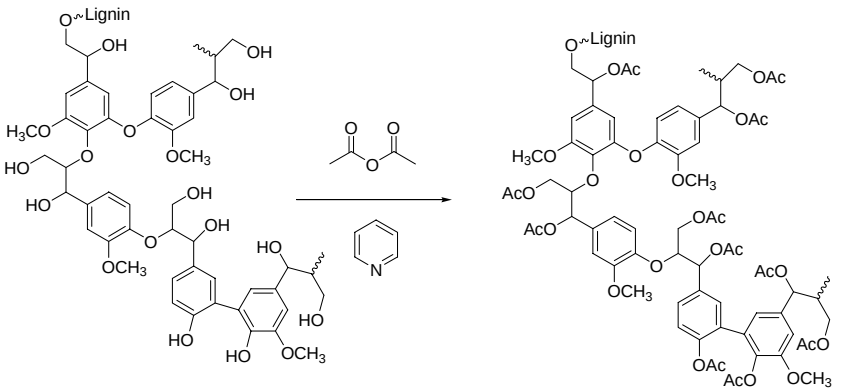
Lignin Acetylation



Acetylation is frequently performed on the residual and cooking liquor lignins. The lignins (dried under vacuum at 40°C for 8-16 hours) were acetylated with acetic anhydride/pyridine (1/1, v/v) at room temperature for 24 hours in 50-ml round-bottom flask. The concentration of the lignin in this solution was approximately 50 mg/ml. After 24 hours, the solution was diluted with ~30 ml of ethanol and stirred for an additional 30 minutes, after which the solvents were removed with a rotary evaporator. Repeated addition and removal of ethanol allowed for the removal of acetic acid and pyridine from the sample. The residue was then dissolved in chloroform, washed twice with filtered de-ionized water in a separatory funnel, and dried with anhydrous sodium sulfate. The chloroform solution (~10 ml) was added drop-wise to approximately 150 ml of anhydrous ether and the product collected as a precipitate. The precipitate was washed twice with ether, each time being collected by centrifugation. The precipitate was dried under high vacuum at 40°C for 24 hours.

Lignin acetates

By far one of the most popular methods to characterize lignin by ^{1}H-NMR is to first derivatize the lignin by acetylation and record the spectrum in chloroform solutions. After being acetylated, the lignins were dried under vacuum for 24 hours at 40°C and accurately weighed out into a 2 ml vial (~22 mg). A standard solution containing pentaflourobenzaldehyde (PFB) and TMS in "100%" $CDCl_3$ was made and added to the lignin. The standard solution was made by first carefully weighing out the PFB (1.3189g) and diluting to 10.0 ml with 100% $CDCl_3$. An aliquot of this solution (1.25 ml) was diluted to 25.0 ml, TMS added, and 0.50 ml added to the lignin. The solution of lignin and internal standard in $CDCl_3$ was stirred vigorously and transferred into a 5 mm NMR tube and the ^{1}H-NMR spectrum recorded.

The ^{1}H-NMR spectra were recorded under quantitative conditions using a 30° pulse and 4 second pulse delay. For each spectrum 800 acquisitions were recorded and a 17 ppm sweep width was used. Manual phasing and baseline corrections were done and an integration file was created so the same integration regions were used for each spectrum. Table 1 is list of the regions integrated for each spectrum.

Quantitative estimates of the various proton containing functional groups were made by performing the following calculation. The signal area of the PFB signal, which

was due to the 0.003297 g of PFB, was integrated and calibrated to 1.0. Since this molecule contains one proton and has a molecular weight of 196.07 g/mol.

Table 1. Functional group frequency and integration regions used for the quantitative ^{1}H-NMR spectra of lignin acetates.

Structure or Functional Group	**Integration region (ppm)**
PFB	10.4-10.2
Aromatic H	8.0-6.2
H_α in β-O-4 structures	6.2-5.8
$-OCH_3$	4.2-3.6
Aromatic acetate	2.6-2.2
Aliphatic acetate	2.2-1.6
TMS	0.0

0.003297/196.07=1.682x10-5 was the number of moles of H present in the internal standard in the sample. Since the integration region of the internal standard was calibrated to 1.0, each unit area in the spectrum is equal to 1.682x10-5 moles of H. For each spectrum this value (or factor) is multiplied by the integration region of interest and divided by the weight of the lignin sample. For example, if the lignin sample weighed 22.03 mg and the integration of the aromatic region equaled 12.437 then: (12.437x1.682x10-5)/.02203=0.0095 mol aromatic H /g lignin are present in the lignin sample. This number was multiplied by 1000 to convert the value into mmol/g lignin.