In situ quantitation of ring-conjugated ethylenic lignin-units in spruce thermomechanical pulps by FT-Raman spectroscopy

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ABTRACT

With the objective of using FT-Raman to quantitatively analyze ethylenic units in lignin in thermomechanical pulps (TMPs), coniferyl alcohol, coniferin, coniferaldehyde, and G-DHP lignin models were used to first demonstrate that the technique was fully capable of quantifying ring conjugated ethylenic units. Based on this result, the amount of ethylenic units in TMP was determined by quantifying the unit-specific contribution to the Raman spectra. The findings were that, in fully bleached spruce TMP (brightness 79.9%), the concentration of coniferyl alcohol ethylenic units was 1.38% and in the case of unbleached TMP, the amount of coniferaldehyde ethylenic units was 1.1%. Another interesting observation was that, compared to spruce wood, the amount of coniferaldehyde ethylenic units was almost 100% higher in unbleached TMP.

INTRODUCTION

As an analytical method, Raman spectroscopy has an important advantage in that it is capable of analyzing materials *in situ*. For Lignocellulosics, it means that a component can be directly analyzed without isolating it first. The technique is also non-destructive which means that the sample can be used in further analysis. Results of some such studies have already been published [1]. In the present research, FT-Raman spectroscopy was used for quantitation of aromatic ring-conjugated ethylenic units in lignin in spruce thermomechanical pulps (TMPs). Considering that ring conjugated-ethylenic groups are present in lignin in small amounts and there is no reliable method to detect them quantitatively [2], FT-Raman seems to hold promise especially because ethylenic groups are known to contribute prominently in the Raman spectra of lignocellulosics [3].

Although Raman spectroscopy is a quantitative method, the analysis of a number of simple and DHP lignin models were used to further demonstrate this capability. In this context, several tasks were accomplished to show that FT-Raman could be used for quantifying ethylenic groups in lignocellulosics. This included selecting Raman bands for quantitation, evaluating effect of substitution on Raman scattering coefficients, developing calibration lines for models, and validating the overall approach with a DHP lignin.

METHODS AND MATERIALS

FT-Raman Spectra were obtained using the Bruker RFS-100 instrument that is equipped with a 1 watt 1064 nm Nd:YAG diode laser. Samples were analyzed in the 180º scattering geometry and the power at the sample was about 300 mW. Two sequential spectra of each sample were obtained to ensure the laser was not modifying the sample in any way. In the pulp and cellulose containing spectra, the 1098 cm^{-1} band was used to calculate relative peak heights; this permitted intensity comparison of bands between spectra.

Coniferaldehyde and coniferyl alcohol were purchased from Sigma-Aldrich. Coniferin was a gift from Noritsugu Terashima and coniferyl alcohol diacetate was prepared in our laboratory. G-DHP lignin was a gift from Ken Hammel and was produced using the conventional method with peroxidase and was chosen because it had appreciable amounts of unsaturated side chains. Acetylated black spruce MWL was prepared in our laboratory. MWL was isolated using the procedure reported elsewhere [4]. TMPs used were from a previous research study where effect of bleaching on pulp chromophores was studied by Raman spectroscopy [5].

RESULTS AND DISCUSSION

The kinds of ring-conjugated ethylenic structures present in guaiacyl lignin are shown in Fig.1. These are unattached coniferaldehyde and coniferyl alcohol end groups (respectively, –CHO and –CH$_2$OH groups at the γ carbon position). Bands associated with these units in the Raman spectra of lignin-containing materials have been identified [1]. Raman data good for this study are summarized in Table 1.

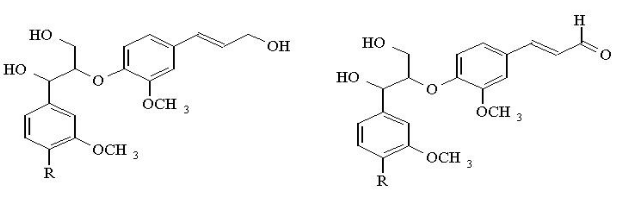

Fig. 1. Lignin β-O-4' dimer structural units with coniferyl alcohol (left) and coniferaldehyde (right) end groups.

Table 1. Useful band positions in the Raman spectra of coniferaldehyde and coniferyl alcohol

Coniferaldehyde, cm^{-1} Solid	Coniferyl alcohol, cm^{-1} Solid
1140	——
1620 C=C stretch	——
1659 C=O stretch	1654 C=C stretch

In Table 1, it is important to note that the two bands (1654 and 1659 cm^{-1}), one each for coniferaldehyde and coniferyl alcohol, overlap due to similar band positions. Moreover, earlier work [6] has shown that the C=O stretch mode at 1659 cm^{-1} is subject to shift depending upon how strongly the C=O is hydrogen-bonded. In that work, the band position varied from 1685 cm^{-1} (in CCl_4) to 1657 cm^{-1} (on cellulose paper). On the contrary, the C=C stretch in coniferyl alcohol (1654 cm^{-1} band) is not expected to vary as this mode is unlikely to be affected by the H– bonding.

As shown in Fig. 2, in the spectrum of spruce MWL, bands belonging to ethylenic units were detected at 1136, 1621, and 1662 cm^{-1}. Additionally, TMP spectra contain some contribution between 1665 and 1690 cm^{-1} due to *p*-quinones [5].

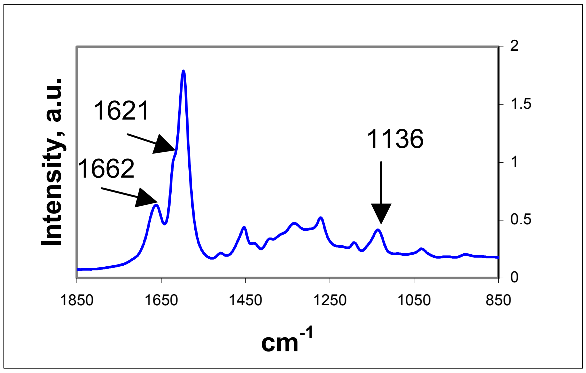

Fig. 2. FT-Raman spectrum of black spruce MWL in the 1850 – 850 cm^{-1} region. Some of the band positions due to coniferaldehyde and coniferyl alcohol are annotated.

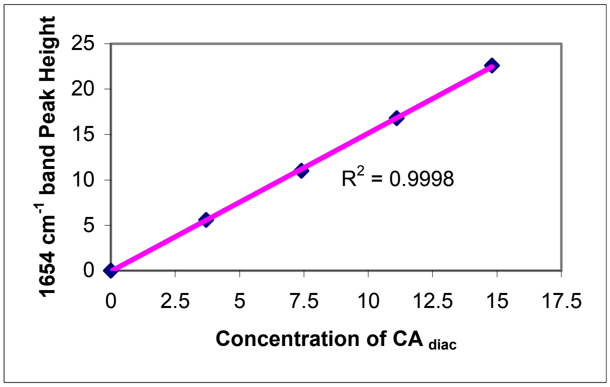

Fig. 3. Calibration line for quantitation of coniferyl alcohol diacetate in bleached kraft pulp (wt %). ■ are the real Raman data points. 1654 cm^{-1} peak height is measured after normalizing spectra on the 1098 cm^{-1} band.

Using some relevant lignin models namely, coniferyl alcohol, coniferin, coniferyl alcohol diacetate, and coniferaldehyde, varying-concentration samples were prepared and analyzed using FT-Raman. The plots of model concentration vs. Raman intensity for different models indicated that indeed the technique was quantitative. For coniferyl alcohol diacetate, such a plot is shown in Fig. 3.

Quantitation of coniferyl alcohol diacetate by Raman was compared with ^{13}C NMR quantitation and the two results were very well correlated. Calibrations similar to plot in Fig. 3 were obtained for other models.

Effect of Substitution on Band Intensity

When the 1654 cm^{-1} band intensities for coniferyl alcohol, its diacetate derivative, and coniferin (glucopyranoside of coniferyl alcohol) were compared on a molar basis, it was found that there was no significant dependency of the band intensity on the substituent group. This is a very useful finding because it indicated that the irrespective of the differences in the state of the derivatization in the aromatic unit, the band intensities associated with the ethylenic unit can be used to calculate concentration of such unit. It is well known that in lignin some units are etherified at the para position whereas others are not. In light of this finding, one need not worry about such structural differences because the impact on intensity of the ethylenic-unit bands is minimal. This observation was further supported by the analysis of the acetylated and unacetylated spruce MWLs. The spectra of these samples produced similar intensities for the bands at 1136 and 1662 cm^{-1}.

G-DHP Lignin Quantitation

Although DHPs prepared from coniferyl alcohol are poor models of natural lignins and/or isolated lignins (MWL), they are very well characterized and therefore, help in structural studies of lignins. In regards to this work, the G-DHP had a high concentration of coniferyl alcohol groups. A detailed structural analysis of this G-DHP has been published [7] and it was estimated that the concentration of the coniferyl alcohol end groups was about 19 %. Nevertheless, another earlier ^{13}C NMR quantitative analysis [8], for the same type of DHP produced a lower value of 16 %. We wanted to see what value a Raman analysis will generate. For coniferyl alcohol quantitation purposes, Fig. 4 shows spectra of coniferin, G-DHP, and coniferaldehyde in dioxane.

The C=C band in G-DHP (1654 cm^{-1}) has a shoulder at 1676 cm^{-1} due to the coniferaldehyde C=O group. However, considering that the shoulder is significantly away from the 1654 cm^{-1} band the former is not likely to influence the peak height measurement at 1654 cm^{-1}. Raman spectrum of coniferin is shown as well and, as one would expect, its C=C mode is at the same position as the C=C band in the G-DHP. For the amount of coniferyl alcohol ethylenic units in G-DHP, Raman calculation generated a value of 13 %. This value is lower than both the earlier reported values [7, 8] but is accurate in our opinion. The reason for the difference is not apparent at this time.

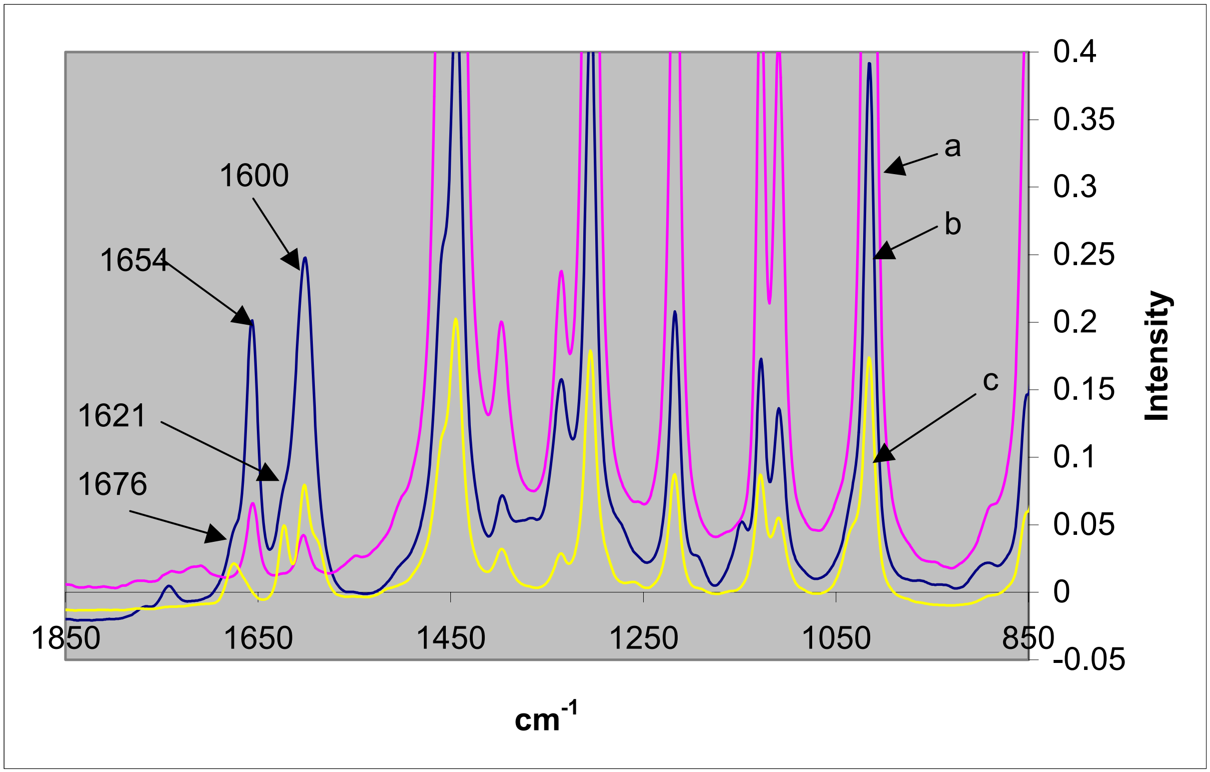

Fig. 4. Raman spectra of coniferin (a), G-DHP lignin (b), and coniferaldehyde (c) in dioxane. Spectra are shifted on the intensity scale for display purposes. 1654 cm^{-1} band of the DHP was used for quantitation purposes.

TMP Pulps

Unbleached and bleached (both oxidative and reductive) TMPs were used in the quantitation work. Coniferaldehyde quantitation was carried out by determining bleaching related decline in the intensity at 1135 cm^{-1} (Fig. 5). It is known that most coniferaldehyde structures in lignin are removed/modified upon alkaline H_2O_2 treatment, and that Raman contribution in the difference spectrum (Fig. 5c) at 1135 cm^{-1} is from such structures [9]. Upon measuring its intensity and using the calibration curve for coniferaldehyde a value of 1.1 % was found. Therefore, the amount of coniferaldehyde units in unbleached TMP is 1.1 %.

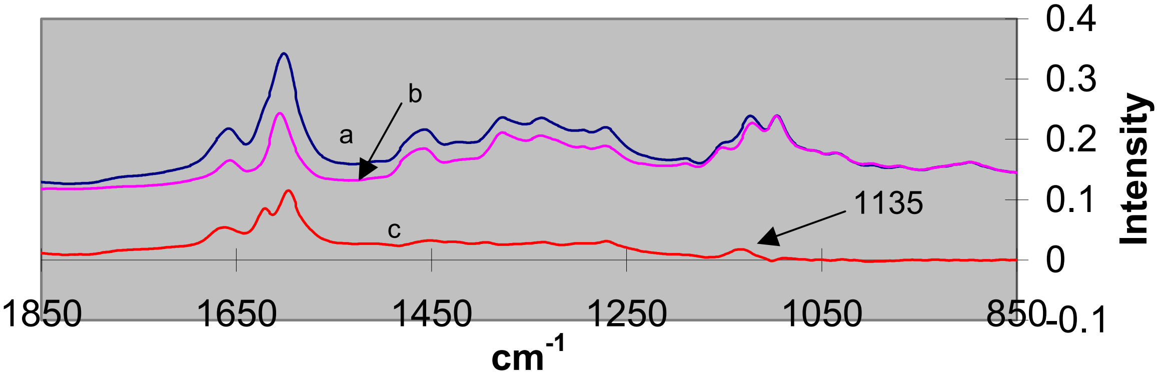

Fig. 5. Effect of alkaline H_2O_2 bleaching on the Raman spectra of spruce TMP; (a) unbleached, (b) bleached , and (c) difference spectrum. Contribution removed at 1135 cm^{-1} is due to coniferaldehyde structures in the TMP.

Another interesting observation was that when similar analysis was done for spruce wood only 0.55 % of coniferaldehyde structures were found to exist (exactly half the amount found in unbleached TMP). This indicated that during thermomechanical pulping some of the lignin structures undergo transformation to coniferaldehyde structure. In authors' knowledge, this is the first time such a finding has been reported. If during pulping the amount of conversion to coniferaldehyde units can be limited, then in the bleaching stage, less bleaching chemicals will be consumed.

Coniferyl alcohol content in TMPs was calculated in all TMPs – unbleached, partially bleached, and fully bleached (Table 2). Because contributions to the 1654 cm^{-1} band from other structures are likely in spectra of most TMPs (such contribution declines upon bleaching), the value calculated for the fully bleached pulp (BR 79.9 %, number 7 in Table 2) is most reliable. For this TMP, a coniferyl alcohol unit concentration of 1.38 % was obtained.

Table 2. Effect of bleaching on coniferyl alcohol content

TMP ID	Description	BR, %	$(I_{1654})/(I_{1098})$	Coniferyl alcohol, %
0	unbleached	52.2	0.55	5.5
1	H_2O_2	71.8	0.278	2.78
2	1 + H_2O_2	77.5	0.224	2.24
3	1 + $Na_2S_2O_4$	70.4	0.255	2.24
4	3 + $NaBH_4$	75.2	0.170	1.7
5	4 + H_2O_2	78.8	0.143	1.43
6	5 + $Na_2S_2O_4$	79.0	0.153	1.53
7	6 + $NaBH_4$	79.9	0.138	1.38

Although, as pointed out earlier, in going from wood to TMP, the amount of coniferaldehyde structure increases, the band intensity ratio (1654 to 1098 cm^{-1}) remains the same. This suggests that unless the 1654 cm^{-1} scattering coefficient between coniferaldehyde and coniferyl alcohol is similar, the new coniferaldehyde structures were produced from some other lignin units. But in case the scattering coefficients are same, it is very likely that coniferyl structures were oxidized to coniferaldehyde units. More work is planned to address this topic.

CONCLUSIONS

The FT-Raman method was successful in the quantitation of ring-conjugated ethylenic structures in G-DHP lignin and thermomechanical pulps. A number of conclusions are as follows. The scattering coefficients of the conjugated C=C bond did not depend on the aromatic ring derivatization. The amount of coniferaldehyde end units in unbleached TMP was 1.1 % whereas the coniferyl alcohol end unit concentration in bleached TMP was determined to be 1.38 %. In addition, studies of black spruce wood indicated that the amount of coniferaldehyde in unbleached TMP was two times its value in wood. FT-Raman spectroscopy is well suited for quantifying such groups in mechanical pulps.

DISCLAIMER

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