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**Novel Spectrochemical Technique for the Facile Calibration of  
Lignin Content in Lignocellulosic Substrates**

**D. Mancosky, L. Schulte, and L. Lucia**

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## Novel Spectrochemical Technique for the Facile Calibration of Lignin Content in Lignocellulosic Substrates

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**Douglas Mancosky,<sup>a</sup> Leah Schulte,<sup>b</sup> and Lucian Lucia<sup>\*a</sup>**

<sup>a</sup> *Institute of Paper Science and Technology, 500 10th St., NW, Atlanta, Georgia, USA*

*Fax: 404-894-4778; Tel: 404-894-9712; E-mail: lucian.lucia@ipst.edu*

<sup>b</sup> *Miami University (OH), 229 Gaskill Hall, Oxford, Ohio, USA*

*Fax: 513-529-2201; Tel: 513-529-2200*

**A simple, rapid procedure has been developed to provide highly accurate spectral characterization and calibration of lignin content in lignocellulosics that consists of freezing the lignocellulosic in liquid nitrogen and pulverizing it to yield a fine powder capable of being cast into traditional KBr pellets for IR analysis.**

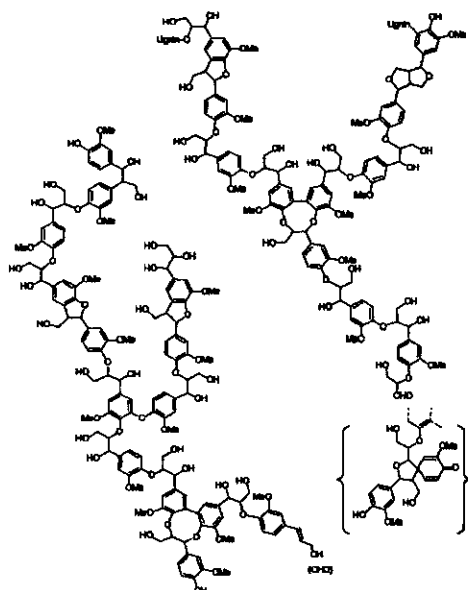
In the pulp and paper industry, methods for quantitatively measuring lignin removal reactions are important to the understanding and improvement of pulping and bleaching. Traditional wet chemical methods for determining the amount of lignin in pulp such as “kappa number (permanganate consumption, mL)”<sup>1</sup> are tedious, time-consuming, and have a low level of accuracy due to organic contaminants and high-lignin content. Native wood contains approximately 30% lignin; a value that varies as a function of

species and other factors, and is reduced when the wood is chemically pulped to about 4% lignin, a lignin level that corresponds to a kappa number of 25. This lignin level can be further reduced to less than 1% through bleaching processes that are essentially an amplification of pulping. Most lignin analytical techniques are destructive, nonspecific, and indirect in nature, often requiring back titration for quantitation. A direct, non-invasive technique based on spectroscopy would provide many benefits. Spectroscopy, with its highly accurate correlation between signal and molecular structure, would be more absolute than standard lignin titration analyses. An accurate on-line testing method would provide faster determination of lignin levels, thus allowing for more responsive, timely, and economic changes in industrial processes.

Lignin is an extremely large and complex polymer constituent of the natural xylem and phloem tissue of trees and other woody plants. During chemical pulping of these tissues, attack and removal of lignin (delignification) causes a variety of chemical modifications to occur to the lignin molecule. Developing an accurate and quick way to track such modifications would be of significant benefit for improving and

directly through spectroscopic techniques because of the complex arrangement of the lignin and carbohydrate polymers and the irreproducible preparation and formation of the fibers for a sheet or disk. Thus, bulk surface analysis is difficult to obtain accurately since a sheet of fibers displays calliper (thickness) differences. Complicating the surface analysis even further is the difference in lignin content that individual fibers display because of the nonuniformity of chemical pulping.

We have simplified the science (and art) of lignin analysis in lignocellulosic fibers by developing a novel liquid nitrogen grinding/preparation technique and analysing the prepared fibers by FT-IR. The genesis of this technique was a preliminary IR study of the lignin in pulp that was subjected to oxygen delignification. Recent studies have shown that a correlation between the aromatic groups and lignin content can be established through FT-IR analysis.<sup>2-6</sup> The novelty of our procedure opens a new window of opportunity for evaluating lignin in its native form. This could ultimately lead to a simple concentration calibration curve



**Fig. 1** Representative lignin structure found in softwood pine pulp.

streamlining the papermaking process. **Figure 1** is an example of a typical lignin structure found in a loblolly pine (*P. taeda*).

The physical and chemical properties of lignocellulosic fibers are difficult to analyze

for the native lignin in the fiber that would otherwise be measured by a kappa test. The method could also be used to monitor the disappearance and appearance of various chemical groups in the lignin as a function of chemical treatments. This technique may also have far-reaching applications in laboratory research for the pulp and paper industry as well as other related industries requiring solid state analysis of specific chemical components.

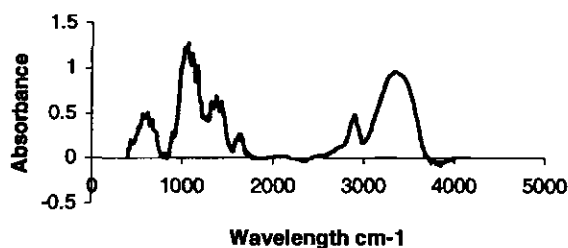
An unbleached, batch-cook kraft pulp sample was obtained and found to have a kappa number of 27.7, corresponding to a dry weight lignin content of 4.2%. Pressurized oxygen bleaching was performed on the kraft pulp at a 10% m/v pulp/water content containing 2% NaOH (m/m to pulp) in a Model 4282 Parr reactor vessel. The reactor was pressurized to 100 psi after attaining a temperature of 90°C and allowed to react for one hour. The pulp was subsequently thoroughly washed to remove the lignin effluent.

The wet pulp was frozen by suspending it for a few minutes in a pestle containing liquid nitrogen; it was immediately powdered using a

mortar. Pulp was frozen in small amounts to ensure complete and effective powdering. The accumulation of water that was observed from the fibers was probably due to the rupturing of the cell walls that was also accompanied by a decrease in fiber volume. The powdering was done at approximately 40% solids content, and the powdered fibers were oven dried. The method allows multiple fibers to be averaged to give a more accurate idea of the chemical content. This fine powder was used to make 200-mg KBr pellets at a 1:50 ratio. Other groups have previously analyzed lignocellulosic species by IR and have ground or filed dried wood or extracted lignin through an instrument such as a Wiley Mill.<sup>3,4,5,7</sup>

The FT-IR measurements in this study were carried out on the Nicolet Magna-IR 860 Spectrometer E.S.P. A DTGS detector was used to collect spectra from the 4000-400  $\text{cm}^{-1}$  region, with an average of 200 scans at a spectral resolution of 4  $\text{cm}^{-1}$ . Baseline correction was carried out using the Nicolet Omnic software. All the measurements were carried out at room temperature and spectrally averaged

over 200 scans. The scans were corrected for baseline and recorded. Ratios of major peaks



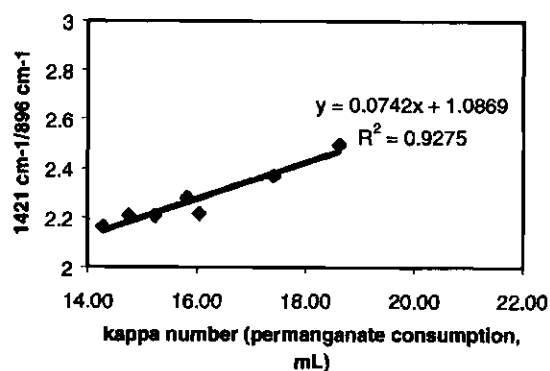
**Fig. 2** The above FT-IR spectrum is representative of the pulverized softwood lignocellulosic samples.

that correspond to well-defined lignin chemical structures were used.

**Figure 2** is a representative IR absorbance spectrum. By ratioing peak signals as opposed to comparing single peak signals, the experimental error accrued by weighing out small samples to make KBr pellets is normalized. This study focused on the peak signals at  $1664\text{ cm}^{-1}$ ,  $1431\text{ cm}^{-1}$ , and  $896\text{ cm}^{-1}$ . The work of Schultz and Glasser demonstrated that a peak at  $1664\text{ cm}^{-1}$  represented an aromatic carbonyl bond, a peak at  $896\text{ cm}^{-1}$  represented an aromatic carbon-hydrogen bond, and a peak at  $1431\text{ cm}^{-1}$  represented an aromatic ring carbon-hydrogen single bond in lignin samples.<sup>7</sup> Lignin contains

aromatic structures that correlate to all of these peaks. In theory, there should be no interference in the aromatic region from cellulose because the glucose units contain no aromatic rings.

A ratio of these peaks ( $1421\text{ cm}^{-1}/896\text{ cm}^{-1}$ ) was then compared to kappa number at different



**Fig. 3** A plot of the  $1421\text{ cm}^{-1}/896\text{ cm}^{-1}$  ratio versus kappa number for a typical softwood lignocellulosic sample.

bleaching levels. The results indicate a relationship between these peaks and the kappa number (**Figure 3**). The method demonstrates great promise for the evaluation of lignin content (kappa number) by analysis of IR. In fact, it may be a more accurate reflection of lignin content than of kappa number since it is well accepted that the kappa test begins to fail at low lignin levels or when lignin is heavily

oxidized due to the nature of the titration method used for the test.<sup>8-10</sup> Further research can help refine the lignin content/IR signal relationship including evaluating more lignocellulosic substrates, encompassing a window of kappa ranges (lignin levels), modifying and changing the pulping/bleaching conditions (other than oxygen delignification), and examining the validity of other peak signal ratios.

The nitrogen grinding technique appears to be a rapid way to examine the chemical structure of lignocellulosics in a laboratory setting. We have <sup>31</sup>P NMR evidence indicating that the procedure does not modify the chemical structure of the lignin that is subjected to IR analysis. We also have examined the physical deformations induced by the procedure through the use of SEM and these demonstrate that the fibers have undergone severe fiber shortening and cell wall lysis, supporting the carbohydrate-fracturing nature of the technique. We intend to continue the fundamental nature of this work by evaluating the influence of process conditions and chemical additives on lignin structure and comparing these values to kappa number to

make more absolute statements about this novel procedure. Work continues on other applications of the grinding technique including solid UV/VIS, fluorescence, and Raman spectroscopy as well as studies into the influence of surface area on pulp chemical processes.

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## Justification

We believe this work deserves immediate publication because of its novel approach to lignin analysis and will lead to wider use of spectroscopic techniques in the pulp and paper industry and other related industries. Current methods demand a dry grind apparatus or file that is generally incompatible to fiber species. Liquid nitrogen and a mortar and pestle are inexpensive and available in most labs where NMR and SEM/TEM microscopy are utilized. The small sample size needed for IR work can be created in minutes with minimal clean up, allowing for the processing of numerous different samples.

This method will also work well for surface area studies. Arguments abound whether certain reactions in lignocellulosics are controlled by surface area and mass transport phenomena. Our initial results show no influence of surface area on a lignin isolation procedure from lignocellulosics. Future work with bleaching, extraction, and washing reactions could ultimately prove interesting.

Our work with kappa number relationships is incomplete, but we believe it is more important to get the initial results of this work in the public domain so that others may benefit from related and unrelated applications. To follow this work to fruition could easily take several years. Although the results of individual studies using the technique are provocative, the technique itself appears as a viable method for surface-area studies and the reduction of lignocellulosics to particles small enough for spectral analysis. We believe that this knowledge could lead to more work in this area and therefore warrants publication in the form of a communication.