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QUICK NON-DESTRUCTIVE ANALYSIS OF LIGNIN CONDENSATION AND PRECIPITATION BY FTIR

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Kraft mills with conventional batch cooking systems sometimes encounter problems related to lignin condensation and its subsequent precipitation. Precipitated lignin increases bleaching chemical consumption and has an adverse effect on pulp quality. Pulp mills must address this issue by improving their digester operation, but it is also important to rapidly analyze and quantify the condensed lignin in brownstock pulp. This paper introduces and discusses a quick method based on Fourier transform infrared (FTIR) spectroscopy to study lignin condensation and precipitation from brownstock pulp. The samples represented two different cooking results of *Eucalyptus camaldulensis* as feedstock: no lignin precipitation on fibers, and apparent condensed approximately lignin precipitation on fibers. The infrared spectra revealed that the sample with condensed lignin had four times more lignin on the fiber surface than the sample without lignin precipitation. Scanning electron microscopy (SEM) images of the fiber surfaces confirmed the lignin precipitation on the fibers. This study therefore proved that the extent of condensed lignin precipitation can be successfully measured using FTIR spectroscopy.

Keywords: conventional batch cooking, *Eucalyptus camaldulensis*, lignin condensation, lignin precipitation, FTIR spectroscopy

INTRODUCTION

The primary objective of kraft pulping is to remove most of the lignin from wood so that the fibers can separate. Approximately 90% of the lignin is dissolved during cooking.[1] This typically converts to a residual lignin content of 3% in unbleached hardwood. In addition, about 50% of the hemicelluloses are removed, as well as more than 10% of the cellulose. The residual cooking liquor, as well as the byproducts and degradation products of lignin, are in the black liquor. During the course of cooking, the reaction pH decreases due to mostly acetate cleavage and peeling byproducts. This in turn increases the risk of undesired side reactions, such as lignin condensation.

A number of condensation reactions are known to occur during kraft pulping. Since carbon-to-carbon linkages are formed between lignin entities, it has been suggested that, as a result of condensation reactions, lignin dissolution is retarded, particularly in the terminal phases of kraft cooking.[2] In a typical case, excessive alkali depletion will lead to lignin condensation, and further dissolution will cease. This means that there must be some free alkali – residual alkali – left after the delignification has been completed. Some 5-15 g/L is considered sufficient.[3]

Lignin condensation increases lignin molecular weight, and if left unaddressed, it can lead to lignin precipitation on the fibers. Lignin precipitation typically occurs when the reaction pH in a digester decreases too much. Lignin solubility is higher at high pH, and a major decrease in pH can lead to lignin precipitation.[4,5]

In conventional batch cooking, pH changes cannot be moderated by adding white liquor at various locations of a digester. Instead, excess alkali must be charged to maintain high enough alkali concentration through the cooking process and have sufficient residual alkali at the end of each cook. Therefore, if delignification continues too long, condensation reactions will occur resulting in the precipitation of lignin on fibers. The problem is further exacerbated if the mill has low sulfidity in cooking, as one of the roles of hydrosulfide ions is to prevent alkali-sensitive groups from condensating.[3] Precipitation of condensed lignin will increase chemical consumption in the subsequent bleaching, and have an adverse effect on pulp properties.

Good process control in cooking operations requires quick and practical analytical methods. On-line continuous measurements are preferable, but many important properties cannot be easily measured on-line. Residual lignin can be measured in a laboratory based on its consumption of certain oxidants, but these methods are complicated and time-consuming, and give information only on the total residual lignin content. More sophisticated wet chemical methods include the analysis of condensed lignin by thioacidolysis, but the method is also very time-consuming.[6] Other demonstrated methods to analyze residual lignin include proton nuclear magnetic resonance (^{1}H NMR) spectroscopy,[7] as well as quantitative C-13 and solid-state C-13 NMR spectroscopy,[8] but they require elaborate and time-consuming sample preparation procedures. In addition, NMR equipment requires relatively high investment costs. On the other hand, Fourier Transform Infrared (FTIR) spectroscopy offers a quick, accurate and non-destructive, yet rather inexpensive method for the analysis of polymers, such as cellulose[9] and lignin,[10,11] or to quantify wood deacetylation.[12] Infrared spectra can be recorded in a few seconds without elaborate preparation. The software of modern FTIR instrumentation automatically evaluates the recorded data. While many traditional analytical tools can give a fairly positive identification of pure substances, they are of little value for complex mixtures. FTIR spectroscopy enables the identification of certain structural features which can result in the identification of intermediates, or by-products, such as condensed lignin structures. Proper sample preparation and measuring techniques ensure reproducible spectra. The recorded transmission spectra are simply recalculated to absorbance spectra. At an industrial plant with limited laboratory resources, the method can be applied to quickly measure condensed lignin on fiber surfaces. However, previous reported experience with FTIR has been limited to the analysis of native lignin structures. Therefore, the analysis of condensed and precipitated lignin structures from kraft mill samples is a novel application of FTIR spectroscopy.

This paper introduces and discusses a novel and rapid method based on FTIR to measure lignin condensation and precipitation directly from dried brownstock pulp collected from a kraft mill that produces *Eucalyptus camaldulensis* pulp. Thin13 mm diameter sheets of fibers were used for recording the FTIR spectra. The method can be modified and applied to, for example, TAPPI standard handsheets with a basis weight of 200 g/m^2.

EXPERIMENTAL

Materials

Industrial brownstock kraft pulp samples made of *E. camaldulensis* were obtained from a South Asian pulp mill. The mill produces paper grade eucalyptus pulp with a conventional batch cooking system. Brownstock pulp typically has a kappa number of about 20. White liquor sulfidity is about 25%. Sample 1 was collected from a normal batch, which apparently had little or no lignin condensation and precipitation. Sample 2, on the other hand, represented an unsuccessful batch, which had caused significant lignin condensation and precipitation on fibers. Thin 13 mm diameter sheets of pressed fibers (1-3 mg) were prepared for recording FTIR spectra of acceptable quality.

FTIR analysis

IR absorption spectra of the samples were registered in the 400-4000 cm^{-1} spectral region with the resolution of 4 cm^{-1} by the Fourier spectrometer Bruker IFS-25. The experimental spectra were normalized on an integral of the absorbance band of stretching vibrations of CH bonds in the range of 2750-3010 cm^{-1}. To eliminate undesired absorbance by water and carbon dioxide, the samples were kept under a constant flow of dry air.

Molecular spectroscopy methods enable the studying of crystalline and amorphous regions of materials. The novel model of cellulose structure was created by developing new spectroscopic criteria for the determination of conformational and phase structural states of cellulose macromolecules.[9,11] This approach allows representing the cellulose physical structure generally as a superposition of CI and CII celluloses with their ordered and disordered regions:

C = CI+CII = CIord+CIdis+CIIord+CIIdis

Specially designed software calculates the concentrations of these four components from the spectra. As a rule, the CIIord component exists in mercerized cellulose. To describe the physical structure of pulp samples, a three-parameter model is used by calculating the relative content of ordered CIord and disordered CIdis regions formed by macromolecules of native cellulose and the relative content of disordered CIIdis regions. Imperfect surface regions of fiber structures and hemicelluloses are the main contributing factors of the CIIdis component.

FESEM imaging

A Hitachi S-4800 field emission scanning electron microscope (FESEM) was used for creating images of the samples. Only a small amount of dried fibers (pulp) was used for FESEM imaging. Prior to the imaging, a Cressingtong 208HR high resolution sputter coater was used for applying a 2.5 or 5.0 nm layer of Pt/Pd on the samples.

RESULTS AND DISCUSSION

The results of the multi-parameter FTIR spectral analysis give information about structural component differences of the samples: Sample 1 – normal pulp; Sample 2 – pulp with precipitation of condensed lignin (Figures 1 and 2).

Carbohydrates

The parameters of molecular and submolecular structure (CIord, CIdis, CIIdis) were calculated for both pulps using the cellulose structure model. The relative content of ordered native cellulose – CIord – in Sample 1 (31%) is about 1.5 times higher than that in Sample 2 (20%). It is a significant difference. The CIIdis parameter (disordered parts of Cellulose of CII modification) value for Sample 1 is less than that for Sample 2. In all, Sample 1 has more native cellulose conformation macromolecules (CIord+CIdis) than Sample 2. Apparently, the inadequate cooking conditions resulted in low-crystalline cellulose fibers in Sample 2, which may have compromised its strength properties, as well.

Residual or bound water

As shown in Figure 1, the spectroscopically tested (band at 1650 cm^{-1}) residual water component is an important parameter (analogous to Water Retention Value, WRV). Sample 2 contains approximately 30% more water than Sample 1, so Sample 2 has somewhat higher hydrophilicity. The other spectroscopic structural water parameters are similar.

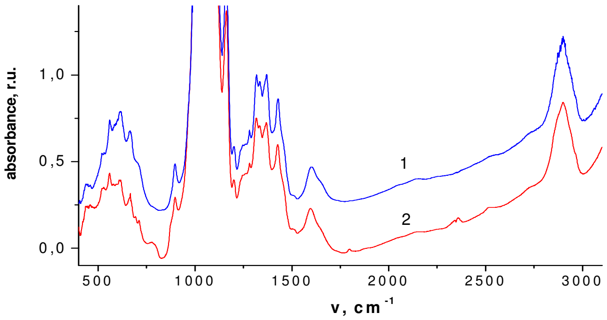

Figure 1: Complete FTIR absorbance spectra of the normal pulp (Sample 1) and pulp with precipitation of condensed lignin (Sample 2)

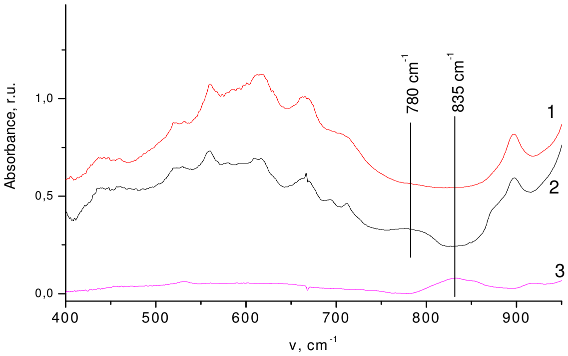

Figure 2:Low-frequency FTIR spectra of the normal pulp (1); pulp with precipitation of condensed lignin (2); and hardwood dioxane lignin (3)

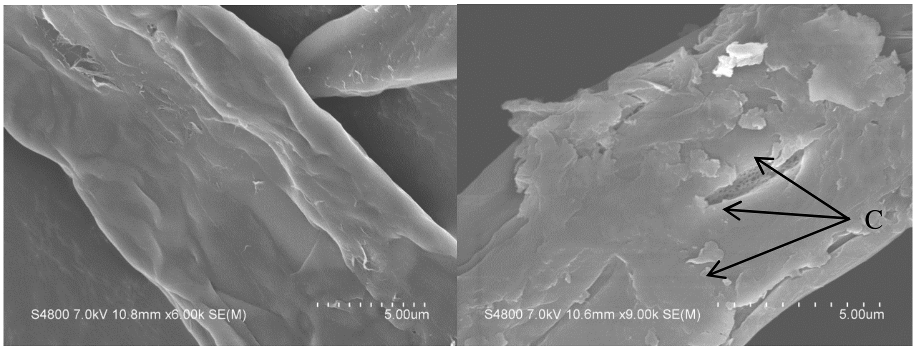

Figure 3: FESEM images of a fiber with no visible lignin precipitation (Sample 1, left) and a fiber with apparent condensed lignin precipitation (Sample 2, right). Thereby precipitation of condensed lignin (C) is easily observable

Residual lignin

Sample 2 has four times more lignin (band at 1508 cm^{-1}) than Sample 1. Moreover, an unusual band near 780 cm^{-1}in Sample 2 can also be observed (Figure 1), which is apparently related to condensed lignin.[13] Moreover, these are obviously associated to the lignin on fiber surfaces.

To gain a better understanding of the condensed lignin, the low-frequency part of the FTIR spectrum of Sample 2 was compared with isolated hardwood lignin. Dioxane lignin was isolated from birch wood by mild acidolysis. A more detailed description of the procedure is presented elsewhere.[14] The normalized spectra of Samples 1 and 2, as well as birch dioxane lignin in the absorption region 400-950 cm^{-1} are shown in Figure 2. There is a clear difference between the spectra of the studied pulp samples in the frequency region of 750-850 cm^{-1}. In this range, the spectrum of Sample 2 demonstrates a broad band with a maximum at about 780 cm^{-1}, which resembles the band at 835 cm^{-1}in the spectral curve of Sample 3, but it is shifted to lower frequencies. The band at 835 cm^{-1} is related to syringyl aromatic C-H out of plane deformation.[15] These results reveal the differences between structure of condensed and native lignin.

The samples were also analyzed by FESEM. The primary purpose of the FESEM analysis was to determine if the samples contained condensed and precipitated lignin on fiber surfaces. FESEM images (Figure 3) show significant absorbed particles on the surface of Sample 2 (pulp with lignin precipitation), while Sample 1 (normal pulp) has no such particles on its surface. Apparently, these are condensed lignin particles, which is in good agreement with the FTIR spectroscopy results.

CONCLUSION

FTIR analysis revealed significant amounts of condensed and precipitated lignin in the sample that represented an unsuccessful batch cook of *E. camaldulensis*. The condensed lignin has a characteristic absorption band near 780 cm^{-1}. The sample with condensed lignin precipitation had four times the amount of lignin on fiber surfaces as the normal sample. This finding was visually confirmed by FESEM imaging. The FTIR results also suggest that the pulp quality has been compromised due to its low cellulose crystallinity values.

FTIR analysis proved to be a quick and easy method to characterize condensed lignin on brownstock pulp. FTIR spectra can be recorded in a matter of a few seconds. Sample preparation is very easy and rapid, without any additional costs for consumables. Simultaneously, other useful information on pulp properties can also be obtained. This offers significant savings in terms of time and costs, when compared to the currently available wet chemical methods.

However, further optimization of the method is essential. To improve FTIR analysis for more accurate quantification of condensed and precipitated lignin, as well as other properties of brownstock pulp, more tests and calibration is needed.

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