Supporting Information

UNDERSTANDING THE EFFECT OF CHEMICAL MODIFICATION ON THE THERMAL BEHAVIOUR OF LIGNIN

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TGA curves



Figure S1. Weigh lost as function of the temperature of (a) OSL and (b) ML lignin.

TGA-FTIR analysis



Figure S2. Evolution of the FTIR spectra at selected temperatures of (a) OSL and (b) ML.



Figure S3. F-TIR spectra of (a) OSL and (b) ML recorded at specific temperatures relating to the maximum formation of each respective species.

(a)

Vibration	Band (cm ⁻¹)	Chemical group	LTA	ML
V1	3390-3460	O—H stretching in Aromatic and Aliphatic groups	3404	3392
V2	3000-2840	C—H stretching of methoxy groups, methyl and methylene groups in side chains	2936	2932
V3	1705-1695	C=O stretching of conjugated aldehydes and carboxylic acids	1696	1698
V4	1590-1600, 1505- 1515, 1420-1430	Aromatic skeletal vibrations	1599, 1514, 1424	1588, 1509, 1419
V5		Aromatic methyl group vibrations	1457	1452
V6		Aliphatic C—H stretching in CH ₃	-	1376
V7		Stretching at the ring, S > G	1326	1262
V8	1210-1220	C=O and C-O stretching in ether linkage	1212	1219
V9	1152-1030	Aromatic C—H in plane deformation	1152, 1112, 1030	1138, 1027
V10	1085	C—O deformation in secondary alcohols and aliphatic ethers	-	1079
V11	930-780	Aromatic C—H out of plane	912, 826	930, 857, 807

 Table 1. Assignment for FTIR resonance bands.

¹³C-NMR analysis

Prior to the ¹³C-NMR analysis, OSL and ML lignins were acetylated in order to improve the spectral resolution in the hydroxyl region. 2 g of each lignin type was placed into a flask. Then, a solution of 20 mL of 50/50 (v/v) Acetic Anhydride/Pyridine was added. Initially, the reaction was carried out for 3 days in complete darkness at room temperature under constant stirring. After that, the temperature of the mixture was raised to 50 °C and the reaction was allowed to continue for 4 more days The sample was precipitated using an acidic (pH 2) solution composed of 240 mL of ultrapure water and 200 μ L of 37% HCl. The solution was cooled down in a crushed-ice bath. The acetylated lignin solution was added drop-wise into the precipitation solution under constant stirring. The solution was then filtered through a paper filter in a Büchner funnel. The precipitate was dried at room temperature for 24 hours under a fume hood. Finally a solution of 100 mg/ml in DMSO-d6 of each lignin was prepared. The ¹³C-NMR analysis was carried out in a Bruker DPX300 with a 5mm QNP probe operating at 300 MHz. Qualitative spectra were recorded at 50 °C using 8000 scans and 12 s of relaxation time.



Figure S4. ¹³C-NMR spectra of OSL and ML lignin. Deconvoluted signals of the acetylated hydroxyl group region (insets).