

QUICK NON-DESTRUCTIVE ANALYSIS OF CONDENSED LIGNIN BY FTIR. PART 2. PULP SAMPLES FROM ACID SULFITE COOKING

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In our previous work, we demonstrated how lignin condensation and precipitation taking place in kraft pulping can be detected and even quantified by Fourier Transform Infrared (FTIR) spectroscopy. Because lignin reactions in acid sulfite pulping are very different from those occurring during kraft cooking, a new analysis method is proposed to rapidly analyze the condensed lignin in acid sulfite pulp. This kind of analysis is useful for sulfite pulp mills to detect the elevated risk of black cook. This paper presents and discusses the novel method using FTIR spectroscopy to rapidly analyze lignin condensation in softwood pulp samples from acid sulfite processes. Several softwood pulp samples from acid sulfite pulping at varying levels of condensation were included in this research. According to the results, FTIR spectroscopy allows indirect quantification of lignin condensation in a difficult matrix of wood constituents, such as in incompletely delignified acid sulfite pulp.

Keywords: chemical pulp, lignin condensation, black cook, FTIR spectroscopy

INTRODUCTION

Sulfite pulping derives its name from the use of bisulfite solution as the cooking liquor, which is the reaction product of sulfur dioxide gas, a base cation, and water. Its advantages – over the kraft process – are that sulfite pulp is easy to bleach, carbohydrate yields are relatively high and the production of specialty pulps with high cellulose contents is feasible.¹ Base cations employed in industrial sulfite pulping processes are ammonium (NH₄⁺), calcium (Ca²⁺), magnesium (Mg²⁺) or sodium (Na⁺). There are also several modifications of sulfite pulping, which are designated according to the pH of the cooking liquor. Currently, acid sulfite pulping process (pH range 1–2) is almost exclusively employed for dissolving pulp production. Dissolving pulp has typically high cellulose content, while lignin, hemicellulose and extractives contents are very low, the desired contents depending on the dissolving pulp grade.

Moreover, dissolving pulp must meet certain quality requirements, such as relatively uniform molecular weight distribution and sufficiently high reactivity.

The reactions occurring during acid sulfite pulping have been studied by many researchers in the past.²⁻⁴ The lignin reactions during an acid sulfite cook are predominantly sulfonation, hydrolysis and condensation. Unlike alkaline kraft pulping, the main goal of acid sulfite pulping is not substantial lignin fragmentation. Instead, the object is to solubilize lignin through the addition of hydrophilic sulfonate groups. This is commonly referred to as sulfonation. The other desirable reaction type, hydrolysis, breaks ether bonds, while also decreasing the molecular weight of lignin. Any lignin-carbohydrate linkages are also cleaved.⁵ At the low pH of acid sulfite pulping, hydrolysis reactions are fast compared to sulfonation,^{6,7} although under these conditions,

lignin is sulfonated to a relatively high degree, thus promoting an extensive dissolution of lignin.⁷

Condensation reactions are also prevalent in acid sulfite pulping (Fig. 1). The molecular weight of lignin is significantly increased, which is detrimental to lignin removal and therefore counteracting the delignification. New, stable carbon-carbon bonds are formed.⁴ In an extreme case, severe condensation reactions may occur to an extent that delignification becomes impossible, which leads to a so-called black cook.^{2,8,9} It causes the resulting pulp to have a very dark color, hence the name. The pulp becomes virtually useless. Our laboratory experiments have shown that even “brownish” pulp that has been cooked close to the conditions of black cook is impractical to re-pulp because of condensed lignin structures, which are very resistant to delignification. A black cook can result from incomplete impregnation of cooking liquor, failure to maintain cooking liquor composition, excessively high cooking temperature, or improper control of the time-temperature schedule of the cook.²

The sulfite pulping does not degrade lignin to the same extent as the kraft process. Neutralized lignin fragments dissolved in sulfite cooking liquor are referred to as lignosulfonates. Their molecular weight (MW) can be as high as 20,000–50,000 g/mol, while the MW of kraft lignin is typically 2,000–3,000 g/mol.¹⁰ Lignosulfonates are useful by-products that have a steadily growing demand and a relatively stable market. In 2010, the total global production of lignosulfonates was approximately 1.2 million tons, which accounted for about 10% of the lignin in the biomass that was pulped.¹¹ In 2020, the global lignosulfonate production is expected to reach to 1.4 million tons.¹⁰ The most important lignosulfonate products include concrete admixtures, animal feed pellets and road dust control. Moreover, substantial research efforts are allocated to the development of new lignosulfonate products. There is an obvious incentive to find new high-value applications, but the desired product quality generally requires a good control of the pulping process. Therefore, for a modern sulfite mill that produces both chemical pulp and lignosulfonates, it is increasingly important to simultaneously monitor and control the quality of both product lines.

In modern sulfite cooking operations, kappa number is typically used for indicating the extent

of delignification in cooking. Kappa number has a certain correlation with the residual lignin content in pulp. It is determined by measuring the amount of potassium permanganate (KMnO₄) consumed by pulp in standard conditions. This analysis is typically carried out by a standard wet chemistry method in the laboratory (*e.g.*, ISO 302:2015 or TAPPI T 236 cm-85).^{12,13} However, the determination of the kappa number using any of these methods is rather cumbersome and time-consuming.

At the beginning of acid sulfite cooking, the kappa number of the pulp decreases as the cooking proceeds. Towards the end of the cooking process – due to the condensation reactions – the average molecular weight of the lignin begins to increase, and so does the kappa number. If the cooking continues too long, it will lead to a black cook. Figure 2 illustrates this phenomenon.

In our previous work, we introduced a novel rapid method by FTIR to analyze lignin condensation in hardwood kraft pulp.¹⁴ However, condensation reactions that occur at the end of kraft cooking are different from those observed in a sulfite cook. In fact, sulfite pulping is a very complex and unsteady reactive process.¹⁵ Unlike kraft cooking, where active chemicals are mainly consumed during delignification reactions and the cooking liquor at the end of the cook is relatively inactive,¹⁶ an acid sulfite cook maintains or increases the acidity of the liquor. This means that some of the reactions do not slow down, but may even accelerate towards the end of the cook,² which creates a necessity to determine a practical end-point to every sulfite cook. A few methods have been suggested,^{2,8} but they generally suffer from disadvantages associated to cumbersome sample preparation and/or time-consuming analysis. It is therefore necessary to develop a rapid analysis method to monitor the condensation reactions taking place in sulfite cooking. FTIR spectroscopy offers an analysis method to rapidly characterize pulp samples and gain valuable information on chemical constituents of wood.

FTIR analysis has proved to be a quick and easy method to characterize condensed lignin on kraft pulp.¹⁴ It only takes a few seconds to record FTIR spectra. Sample preparation is also easy and quick, without any additional costs for expensive chemicals or consumables.

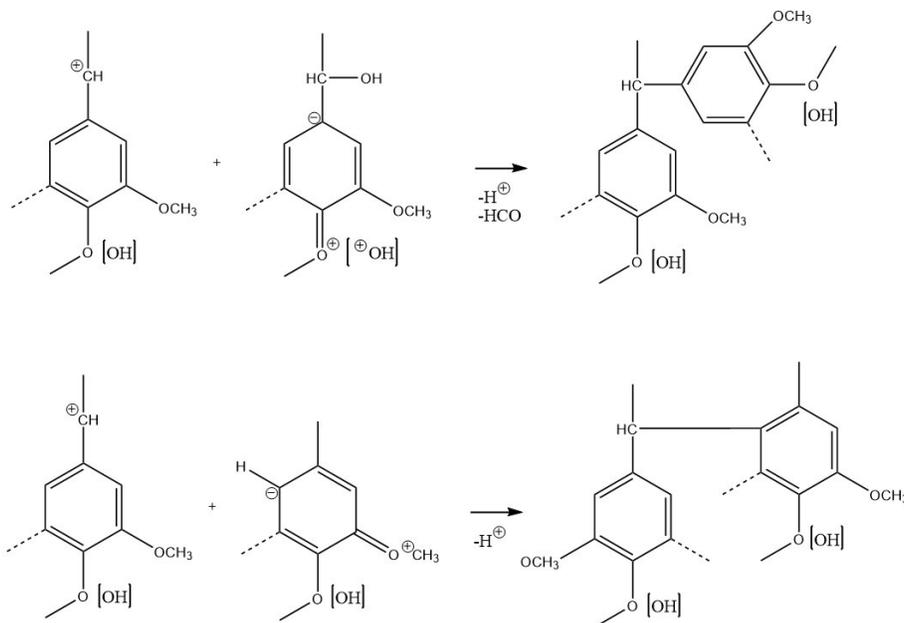


Figure 1: Examples of lignin condensation reactions during acid sulfite pulping (adapted from Gierer (1970))³

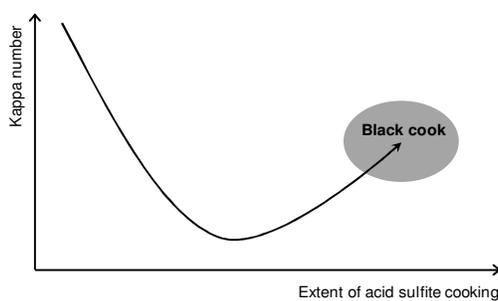


Figure 2: Kappa number in acid sulfite pulping as a function of the extent of cooking (combined cooking temperature and time)

The method also offers the possibility to simultaneously obtain useful information on other pulp properties. In all, the method generates significant savings in terms of time and costs, when compared to the available wet chemical methods. To the best of the authors' knowledge, FTIR has not previously been suggested as a method for lignin condensation analysis using pulp samples from acid sulfite cooking.

EXPERIMENTAL

Materials

All unbleached sulfite pulp samples used in this study derived from Norway spruce (*Picea abies*). Sample 1 represented industrial unbleached pulp from a calcium-base acid sulfite pulping process and it did not exhibit any noticeable lignin condensation. Samples 2 and 3 were collected from a continuous acid sulfite pulping process with sodium as the base; they

presented unsuccessful sulfite cooking, which had resulted in substantial lignin condensation. Thin 13 mm diameter sheets of pressed fibers (1-3 mg) were prepared to facilitate the recording of FTIR spectra with acceptable quality.

Kappa number

Samples 1 and 2 were characterized in terms of their kappa number according to the common standard method ISO 302:2004.

FTIR analysis

IR absorption spectra of the samples were registered in the $400\text{-}4000\text{ cm}^{-1}$ spectral region, with the resolution of 2 cm^{-1} , by an IRAffinity-1 Fourier spectrometer (Shimadzu). The experimental spectra were normalized on an integral of the absorbance band of stretching vibrations of CH bonds in the range of $2750\text{-}3010\text{ cm}^{-1}$.

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.¹⁷ This approach allows representing the cellulose physical structure generally as a superposition of CI and CII celluloses with their ordered and disordered regions:

$$C = CI + CII = CI_{ord} + CI_{dis} + CII_{ord} + CII_{dis} \quad (1)$$

Specially designed software calculates the concentrations of these four components from the spectra. As a rule, the CII_{ord} 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 CI_{ord} and disordered CI_{dis} regions formed by macromolecules of native cellulose and the relative content of disordered CII_{dis} regions. Imperfect surface regions of fiber structures and hemicelluloses are the main contributing factors of the CII_{dis} component.

To have more details about the bands, the quantum-chemical calculation of the IR spectrum of dimmer model of softwood lignin with β -O-4 linkage between aromatic rings was carried out by the method of density functional theory with the B3LYP functional in the basis of 6-31 + G (d, p), using a software package Gaussian03.¹⁸

On the accuracy and precision of FTIR analysis

In our research, FTIR spectra were recorded after an average of 150 scans. This resulted in a high signal/noise relation. In that way, the spectral curves became smooth and they gave a very small input to errors in band intensities. Moreover, the spectra of three probes for each sample were recorded and used for calculations. It allowed us to evaluate the values of spectral parameters and their errors.

According to the literature, there is ample research experience related to the accuracy and precision of the FTIR analysis of lignin. For example, Rodrigues *et al.* compared the accuracy of FTIR spectroscopy and acetyl bromide analysis in lignin quantification.¹⁹ They observed that the standard errors of both analysis methods were very low and differed only slightly. An earlier study by Backa and Brodin demonstrated that FTIR is a very precise method to analyze carbohydrate and lignin contents, as well as pulp yield.²⁰

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

Cressington 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 sulfite pulps were characterized in terms of carbohydrates, lignin and water contents, using IR absorbance spectra of the samples. For illustration, the IR spectra of Samples 1 and 2 are shown in Figure 3. The presented spectra are mainly related to cellulose absorbance, in addition to the absorbance bands of residual lignin and other non-cellulosic components. The parameters of molecular and sub-molecular structure (CI_{ord}, CI_{dis}, CII_{dis}) were calculated from the FTIR spectra of the pulp samples using the cellulose structure model. Values of the cellulose structural parameters are presented in Table 1.

Carbohydrates

The data in Table 1 show that the relative content of ordered native cellulose – CI_{ord} – in Sample 1 (31%) is about 1.3 times lower than that in Sample 2 (40%). The CII_{dis} parameter (disordered parts of cellulose of CII modification) value for Sample 1 is higher than that for Sample 2. In all, Sample 1 has less native cellulose conformation macromolecules (CI_{ord}+CI_{dis}) than Sample 2. Apparently, the inadequate cooking conditions resulted in high-crystalline cellulose fibers in Sample 2 and 3, which may probably have compromised their usefulness as dissolving pulp. Moreover, unfavorable cooking conditions have resulted in the hydrolysis of carbohydrates. Furthermore, FTIR spectral analysis showed a strong decreasing absorbance band at 1740 cm⁻¹ (Table 2) as a marker of cleavage of acetyl groups of xylans or hydrolysis xylans.

Besides the cellulose bands, the lignin band at 1510 cm⁻¹, the water band at 1650 cm⁻¹, and the bands of C=O bonds stretching vibration at 1705 and 1740 cm⁻¹ were observed. Calculated intensities of these bands are summarized in Table 2. It is noteworthy that the estimation of the spectral parameters errors for each sample revealed that the errors were greater for Samples 2 and 3 than for Sample 1, which indicated a more pronounced inhomogeneity.

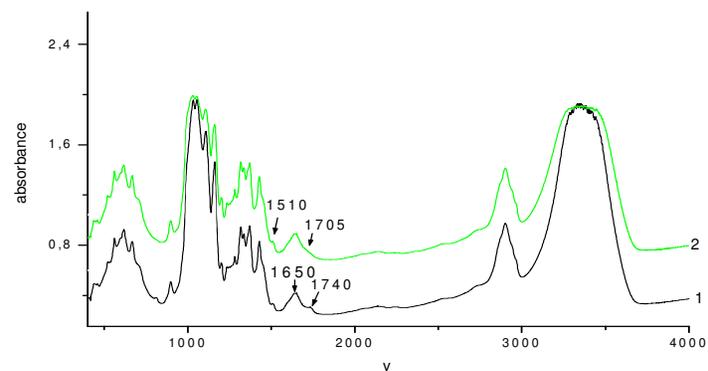


Figure 3: FTIR absorbance spectra of the spruce sulfite pulps: low lignin condensation (Sample 1) and high lignin condensation (Sample 2)

Table 1
Cellulose structure parameters (CIord, CIdis, CIIdis) of the investigated pulp samples

	Lignin condensation	Cellulose structure parameters		
		CIord, %	CIdis, %	CIIdis, %
Sample 1	low or no	31.5	29.5	39.0
Sample 2	high	40.5	25.0	34.5
Sample 3	high	34.5	27.0	38.5

Table 2
Lignin-related structure parameters of the investigated pulp samples

	Lignin condensation	Kappa no.	Residual lignin	Bound water	Appeared C=O groups	C=O acetyl groups of hemicelluloses
			Band at 1510 cm ⁻¹	Band at 1650 cm ⁻¹	Band at 1705 cm ⁻¹	Band at 1740 cm ⁻¹
Sample 1	low or no	17.7	0.78	0.84	0.00	0.50
Sample 2	high	60	0.88	0.86	0.07	0.11
Sample 3	high	n.a.	3.65	0.70	0.67	0.00

Residual lignin

Table 2 shows that both pulp samples (Samples 1 and 2) contain approximately the same amount of lignin (the band at 1510 cm^{-1}). Despite the quite similar band intensities at 1510 cm^{-1} , which are used to estimate the content of residual lignin in pulps,^{19,21} one can observe a strong attenuation of the lignin absorption bands at 814 and 870 cm^{-1} in the spectrum of Sample 2 (see Fig. 4). Both bands are a marker for the presence of guaiacyl aromatics. These bands are related to guaiacyl aromatic C-H out-of-plane deformation. To provide more information about these bands, the normalized spectrum of spruce wood in the absorption region $750\text{--}950\text{ cm}^{-1}$ is shown in Figure 4, as well. We can see both bands in the wood spectrum at 808 and 864 cm^{-1} , while they are completely absent from the spectrum of Sample 2.

The dimmer model after optimization of its geometry and two modes of dimmer vibrations with frequencies near 814 cm^{-1} are presented in Figure 5. Arrows show the vectors of atomic displacements for a given vibration mode according to the calculations.²² It can be seen that these vibration modes are associated with the out-of-plane deformation vibrations of C_2H , C_3H , and C_6H groups of a phenolic ring at 807 cm^{-1} , as well as a non-phenolic ring at 816 cm^{-1} . Altogether, these both closely located bands contribute to the

common absorbance near 810 cm^{-1} . As Figure 1 shows, during acid sulfite pulping, lignin condensation results from the reaction of carbonium ion with weak nucleophilic sites in the benzene ring.⁶ A structural lignin change, such as that, naturally results in an absorbance decrease close to 810 cm^{-1} .

Thus, these experimental and theoretical spectral observations are apparently related to condensed lignin.

Bound water

As shown in Table 2, the spectroscopically tested water component (the band at 1650 cm^{-1}) is an important parameter (analogous to Water Retention Value, WRV). Samples 1 and 2 contain approximately equal amounts of water inside, as well as on the surface of the fibers, so the pulp samples had comparable hydrophilicity.

FESEM was used to record images of the fiber surfaces. Sample 1 (with little or no condensed lignin) has undergone successful delignification and characteristic details of a softwood tracheid, such as pits, are more apparent in the image (Fig. 6, left). The image of Sample 3 with apparent condensed lignin demonstrates visible incomplete delignification and the precipitation of condensed lignin on the surface of the fibers is easily observable (Fig. 6, right).

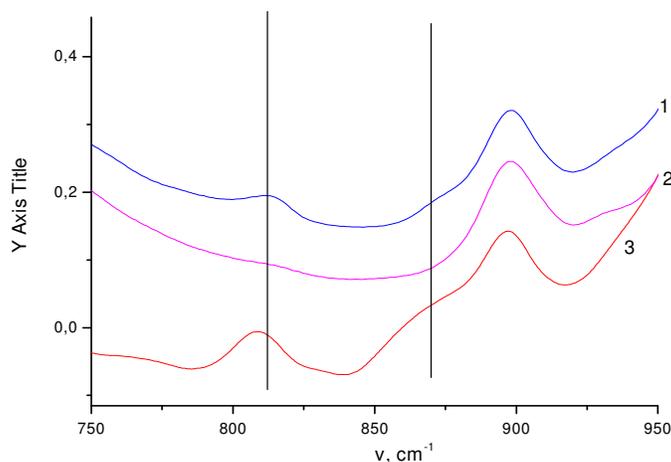


Figure 4: Low-frequency FTIR spectra of the normal spruce sulfite pulp (Sample 1 – 1); spruce sulfite pulp with high lignin condensation (Sample 2 – 2); spruce wood (3)

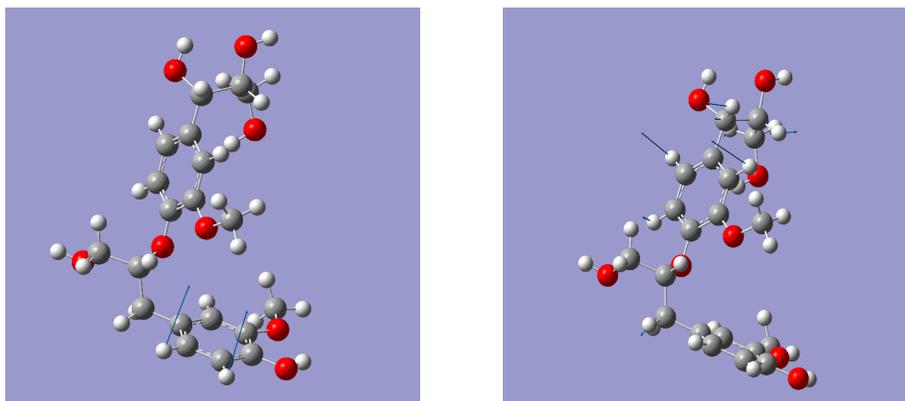


Figure 5: Guaiacyl–guaiacyl dimer model with β -O-4 bond: C-H out-of-plane deformation vibration modes of guaiacyl ring at 807 cm^{-1} (left) and at 816 cm^{-1} (right)

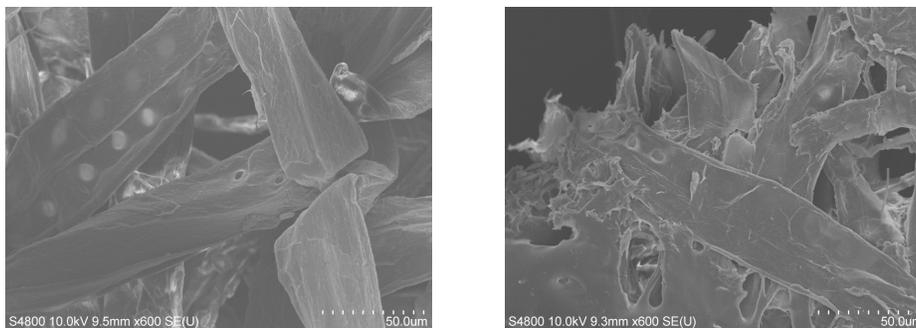


Figure 6: FESEM images of fibers with no visible condensed lignin (Sample 1, left) and fibers with apparent condensed and precipitated lignin (Sample 3, right)

CONCLUSION

FTIR analysis revealed significant amounts of condensed and precipitated lignin in the sample, which represented an unsuccessful acid sulfite cook of spruce. The non-condensed (near-native) lignin has characteristic absorption bands near 814 and 865 cm^{-1} , while condensed lignin exhibited a marked decrease in these bands. Further, it was also observable that the samples with condensed lignin had higher lignin contents than the reference sample. These findings were visually confirmed by FESEM imaging. Moreover, the FTIR results also suggest that the pulp quality had also been compromised because of its high cellulose crystallinity values, which is apparently another negative attribute related to sulfite pulp from black or “brownish” cooks.

In all, FTIR analysis proved to be a quick and easy method to characterize condensed lignin in acid sulfite pulp samples. Sample preparation is very easy and rapid, without any additional costs for consumables. Thereafter, FTIR spectra can be

recorded in a matter of a few seconds. Simultaneously, other useful information on pulp properties can 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 lignin, as well as other properties of brownstock pulp, more tests and calibration are needed.

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