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Short communication

Response of near infrared diffuse reflectance spectra to blue stain and wood age

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We analysed 320 increment cores at 10 different growth ring positions for a net total of 2691 ring samples, all taken from breast height. The objective of this research was to (a) detect which wavelengths were sensitive to blue stain and (b) determine which wavelengths were sensitive to age when subjected to chemometric interpretation. It was found that wood chemistry-associated wavelengths 1115–1195 nm were most sensitive to blue stain while those at 1335–1415 nm and 1655–1685 nm were also influenced by blue stain, but to a lesser extent. When blue stained samples are not included in the calibration set, but blue stain then occurs in the field, bias in lignin prediction may be more likely, since wavelengths associated with lignin were more sensitive to blue stain. Alternatively, lignin-associated wavelengths showed clear delineation in absorbance with age while the relationship between cellulose-associated wavelengths and age was apparent, but less clear.

Keywords: lignin, cellulose, biomass, feedstock, NIR, blue stain, *Leptographium*

Introduction

Longleaf pine (*Pinus palustris*) may become more popular for value added wood products since loblolly pine (*Pinus taeda*) plantations are under increased demand for lumber and strand board composites. Previous studies have found longleaf pine to be competitive in mechanical properties.[1] Additionally, longleaf pine thinnings can still end up in pulp mill and biomass processing facilities. Being able to monitor longleaf pine for potential shifts in wood chemistry prior to processing would result in reduced costs and improved product performance.

The ability to detect blue stain is also important when monitoring the raw material prior to processing. Blue stain occurs in the sapwood of trees and is caused by several genera of fungi. The absence of blue stain helps to provide a bright pulp for paper processing.[2] The presence of blue stain may also be an indication of an increase in extractives content since invasion of bark beetles can result in increased resin soaking within loblolly pine[3] which, in turn, can result in poor bond capability for paper products. The objective of this research was to (a) detect which wavelengths were sensitive to blue stain and (b) determine which wavelengths were sensitive to age when subjected to chemometric interpretation.

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Methods and materials

Sample collection

Three hundred and twenty increment cores were collected at breast height from a 41-year-old longleaf pine (*Pinus palustris*) plantation on the Harrison Experimental Forest, Saucier, Mississippi, USA. The breast height was 1.4 ± 0.3 m above ground surface with the range around the mean a function of tree defects such as knots and gaul. A total of 2318 ring samples were absent of blue stain, knots and other defects; while 373 ring samples were blue stained for a total of 2691 ring samples. One increment core was collected per tree. An increment core is defined as a 12 mm diameter (green sample) by variable length sample drilled at an angle perpendicular to the tree.[1] After collection, each increment core was sealed in a plastic bag and stored in a freezer. Because of a recent beetle infestation, a random number of cores were naturally inoculated prior to drilling. The bags of increment cores were taken out of the freezer and remained sealed for one week in a room at 28–32°C which allowed for blue stain development on naturally inoculated cores. The cores were then taken out and allowed to dry.

The genera of blue stain was not controlled and it was possible that the increment core borer could have inoculated new trees although the temperature of the increment borer was extremely hot (too hot to touch), making it unlikely for genera transport. Nevertheless, since control of genera was not an objective, potential transport of genera by drill was allowed. Each increment core was sawn with a twin blade circular saw to expose the radial–longitudinal face for near infrared (NIR) reflectance spectra collection. The growth rings were counted backward from the bark to track tree age since it was known that the outermost ring was 41 years in age and the pith was not always present in the sample. Additionally, longleaf pine takes several years to grow out of the grass stage, resulting in added variance to the number of growth rings on the increment core present at breast height between trees.

NIR spectroscopy and spectra pre-treatment

A Nexus 670 FT-IR spectrometer (Thermo Nicolet Instruments, Madison, WI, USA) was used to acquire absorbance between 1000 nm and 2500 nm. A spot size of approximately 8 mm was used to scan samples and the Nexus NIR updrift accessory was used. A reference check was run every 10 minutes. All scans were acquired at 1 nm intervals and the final spectra were an average of 40 scans. To facilitate analysis, the spectra were then reduced into 10 nm intervals through further averaging, a procedure typically performed on wood samples without compromise in model precision.[4] Growth rings at ages 3, 4, 5, 7, 9, 12, 15, 22, 30 and 40 at breast height were scanned for their spectra. After spectra acquisition, the Savitzky–Golay method of transformation was used to convert the spectra to the 1st and 2nd derivative.[5] Only the 1st derivative is reported here, since analysis of variance tests found no additional benefit in using the 2nd derivative ($\alpha = 0.05$). Finally, the literature was reviewed to determine which wavelengths, and consequent wood chemistry bonds or polymer, were important for interpretation (Table 1).[6–10]

Results and discussion

The effect of blue stain

When all ring numbers with blue stain were combined the first derivative of absorbance values (da/dw), between 1115 nm and 1195 nm wavelengths, were most influenced by the presence of stain followed by 1335–1415 nm and 1655–1685 nm (Figure 1). These findings were in agreement with Via *et al.*[11] where *Ophiostoma minus* and *Leptographium serpens* isolates were inoculated onto the wood prior to scanning. In that study, more wavelengths were found to be influenced by stain due to better sample preparation and wavelengths in the visible region were investigated. Since this study reviewed a sample size six times greater and has, potentially, a greater diversity of genera and species, these blue stain-associated wavelengths may be more important during calibration of NIR equipment for blue stain detection in a manufacturing environment.

While using NIR spectra to detect blue stain can be advantageous, the presence of blue stain can be detrimental when trying to predict other traits. Lignin is one trait commonly important for wood because it impacts yield both in bioprocessing and pulping. The absorbances at 1135 nm and 1672 nm have been found to be important for lignin determination (Table 1). Figure

Table 1. Assignment of wavelengths to cellulose, hemicelluloses and lignin composition.

Wavelength (nm)	Chemical constituent	Reference
1135	Aromatic portion of lignin	6
1423	Amorphous region of cellulose	6
1580	Crystalline region of cellulose	6
1672	Aromatic portion of lignin	6–10
1758	Alpha cellulose	10
1900	Lignin from foliar and branch material	6
2330	CH stretch in hemicellulose	8

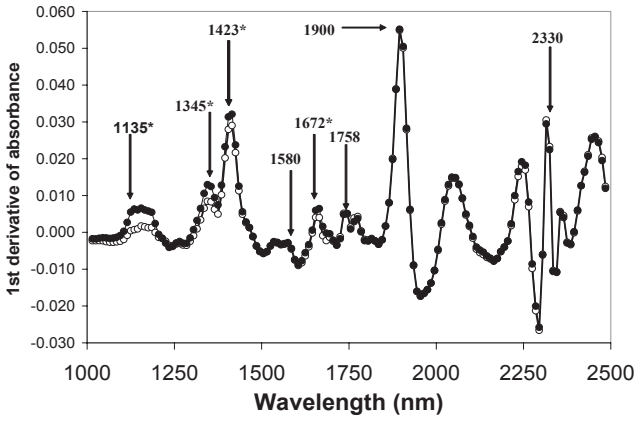

Figure 1. The effect of blue stain on the first derivative of absorbance between the 1000 nm and 2500 nm wavelengths. Important benchmark wavelengths from Table 1 are inscribed. A star (*) is listed next to those wavelengths that were statistically influenced by blue stain ($\alpha = 0.05$). Key: ○ blue stained and ● non-blue stained.

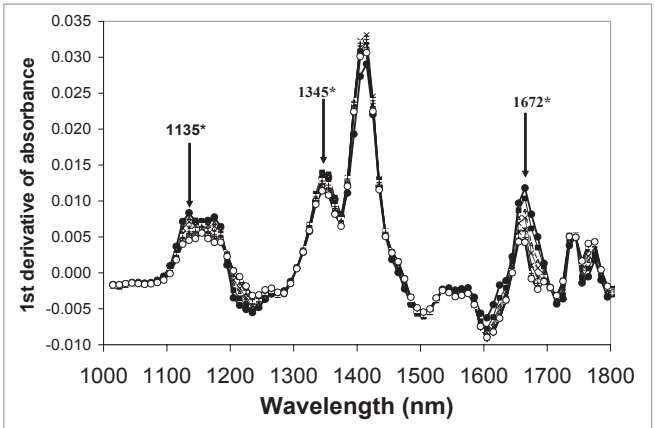

Figure 2. The response in spectra with age. Important benchmark wavelengths from Table 1 are inscribed. A star (*) is listed next to those wavelengths that exhibited a significant relationship between absorbance and age ($\alpha = 0.05$). Key: ● age 4, ■ age 5, △ age 7, x age 9, * age 12, ' age 15, ◆ age 22, □ age 30 and ○ age 40.

1 demonstrates that blue stain did impact d*a*/d*w* at these two wavelengths, suggesting that bias in prediction of lignin will occur for blue stained wood. To alleviate this problem, Via *et al.*[12] attempted to use principal components regression to hedge the effect of stain on lignin calibration by incorporating all wavelengths. However, significant bias in lignin prediction still occurred when blue stain was present.

In Figure 1, blue stain had minimal influence on d*a*/d*w* at 1580 nm, a wavelength particularly sensitive to the crystalline region of cellulose (Table 1). Since cellulose concentration is high in wood, relative to lignin, hemicellulose and nitrogen, it was likely that cellulose had a dominant effect on spectra response relative to the nitrogen-rich blue stain. This finding was further supported by Riley and Cánaves who found nitrogen not to be influential on the spectra at 1580 nm.[13] It may thus be possible to use 1580 nm to predict cellulose and/or crystallinity content in the presence of stain.[13] However, the wavelength associated with the amorphous region of cellulose (Table 1) was influenced by blue stain, followed by alpha-cellulose (Figure 1).

The effect of age

The aromatic structure of lignin has been shown to influence absorbance response at 1135 nm and 1672 nm (Table 1). The d*a*/d*w* at both of these wavelengths showed significant variation with age (Figure 2). At both 1135 nm and 1672 nm, the d*a*/d*w* decreased with age. The decrease in the d*a*/d*w* can probably be explained by the decrease in lignin content from pith to bark that occurs in longleaf pine.[14]

While the spectra near the 1423 nm (wavelengths associated with amorphous cellulose) region showed increased variation (Figure 2), there was no clear delineation between age and d*a*/d*w*. Likewise, crystalline cellulose-associated wavelengths (1580 nm) showed significant variation in d*a*/d*w* (Figure 2), but it was harder to delineate d*a*/d*w* trends with age. At 1758 nm, d*a*/d*w* increased with age due to the increase in alpha-cellulose that occurs with age in most pine species. Given the lower variation in d*a*/d*w* with age for cellulose-associated wavelengths, more factors may be required during calibration.

In conclusion, the variation in d*a*/d*w* for cellulose-associated wavelengths was less influenced by stain than lignin-associated wavelengths. Lignin-associated wavelengths exhibited higher d*a*/d*w* variation than cellulose content for the entire range of ring numbers considered. The results suggest that lignin-associated wavelengths may require fewer factors for prediction than cellulose-associated wavelengths. Such was the case for two studies of pine, where cellulose calibrations required slightly more factors than lignin calibrations.[15,16] Alternatively, in Jones *et al.*,[17] prediction of cellulose and lignin required the same number of factors, suggestive that more studies are needed to confirm or disprove our hypothesis.[17] However, when blue stain was present, cellulose-associated wavelengths were less influenced by stain than lignin-associated wavelengths, suggesting that cellulose calibration equations may be more robust under a blue stained environment that extrapolates from the calibration curve. Finally, significant variation in d*a*/dw mostly occurred at wavelengths outlined in Table 1. Such an observation was important because it strengthens the validity of recent work where important fundamental wood chemistry wavelengths were identified (Table 1).

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