

FINAL RESEARCH PROJECT: New Uses for Lignin

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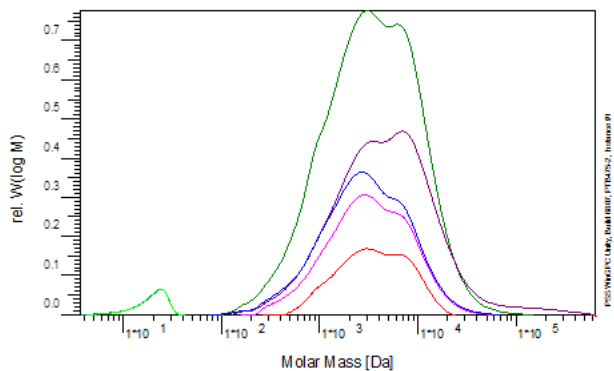
PROJECT OBJECTIVE: The GA Tech deliverable in this project was to provide training, access and testing of a series of lignin samples generated at Imperial College and analyzed at the research laboratories of Dr. Ragauskas.

Dr. C. Conner (post doctoral research fellow from ICL) arrived at IPST@GT in March 2011 and was trained in Ragauskas research protocols for hydrogenation of lignin, NMR and GPC analysis of lignin followed by well established published procedures.^{i,ii,iii,iv}

A series of ICL lignin samples were analyzed by (i) NMR and (ii) acetylated and GPC by Ragauskas research team and this data was subsequently emailed to ICL. The results of this analysis are also summarized below:

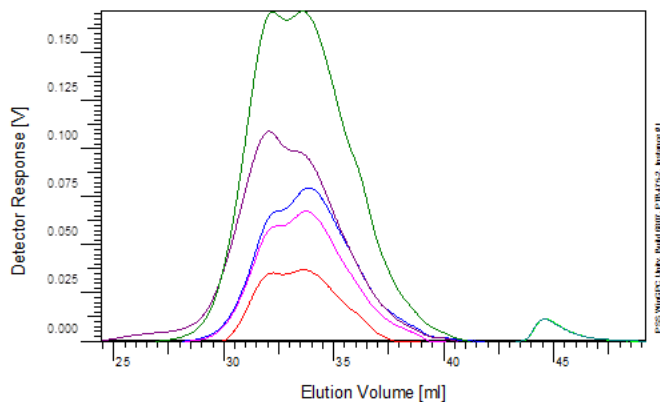
Samples

1. Lig-AC (Chris Conifer's commercial sample of lignin that had undergone our 3 days acetylation process)
2. Lig (Chris Conifer's commercial sample of "Ethanol Organosolv Lignin Acetate")
3. 503 (The 500 series are largely unknown, based on the Mass distribution profiles, they're various samples of EOL), 504, 506, 508 and 509



Curve 1: Vial 91: Lg-AC
 Curve 2: Vial 92: Lg
 Curve 3: Vial 93: 503
 Curve 4: Vial 94: 504
 Curve 5: Vial 95: 505
 Curve 6: Vial 96: 508
 Curve 7: Vial 97: 509

	Aqilent UV	Aqilent UV	Aqilent UV	Aqilent UV	Aqilent UV	Aqilent UV	Aqilent UV	
Mn:	2.5383e3	1.8187e3	1.7187e1	2.0025e3	2.3465e3	1.7660e1	1.8706e3	g/mol
Mw:	4.6721e3	5.6329e3	2.0085e1	4.7889e3	1.0839e4	2.0189e1	4.5255e3	g/mol
Mz:	7.4052e3	1.4199e4	2.2220e1	9.6903e3	9.6904e4	2.2152e1	9.9833e3	g/mol
Mu:	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	g/mol
D:	1.8407e0	3.0971e0	1.1699e0	2.3917e0	4.6191e0	1.1432e0	2.7089e0	g/mol
[η]:	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	ml/g
Vp:	3.3655e1	3.3686e1	4.4671e1	3.3768e1	3.2057e1	4.4592e1	3.3884e1	ml
Mp:	3.1217e3	3.2683e3	2.4268e1	2.9823e3	7.1849e3	2.4059e1	2.8084e3	g/mol
A:	1.673e-1	9.776e-1	2.056e-2	3.299e-1	5.909e-1	2.053e-2	4.010e-1	ml/V
0.0e D	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	g/mol
0.0e D	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	g/mol
0.0e D	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	g/mol
0.0e D	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	g/mol
0.0e D	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	g/mol



Overlay	
<u>Curve 1</u> :	Vial 91: Lg-AC
<u>Curve 2</u> :	Vial 92: Lg
<u>Curve 3</u> :	Vial 93: 503
<u>Curve 4</u> :	Vial 94: 504
<u>Curve 5</u> :	Vial 95: 506
<u>Curve 6</u> :	Vial 96: 508
<u>Curve 7</u> :	Vial 97: 509

Several lignin related were also analyzed by NMR and these results are summarized below:

Two-dimensional ^1H - ^{13}C *heteronuclear single quantum coherence* (HSQC) correlation NMR spectra were recorded in a Bruker III 400 spectrometer. The HSQC analysis was performed using a standard Bruker pulse sequence with a gradient field in the Z direction. The lignin sample (60~100 mg) was dissolved in deuterated dimethyl sulfoxide (DMSO- d_6) (0.50 mL). The mixture was allowed to shake in a Vertex shaker for dissolution. The sample was then transferred into a 5-mm NMR tube. The HSQC experiments were acquired with a 1.5 s interscan delay, a $^1J_{CH}$ of 145 Hz (i.e. CNST2), and 32 or 64 scans at 50 °C. The central solvent peak (δ_C 39.5 ppm; δ_H 2.5 ppm) was used for chemical shifts calibration. Spectra processing was carried out with Bruker Topspin software 2.1.

The ^1H - ^{13}C HSQC NMR spectra were presented below in Figures 1-5.

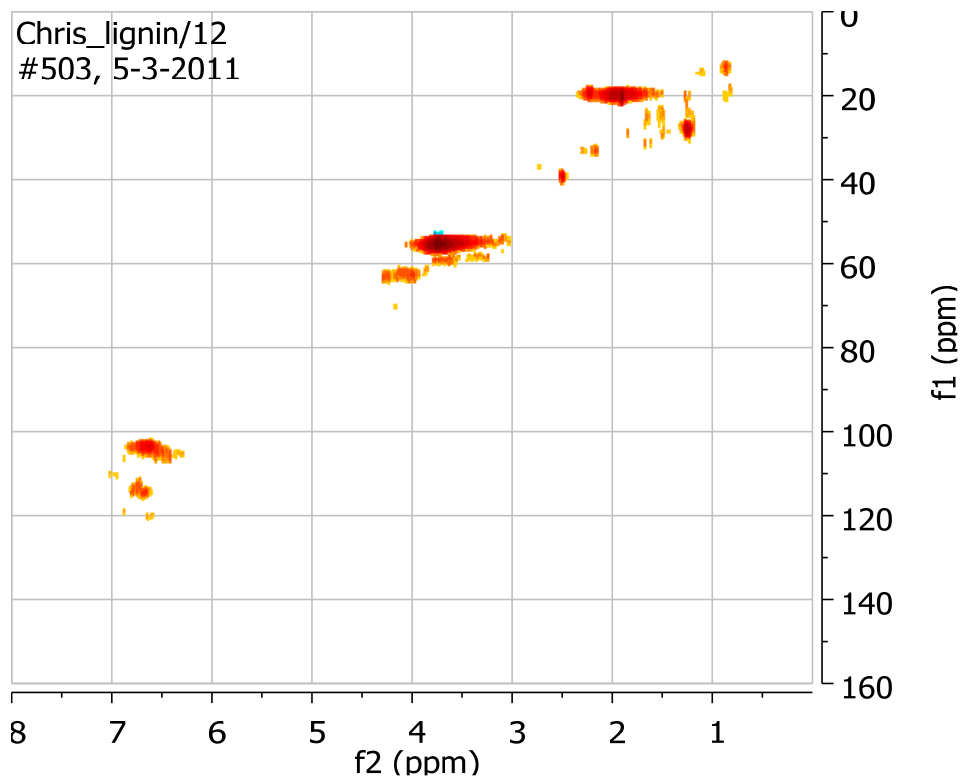


Figure 1. HSQC spectrum of sample # 503.

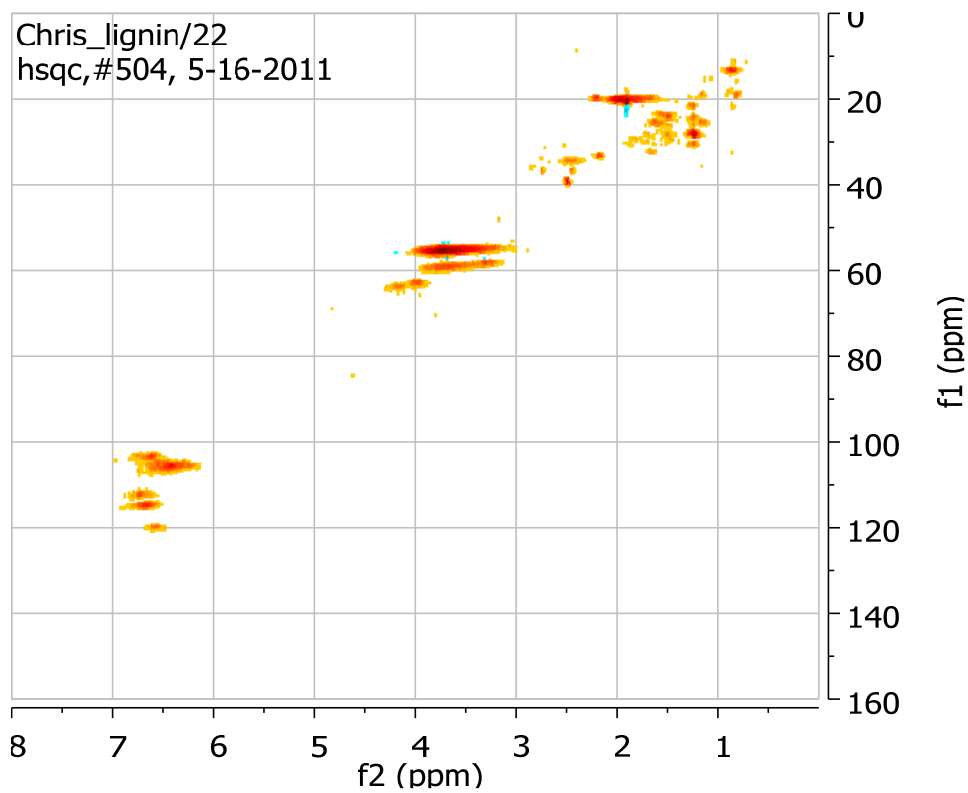


Figure 2. HSQC spectrum of sample # 504.

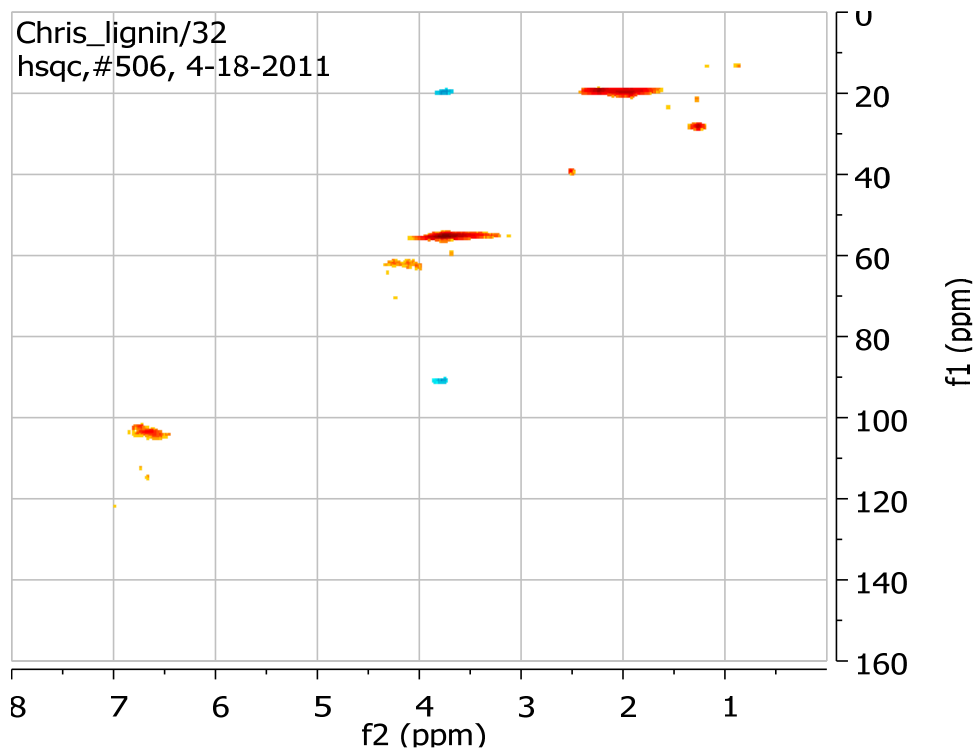


Figure 3. HSQC spectrum of sample # 506.

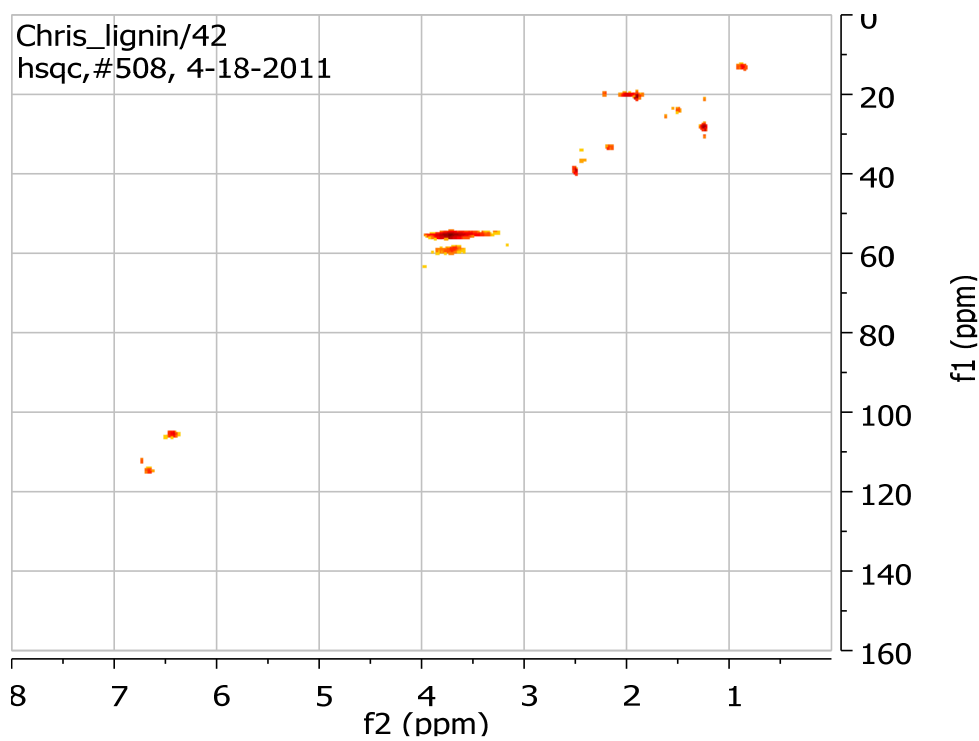


Figure 4. HSQC spectrum of sample # 508.

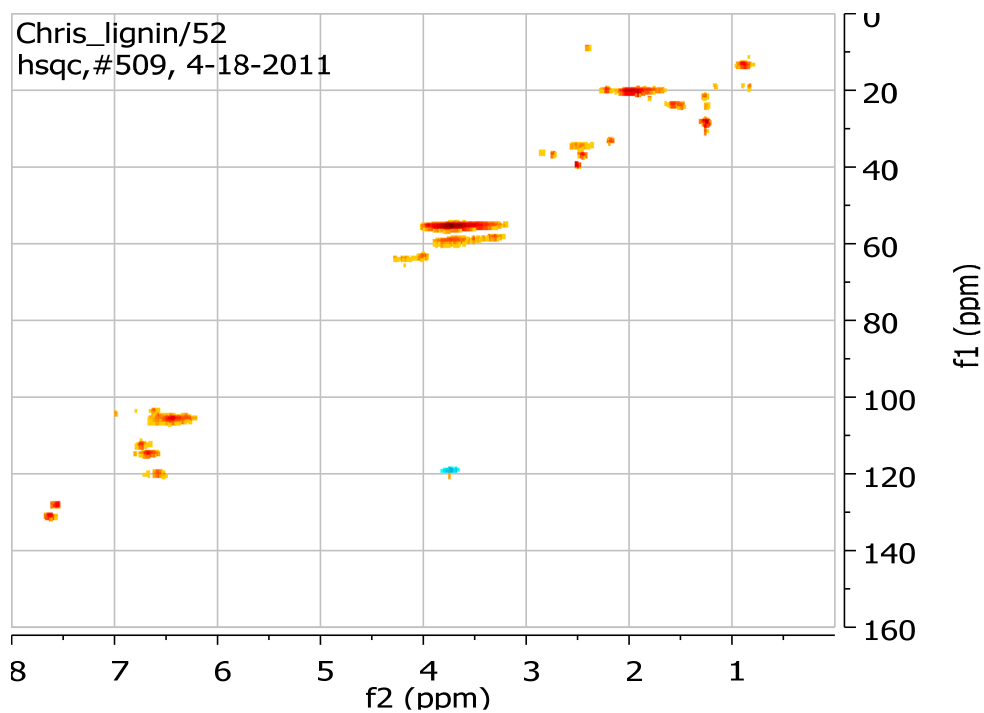


Figure 5. HSQC spectrum of sample # 509.

References:

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- ⁱ Structural characterization and comparison of switchgrass ball-milled lignin before and after dilute acid pretreatment. Samuel, R.; Pu, Y.; Raman, B.; Ragauskas, A.J., *Applied Biochemistry and Biotechnology* (2010), 162(1), 62-74.
- ⁱⁱ Characterization of CO₂ precipitated Kraft lignin to promote its utilization. Nagy, M.; Kosa, M.; Theliander, H.; Ragauskas, A.J., *Green Chemistry* (2010), 12(1), 31-34.
- ⁱⁱⁱ Chemical transformations of *Buddleja davidii* lignin during ethanol organosolv pretreatment. Hallac, B.B.; Pu, Y.; Ragauskas, A.J., *Energy & Fuels* (2009), 24(4), 2723-2732.
- ^{iv} Catalytic hydrogenolysis of ethanol organosolv lignin. Nagy, M.; David, K.; Britovsek, G.J. P.; Ragauskas, A.J., *Holzforschung* (2009), 63(5), 513-520.