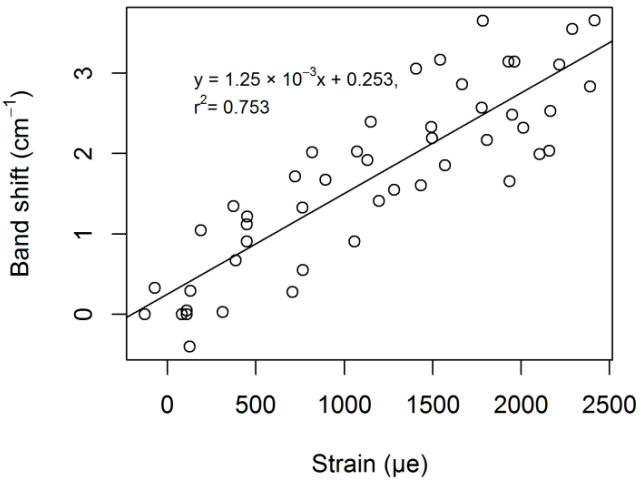

Figure 7: Band position of the 6290 cm^{-1} signal dependent on tensile strain for 3 fully saturated eucalyptus samples under strain (duplicate measurements).

CONCLUSION

1) Abundant free water in fully water saturated eucalyptus wood samples resulted in strong water signals in NIR spectra. These signals were mainly in the regions between 5000 and 5300 cm^{-1} as well as 6100 and 7200 cm^{-1}. The region between 5700 and 6080 cm^{-1} was less affected.

2) When spectra were normalised between 6100 and 7200 cm^{-1}, air-drying during spectra acquisition overrode the effect of mechanical strain in fully water saturated wood.

3) Clear band shifts caused by tensile strain were observed in the 2nd derivative spectra for both, air-dry (r^2 = 0.78) and fully water saturated (r^2 = 0.75) samples.

4) The rate of band shift for air-dry eucalyptus (0.94×10^{-3} $cm^{-1}/\mu\varepsilon$) was similar to that of previously reported air-dry radiata pine (1.04×10^{-3} $cm^{-1}/\mu\varepsilon$).

5) Compared to the air-dry samples the band affected by strain was found at lower wavenumbers in fully water saturated samples. This could be mainly an effect of baseline distortion due to a large neighbouring water signal.

6) The band shift caused by tensile strain in the fully water saturated sample matched that of the air-dry sample when the observed band shift was corrected for the effect of moisture loss.

As a consequence of these observations it seems possible to measure growth-strain in stems by NIR spectroscopy. However, the moisture content affects the position of the signal of interest. Therefore, it seems more realistic to measure growth-strain in standing trees or freshly felled/debarked logs rather than in debarked logs in a sawmill, which might have lost some moisture. Alternatively a spectra processing method capable of removing the influence of moisture of a measurement technique which is less affected by moisture could improve this technique.

ACKNOWLEDGEMENTS

This research project is financially supported by the Ministry of Business, Innovation & Employment (MBIE) – Specialty Wood Partnership of New Zealand. Fei Guo would also like to thank Chinese Scholarship Council (CSC) for supporting his study at the University of Canterbury.

REFERENCES

Altaner, C. M., Horikawa, Y., Sugiyama, J., and Jarvis, M. C. (2014). Cellulose Iβ investigated by IR-spectroscopy at low temperatures. *Cellulose*, 1-9.

Guo, F., and Altaner, C. (2016). "Literature Review: Measuring growth-strain by IR-spectroscopy." Speciality Wood Products Research Partnership, New Zealand.

Guo, F., and Altaner, C. (2017). "Predicting strain levels in air-dried wood using near infrared spectroscopy." Speciality Wood Products Research Partnership, New Zealand.

Osborne, B. G., Fearn, T., and Hindle, P. T. (1993). "Practical NIR spectroscopy with applications in food and beverage analysis," Longman Scientific & Technical, Harlow, Essex, England;New York;.

Schwanninger, M., Rodrigues, J. C., and Fackler, K. (2011). A review of band assignments in near infrared spectra of wood and wood components. *Journal of near Infrared Spectroscopy* **19**, 287-308.

Workman, J., and Weyer, L. (2008). "Practical guide to interpretive near-infrared spectroscopy," Taylor & Francis, Boca Raton, FL.