Supplementary Materials

Unfolding of Lignin Structure Using Size-Exclusion Fractionation

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List of Figures and Tables

Table S1. Calibration data for PS, PMMA standards obtained for analytical SEC

TYPE	MW	log MW	tr, min
PMMA	550	2.740363	9.783
PMMA	960	2.982271	9.404
PMMA	1780	3.25042	8.739
PMMA	2800	3.447158	8.401
PMMA	4640	3.666518	8.019
PMMA	6850	3.835691	7.710
PMMA	10280	4.011993	7.338
PMMA	17810	4.250664	6.856
PMMA	26080	4.416308	6.550
PS	580	2.763428	9.675
PS	1480	3.170262	8.879
PS	2340	3.369216	8.496
PS	5030	3.701568	7.860
PS	8450	3.926857	7.395
PS	19760	4.295787	6.655

Figure S1. Calibration curve for PS, PMMA standards obtained for analytical SEC separation

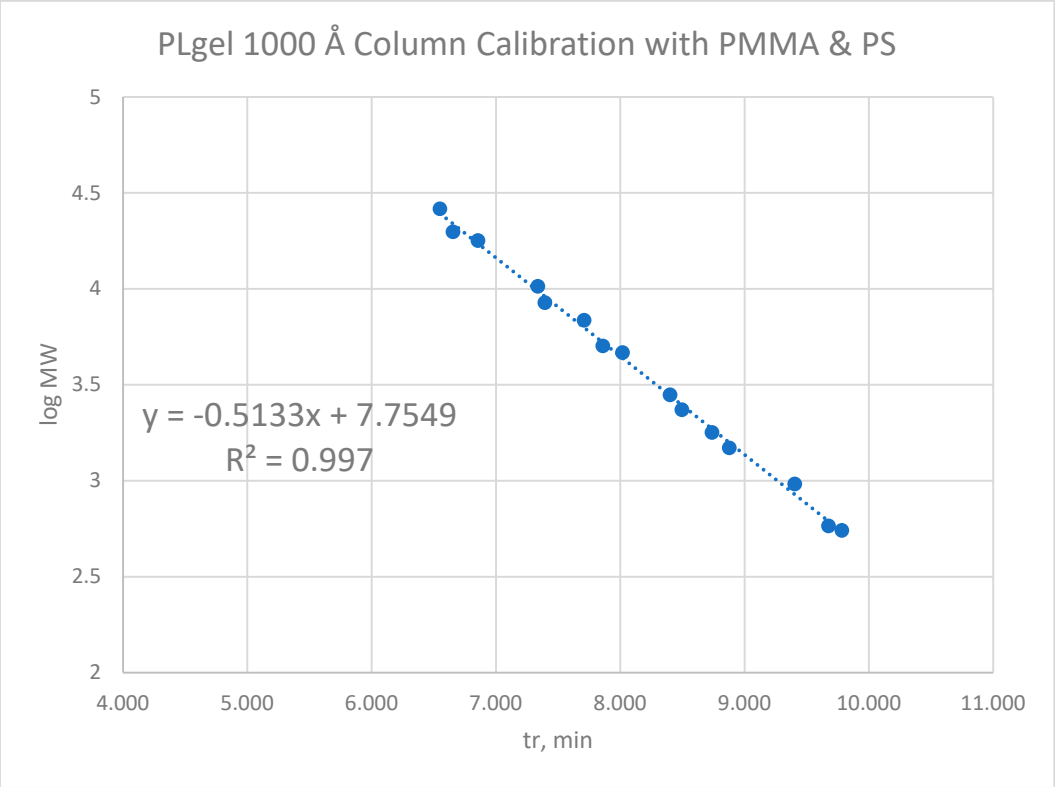
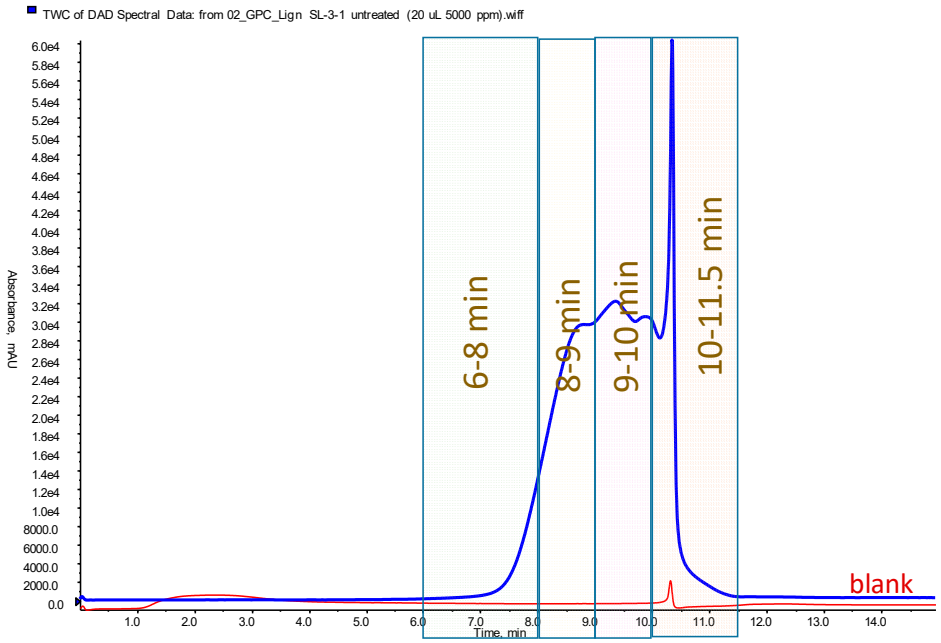
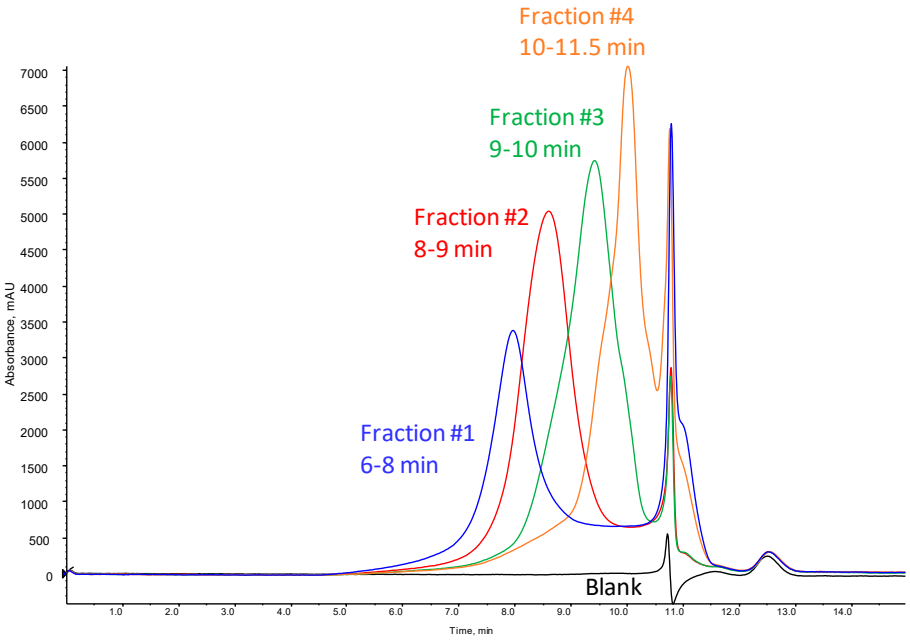


Figure S2. SEC preparative and analytical chromatograms for preliminary fractionation experiments

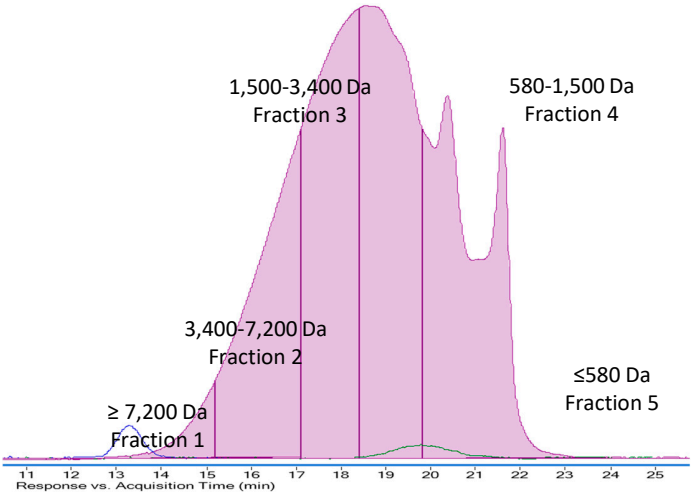
a) Preparation SEC - Fractionation 1 – focus on specific MW (not equal time intervals)



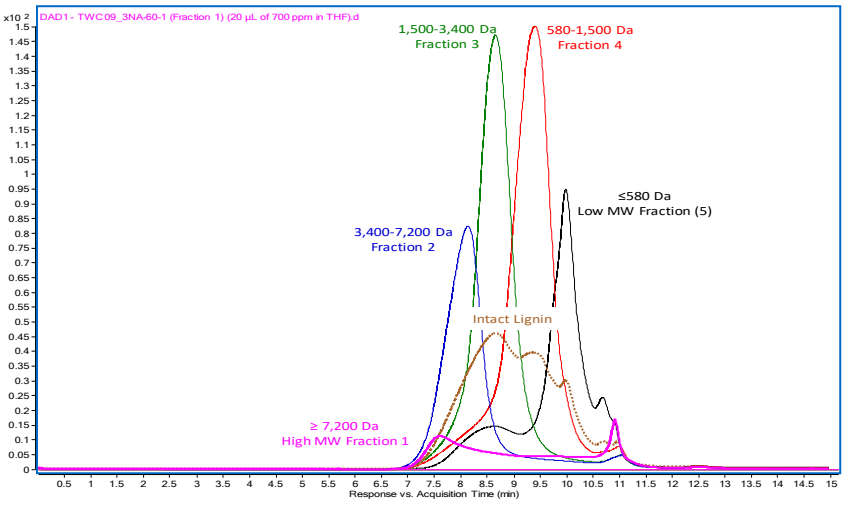
b) Analytical SEC - Fractionation 1 – focus on specific MW (not equal time intervals)



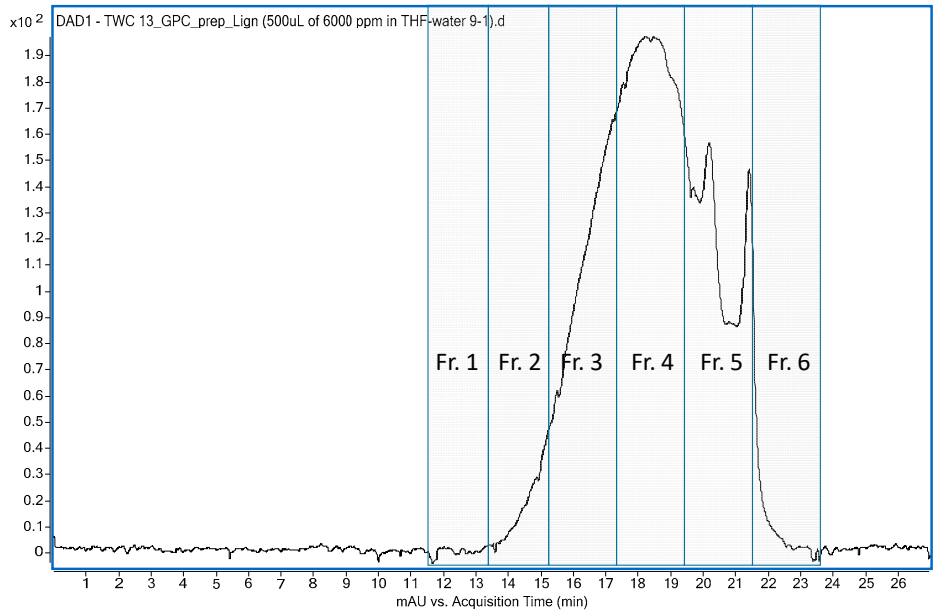
c) Preparation SEC - Fractionation 2 – focus on specific MW (not equal time intervals)



d) Analytical SEC - Fractionation 2 – focus on specific MW (not equal time intervals)



e) Preparation SEC - Fractionation 3– including pre and post-eluate



f) Analytical SEC - Fractionation 3 – – including pre and post-eluate

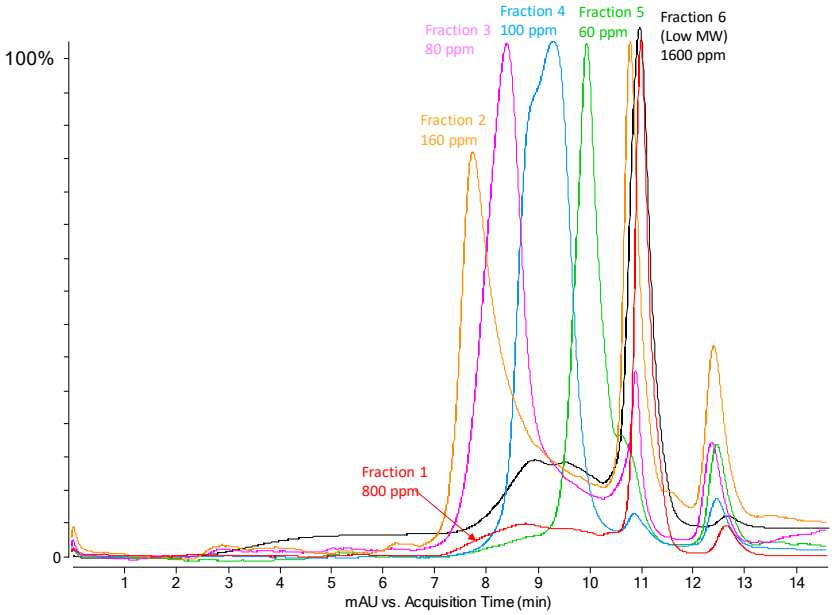


Table S2. MW characterization of the five fractions obtained by preparative SEC and unfractionated alkali lignin conducted with ESI-TOF HR MS.

	ESI-TOF HR TOF MS					
Fractions	**1**	**2**	**3**	**4**	**5**	**Alkali Lignin**
M_n	1330	1634	1028	1188	522	869
M_w	3160	3547	2266	2853	1335	1881
M_z	5261	5557	4500	4820	3321	3767
PDI	2.4	2.2	2.2	2.4	2.6	2.2

Figure S3. ESI-TOF HR MS spectra for SEC lignin fractions 1 – 5

MS data shown as the direct acquisition (m/z) and upon deconvolution (Da). All fractions were diluted 5 times except fraction 1, which was diluted 2 times.

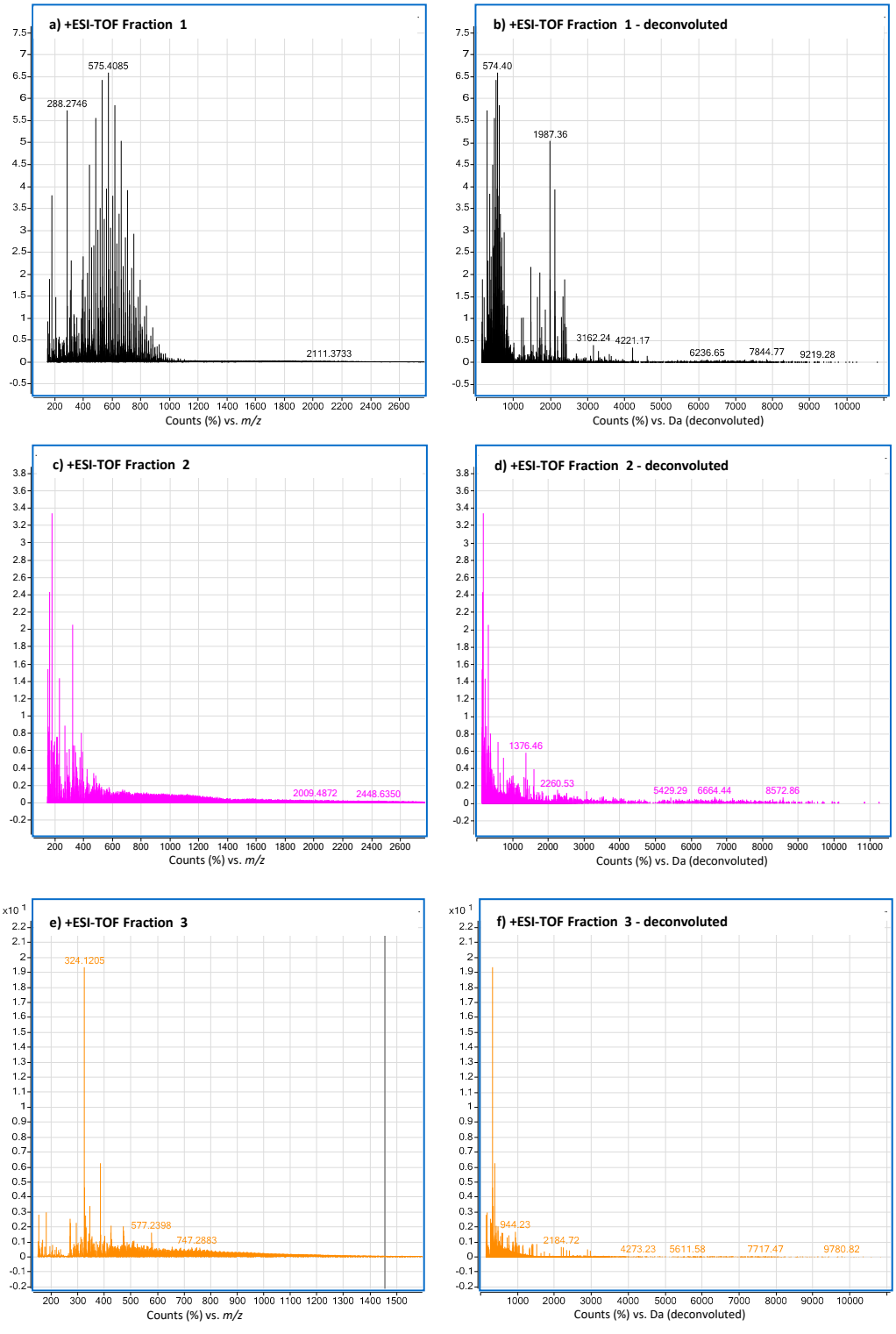


Figure S3 count.

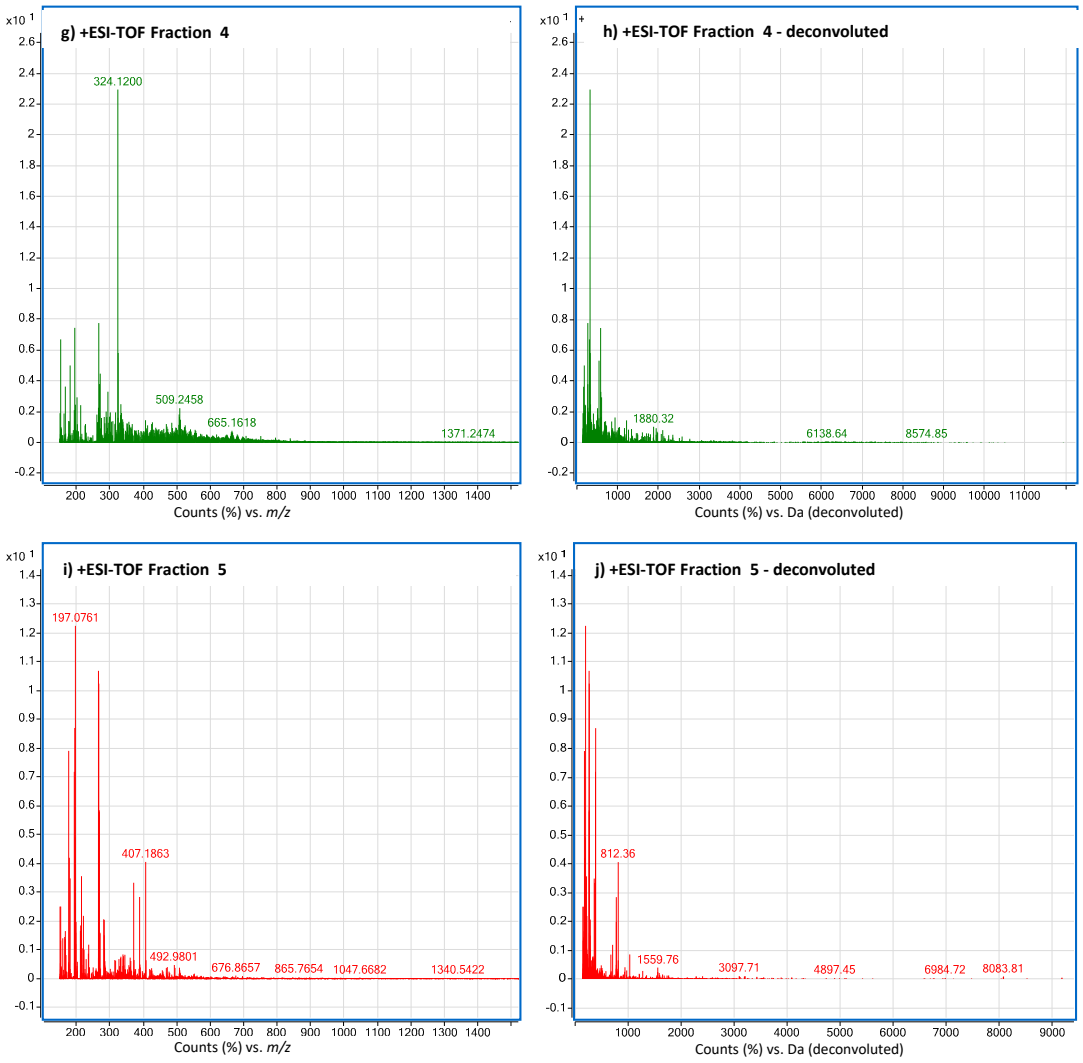


Figure S4. Aggregated TD-Py-GC-MS peak areas based on the GC-MS TIC response

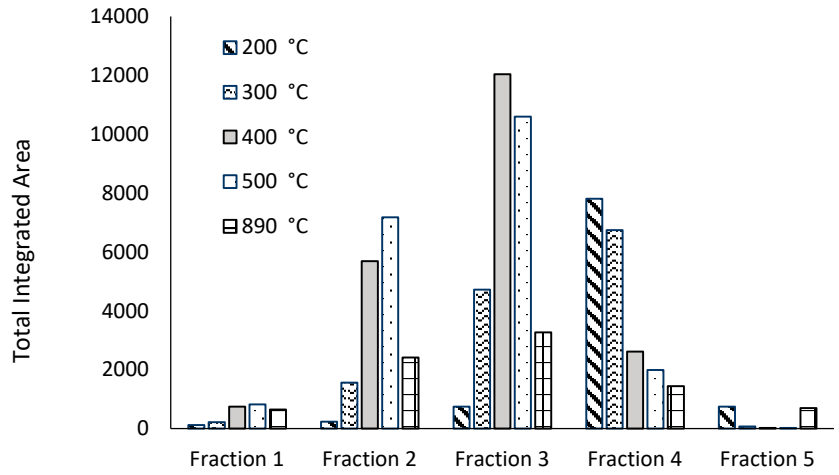


Figure S5. TD-Py-GC-MS profiles for each SEC fraction based on the TIC peak areas response

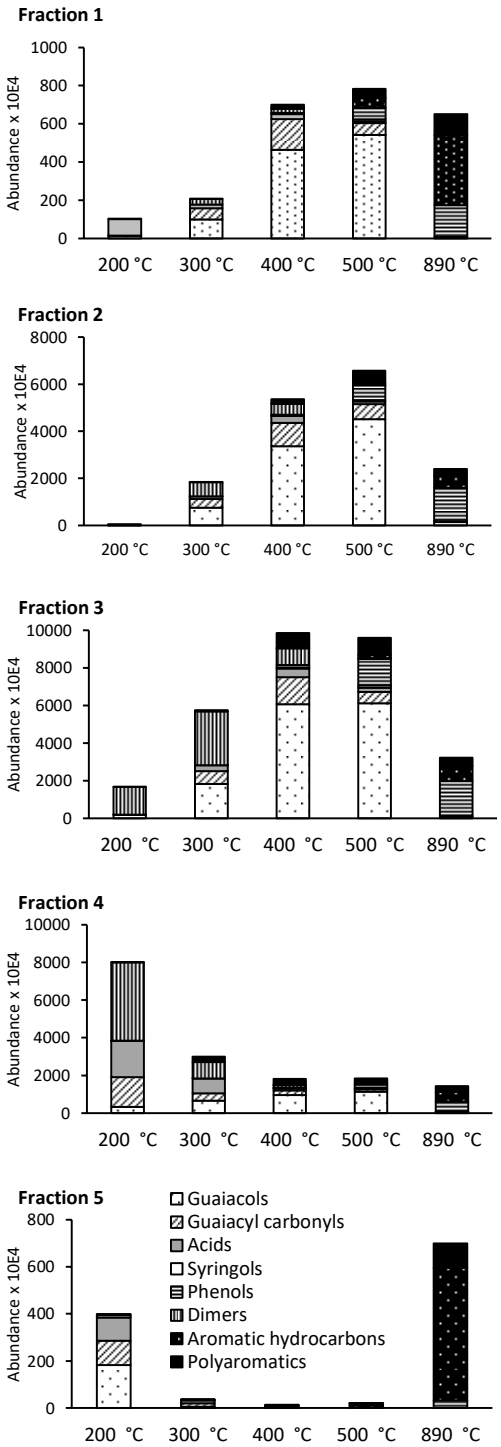


Figure S6. ^{31}P NMR spectra of SEC weight fractionated lignin samples.

The top spectrum belongs to the lowest molecular weight fraction, 3NA-81-6, while the second spectrum from the bottom is for the highest molecular weight fraction, 3-NA-2. The bottom spectrum is a pre-eluate fraction comprised mostly of impurities of carbohydrate origins.

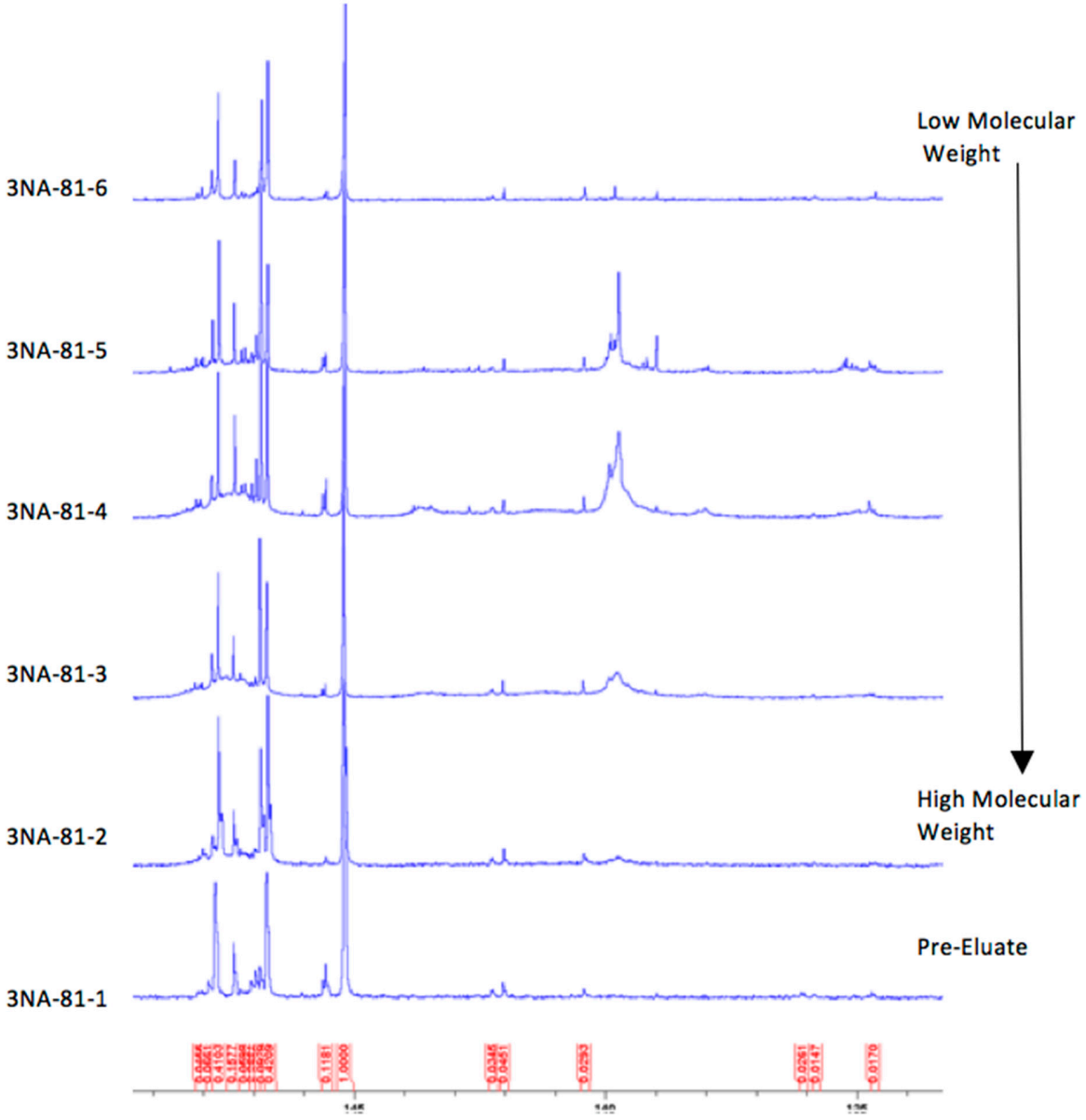
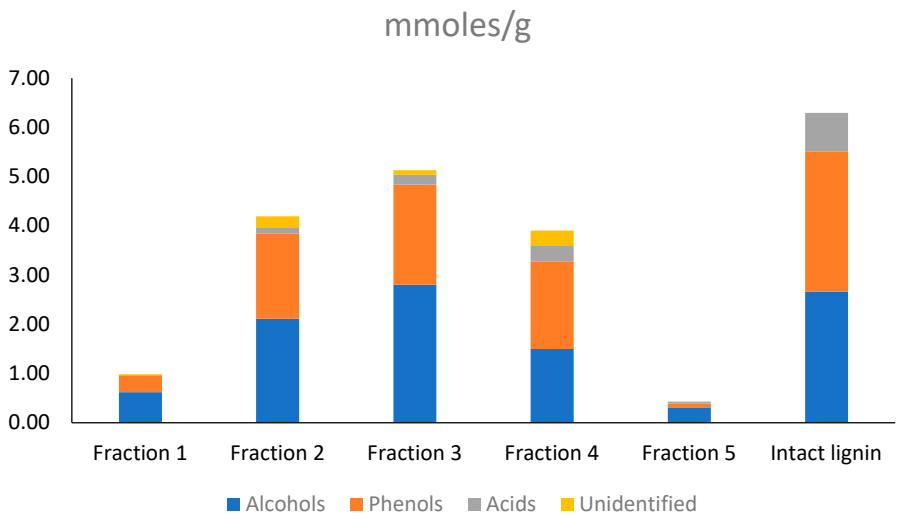


Figure S7. Relative abundance of characteristic functional groups determined by ^{31}P NMR

a) Relative abundance



b) Normalized