

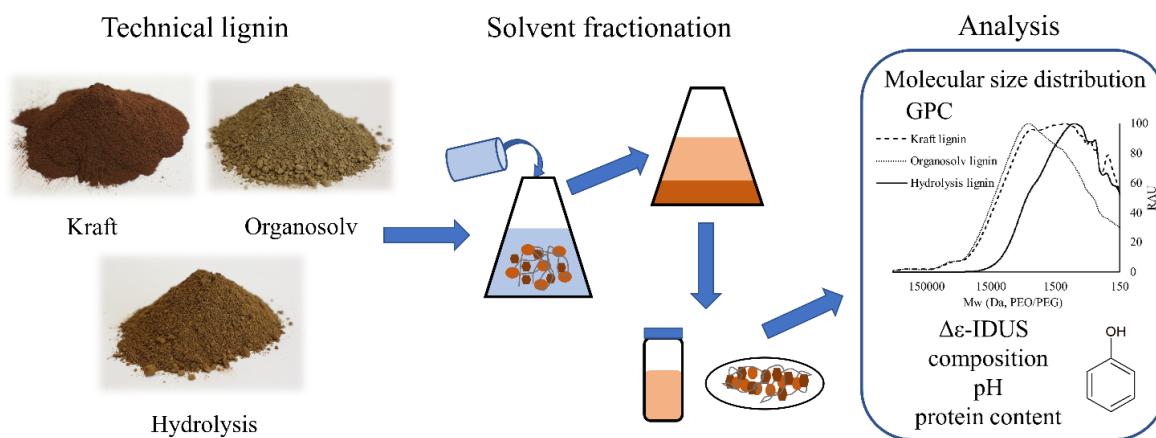
## Supplement

# Solvent Fractionation of Technical Lignin Materials with Industrially Relevant Solvents

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**Fig. S1** Illustration of the lignin solvent fractionation procedure

**Table S1** Properties of the soluble Kraft lignin fractions

Solvent	Kraft lignin soluble fractions					
	S/L* [g/L]	Dissol. [wt%]	M <sub>w</sub> [Da]	M <sub>n</sub> [Da]	PDI	OH <sub>ph</sub> [mmol <sub>OH</sub> /g <sub>lignin</sub> ]
Reference (DMF)	10	98	4 800	930	5.1	2.51
Water	10	13	1 300	370	3.5	2.20
	150	10	710	380	1.9	1.53
50% Isopropanol	10	89	2 700	650	4.1	2.67
	150	72	2 800	740	3.8	2.53
Isopropanol	10	11	560	380	1.4	1.17
	150	10	550	380	1.5	0.46
30% Ethanol	10	40	1 400	430	3.2	3.05
	150	21	1 000	440	2.3	2.56
70% Ethanol	10	88	3 100	700	4.4	2.81
	150	70	2 500	740	3.4	2.58
Ethanol	10	37	1 600	460	3.5	2.58
	150	23	680	440	1.6	2.27
Dimethyl sulfoxide	10	99	4 500	920	4.8	2.55
30% γ-valerolactone	10	47	850	410	2.1	2.64
70% γ-valerolactone	10	99	3 400	720	4.8	2.78
γ-valerolactone	10	93	3 200	850	3.7	2.43
90% Sulfolane	10	98	3 800	760	4.9	2.67

\* S/L: Solid/Liquid, initial solid concentration

**Table S2** Properties of the soluble organosolv lignin fractions

Solvent	Organosolv lignin soluble fractions					
	S/L* [g/L]	Dissol. [wt%]	M <sub>w</sub> [Da]	M <sub>n</sub> [Da]	PDI	OH <sub>ph</sub> [mmol <sub>OH</sub> /g <sub>lignin</sub> ]
Reference (DMF)	10	97	5 800	1 200	4.7	2.30
Water	10	4	1 200	410	2.9	0.34
	150	1	640	270	2.4	0.26
50% Isopropanol	10	54	1 600	620	2.6	2.46
	150	34	1 000	460	2.3	2.14
Isopropanol	10	17	620	410	1.5	2.14
	150	10	520	350	1.5	1.29
30% Ethanol	10	13	880	390	2.2	2.21
	150	4	500	310	1.6	1.78
70% Ethanol	10	59	1 900	680	2.8	2.55
	150	38	1 200	510	2.4	2.48
Ethanol	10	31	930	510	1.8	2.52
	150	18	740	450	1.6	2.74
Dimethyl sulfoxide	10	97	5 700	1 200	4.7	2.32
30% $\gamma$ -valerolactone	10	27	910	450	2.0	1.81
70% $\gamma$ -valerolactone	10	95	3 900	780	5.0	2.05
$\gamma$ -valerolactone	10	92	5 900	1 200	4.8	2.29
90% Sulfolane	10	92	5 600	1 100	5.4	2.41

\*S/L: Solid/Liquid, initial solid concentration

**Table S3** Properties of the soluble hydrolysis lignin fractions

Solvent	Hydrolysis lignin soluble fractions					
	S/L* [g/L]	Dissol. [wt%]	M <sub>w</sub> [Da]	M <sub>n</sub> [Da]	PDI	OH <sub>ph</sub> [mmol <sub>OH</sub> /g <sub>lignin</sub> ]
Reference (DMF)	10	32	1 800	700	2.6	1.95
Water	10	5	740	350	2.1	0.52
	150	7	480	260	1.8	1.03
50% Isopropanol	10	20	1 000	470	2.2	2.51
	150	16	690	370	1.9	2.20
Isopropanol	10	10	500	360	1.4	1.71
	150	12	480	310	1.5	0.77
30% Ethanol	10	12	910	380	2.4	2.49
	150	8	500	300	1.7	1.67
70% Ethanol	10	23	1 100	500	2.2	2.56
	150	16	780	400	1.9	2.10
Ethanol	10	16	750	440	1.7	2.27
	150	15	550	360	1.5	2.16
Dimethyl sulfoxide	10	33	1 900	720	2.7	2.21
30% $\gamma$ -valerolactone	10	17	820	430	1.9	1.97
70% $\gamma$ -valerolactone	10	30	1 700	590	2.8	1.56
$\gamma$ -valerolactone	10	19	1 400	640	2.3	0.90
90% Sulfolane	10	22	1 900	670	2.8	2.70

\* S/L: Solid/Liquid, initial solid concentration

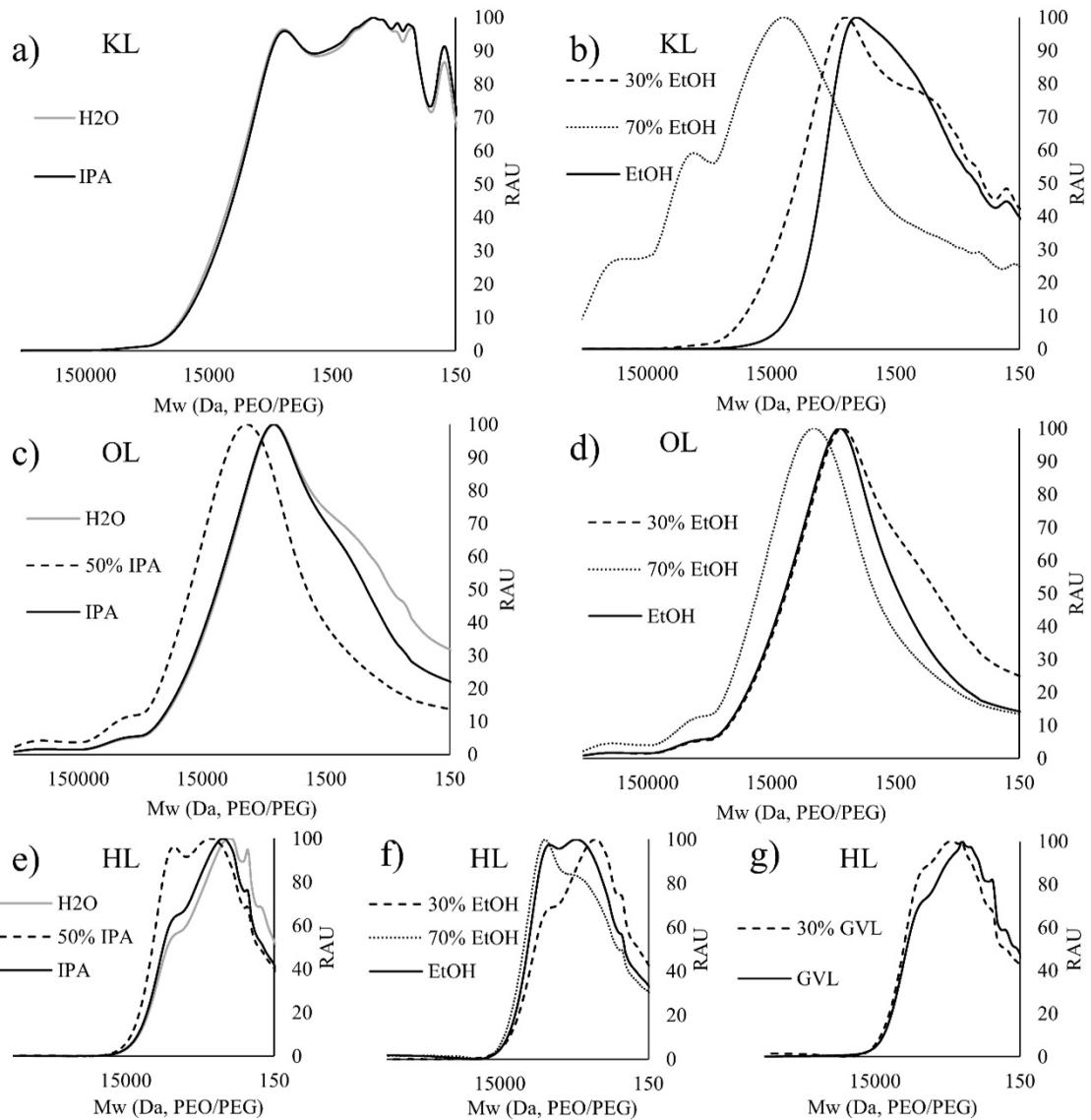
**Table S4** Properties of the insoluble lignin fractions. The initial solid concentration 10 g/L

Solvent	Kraft			Organosolv			Hydrolysis		
	M <sub>w</sub> [Da]	M <sub>n</sub> [Da]	PDI	M <sub>w</sub> [Da]	M <sub>n</sub> [Da]	PDI	M <sub>w</sub> [Da]	M <sub>n</sub> [Da]	PDI
Water	3 300	820	4.0	5 400	1 200	4.5	1 800	670	2.7
50% Isopropanol	N/A*	N/A	N/A	9 800	2 100	4.8	2 400	880	2.7
Isopropanol	3 200	810	4.0	5 900	1 400	4.2	1 900	750	2.6
30% Ethanol	3 900	1 000	3.8	5 800	1 300	4.4	2 100	770	2.7
70% Ethanol	20 000	2 100	9.6	10 000	2 100	4.8	2 700	1 000	2.7
Ethanol	2 400	920	2.6	6 800	1 700	3.7	2 400	930	2.5
30% $\gamma$ -valerolactone	N/A	N/A	N/A	N/A	N/A	N/A	2 300	860	2.7
$\gamma$ -valerolactone	N/A	N/A	N/A	N/A	N/A	N/A	2 100	780	2.8

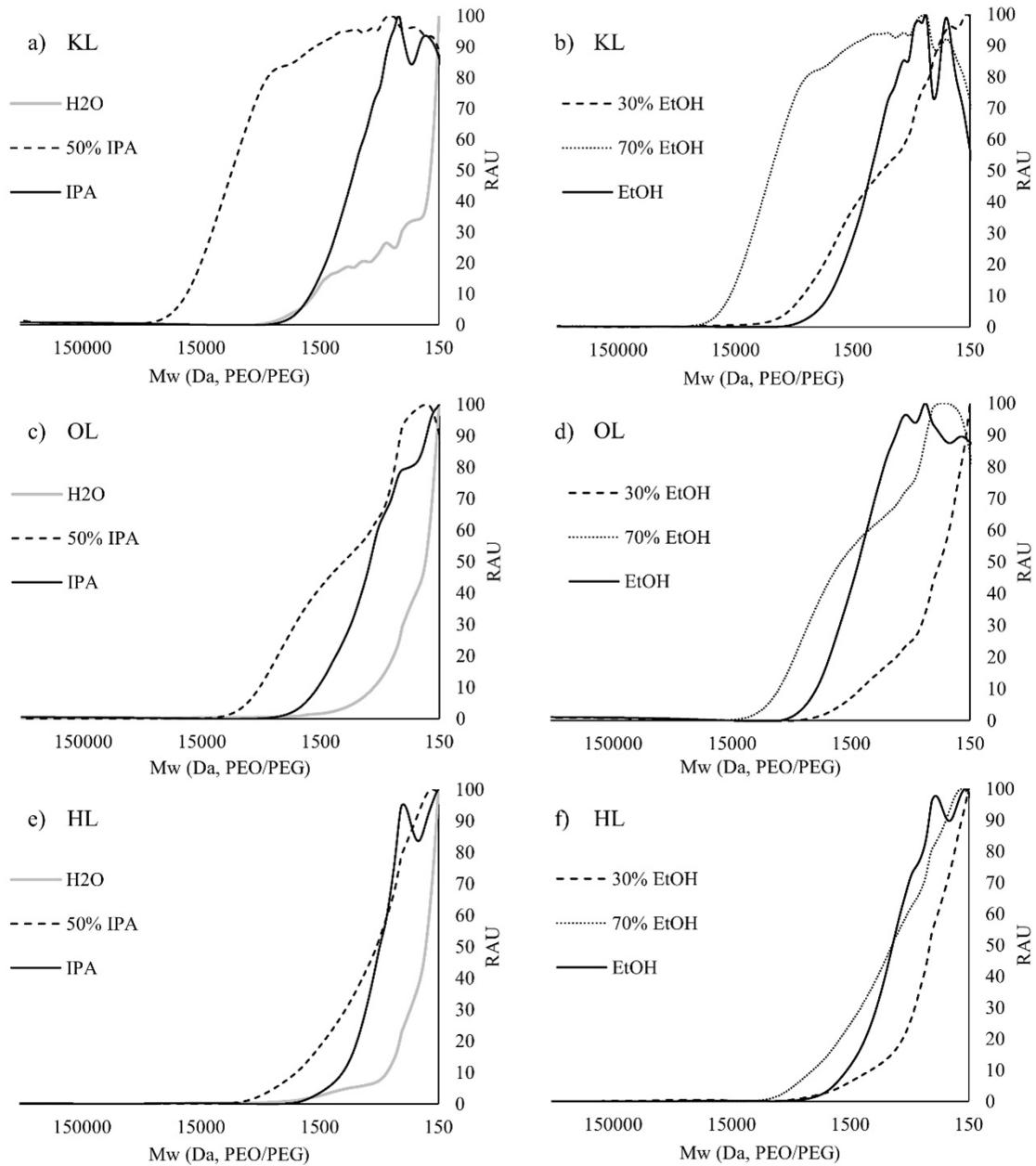
\* N/A: Not applicable, measurement did not give feasible results.

**Table S5** Properties of the insoluble lignin fractions. The initial solid concentration 150 g/L

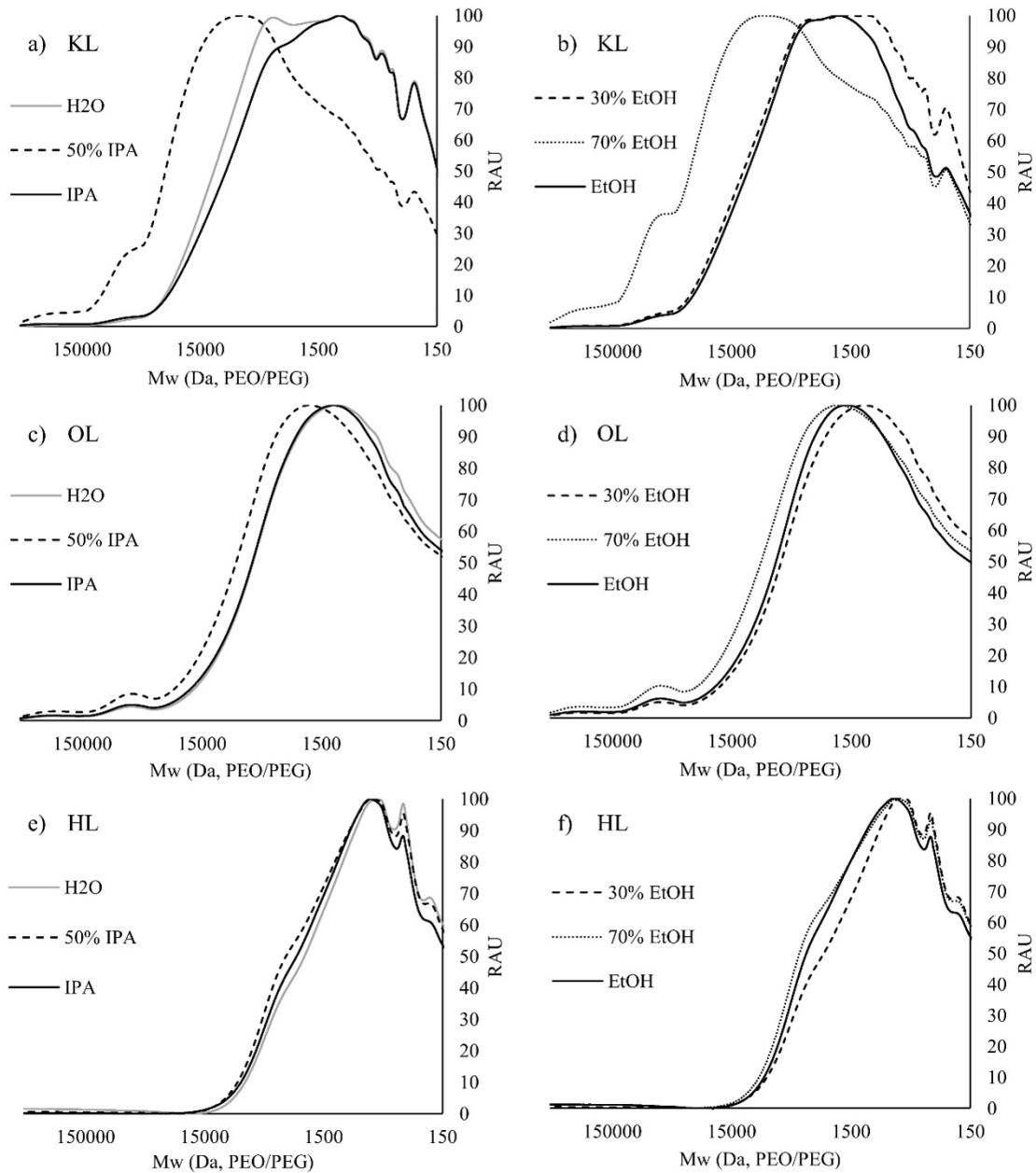
Solvent	Kraft			Organosolv			Hydrolysis		
	M <sub>w</sub> [Da]	M <sub>n</sub> [Da]	PDI	M <sub>w</sub> [Da]	M <sub>n</sub> [Da]	PDI	M <sub>w</sub> [Da]	M <sub>n</sub> [Da]	PDI
Water	3 900	930	4.2	3 300	800	4.1	1 300	580	2.2
50% Isopropanol	9 800	1 500	6.6	4 600	930	5.0	1 500	630	2.4
Isopropanol	3 900	880	4.4	3 500	830	4.3	1 400	620	2.3
30% Ethanol	4 600	990	4.7	3 500	820	4.3	1 400	610	2.4
70% Ethanol	11 000	1 400	7.6	5 100	950	5.4	1 600	660	2.5
Ethanol	4 600	1 100	4.3	4 000	900	4.5	1 500	660	2.3



**Fig. S2** Normalized size distributions of the insoluble fractions: (a) Kraft lignin (KL) water and pure IPA insoluble fractions, (b) KL 30%, 70% and pure EtOH insoluble fractions, (c) organosolv lignin (OL) water, 50% and pure IPA insoluble fractions, (d) OL 30%, 70% and pure EtOH insoluble fractions, (e) hydrolysis lignin (HL) water, 50% and pure IPA insoluble fractions, (f) HL 30%, 70% and pure EtOH insoluble fractions and (g) HL 30% and pure GVL insoluble fractions. The initial solid concentration 10 g/L



**Fig. S3** Normalized size distributions of the soluble fractions: (a) Kraft lignin (KL) water, 50% and pure IPA soluble fractions, (b) KL 30%, 70% and pure EtOH soluble fractions, (c) organosolv lignin (OL) water, 50% and pure IPA soluble fractions, (d) OL 30%, 70% and pure EtOH soluble fractions, (e) hydrolysis lignin (HL) water, 50% and pure IPA soluble fractions, (f) HL 30%, 70% and pure EtOH soluble fractions. The initial solid concentration 150 g/L



**Fig. S4** Normalized size distributions of the insoluble fractions: (a) Kraft lignin (KL) water, 50% and pure IPA insoluble fractions, (b) KL 30%, 70% and pure EtOH insoluble fractions, (c) organosolv lignin (OL) water, 50% and pure IPA insoluble fractions, (d) OL 30%, 70% and pure EtOH insoluble fractions, (e) hydrolysis lignin (HL) water, 50% and pure IPA insoluble fractions, (f) HL 30%, 70% and pure EtOH insoluble fractions. The initial solid concentration 150 g/L