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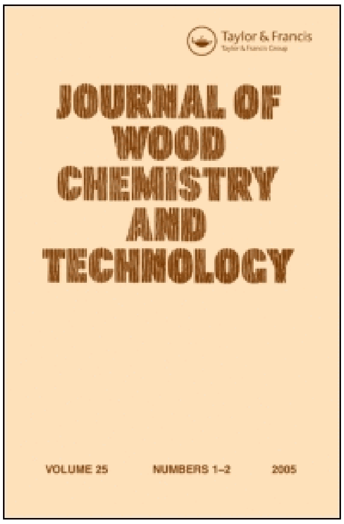

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# $^{13}$C NMR Characterization of Soda and Soda/Aq Spent Liquor Fractions

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# $^{13}$C NMR CHARACTERIZATION OF SODA AND SODA/AQ SPENT LIQUOR FRACTIONS

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## ABSTRACT

Spent liquor fractions from soda and soda/anthraquinone cooks of loblolly pine wood meal were examined by C-13 NMR spectroscopy. The material which precipitated from the liquors at pH 7 as well as that remaining in solution were acetylated and fractionated on a styrene-divinylbenzene gel column. This technique was an attempt to simplify spectral interpretation and to elucidate the distribution of anthracenyl structures within the spent liquor components. The NMR spectra of fractions of the precipitated material revealed that anthracenyl structures chemically bound to lignin increased with decreasing molecular weight (MW), whereas, polysaccharide content decreased markedly with decreasing MW. The NMR spectra of the soluble material had no anthracenyl peaks, but did contain a significant peak at 105 ppm. This is in the same location as a predominant peak observed in C-13 NMR spectra of hardwood lignins, and which has been assigned to C2 and C6 of syringyl structures. However, in the present study the 105 ppm peak has been tentatively assigned to a carbohydrate carbon since it is prominent only in carbohydrate-rich fractions. Also, its aliphatic nature was confirmed by double resonance NMR experiments.

## INTRODUCTION

Recent results of $^{13}$C NMR characterization of lignin from soda, soda/anthraquinone (AQ), and soda/9,10-$^{13}$C enriched AQ spent liquors confirmed the presence of chemically bound AQ, or more appropriately, "anthracenyl adducts."[1] These catalytically

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inactive adducts, which persist throughout delignification, result from reactions of the AQ reduction products anthrahydroquinone and anthranol with lignin quinone methides.[1,2] They may be the main causes of extensive AQ loss during alkaline pulping. It is expected that modification of pulping conditions aimed toward improving the efficiency of AQ as a catalyst will be facilitated by the characterization of these adducts.

In a previous study[1] the total lignin precipitated from the liquors at pH 7, as well as that obtained following removal of low molecular weight products (monomers and dimers), was examined. However, interpretation of the $^{13}C$ NMR spectra of these lignins was very limited due to their complexity. This study describes initial attempts to simplify interpretation by separation of the precipitated lignins into four molecular size fractions prior to $^{13}C$ NMR examination. Similarly, the material which remains dissolved upon neutralization of the spent liquors was also isolated and separated into fractions.

The main purpose of the NMR comparisons described here is to emphasize major differences between the soda, soda/AQ, and soda/$^{13}C$ AQ lignins, rather than detailed peak assignments. Since the conditions of the three cooks and lignin preparations were essentially identical, differences between the two AQ lignins should only reflect the 9,10-$^{13}C$ label whereas differences between the soda and soda/AQ reflect, in general, the incorporation of anthracenyl structures and the effect of more extensive lignin depolymerization due to the catalyst.

## RESULTS AND DISCUSSION

### Separation Scheme

Spent liquors from soda, soda/AQ, and soda/9,10-$^{13}C$ (50%) AQ cooks of loblolly pine wood meal[1] were treated as illustrated in Fig. 1. Following neutralization with acetic acid, the suspensions were filtered through a molecular membrane (nominal MW cutoff = 100,000), instead of filter paper, to assure a clean

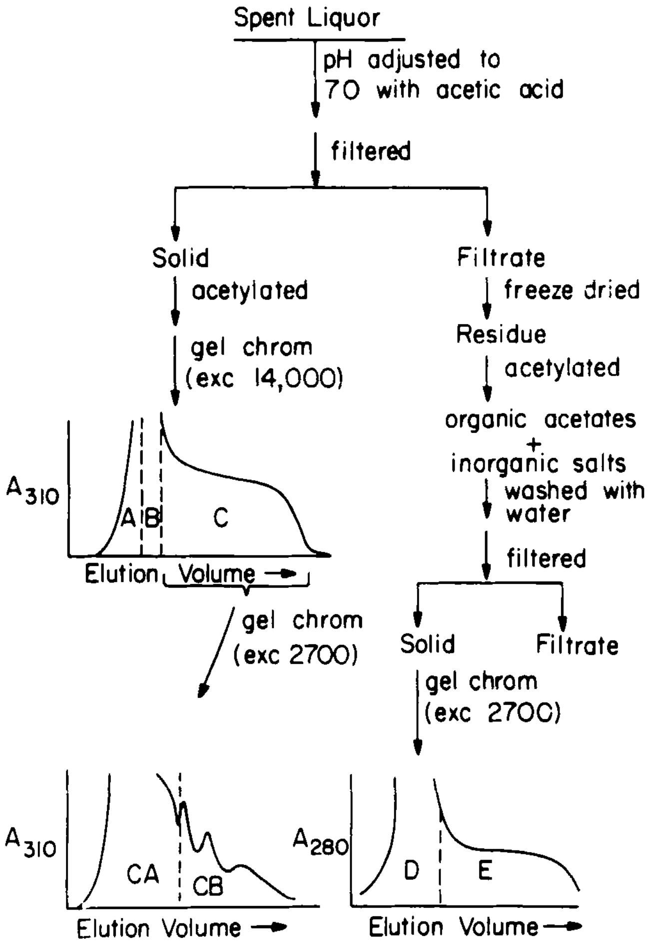

Figure 1.--Separation scheme.

and quantitative recovery of the precipitated material. The precipitates were washed thoroughly with water, freeze-dried, and finally acetylated. The filtrates were also freeze-dried and the residues were acetylated. With both the soda and soda/AQ liquors, the precipitates represent 62% and the filtrate residues represent 38% of the total isolated spent liquor components.

TABLE 1

Contribution of Fractions to Total Isolated Liquor Components

| Cook | Precipitate fractions, % | | | | Filtrate fractions, % | |
|---|---|---|---|---|---|---|
| | A | B | CA | CB | D | E |
| Soda | 20 | 16 | 19 | 7 | 27 | 11 |
| Soda/AQ | 15 | 13 | 27 | 7 | 28 | 10 |
| Soda/$^{13}$C-AQ | 17 | 12 | 26 | 8 | 28 | 9 |

The acetylated products were fractionated on the appropriate gel columns (see Experimental section) by chloroform elution, giving the fractions shown in Fig. 1. The contribution of individual fractions to the total isolated material is shown in Table 1. The only significant difference between the soda and soda/AQ distributions is a shift in quantity of material from fraction A (high MW) to fraction CA (low MW). This is not surprising considering the increased depolymerization caused by the catalyst.[2,3] Fraction CB is composed of a complex mixture of monomers and dimers and has not been investigated.

## Fractions From Precipitated Material

$^{13}$C NMR spectra of the highest MW fractions (A) are compared in Fig. 2. The only significant difference in the spectra of the AQ lignins is the small cluster of peaks at 180-185 ppm (region a) which is assigned to $^{13}$C enriched carbonyl groups of anthracenyl structures attached to the lignin. A notable feature in the spectrum of the soda lignin is the peak at 30 ppm which is very weak in the spectra of the AQ lignins. This peak and the weaker peaks in the same vicinity have been assigned to methylene groups based on their inversion in an APT (attached proton test)[4] spectrum as shown in Fig. 3. Likely structures are methylene "bridges" between aromatic rings resulting from condensation reactions of lignin with liberated formaldehyde.[5,6] The location of the methylene peak in a

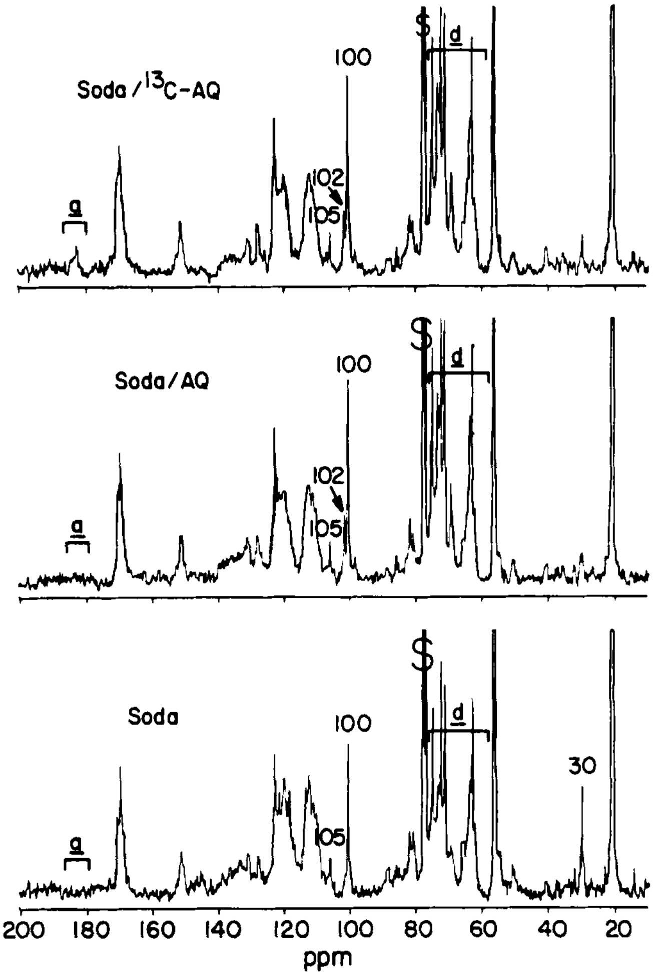

Figure 2.--$^{13}$C NMR spectra of acetylated lignin fraction A (high MW).

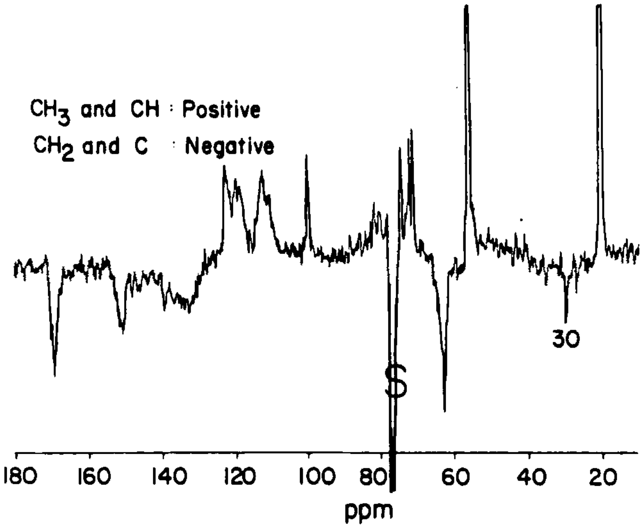

Figure 3.--APT spectrum of soda lignin, fraction A.

highly shielded region indicates that the aryl-$CH_2$-aryl moiety is nonplaner due to ortho substituents in both rings. For example, it has been reported that the methylene bridge carbon in aryl-$CH_2$-aryl structures with no ortho substituents, an ortho substituent in one ring, and an ortho substituent in both rings, resonates at approximately 40, 35, and 30 ppm respectively.[7-9] The significant peak at 102 ppm appearing in the spectra of the AQ lignins (Fig. 2) has not yet been assigned. It presumably originates from carbohydrates as does the intense peak at 100 ppm which is present in the spectra of both the soda and soda/AQ lignins. Peaks in the region of 98-103 ppm have been reported previously in $^{13}C$ NMR spectra of acetylated milled wood lignins of hardwoods, bamboo, wheatstraw, and cornstalks,[10,11] and to a very small extent in spruce kraft lignin.[6] Generally, they have been either unassigned or assigned to C1 in hemicelluloses. The intense peak at 100 ppm, along with several sharp peaks at 60-75 ppm (region d), clearly establish that fraction A has a large polysaccharide content.[12]

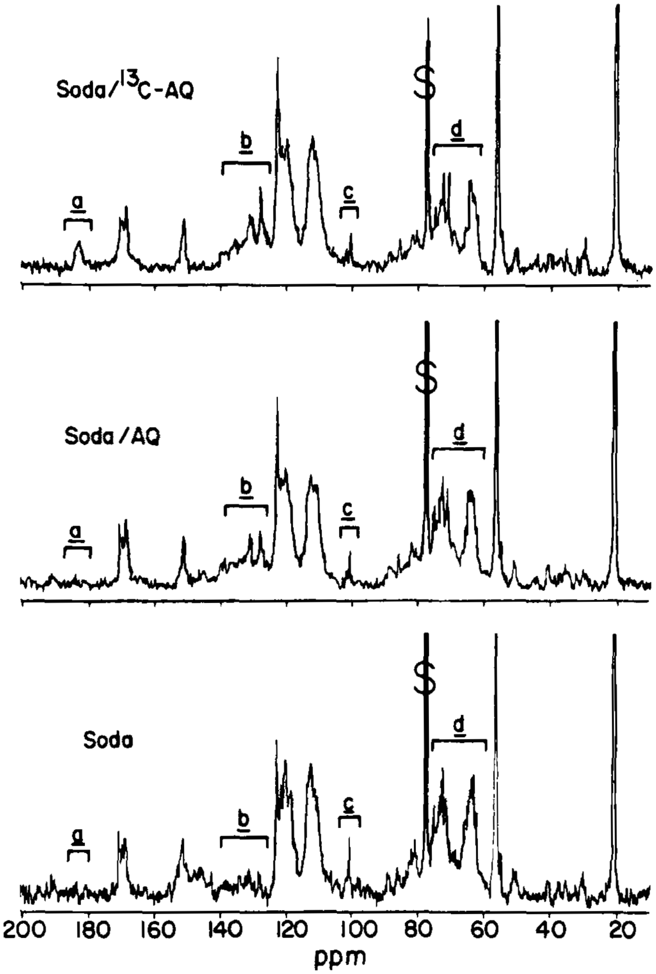

Figure 4.--$^{13}$C NMR spectra of acetylated lignin, fraction B.

The spectra of fraction B lignins are compared in Fig. 4. Again, the cluster of peaks in region a appears in the spectrum of the labeled AQ lignin. Also, the greater intensities at 125-140 ppm (region b) in the spectra of the AQ lignins than that of the soda lignin is consistent with the presence of incorporated anthracenyl structures.[1] Diminished carbohydrate content in fraction B is apparent from decreased intensities of peaks at

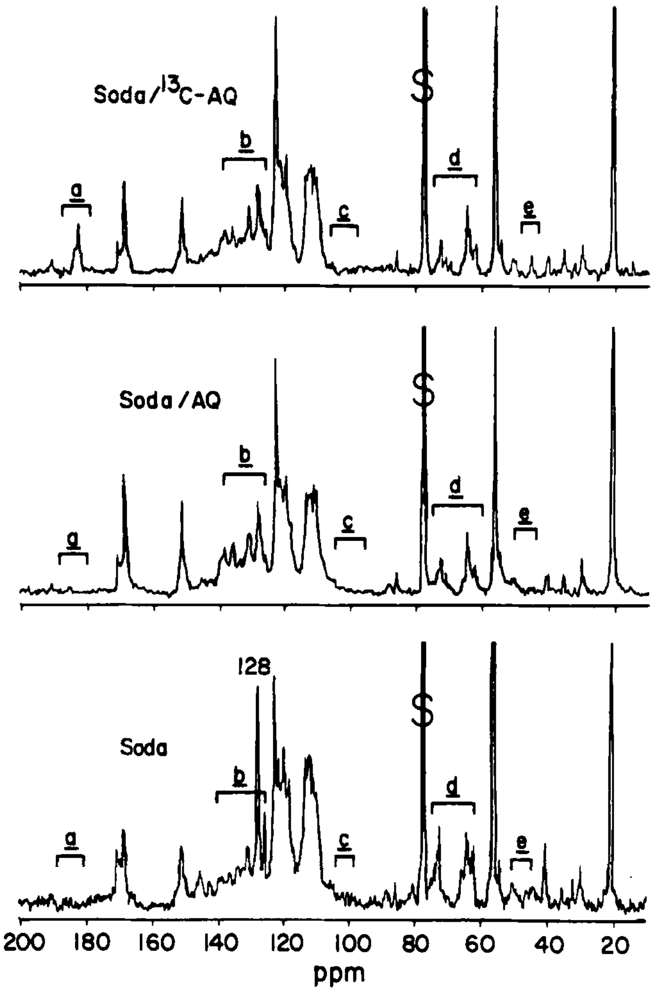

Figure 5.--$^{13}$C NMR spectra of acetylated lignin, fraction CA (low MW).

98-102 ppm (region c), and at 60-75 ppm (region d) which were very intense in the fraction A spectra.

Finally, $^{13}$C NMR spectra of the lowest MW fractions (CA) which can still be considered polymeric are illustrated in Fig. 5. Fraction CA appears to be carbohydrate free because of the absence of peaks in region c and the decreased intensity in region d. In this fraction, anthracenyl structures are more predominant than in fractions A or B, as indicated by the greater intensity in region a in the spectrum of the labeled AQ lignin. In addition, a small, but significant, cluster of peaks at 43-47 ppm (region e) has been assigned to labeled C10 carbons of incorporated anthranol adducts in accordance with earlier model studies.[13-15] The greater anthracenyl content in the low MW fraction CA is explained by increased phenolic content in the more extensively degraded lignin. The greater phenolic content results in more quinone methide formation and more extensive reaction with AHQ and anthranol.[13] The intense peak at 128 ppm in the spectrum of the soda lignin, which is much weaker in the spectra of the soda/AQ lignins, is consistent with Cα of stilbene structures.[6,16] Stilbenes reportedly arise from β-aryl units in lignin and have been isolated from soda and kraft spent liquors.[17]

The trends of increasing anthracenyl content and decreasing carbohydrate content with decreasing MW can be more clearly seen in a comparison of the soda/$^{13}$C AQ fractions in Fig. 6. A noteworthy feature of the spectrum of fraction CA is the lack of strong peaks in the aliphatic region at 60-90 ppm (with the exception of the solvent peak), which is indicative of extensive side chain degradation. However, this cannot be attributed to a MW effect since this region is obscured by carbohydrate peaks in fractions A and B (region d).

### Soluble Liquor Components

Upon fractionation of the soluble components as in Fig. 1, over 70% of the material was found in the high MW fractions, D, as is illustrated in Table 1. The $^{13}$C NMR spectra of fractions D and E from the soda/AQ experiment were essentially the same as the corresponding fractions from the soda/$^{13}$C-AQ experiment, thus indicating an absence of anthracenyl structures. Likewise, the spectra of fractions D and E from the soda experiment were not appreciably different from those of the AQ experiments. Therefore, the spectra of fractions D and E from the soda/AQ experiment are

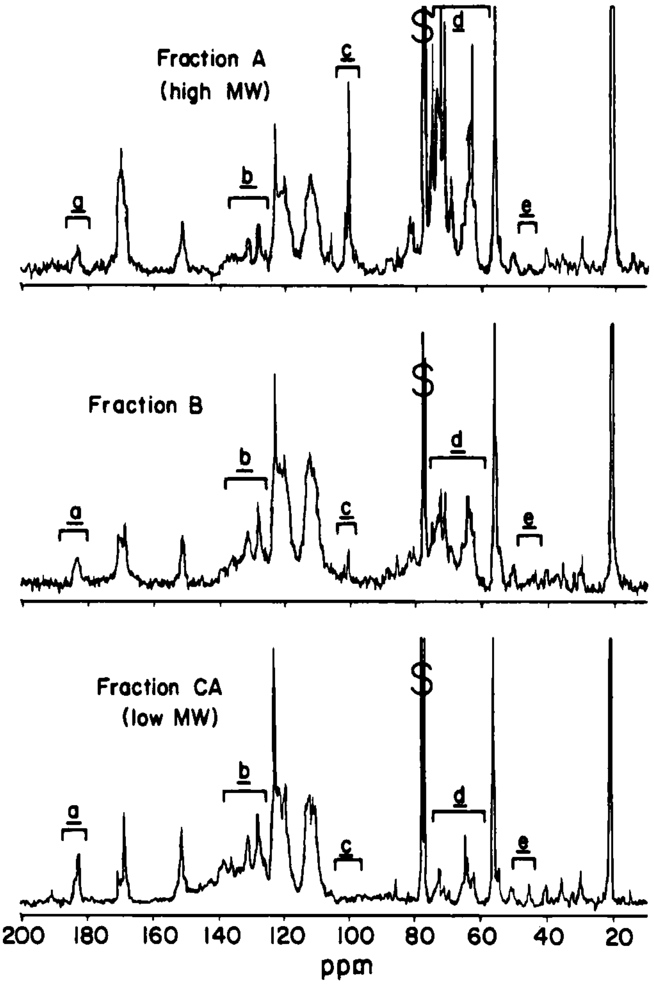

Figure 6.--$^{13}$C NMR spectra of acetylated soda/$^{13}$C-AQ lignins.

representative of the soluble components and are illustrated in Fig. 7. The minor fraction E is a complex mixture consisting largely of monomers and dimers and was not investigated. The carbohydrate content of the major fraction D is evident from the clusters of peaks in region c as well as the intense peaks in region d. The peak at 105 ppm is interesting in that in the past

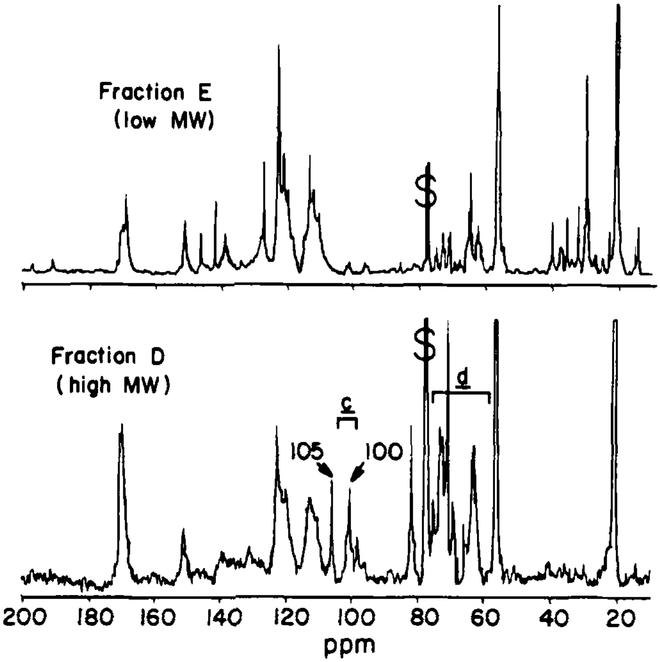

Figure 7.--$^{13}$C NMR spectra of acetylated soluble components (soda/AQ).

it has been assigned exclusively to C2/C6 of syringyl units in hardwood lignins.[10] Only a trace of this peak is occasionally seen in the spectra of softwood lignins.[16] It is noteworthy that this peak is also present in the spectra of carbohydrate rich fractions A of the precipitated lignins (Fig. 2). Because of its appearance in only the carbohydrate-rich fractions and its relatively high intensity, it is likely that it is carbohydrate in origin.

The aliphatic nature of the carbon responsible for the 105 ppm peak in fraction D was confirmed by a double resonance experiment. In this experiment a narrow portion of the proton frequency range is coherently irradiated, with relatively low power, during acquisition of the $^{13}$C NMR spectrum. Therefore, only those car-

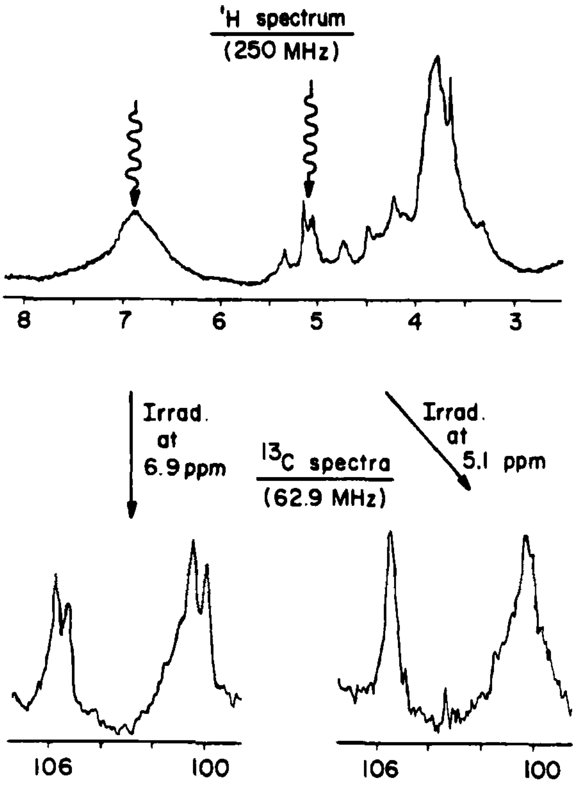

Figure 8.--'H NMR spectrum and $^{13}$C double resonance experiments on fraction D.

bons attached to the irradiated protons will display reduced multiplicity. As illustrated in Fig. 8, coherent irradiation of the aromatic protons in fraction D did not collapse the CH doublet at 105 ppm. The carbon at 100 ppm also retained its multiplicity, which was expected since it has been assigned to C1 in hemicellulose.[6,10,11] A second experiment in which the protons at 5.1 ppm were irradiated resulted in the collapse of the 105 ppm peak into a singlet, and reduced multiplicity of the 100 ppm carbon (Fig. 8). This result confirmed that the proton attached to the 105 ppm carbon is very close to 5.1 ppm and the proton attached to the

100 ppm carbon is within a few tenths of a ppm of the irradiation frequency. Because of the prominence of the 105 ppm peak in carbohydrate rich fractions (A and D) it can be tentatively assigned to a carbohydrate carbon. However, further research is needed to confirm this assignment.

## SUMMARY

Gel fractionation of acetylated spent liquor components, from soda and soda/AQ loblolly pine cooks prior to $^{13}$C NMR characterization, revealed considerably more information than could be obtained from studies of unfractionated material. For example, chemically attached anthracenyl structures were found to increase with decreasing MW of the precipitated lignins. Conversely, polysaccharide content drastically decreased with decreasing MW of the precipitate.

Over 70% of the material which remained in solution following neutralization had a relatively high MW. A peak at 105 ppm, which is the location of a predominant syringyl peak in hardwoods, was present in the spectra of the soluble material in much greater intensity than would be expected from the trace occasionally observed in the spectra of softwood lignins. It was confirmed by a $^{13}$C NMR double resonance experiment that this peak is not due to an aromatic carbon. It was tentatively assigned to a carbohydrate carbon.

## EXPERIMENTAL

### Wood Cooks and Spent Liquor Treatment

Cook conditions were the same as previously described.[1] The spent liquors were neutralized with glacial acetic acid and the resulting suspensions were concentrated to 30-40 ml (50°/25 mm) and filtered through a Millipore Pellicon PT series molecular membrane (nominal cutoff = 100,000 MW). The retentates were washed several times with water, then freeze-dried and acetylated with 1/1 acetic anhydride/pyridine for 18 hr at room temperature. Similarly, the filtrates plus retentate washings were freeze dried, and the resulting residues were acetylated, followed by water washings to remove inorganic salts.

## Gel Chromatography

Precipitated lignins.--The acetylated material (400-700 mg) was dissolved in $CHCl_3$ and applied on a 93 x 5-cm column of porous styrene-divinylbenzene copolymer beads with 1% crosslinkage (BIO-RAD Bio-Beads S-X1, exclusion limit 14,000), followed by gravity elution with $CHCl_3$ (approx. 1.5 ml/min). The eluant was monitored at 310 nm with an ISCO UA-5 absorbance monitor and divided into three fractions as shown in Fig. 1.

The lowest molecular weight fraction (C) was then applied on a 104 x 3.8-cm column of 2% crosslinked copolymer beads (Bio-Beads S-X2, exclusion limit 2700) and eluted with $CHCl_3$ as described above.

Association between lignin fragments (which lead to anomalous MW profiles)[18] in this chromatographic system was shown to be negligible by reinjection of isolated samples onto the same column. Upon elution with $CHCl_3$ individual peaks emerged at their characteristic elution volumes.

Filtrate residues.--The acetylated material (400-450 mg) was applied on the same column as used for fraction C of the precipitated lignins and eluted in the same manner.

## $^{13}C$ NMR Spectra

Proton decoupled $^{13}C$ NMR spectra of $CDCl_3$ solutions (40-80 mg in 0.3 ml solvent) were determined at a frequency of 62.9 MHz with a Bruker WM-250 FT spectrometer equipped with a 5-mm broadband probe. All spectra were obtained at 30°C. from approximately 6000 to 100,000 transients with 4-8K data points and zero-filling to 8-16K. A pulse angle of 75°, and relaxation delays of 0.3-1.0 sec were used. For comparison purposes the spectra were scaled to a constant methoxyl peak. The APT spectrum (Fig. 3) was obtained by the double spin echo version,[4] in which the observe pulse was 75°, the relaxation delay was 1 sec, $\tau = 7$ μsec, and $\Delta = 2$ μsec. In the double resonance experiments an irradiation power of 0.2 watt was used in the CW mode at frequencies corresponding to 5.1 or 6.9 ppm in the proton spectrum.

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