

# Impact of Industrial Source on the Chemical Composition of Loblolly Pine Bark

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## Abstract

The chemical compositions of loblolly pine (*Pinus taeda* L.) bark samples from two industrial sources were determined for whole bark as well as the inner and outer bark components. Differences in extractive contents of the whole bark samples were primarily attributed to the different debarking methods which afforded different proportions of inner and outer bark. Treatment of the extractive-free bark samples with 1 percent NaOH to remove interfering phenolic compounds impacted the lignin contents determined by the Klason method, but not those determined by the acetyl bromide method. Upon determining the proportions of inner and outer bark, the data provided here can be used to estimate the chemical compositions of other southern yellow pine bark resources.

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Most bark residues currently generated by the forest products industry sector are burned as fuel. Therefore, while the processing of southern yellow pine (SYP) timber affords large volumes of bark, little of this biomass resource is wasted. Concerns have been raised about reductions in fuel value from deterioration and process problems from high moisture and ash contents. Recently, inquiries about the use of SYP bark as a source of extractives have increased. Interest has also been expressed in recovering value from the structural polymers (lignin, cellulose, hemicelluloses) comprising extractive-free bark residues. Literature reports validate that there is continued interest in bark characterization with the ultimate objective(s) of developing chemical products such as nutraceuticals, adhesives, and biofuels (Ingram et al. 2008, Şen et al. 2010, Ku et al. 2011).

A variable with industrial bark supplies that can bring consternation is the proportion of outer bark (rhytidome) and inner bark (phloem). In a prior study, outer:inner bark ratios were 5.8 and 1.5 from loblolly pine (*Pinus taeda* L.) bark residues collected from a plywood plant and paper mill, respectively (Eberhardt et al. 2009). These different ratios reflect both the differences in the sizes of the logs being processed and the debarking methods. Whereas ring debarking at the plywood plant afforded large pieces of relatively intact bark, drum debarking at the paper mill afforded stringy pieces of inner bark with less outer bark, the latter being highly abraded (Eberhardt and So 2005). In the present study, chemical composition data for these two bark supplies are reported. Differentiating these data from those in the literature (McGinnis and Parikh 1975, Labosky 1979, Huang et al. 2011) are values for the inner and outer bark components; also, lignin contents are from direct

determinations and not simply calculated by difference (Pearl and Buchanan 1976). The primary objective of this very brief report is to provide updated chemical composition data that can be used as a practical reference to direct new utilization ventures toward potential SYP bark suppliers in the forest products industry sector.

## Materials and Methods

### Bark collection and processing

Bark samples were obtained from two local forest products companies (plywood plant, paper mill) processing loblolly pine logs. It should be noted that in such industrial settings, there is the distinct possibility of some bark from the other southern yellow pines being included. Whole bark samples were ground as received with drying under ambient conditions. Essentially debris-free inner and outer bark samples were prepared by carefully peeling bark chips/strands by hand before freeze-drying. All bark samples were ground to pass a 2-mm-mesh sieve plate before extraction.

### Chemical analyses

Bark samples were sequentially extracted in a Soxhlet apparatus using reagent grade hexane, ethyl ether, ethanol (95%), and water. Organic solvents were removed by rotary

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evaporation, whereas water in the aqueous extracts was removed by freeze-drying. After oven drying (100°C) to confirm the dry weights of the extractive-free bark residues, samples of these residues were subjected to alkaline extraction by heating (ca. 97°C) for 1 hour in 1 percent NaOH in water (McGinnis and Parikh 1975, Labosky 1979). Extractive-free and alkaline-treated bark samples were ground to pass a 20-mesh screen before Klason lignin (American Society for Testing and Materials [ASTM] 1996) and polysaccharide sugar analyses (Davis 1998). Lignin contents were also determined by the acetyl bromide method (Morrison 1972) using an extinction coefficient of 23.7 liters g<sup>-1</sup> cm<sup>-1</sup> (Johnson et al. 1961). Extractive-free loblolly pine wood was used as a control for all analyses. Data were corrected for moisture content and represent averages of duplicate analyses.

## Results and Discussion

Representative chemical composition data are readily available for many different wood species (Pettersen 1984). On the contrary, bark chemical composition data are much less common, and those few data that are available vary widely as a result of differences in sampling and the methods of analysis; confounding these data further is the common practice of using methods developed for wood that may not be directly applicable to nonwood plant tissues (Hatfield and Fukushima 2005). In the present study, results from a control sample of loblolly pine wood verified that all analytical methods were properly performed.

Sequential extraction of the plywood plant whole bark sample with neutral solvents gave extractive yields (Table 1) that were similar to those reported in the literature for loblolly pine whole bark peeled by hand (McGinnis and Parikh 1975, Labosky 1979). The high proportion of outer bark in the plywood plant whole bark sample gave a total extractive yield of 10.1 percent; the values for the outer bark and inner bark were 13.4 and 33.7 percent, respectively. Debris (e.g., dirt, wood) observed in this whole bark sample (Eberhardt et al. 2009) undoubtedly resulted in a value below that for the debris-free outer bark sample. Conversely, the high proportion of inner bark in the paper mill whole bark sample gave a much higher total extractive yield of 28.1 percent; the values for the outer bark and inner bark were 17.3 and 31.1 percent, respectively. Although the abraded and stringy bark obtained by drum debarking is less intact, it is not necessarily of lower quality. In this regard, the accumulation of extractive-rich inner bark may make a paper mill the preferable industrial source for bark in

applications focused on extractives recovery. It is interesting to note that for the two inner bark samples, the plywood plant sample had a lower yield (0.2% vs. 3.3%) in the ethyl ether fraction and a greater yield (21.1% vs. 16.4%) in the ethanol fraction. It is well beyond the scope of this study to identify the individual compounds contributing to these differences; however, it would appear that some of the lipophilic extractives in the plywood plant inner bark sample could have been oxidized as reported to occur for pine bark undergoing fungal decay (Valentín et al. 2010).

Although pine bark may provide a useful source of lipophilic extractives (e.g., resin and fatty acids), it is the polar extractives, in particular the proanthocyanidins (condensed tannins), that are more commonly sought. One high-volume application is their use in adhesives. A lower volume, but high-value application, is their use as antioxidants (Ku et al. 2011). Because ageing of the outer bark results in secondary reactions, thereby reducing the solubility of the proanthocyanidins, the yields for Scots pine (*Pinus sylvestris*) bark were shown to be much greater with the inner bark compared with the outer bark (Matthews et al. 1997). The extractive yields presented here for loblolly pine parallel those results. Thus, for the recovery of polar extractives from SYP bark, a bark supply rich in inner bark, such as that obtained from the paper mill, may be preferable.

Application of the Klason (acid-insoluble lignin) method to bark can give inflated values for lignin content; Labosky (1979) reported a Klason lignin content of 52 percent for loblolly pine whole bark. Klason lignin contents for the extractive-free whole bark samples from the plywood plant and paper mill were carried out for comparison and gave values of 42.6 and 28.9 percent, respectively (Table 2). After alkaline treatment, used to remove interfering phenolic compounds, the respective Klason lignin contents were 28.9 and 16.8 percent. Alternatively, analyses of extractive-free samples by the acetyl bromide method gave even lower lignin contents. The observation that the acetyl bromide method afforded similar lignin contents for the extractive-free and alkaline-treated whole bark samples (plywood plant, 20.6% vs. 19.9%; paper mill, 13.5% vs. 10.6%) demonstrated limited interference from nonlignin constituents (Hatfield and Fukushima 2005). Correcting for the large loss of material resulting from the alkaline treatment can be a source for error when calculating the lignin contents. Thus, determining the lignin contents of the extractive-free samples by the acetyl bromide method would appear to give the most representative data.

Determination of the polysaccharide sugars gave similar values for inner and outer bark samples from both industrial

Table 1.—Yields of soluble materials from sequential extraction and subsequent alkaline treatment of loblolly pine bark samples from two different industrial sources.<sup>a</sup>

Solvent or treatment	Whole bark (%)		Inner bark (%)		Outer bark (%)	
	Plywood plant	Paper mill	Plywood plant	Paper mill	Plywood plant	Paper mill
Hexane	1.7	3.1	3.5	3.3	1.7	1.3
Ethyl ether	0.6	4.4	0.2	3.3	0.3	2.6
Ethanol	4.3	14.5	21.1	16.4	6.5	6.9
Water	3.5	6.1	8.9	8.1	4.9	6.5
Total	10.1	28.1	33.7	31.1	13.4	17.3
1% NaOH	21.4	26.2	27.0	32.9	20.9	23.7

<sup>a</sup> Values are expressed as a percentage of oven-dry material and represent averages of replicate determinations; typical standard deviation was 2 percent of the reported value.

Table 2.—Lignin contents for extractive-free and alkaline-treated loblolly pine bark samples from two different industrial sources.<sup>a</sup>

Lignin analysis method	Sample	Whole bark (%)		Inner bark (%)		Outer bark (%)	
		Plywood plant	Paper mill	Plywood plant	Paper mill	Plywood plant	Paper mill
Klason	Extractive-free	42.6	28.9	16.8	15.6	46.2	42.1
	Alkaline-treated	28.9	16.8	10.5	4.1	30.2	27.6
Acetyl bromide	Extractive-free	20.6	13.5	8.3	6.4	21.0	19.8
	Alkaline-treated	19.9	10.6	7.3	3.9	19.9	17.1

<sup>a</sup> Values are expressed as a percentage of oven-dry material and represent averages of replicate determinations; typical standard deviation was 2 percent of the reported value.

Table 3.—Polysaccharide sugar contents for extractive-free loblolly pine bark samples from two different industrial sources.<sup>a</sup>

Polysaccharide sugar	Whole bark (%)		Inner bark (%)		Outer bark (%)	
	Plywood plant	Paper mill	Plywood plant	Paper mill	Plywood plant	Paper mill
Arabinose	1.4	3.5	4.4	5.9	1.1	2.2
Galactose	2.3	3.4	2.2	2.8	2.4	3.3
Rhamnose	0.2	0.4	0.4	0.6	0.2	0.3
Glucose	18.3	18.9	27.1	24.7	19.2	17.6
Xylose	5.2	3.5	2.6	2.4	5.6	4.8
Mannose	3.5	2.6	1.9	2.6	3.6	2.9
Total	30.9	32.3	38.6	39.0	32.1	31.1

<sup>a</sup> Values are expressed as a percentage of oven-dry material and represent averages of replicate determinations; typical standard deviation was 2 percent of the reported value.

sources (Table 3). Coinciding with their lower lignin contents, the inner bark samples had higher contents of polysaccharide sugars. It should be noted that those sugars found in the hemicelluloses (e.g., arabinose, galactose) were reduced by the alkaline treatment (data not shown). Accordingly, whereas alkaline treatment may generate more appropriate values for lignin content by the Klason method, data from analysis of the polysaccharide sugars remaining after the hydrolysis of the alkaline-treated bark must be interpreted with caution. Note that the removal of some hemicelluloses was anticipated since an alkaline treatment, albeit harsher, is used to remove hemicelluloses in the preparation of holocellulose (ASTM 1971). For applications targeting the bark polysaccharides, the source of the bark may still be important, with industrial sources rich in inner bark being preferable since they would have less lignin to interfere with the accessibility of the polysaccharide sugars.

Finally, given the reasonable agreement in the data for the inner and outer bark samples, rough estimates of chemical composition may be made for other industrial bark resources knowing the relative ratio of inner to outer bark. Multivariate models based on near infrared spectroscopic data can be used to predict these ratios (So and Eberhardt 2006) as an alternative to simple partitioning and weighing the two bark components. Thus, in addition to showing chemical composition differences for two industrial bark sources, data presented here may allow assessments to be made on a wide spectrum of SYP bark resources.

## Conclusions

Industrial supplies of loblolly pine bark can have significantly different chemical compositions. This can be primarily attributed to the different proportions of inner and outer bark. Chemical composition data for the inner and outer bark samples can be used by extension to predict the chemical composition of other SYP bark resources.

Accordingly, data presented in the current study can be used as a practical reference to direct new utilization ventures toward the most appropriate industrially available bark resources.

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