

Supporting Information

Selective lignin fractionation using CO₂-expanded 2-methyltetrahydrofuran (2-MTHF).

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Table S1: Precipitated lignin fractions for six experiments.

p(CO ₂) [bar]	w(Lignin) (1) [wt%]	w(Lignin) (2) [wt%]	w(Lignin) (3) [wt%]	w(Lignin) (4) [wt%]	w(Lignin) (5) [wt%]	w(Lignin) (6) [wt%]
0	0	0	0	0	0	0
10	13.8	12.9	12.8	19.1	15.9	18.2
20	21.2	17.8	16.7	10.8	14.8	18.0
30	7.0	11.5	13.1	11.8	10.9	16.1
40	8.7	22.7	11.0	9.3	14.0	14.0
50	15.0	10.6	17.8	10.7	6.2	10.7
Dissolved	20.6	22.3	16.2	31.4	36.2	41.1

Table S2: Chemical composition of different lignin fractions for three experiments (Exp.).

Exp.	p(CO ₂) [bar]	β -O-4 [%]	β - β [%]	β -5 [%]	H [%]	G [%]	S [%]	Monomers [%]
1	0	12.2	7.2	1.2	6.9	43.1	50.0	2.3
1	10	25.6	8.0	1.6	1.9	41.0	57.2	1.2
1	20	22.0	7.3	1.4	1.7	42.2	56.1	1.2
1	30	19.1	7.6	1.6	1.7	44.2	54.1	1.1
1	40	13.6	7.4	1.6	2.1	44.2	53.8	1.3
1	50	7.1	6.9	1.3	2.5	43.9	53.6	1.6
1	Dissolved	2.6	5.9	0.6	15.9	42.6	41.5	4.5
2	0	12.2	7.1	1.3	6.5	43.8	49.7	2.3
2	10	24.7	8.4	1.7	1.6	41.4	57.0	1.0
2	20	22.5	7.6	1.5	1.5	42.6	55.9	1.0
2	30	16.7	7.5	1.6	1.7	44.5	53.8	1.2
2	40	12.0	7.3	1.6	2.0	44.2	53.8	1.2
2	50	5.7	7.2	1.1	3.1	43.6	53.3	1.9
2	Dissolved	3.8	5.9	0.6	16.4	46.1	37.4	5.0
3	0	12.9	7.3	1.3	6.5	44.1	49.4	2.7
3	10	24.4	8.1	1.6	1.5	40.9	57.6	1.0
3	20	23.1	7.8	1.7	1.8	42.4	55.7	1.1
3	30	19.2	7.4	1.6	1.7	45.0	53.3	1.1
3	40	13.6	7.2	1.5	2.1	45.8	52.2	1.4
3	50	6.2	7.0	1.3	2.7	44.7	52.6	1.6
3	Dissolved	3.8	5.6	0.5	16.6	45.2	38.1	4.2

Table S3: Amount of hydroxy functions of different lignin fractions for three experiments.

Exp.	p(CO ₂) [bar]	H [mmol g ⁻¹]	G [mmol g ⁻¹]	S [mmol g ⁻¹]	Aliphatic-OH [mmol g ⁻¹]	COOH [mmol g ⁻¹]
δ [ppm]		140.1 - 138.8	143.5 - 141.5	145.3 - 145.0	149.0 - 145.7	135.2 - 134.4
1	0	0.048	0.732	1.783	1.594	0.292
1	10	0.048	0.673	1.597	2.468	0.112
1	20	0.047	0.727	1.841	1.947	0.120
1	30	0.053	0.807	1.966	1.912	0.114
1	40	0.045	0.871	2.166	1.643	0.131
1	50	0.054	0.930	2.540	1.193	0.124
1	Dissolved	0.064	1.015	2.523	1.221	0.558
2	0	0.055	0.770	1.941	1.614	0.246
2	10	0.040	0.639	1.533	2.453	0.108
2	20	0.042	0.637	1.536	2.135	0.164
2	30	0.057	0.810	2.142	1.969	0.112
2	40	0.051	0.848	2.247	1.731	0.126
2	50	0.050	0.896	2.491	1.397	0.156
2	Dissolved	0.076	1.051	2.735	1.344	0.459
3	0	0.036	0.701	1.733	1.546	0.319
3	10	0.046	0.695	1.628	2.555	0.105
3	20	0.037	0.705	1.697	2.253	0.112
3	30	0.047	0.792	1.900	1.989	0.138
3	40	0.044	0.834	2.128	1.524	0.129
3	50	0.044	0.803	2.238	1.108	0.143
3	Dissolved	0.059	0.938	2.334	1.472	0.533

Table S4: Mw, Mn and PDI of different lignin fractions for three experiments.

p(CO ₂) [bar]	Mw(1) [g mol ⁻¹]	Mn(1) [g mol ⁻¹]	PDI(1) []	Mw(2) [g mol ⁻¹]	Mn(2) [g mol ⁻¹]	PDI(2) []	Mw(3) [g mol ⁻¹]	Mn(3) [g mol ⁻¹]	PDI(3) []
0	2353	604	3.90	2088	564	3.70	2136	603	3.54
10	4909	3105	1.58	4182	1180	3.54	4759	2187	2.18
20	3066	1012	3.03	3087	1073	2.88	3184	1427	2.23
30	2503	1160	2.16	2065	751	2.75	2296	882	2.60
40	1658	786	2.11	1428	599	2.39	1610	680	2.37
50	1102	513	2.15	936	432	2.17	1082	475	2.28
Dissolved	552	274	2.01	572	204	2.81	612	286	2.14

Table S5: Calibration of SEC using an external standard.

No.	M [g mol ⁻¹]	t [min]
1	62500	21.18
2	42600	22.32
3	25700	23.62
4	15500	24.86
5	8670	26.45
6	6670	27.18
7	4880	27.92
8	3460	28.70
9	2250	29.70
10	1220	30.89
11	498	32.34
12	266	33.00

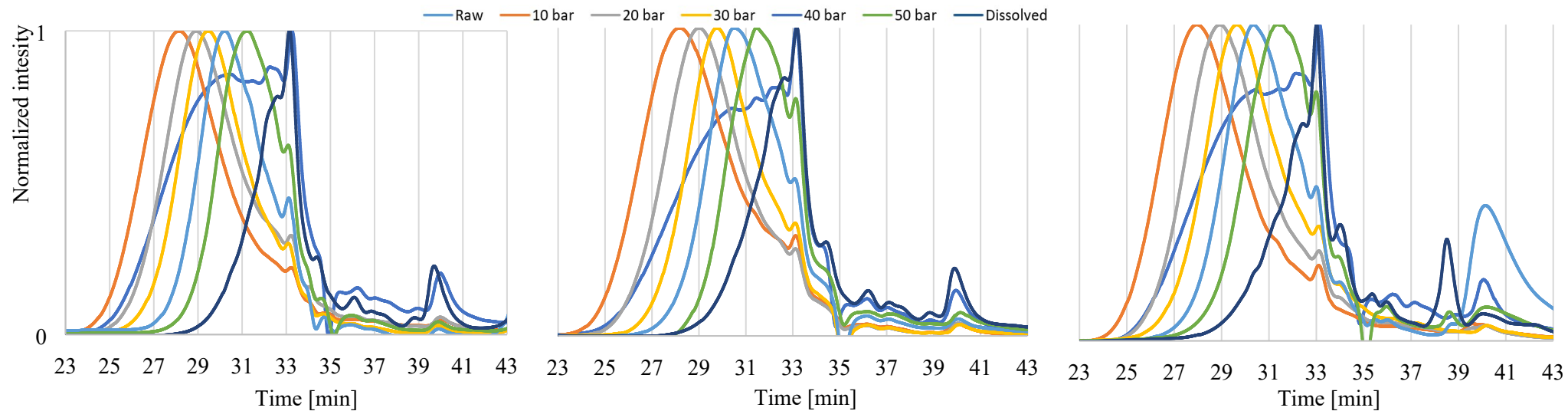


Figure S1: Size Exclusion chromatograms for different three experiments.

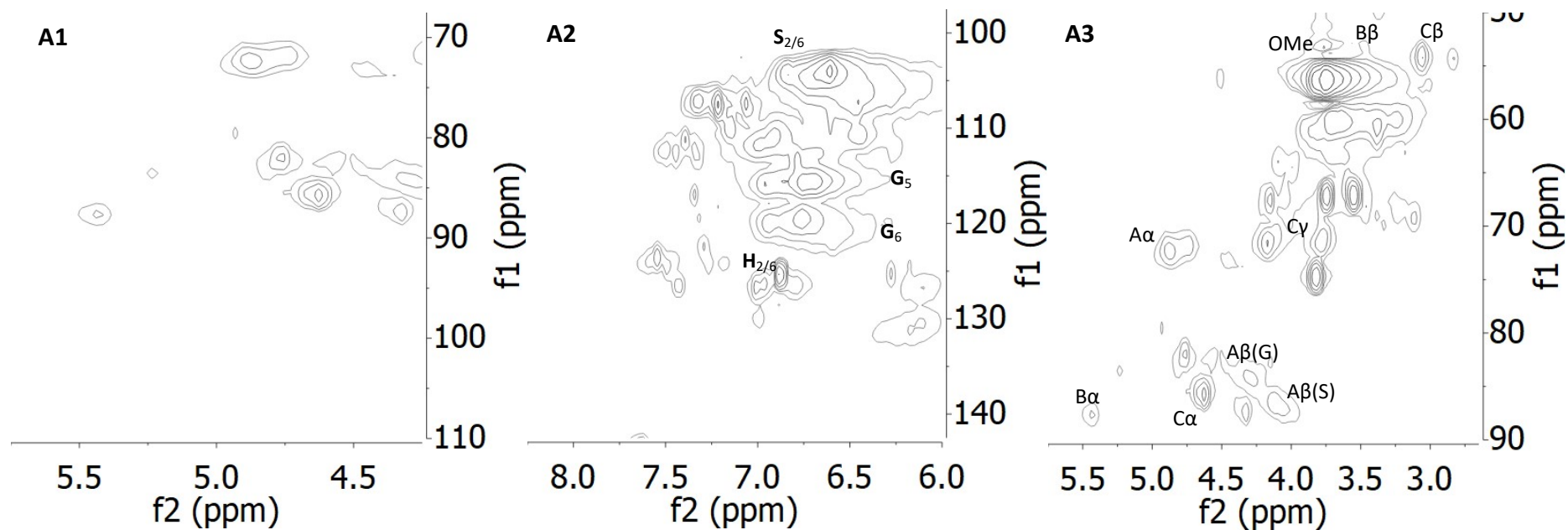


Figure S2: Expansion of HSQC NMR spectrum of OrganoCat lignin, A1 (carbohydrate region), A2 (lignin region) and A3 (aliphatic region).