Supplementary Information

Synthesis and characterization of lignin-based carbon materials with tunable microstructure

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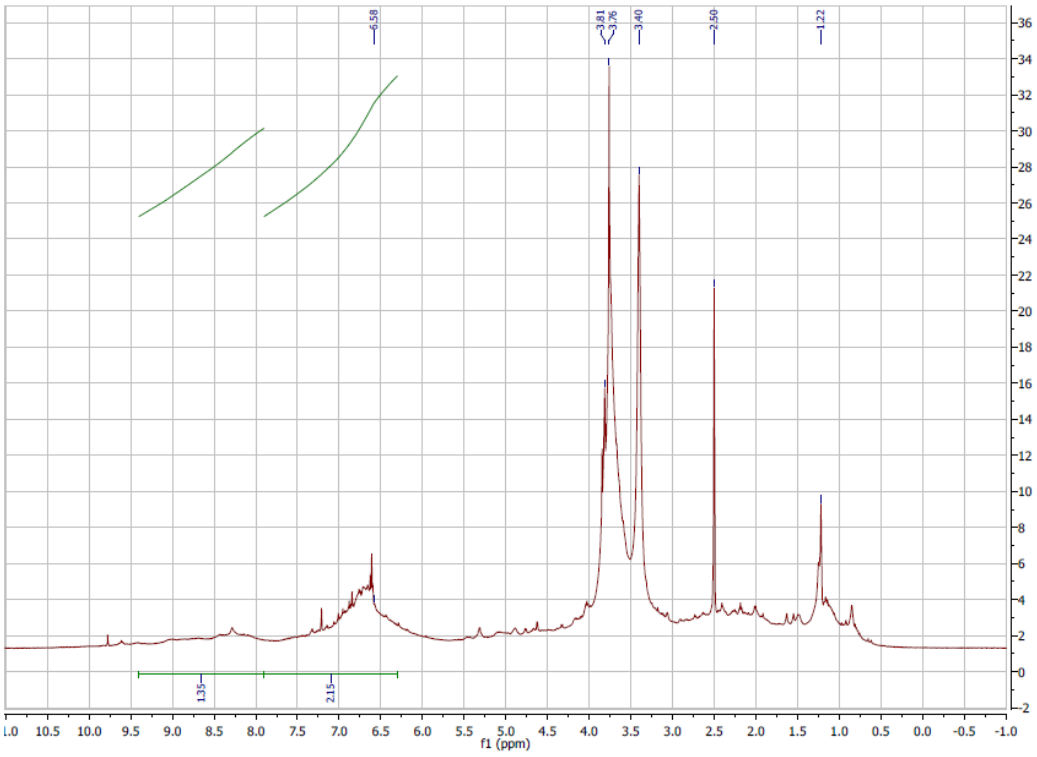

Figure 1. ^{1}H NMR spectrum of unmodified organosolv lignin. Integrations are done based on the assumptions of 2.15 aromatic protons per average phenylpropane (C_9) unit.[1-2]

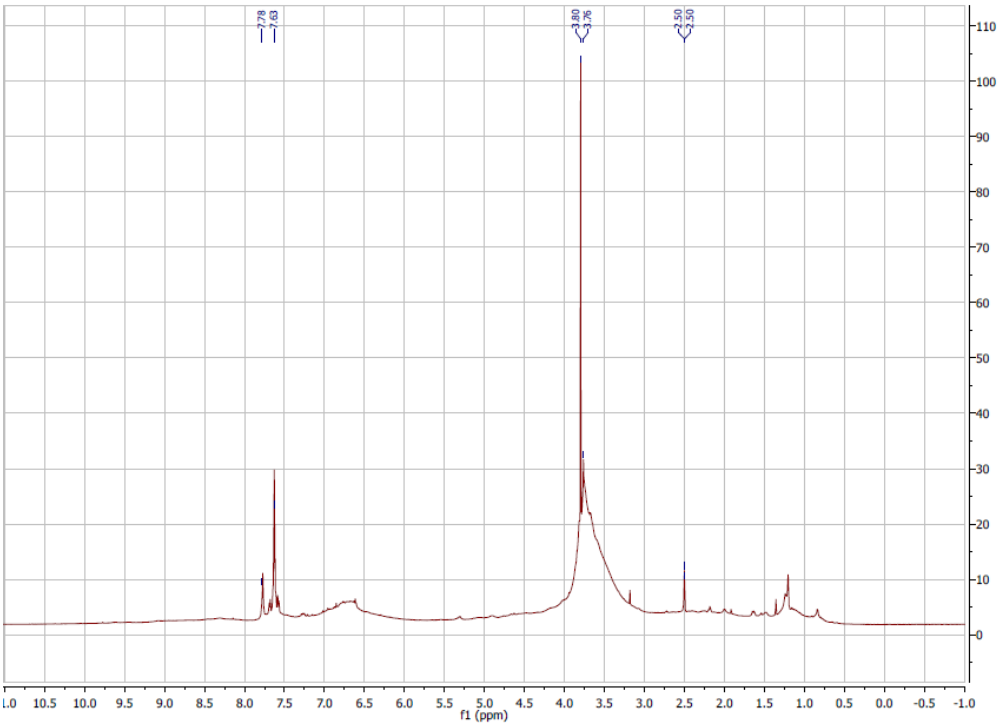

Figure 2. ^{1}H NMR spectrum of Phthalic anhydride modififed organosolv lignin. [1-2]

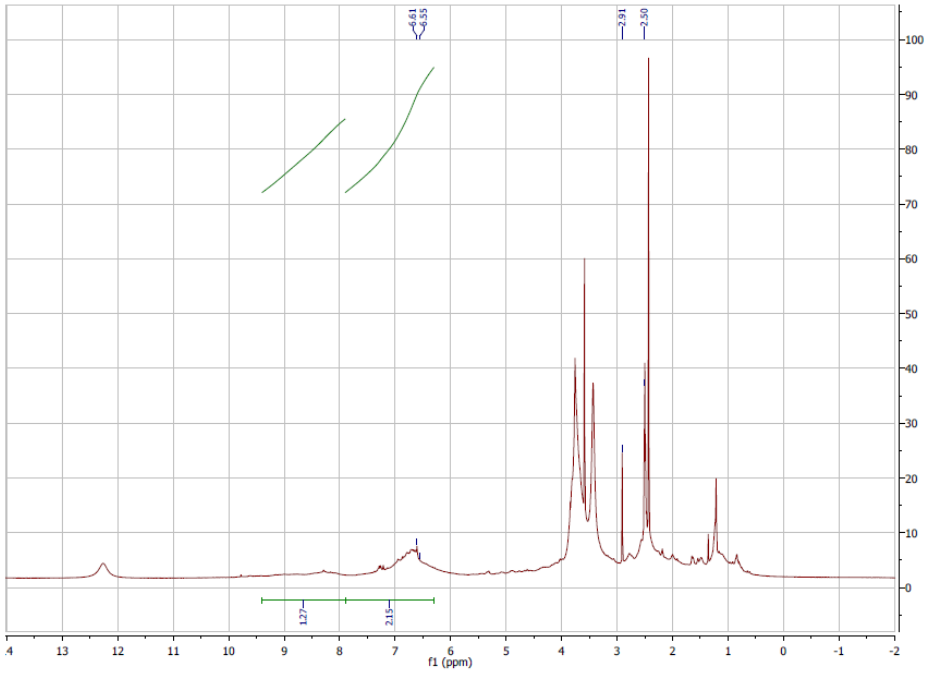

Figure 3. ^{1}H NMR spectrum of succinic anhydride modified organosolv lignin. Integrations are done based on the assumptions of 2.15 aromatic protons per average phenylpropane (C_9) unit.[1-2]

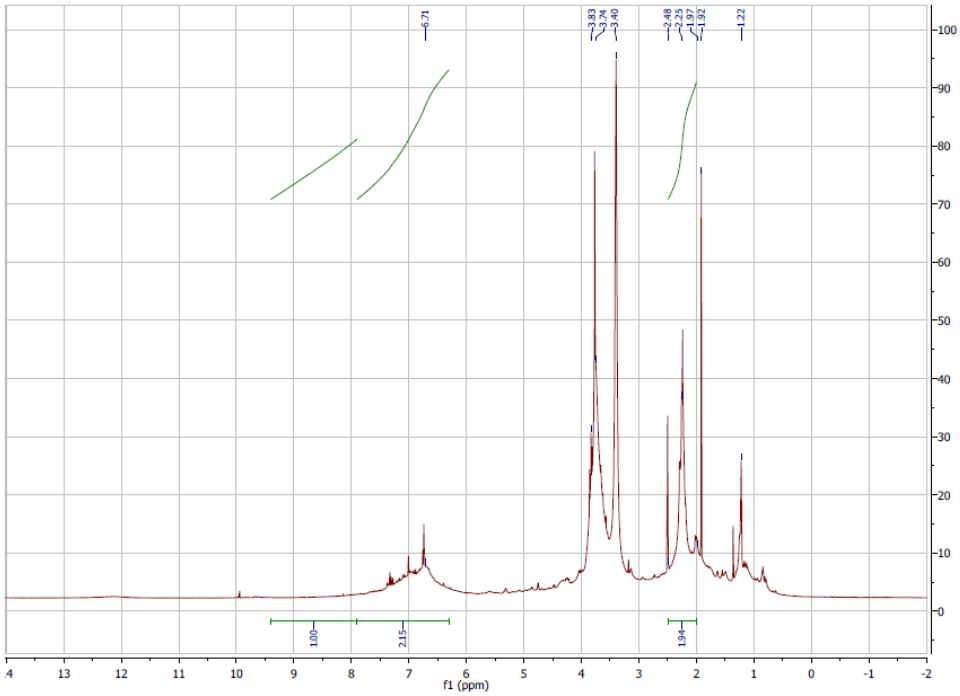

Figure 4. ^{1}H NMR spectrum of acetic anhydride modified organosolv lignin. Integrations are done based on the assumptions of 2.15 aromatic protons per average phenylpropane (C_9) unit.[1-2]

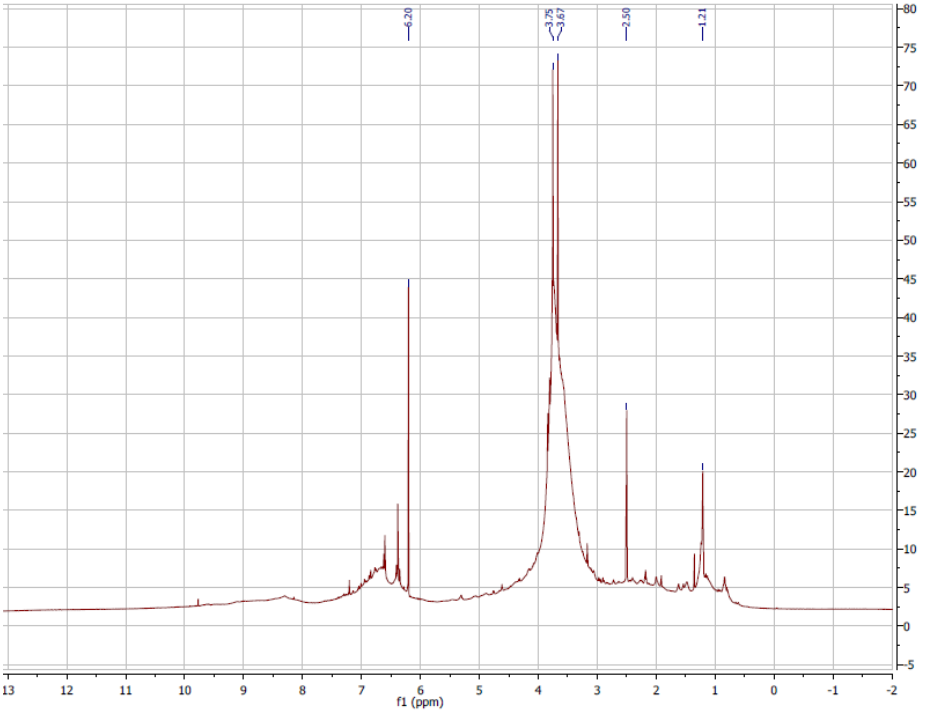

Figure 5. ^{1}H NMR spectrum of maleic anhydride modified organosolv lignin. Integrations are done based on the assumptions of 2.15 aromatic protons per average phenylpropane (C_9) unit.[1-2]

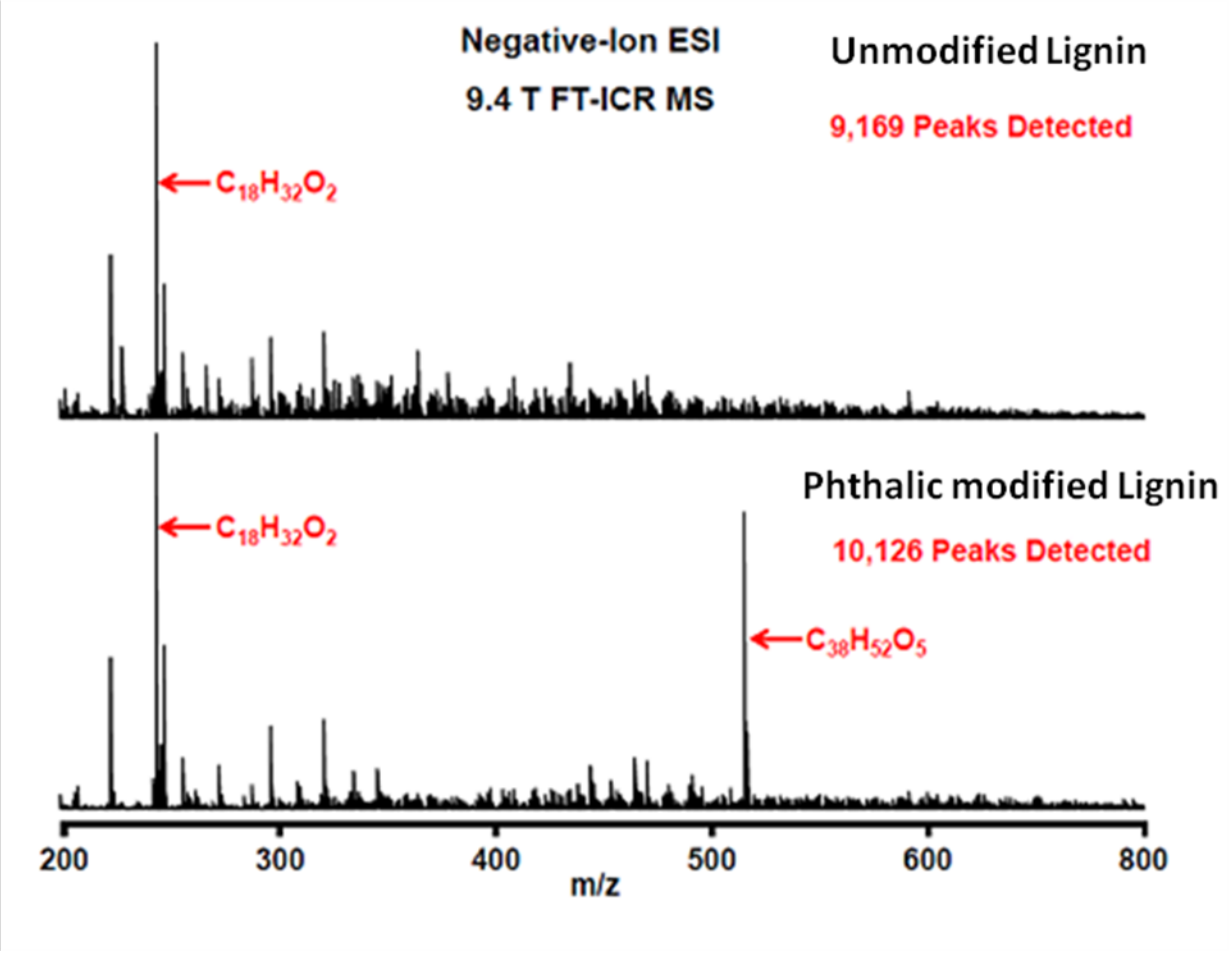

Figure 6. Mass spectra of unmodified and phthalic anhydride modified lignins.

Table 1. HMQC analysis of the unmodified lignin[1]

Typical signal location ($^{1}C/ ^{1}H$)	assignment
Aromatic Region	
127.31/ 7.28	$C_{2,6}$, $H_{2,6}$ in P units with α-OH or -OR
120.20/ 7.27	C_6, H_6 in G units
118.04/ 6.78	C_β, H_β in P units with esterified γ-OH and α,β unsaturation
114.96/ 6.77	C_β, H_β in ferulates
112.37/ 6.73	C_6, H_6 in G units with α,β unsaturated carbonyl group
110.52/ 7.06	C_2, H_2 in esterified felurates or free feluric acid
106.72/ 7.21	$C_{2,6}$, $H_{2,6}$ in P units with carbonyl at α position of side chain
105.59/ 6.43	$C_{2,6}$, $H_{2,6}$ in S units with carbonyl at α position of side chain
103.60/ 6.85	$C_{2,6}$, $H_{2,6}$ in S units
103.35/ 6.62	$C_{2,6}$, $H_{2,6}$ in S units
Side Chain Region	
85.72/ 4.15	unidentified
84.81/ 4.63	C_β, H_β in β-O-4
81.27/ 4.76	Furanose-OH
71.74/ 4.90	C_α, H_α in β-O-4
70.72/ 4.19	Pyranose -OH
63.93/ 3.36	C_γ, H_γ with esterified γ-OH
59.53/ 4.04	C_γ, H_γ in P units
55.77/ 4.64	unidentified
55.53/ 3.73	methoxy
53.37/ 3.07	C_β, H_β in β-1
50.96/ 3.57	unidentified
Alkyl Region	
39.50/ 2.50	solvent
33.35/ 2.19	Benzylic CH_2
33.08/ 2.40	Benzylic CH_2
32.99/ 2.28	Benzylic CH_2
30.85/ 1.21	Alkyl group α to a carbonyl/ solvent
30.04/ 1.65	Alkyl group α to a carbonyl/ solvent
29.20/ 2.11	Alkyl group α to a carbonyl/ solvent
28.58/ 1.22	CH signals in extractives and aliphatic lignin chains
26.31/ 2.00	CH signals in extractives and aliphatic lignin chains
25.20/ 1.63	CH signals in extractives and aliphatic lignin chains
24.14/ 1.49	CH signals in extractives and aliphatic lignin chains
22.86/ 1.63	CH signals in extractives and aliphatic lignin chains
14.92/ 1.09	High field alkyls
13.77/ 1.16	High field alkyls
13.52/ 0.85	High field alkyls

[1] Chemical shifts are reported in ppm[3]

Table 2. HMQC analysis of phthalic anhydride modified lignin[1]

Typical signal location ($^{1}C/ ^{1}H$)	assignment
Aromatic Region	
131.65/ 7.63	C,H from phthalic moiety
131.22/ 7.61	$C_{2,6}$, $H_{2,6}$ in P units with esterified 4-OH
129.21/ 5.32	Unidentified
128.84/ 7.69	C,H from phthalic moity
128.81/ 7.76	C,H from phthalic moity
128.24/ 7.65	$C_{2,6}$, $H_{2,6}$ in P units esterified at C-4
127.64/ 5.31	unidentified
118.78/ 7.34	C_{β}, H_{β} in P units with esterified γ-OH and α,β unsaturation
118.48/ 6.76	C_{β}, H_{β} in P units with esterified γ-OH and α,β unsaturation
115.25/ 6.94	C_{β}, H_{β} in ferulates
114.94/ 6.76	C_{β}, H_{β} in ferulates
109.86/ 6.92	unidentified
106.02/ 7.34	$C_{2,6}$, $H_{2,6}$ in P units with carbonyl at α position of side chain
105.78/ 6.18	$C_{2,6}$, $H_{2,6}$ in S units with carbonyl at α position of side chain
104.29/ 6.49	$C_{2,6}$, $H_{2,6}$ in S units with carbonyl at α position of side chain
103.92/ 6.55	$C_{2,6}$, $H_{2,6}$ in S units
Side Chain Region	
88.64/ 4.14	unidentified
84.78/ 4.63	C_{β}, H_{β} in β-O-4
81.03/ 4.78	Furanose-OH
71.82/ 4.92	C_{α}, H_{α} in β-O-4
70.82/ 3.84	Pyranose -OH
70.79/ 4.17	Pyranose -OH
63.71/ 3.33	C_{γ}, H_{γ} with esterified γ-OH
55.45/ 3.73	methoxy
55.29/ 4.56	unidentified
53.37/ 3.07	C_{β}, H_{β} in β-1
52.06/ 3.80	C_{β}, H_{β} in β-1
50.90/ 3.54	unidentified
Alkyl Region	
39.57/ 2.49	solvent
33.40/ 2.19	Benzylic CH_2
33.11/ 2.26	Benzylic CH_2
30.08/ 1.36	Benzylic CH_2
26.22/ 1.99	CH signals in extractives and aliphatic lignin chains
24.97/ 2.73	CH signals in extractives and aliphatic lignin chains
20.64/ 1.92	CH signals in extractives and aliphatic lignin chains
14.85/ 1.09	High field alkyls
13.67/ 0.89	High field alkyls
13.62/ 1.15	High field alkyls

[1] Chemical shifts are reported in ppm[3]

References

1. G. Glasser Wolfgang and K. Jain Rajesh, *Holzforschung*, 1993, **47**, 225.
2. S. Li and K. Lundquist, *Nord. Pulp Pap. Res. J.*, 1994, **9**, 191-195.
3. J. J. Bozell, C. J. O'Lenick and S. Warwick, *J. Agri. Food Chem.*, 2011, **59**, 9232-9242.