# Variability in southern yellow pine bark from industrial sources

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## ABSTRACT

Bark utilization requires the development of quality control protocols to assess variability and predict product yields. Southern yellow pine (SYP) bark samples from two industrial sources were separated into inner and outer bark tissues prior to characterization. Results suggest that simple screening operations can remove much of the grit contributing to high ash contents. Differences in Klason lignin and polysaccharide values were attributed to different relative ratios of inner and outer bark tissues for the two sources of bark. Near Infrared (NIR) spectroscopy coupled with multivariate analysis was used to develop a model to predict relative amounts of inner bark and outer bark in an industrial bark sample.

## INTRODUCTION

Trees harvested by the forest products industry sector are commonly transported from the forest to the processing site as bark-covered logs. For SYP, about 18% of the transported load is bark (1). Most bark, especially at pulp mills, finds its way to the power boilers where it is used for its fuel value. In some cases, bark still presents a disposal issue at plywood plants. Efforts to obtain greater value from this biomass resource have generally focused on developing products from the extractives component. Extractions of SYP bark with sodium sulfite and sodium carbonate can afford tannin sulfonate yields of about 20% (2). Condensed tannins have been widely studied as a substitute for phenol in the production of phenol formaldehyde adhesive systems. Obstacles to be addressed for the widespread industrial use of condensed tannins are their high reactivity and natural variability (3), the latter being a function of the variability between bark supplies.

Controlling the variability of a bark supply for a target end use necessitates the development of quality control protocols. In addition, a thorough understanding of bark anatomy and chemistry is needed. With relatively fresh bark supplies, one variable of interest is the relative amounts of inner (living phloem) and outer (rhytidome) bark (see Figure 1). Results from more detailed studies on bark have demonstrated that there are chemical differences between inner and outer bark tissues (4-6). For example, the extractives and lignin content of *Picea orientalis* (L.) Link is higher for the outer bark than the inner bark (7). Accordingly, bark utilization warrants the development of facile quality control measures to allow the prediction of yields of products (e.g., extracts and fiber) that are dependent upon the amounts of inner and outer bark present in the available bark supply.

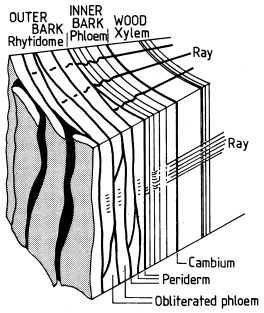


**Figure 1. Inner and outer bark tissues (8)**

The use of NIR spectroscopy by the forest products sector is becoming increasingly popular (9). However, there are only a few reports in the literature applying this technique to the characterization of bark. Donkin and Pearce (10) have utilized NIR for tannin analysis of Black Wattle (*Acacia mearnsii* De Wild.) bark while Schimleck and Yazaki (11,12) have applied this to a range of bark properties from *Pinus radiata* D. Don (11) and *Acacia mearnsii* De Wild. (12). This includes determining the Stiasny value, amounts of hot water and NaOH extractives, and extractives yields, based on the NIR spectra from milled bark samples. In these studies, the authors have utilized the bark as a whole, rather than differentiating between inner and outer bark. This initial study will first determine the ratio of inner to outer bark prior to an in-depth study of bark properties.

## MATERIALS AND METHODS

### Preparation of Bark Samples

SYP bark (essentially all *Pinus taeda* L.) was obtained from a local plywood plant and a local pulp mill. Samples of air-dried bark were ground as received in a Wiley mill equipped with a No. 10 mesh screen. Samples of inner and outer bark were prepared by peeling bark fragments apart, freeze-drying, and grinding as above.

### Bark Characterization

Aliquots of whole, inner, and outer bark samples were subjected to sequential Soxhlet extraction with solvents of increasing polarity (hexane, diethyl ether, 95% ethanol, and water, respectively). Organic solvent extracts were dried *in vacuo*; water extracts were freeze-dried. Extractive-free bark samples were ground further in a laboratory Wiley mill equipped with a No. 20 mesh screen and dried *in vacuo* at 45ºC. Aliquots of these samples were digested in 72% sulfuric acid to afford an acid insoluble residue (Klason lignin) that was quantified gravimetrically; hydrolysates were analyzed by anion exchange HPLC, coupled with pulsed amperometric detection, to determine sugar contents (13). Ash contents were determined for unextracted samples in a muffle furnace heated to 450ºC.

### Spectroscopy and Model Development

Near-infrared (NIR) spectra of milled bark samples were obtained with an ASD Field Spec Pro (Analytical Spectral Devices, Boulder, CO) spectrometer at wavelengths between 350 and 2500 nm. Samples were transferred to a bottle cap, leveled, and rotated at 45 rpm to minimize specular interference and surface heterogeneity (14). Spectra were collected with a fiber optic probe oriented perpendicular to the sample surface while illuminated with a DC lamp oriented at 30 degrees above the surface (14).

## RESULTS AND DISCUSSION

Given that there are anatomical and chemical differences between the inner and outer barks of trees, either the inner or outer bark may be more suitable for a target application. Nevertheless, most efforts to utilize or characterize bark do not differentiate between these two bark tissues. This likely stems from an inability to efficiently separate the inner bark from the outer bark.

We have observed that SYP bark from different sources differ in the amounts of outer bark relative to inner bark. This undoubtedly results from the age/size of the roundwood processed, the debarking system, and handling operations for the bark residues. Accordingly, should a target application for bark residues perform better with either inner or outer bark, quality control measures would be needed to select bark supplies for processing and predict product yields.

### Bark Chemistry

Samples of SYP bark were obtained from two different sources, a plywood plant and a paper mill. The bark from the plywood plant contained many small pieces of friable outer bark whereas the bark from the paper mill was mostly a stringy inner bark with attached outer bark. Grab samples of the barks from the two sources were separated into inner and outer bark components for chemical characterization. The results from the ash determinations showed that the plywood plant bark contained significantly higher amounts of ash (Table 1). The lower amounts of ash for the inner and outer barks were attributed to losses of grit while the bark was being separated. In addition, the whole bark sample was ground as received whereas inner and outer bark samples were taken from the larger bark segments. This demonstrated that simple screening operations could dramatically reduce ash levels.

**Table 1.**
**Ash contents for bark samples from two industrial sources.**

| Sample | Ash Content (%)[a] | |
|---|---|---|
| | Plywood Plant Bark | Paper Mill Bark |
| Whole Bark | 6.9 | 2.3 |
| Inner Bark | 3.8 | 3.2 |
| Outer Bark | 1.6 | 1.2 |

a) Percent of oven-dry bark.

In the case of the paper mill bark, the whole bark sample gave an ash content that was intermediate of that for the respective inner and outer bark samples. It should be noted that our values for ash were higher than that reported in the literature for *P. taeda* (15,16). Accordingly, a significant proportion of the ash in this bark

supply could also be attributed to grit carried over from handling operations.

Samples of extractive-free inner, outer and whole bark were prepared by sequentially extracting the target tissues with solvents of increasing polarity. Bark samples were then digested by the Klason method to afford the lignin as an insoluble residue and hydrolysates for sugar analysis. Results show that the lignin contents of the outer bark samples are twice those for the corresponding inner bark (Table 2): the lower degree of lignification of the inner bark is reflected by higher amounts of polysaccharides.

**Table 2.**
**Klason lignin and sugar contents of bark samples from two industrial sources.**

| Bark Source | Bark Fraction | Analysis | |
|---|---|---|---|
| | | Klason Lignin (%) | Total Sugars |
| Plywood Plant | Whole | 47.4 | 34.4 |
| | Inner | 25.3 | 58.2 |
| | Outer | 53.3 | 37.1 |
| Pulp Mill | Whole | 40.2 | 45.0 |
| | Inner | 22.6 | 56.6 |
| | Outer | 50.9 | 37.6 |

It should be noted that these values for Klason lignin content include phenolic materials not considered to be lignin, specifically, phenolic acids that are extractable with aqueous NaOH (16). Nevertheless, the values for our solvent extracted inner and outer bark fractions are similar between the two bark sources and consistent with those reported in the literature (16). For the whole bark samples, the values for Klason lignin and sugars are starkly different. This reflects the different relative amounts of inner and outer bark in these samples. Accordingly, with a measurement of the relative ratio of inner and outer bark, one could predict values for the above bark constituents (e.g., lignin, polysaccharides).

**Spectroscopy and Model Development**

Samples used for multivariate analysis were made to five predetermined compositions (0, 25, 50, and 100% inner bark) in triplicate, and another fifteen test samples of random composition. A principal component analysis (PCA) was carried out prior to predicting inner bark percentages. The resultant PCA scores plot (Figure 2) shows a gradation in inner bark composition, from 100 to 0%, along principal component 1. The test samples, when incorporating their true values, were found to be fairly accurately interspersed between the calibration samples (Figure 2).

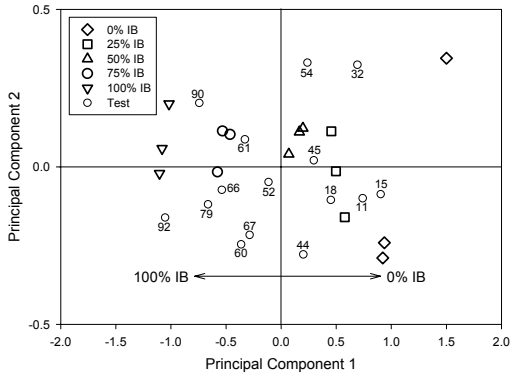


**Figure 2. PCA scores plot of bark samples.**

Projection to latent structures (PLS) modeling was performed on the NIR spectra to predict inner bark content. The predetermined compositions were used for calibration with the (known) random compositions as the test set. An excellent correlation (Figure 3) was obtained between the measured and NIR-predicted inner bark contents for the calibration samples. The test samples, with their random compositions, can be seen to fit very well with the calibration. Thus, additional samples with unknown compositions can be estimated with a certain degree of confidence using this method.

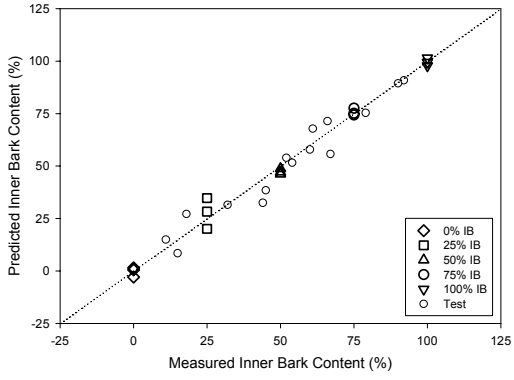


**Figure 3. Relationship between predicted and measured inner bark content.**

The spectral range used for modeling was between 500 – 2500 nm. Additional models

were produced using reduced wavelength ranges (500 - 1100 nm and 110 – 2500 nm) for comparison (Table 3) While the higher NIR range gave excellent results, the low visible-NIR range gave comparable results to the full wavelength range. This allows the possibility of using lower cost, portable, shorter-wavelength spectrometers for field or process monitoring.

**Table 3.**
**Regression statistics for prediction of inner bark content.**

| | $R^2$ | RMSEC/P | %RMSEP of mean |
|---|---|---|---|
| 500-1100 nm | | | |
| Calibration | 0.99 | 3.95 | - |
| Test | 0.96 | 4.99 | 9.5 |
| 1100-2500 nm | | | |
| Calibration | 0.95 | 8.04 | - |
| Test | 0.83 | 12.02 | 22.9 |
| 500-2500 nm | | | |
| Calibration | 0.99 | 3.45 | - |
| Test | 0.94 | 6.05 | 11.5 |

## CONCLUSIONS

Significant differences in the Klason lignin and polysaccharide compositions of bark from different industrial sources reflect different relative amounts of inner and outer bark. NIR spectroscopy coupled with multivariate analysis can be used to develop models to predict relative amounts of inner bark and outer bark in industrial bark samples. Since, the low visible-NIR range gave comparable results to the full wavelength range, the possibility of using lower cost, more portable shorter-wavelength spectrometers for field or process monitoring is particularly appealing.

## FUTURE WORK

Near infrared spectroscopy, coupled with multivariate analysis, is currently being evaluated as a means to predict the yields of different extractive types while taking into account the ratios of inner and outer bark.

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