AN FT-RAMAN STUDY OF SOFTWOOD, HARDWOOD, AND CHEMICALLY MODIFIED BLACK SPRUCE MWLS

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ABSTRACT

Raman spectroscopy is being increasingly used to carry out *in situ* analysis of wood and other lignocellulosics. To obtain useful information from the spectra, the vibrational bands need to be assigned in terms of contributions from various chemical components and component sub-structures. In additional, so that the technique can be better applied as an analytical tool, an understanding of chemical-treatment induced spectral changes is important. In the present work, Raman spectra of four MWLs (black spruce, loblolly pine, aspen, and sweet gum) were compared and, for black spruce MWL, spectral changes due to bleaching, hydrogenation, acetylation, and methylation reactions were studied.

INTRODUCTION

After FT-Raman instruments became commercially available, the use of Raman spectroscopy in the field of lignocellulosics has increased significantly. This can be noted from the work described in a recent review on this subject[1]. Although the application of this technique has already provided useful information, fundamental Raman information on lignocellulosics is still being developed. The present study is aimed at generating such basic information on selected softwood and hardwood lignins.

EXPERIMENTAL

Black spruce (spruce) MWL was isolated using the modified Bjorkman procedure outlined in reference 2. The MWTs from loblolly pine, sweet gum, and aspen were provided by the researchers at the Forest Products Laboratory, Madison, WI. These were also isolated using methods similar to the Bjorkman method described in reference 2.

using standard procedures, spruce MWL was treated with the following reagents: alkaline hydrogen peroxide (bleaching), sodium borohydride (bleaching) followed by diimide (hydrogenation), pyridine and acetic anhydride (acetylation), and diazomethane (methylation). The acetylated and methylated MWLs were analyzed using NMR to verify that the derivatization reactions were successful.

Except for the methylated spruce MWL all others were studied in solid state using a Bruker RFS 100 instrument. The methylated MWL had some residual deuterated acetone in it and was analyzed as a liquid. Samples were excited using a 1064-nm Nd:YAG laser.

Qualitative comparisons among spectra (band positions, band shapes etc.) can be carried out without any difficulty. However, for quantitative comparisons, the spectra were normalized on the aromatic C-H stretch (~3070 cm^{-1}, Fig. 3 or Fig 6). Such a normalization not only removed the effect of experimental variables on the band intensities but also minimized differences due to lower amount of lignin in hardwoods MWLs (the baud intensities can therefore be considered as per aromatic unit of lignin).

RESULTS AND DISCUSSION

Spruce, loblolly pine, aspen, and sweet gum MWLs

Raman spectra obtained from spruce, loblolly pine, aspen, and sweetgum MWLs are shown in Figures 1-3. To be able to better visualize features in a spectrum, the three Figures show different regions of a MWL Raman spectrum - Figure 1,250 - 1450 cm^{-1}; Figure 2, 1350 - 1850 cm^{-1}; and Figure 3, 2500 - 3500 cm^{-1}.

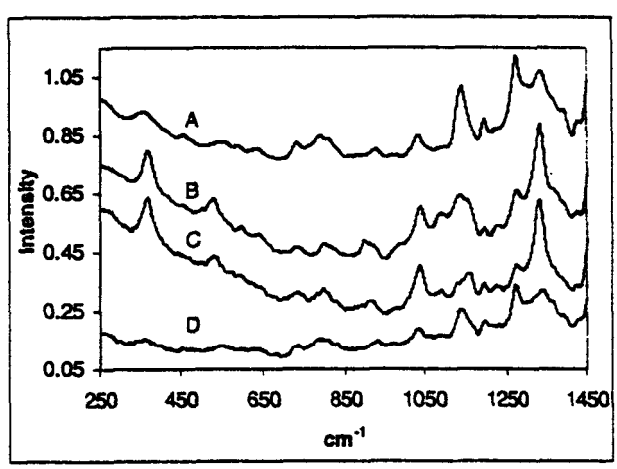

Fig. 1: Raman spectra of MWLs in the region 250 - 1450 cm^{-1}; (A) spruce, (B) aspen, (C) sweet gum, and (D) loblolly pine

Compared to bands at 370 cm^{-1} in the aspen and sweetgum MWL spectra, the spruce MWL spectrum had the 370 cm^{-1} band broader and weaker (spectrum A in Fig. 1). This was even more so for loblolly pine (spectrum D in Fig. 1). This behavior of intensity variation was also seen for hardwood (HW) MWL bands at 531, 1033, and 1334 cm^{-1}. On the other hand, the band intensity at 1272 cm^{-1} was higher in the case of softwood (SW) MWL Raman spectra (spectra A

and D respectively for spruce and loblolly pine). These differences seem to be associated mostly with lignin but because hemicelluloses are also present in MWLs differences in hemicellulose structures are also expected to play a role. Further investigations are underway in our laboratory which are likely to provide more information on this issue.

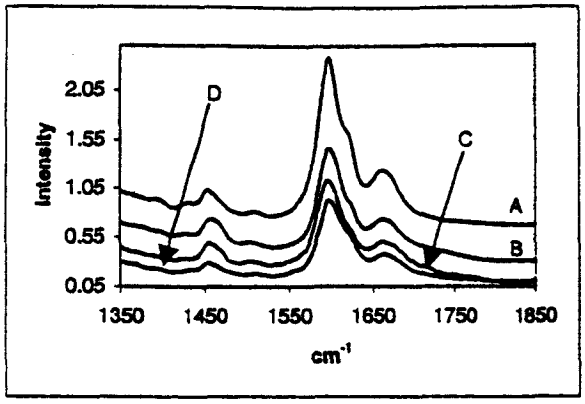

Figure 2: Raman spectra of MWLs in the region 1350 - 1850 cm^{-1}; (A) spruce, (B) aspen, (C) sweet gum, and (D) loblolly pine

The region 1350 - 1850 cm^{-1} is the most important region for lignin contributions as most group frequencies are present here[1,3]. Of the four spectra, the one for loblolly pine MWL shows the smallest 1454 cm^{-1} baud (spectrum D, Fig 2) indicating that this lignin has the least amount of alipharic -CH_2 and/or -CH_3 groups.

Although lignin structures and amomts of the two SW MWLs are similar, it was surprising that the intensity of the 1600 cm^{-1} band was significantly lower for the loblolly pine MWL compared to spruce MWL. One plausible interpretation is that the concentration of aromatic ring-conjugated structures is different between the two lignins. In this regard noteworthy is our previously reported finding that the ring-conjugated structures significantly impact the intensity of the benzene-ring mode at 1600 cm^{-1}[4]. Further support for this interpretation comes from the presence of comparatively weaker bands at 1622 and 1662 cm^{-1} (compared to their intensity in spruce MWL spectrum). Contribution from coniferaldehyde units is expected at 1622 and 1662 cm^{-1}, whereas coniferyl alcohol and *p*-quinones contribute at 1662 cm^{-1}. The first two compounds have bonds that are aromatic-ring conjugated and such conjugation is known to affect the intensity of the 1600 cm^{-1} band. As expected, HW MWL spectra showed features at 1622 and 1662 cm^{-1}, indicating that sinapaldehyde, sinapyl alcohol, and other chromophore structures analogous to those in SW MWLs were present.

For HW MWLs (Fig. 2, spectra B and C), significant contribution due to unconjugated carbonyl groups could not be detected. Usually such groups have been detected in hardwoods (in the frequency range 1715 - 1750 cm^{-1}) and are considered to arise due to the acetoxy groups in xylan and other hemicelluloses. The absence of a feature at about 1738 cm^{-1} in aspen or sweet gum MWL spectrum is especially puzzling because the other acetoxy group contribution at 2940 cm^{-1} in the C-H stretch region was easily detected (Fig. 3). There are a couple of explanations for this. One possibility is that the concentration of carbonyls in MWLs is lower than in hardwoods and given that such groups are not easy to detect in Raman, their contribution remains unobserved. The other possibility is that insignificant amounts of xylans are present in HW MWLs and the C-H stretch at 2940 cm^{-1} is really due to the extra methoxy C-H stretch in syringyl units.

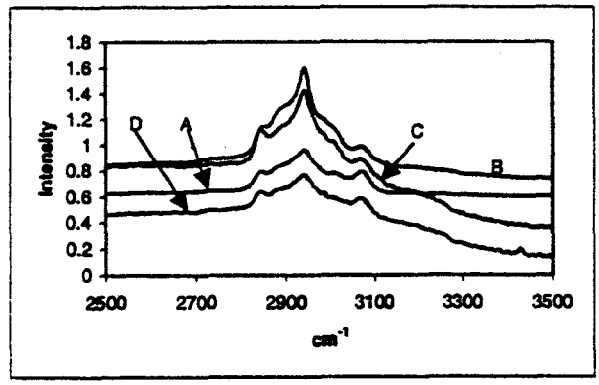

Figure 3: Raman spectra of MWLs in the region 2500 - 3500 cm^{-1}; (A) spruce, (B) aspen, (C) sweet gum, and (D) loblolly pine

In the C-H stretch region all MWL spectra showed bands at 2845, 2895, 2940, and 3070 cm^{-1}. The last band being due to the aromatic C-H stretch, the remaining three contributions are due to aliphatic C-H's of various types. The spectral features were very similar between the spruce and loblolly pine MWLs (Fig. 3, spectra A and D) and for the HW MWLs, with the exception of 2845 cm^{-1}, the features were also very similar (Fig. 3, spectra B and C). It remains unclear why the 2845 cm^{-1} was stronger for the sweetgum MWL compared to aspen MWL.

Compared to SW MWLs, the higher intensity of the 2940 cm^{-1} band in the Raman spectra of two HW MWLs can be explained by the fact that either the

methoxy (syringyl) or acetoxy (xylans) groups are present in amounts greater than their concentration in SW MWLs. It has also been reported that the HW xylans contain acetoxy groups[5] (which are not present in SW xylans) whose C-H stretch is responsible for a significant portion of the Raman scattering at 2940 cm^{-1}[6]. This is also supported by the observation in our 1aboratory that when acetoxy groups in HWs were hydrolyzed (using sodium borohydride) the intensity of this band declined.

Chemical treatment induced spectral changes

Raman spectra of control and chemically modified spruce MWLs that were bleached (alkaline hydrogen peroxide), hydrogenated (diimide treament after sodium borohydride), acetylated (pyridine and acetic anhydride), and methylated (diazomethane) were compared to determine what spectral changes occurred after each treatment. The spectra are shown in Fig. 4 (250 - 1450 cm^{-1}), Fig. 5 (1350 - 1850 cm^{-1}), and Fig. 6 (2500 - 3500 cm^{-1}).

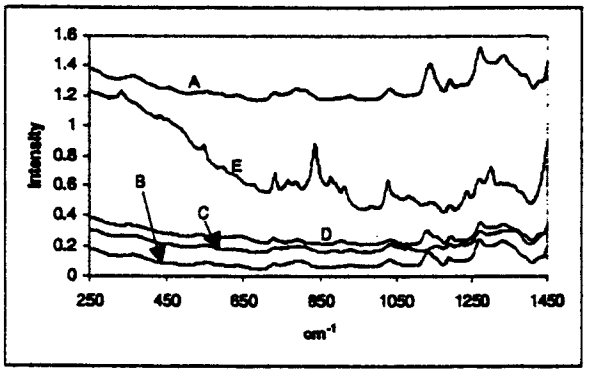

Figure 4: Raman spectra of spruce MWLs in the region 250 - 1450 cm^{-1}; (A) untreated, (B) peroxide bleached, (C) hydrogenated after borohydride bleaching, (D) acetylated, and (E) methylated

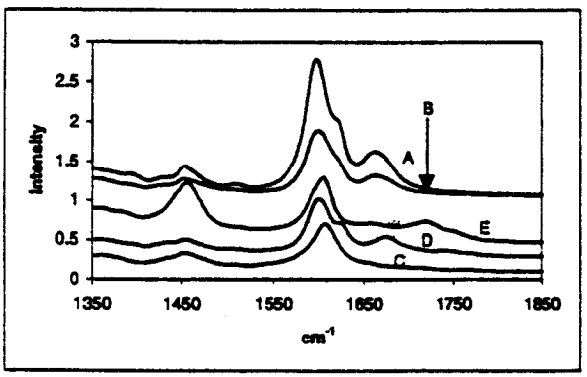

Figure 5: Raman spectra of spruce MWLs in the region 1350 - 1850 cm^{-1}; (A) untreated, (B) peroxide bleached, (C) hydrogenated after borohydride bleaching, (D) acetylated, and (E) methylated

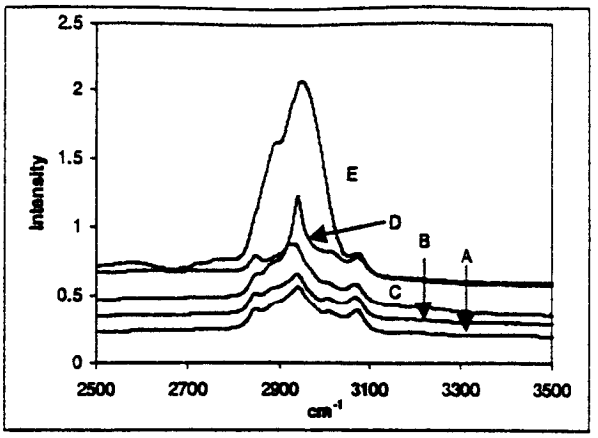

Figure 6: Raman spectra of spruce MWLs in the region 2500 - 3500 cm^{-1}; (A) untreated, (B) peroxide bleached, (C) hydrogenated after borohydride bleaching, (D) acetylated, and (E) methylated

Peroxide bleaching

Upon peroxide bleaching Fig. 4 shows significant changes in the intensity of most bands in the region 250 - 1450 cm^{-1} (Fig. 4, spectra A and B). Because bleaching primarily affects chromophore structures in lignin, decline in intensity indicated that significant Raman contribution due to chromophore structures is present in the 250 - 1450 cm^{-1} region of the spectrum. Although contributions were significantly diminished, most Raman bands could still be detected. This indicated that spruce lignin structure was not altered significantly and most of the originally present lignin sub-structures were still present. Even some coniferaldehyde structures survived bleaching as its contribution at 1135 cm^{-1}[7] was not completely removed.

In the 1350 - 1850 cm^{-1} region, all bands declined in intensity (Fig. 5, spectra A and B). This can be accounted for by noting that upon bleaching coniferaldehyde contributions at 1600, 1622, and 1662 cm^{-1} are mostly removed. This bleaching related effect on band intensities has previously been reported[7,8]. Additionally, contributions in the range 1660 - 1690 cm^{-1} due to *p*-quinones were also removed[9].

In Figure 6 (spectra A and B), normalized spectra of untreated and bleached spruce MWLs are very similar. This indicated that peroxide bleaching does not modify the amount of aliphatic C-H groups in lignin.

Diimide treatment of borohydride bleached MWL

When one compares the Raman features in Fig. 4 (spectra A and C), it becomes clear that although most bands declined in intensity the bands at 558, 895, 975, and 1135 were more or less completely diminished. This suggests that these contributions are likely to be due to lignin units that have unsaturated side chains containing either C=C or C=O groups because hydrogenation primarily modifies such functional groups. Because no Raman intensity can be seen at 1135 cm^{-1} band in the spectrum of the bleached and hydrogenated MWL, it is likely that nearly all coniferaldehyde units were modified. The other differences in the spectra indicated that a new feature appeared at 882 cm^{-1}. Its assignment remains unknown at the present time.

In addition the drastic reduction in the intensity of the 1600 cm^{-1} band and the disappearance of the 1662 cm^{-1} band in the spectrum of the hydrogenated MWL clearly showed that all of the coniferyl alcohol units were reduced upon treatment with diimide. In the photoyellowing studies of mechanical pulps, such evidence was used to ensure that ring-conjugated groups were fully reduced[10]. A consequence of the diimide treatment was that the aromatic ring-stretch mode of lignin had shifted to 1607 cm^{-1}. This is likely to be due to modification of aromatic units that contributed at 1600 cm^{-1} or lower wavenumbers. The spectrum of hydrogenated MWL also showed reduced band intensities at 1454 and 1508 cm^{-1}.

Upon reduction, the C-H stretch region showed higher intensity (Fig. 6, spectra A and C) and this is to be expected The ethylenic and carbonyl bonds upon reduction would produce aliphatic C-H bonds and this explains why more band intensity is present at 2845, 2900, and 2930 cm^{-1}.

Acetylation

In the spectrum of acetylated MWL (250 - 1450 cm^{-1}), in addition to general decline in band intensities several specific changes were detected (Fig. 4, spectra A and D). The bands at 557 and 787 cm^{-1} were better resolved. Raman band intensity increased at 637 and 787 cm^{-1}. Moreover, upon acetylation some weak but distinct peaks emerged from the broadness of the bands (in the spectrum of the untreated MWL).

In the region 1350 - 1850 cm^{-1}. intensity was also lower for all of the acetylated MWL Raman bands (Fig. 5, spectra A and D). A new weak feature at 1739 cm^{-1} due to the acetyl carbonyl group was detected. The band at 1662 cm^{-1} present in the spectrum of the untreated MWL was found to have shifted to 1673 cm^{-1}. The latter band shift was caused by lack of hydrogen bonding in the acetylated lignin and is supported by our salvation studies of coniferaldehyde[11].

Effect of acetylation on the C-H stretch region is shown in Fig. 6 (spectra A and D). It can be easily noted that acetylation resulted in the weakening of the band at 2845 cm^{-1}. On the contrary, the 2940 cm^{-1} band showed a significant enhancement As previously pointed out, the increased contribution at the latter band position is due to the C-H stretches present in the acetoxy groups in acetylated lignin. It is likely that this band could be used for quantitative monitoring of the acetylation reaction in lignin and lignocellulosics[1].

Methylation

In the low vibrational frequency region, like acetylation, methylation also resulted in significant changes in band profiles and appearance of new features (Fig. 4, spectra A and E). New bands appeared at 333, 766, 837, 879, 913, 1027, 1082, 1237, and 1301 cm^{-1}. Wherever bands were in the proximity of the band positions of the untreated MWL, the bands in the methylated MWL spectrum were stronger.

Whereas the 1454 cm^{-1} band intensity increased, the band at 1600 cm^{-1} declined upon methylation (Fig. 5, spectra A and E). The methylation (or the reaction conditions under which methylation was carried out) was also responsible for the reduced 1657 cm^{-1} band. It is not clear why the intensity of this band would decrease upon methylation. The appearance of two carbonyl peaks at 1718 and 1748 cm^{-1} is also unexpected and may have something to do with either the conditions under which this reaction was carried out or residual deuterated acetone (although no significant intensity for C-D stretch mode was detected). We are investigating the reaction (diazomethane methylation) further to find out why such effects were observed.

The C-H stretch region is compared in Figure 6 (spectra A and E). There is very significant increase in the intensity of bands at 2850 and 2950 cm^{-1}. Such an enhancement implies that a large number of hydroxyl groups were successfully methylated. In spruce MWL, such groups are likely to be both in lignin and residual hemicelluloses.

CONCLUSION

Most of the Raman spectral features were common in both HW and SW MWLs. Small as well as significant differences in intensity were detected for some of the bands. Role of hemicelluloses in such differences needs to be better understood.

Important changes occured in the Raman spectrum of spruce MWL when it was chemically modified. Such spectral changes were present in all regions of the spectrum. For the most part, spectral changes could be successfully interpreted in terms of chemical-treatment related structural changes in lignin.

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