Supplementary

High-purity lignin from selective biomass fractionation with ternary deep eutectic solvents

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Contents

1. Preparation and characterization of DES

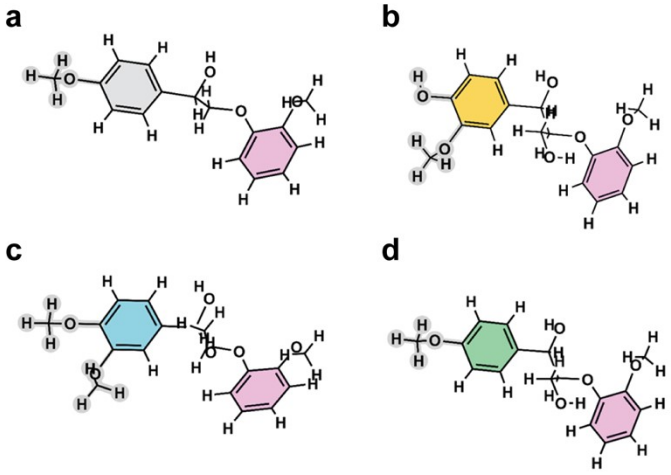

Fig. S1: a – d. β-O-4 Lignin model compounds for molecular simulations and theoretical calculations.

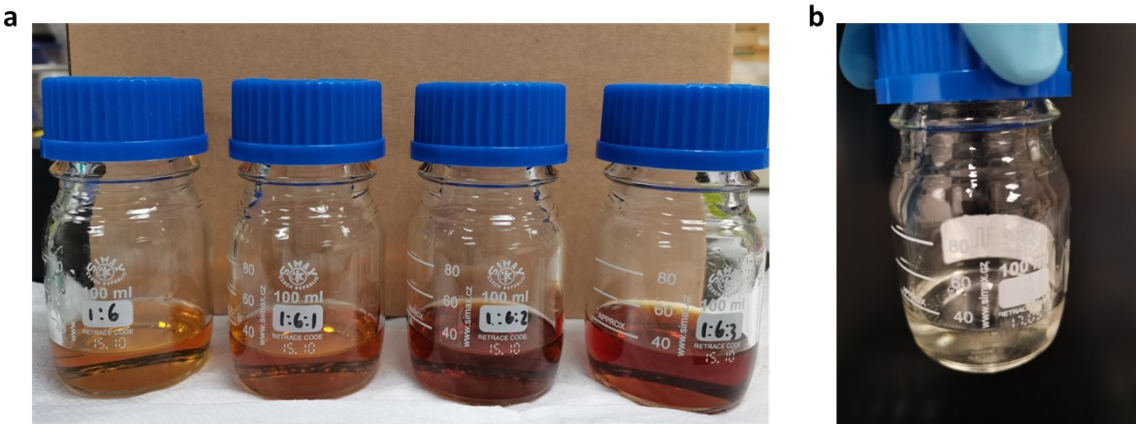

Fig. S2: Image of **a.** prepared BDES and TDES samples based on alanine, lactic acid, and ethylene glycol at different molar ratios, and **b.** lactic acid, tartaric acid, and choline chloride at molar ratio 4:1:1.

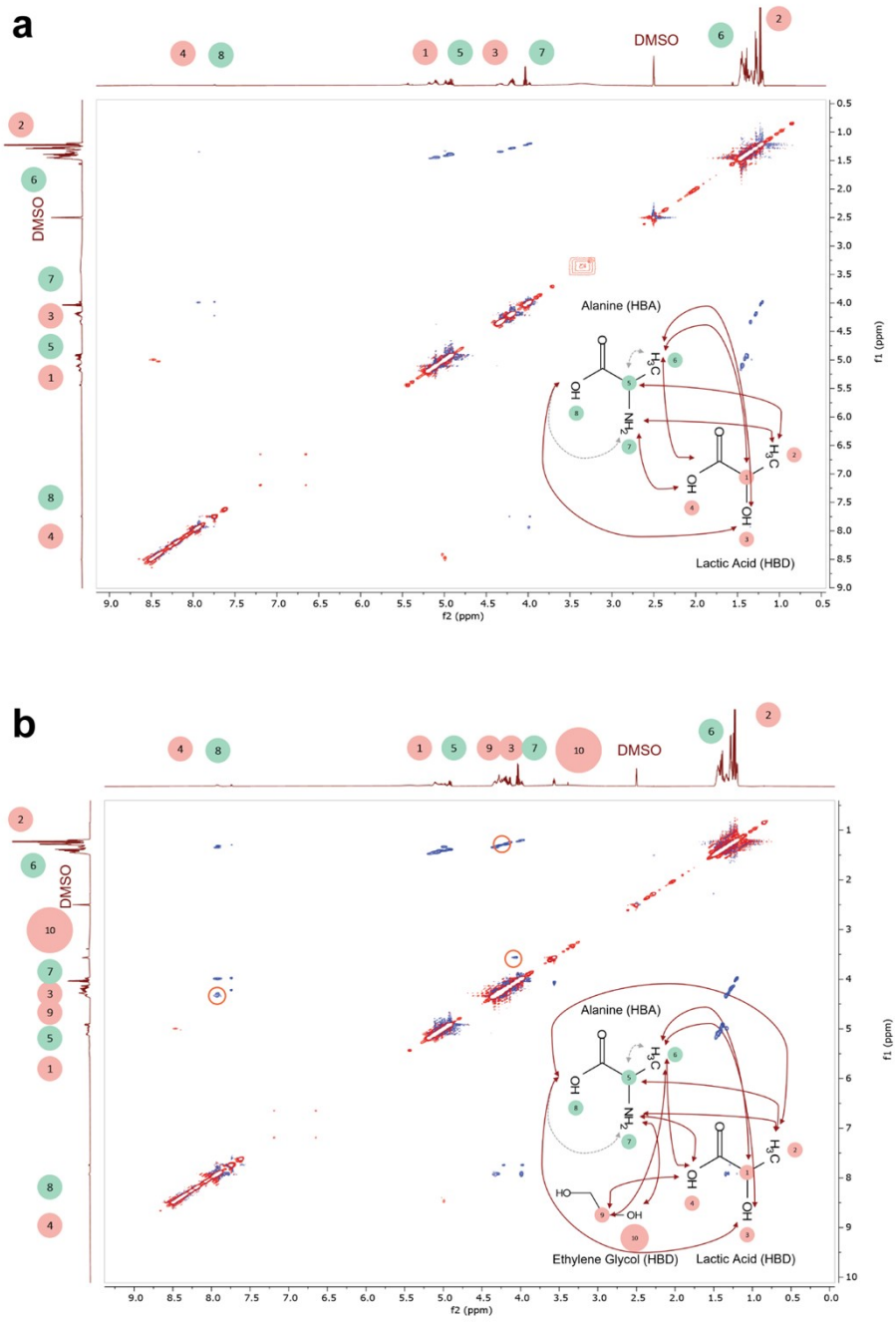

Fig. S3: ^{1}H-^{1}H 2D NOESY NMR spectra of **a.** BDES and **b.** TDES with illustration of intramolecular and intermolecular hydrogen bond interactions.

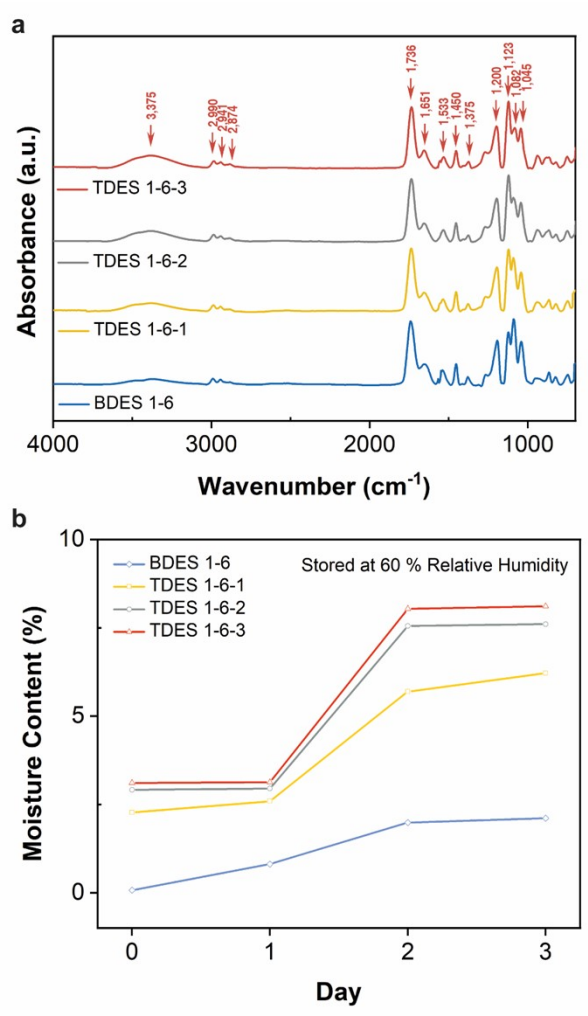

Fig. S4: a. ATR-FTIR spectra and **b.** moisture stability of deep eutectic solvent samples (stored in relative humidity 60 % and 24 °C).

Table S1: DSC & rheological analysis results of DES samples.

Sample	DSC Analysis		Viscosity (cP at 80 °C)
	Glass Transition Temperature (°C)	Vitrification Temperature (°C)	
BDES 1-6	-10.1	-	21.2
TDES 1-6-1	-61.7	-	80.7
TDES 1-6-2	-59.2	-	39.1
TDES 1-6-3	-56.8	-8.1	25.9

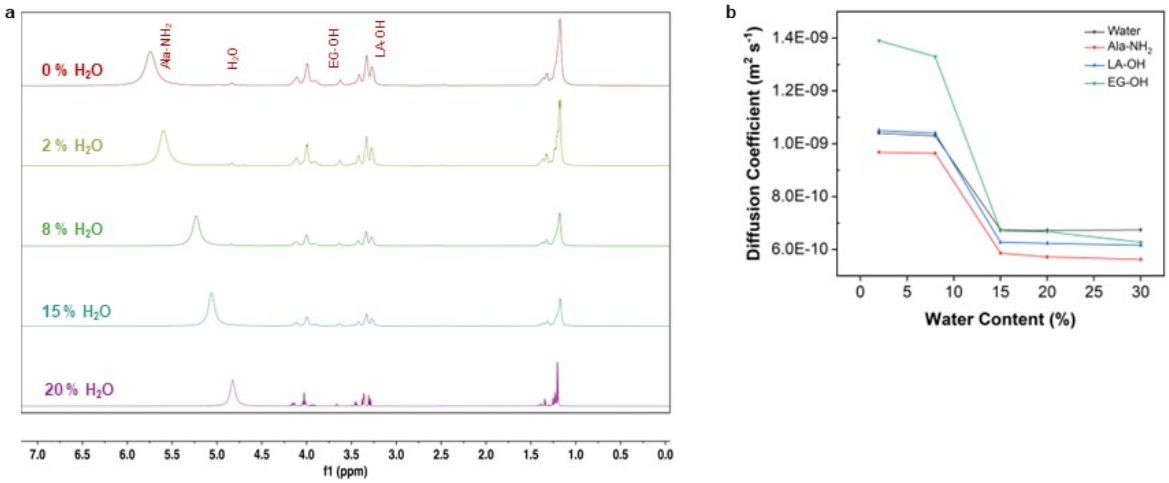

Fig. S5: a. ^{1}H {^{13}C-decoupled} NMR spectra and **b.** diffusion coefficient determined from ^{1}H DOSY NMR analysis of TDES 1-6-3 with different water content.

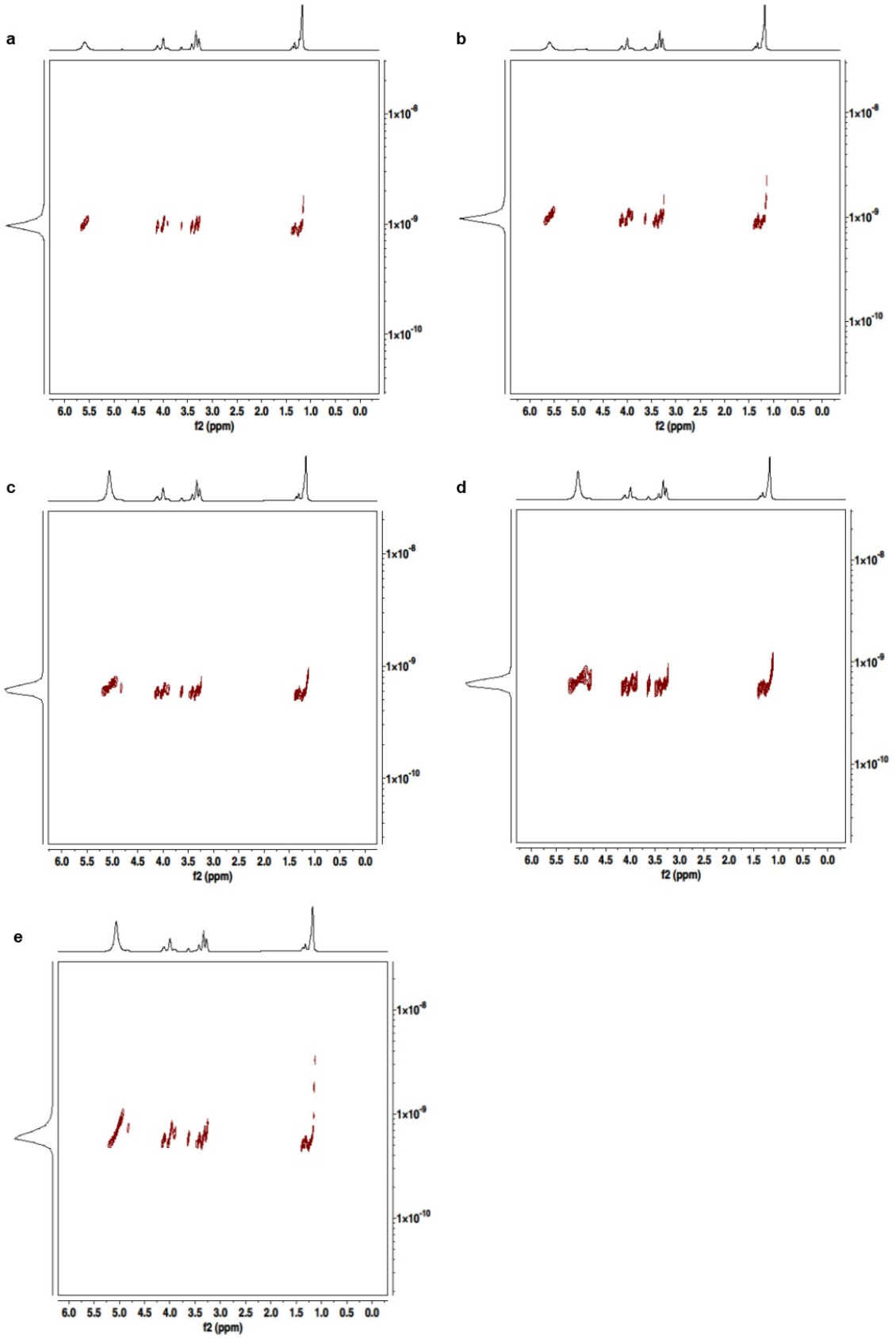

Fig. S6: ^{1}H DOSY NMR spectra (Bayesian transform) of TDES 1-6-3 with **a.** 2 %, **b.** 8 %, **c.** 15 %, **d.** 20 %, and **e.** 30 % w/w water content.

2. DES dissolution of ground rice husks

Table S2: DES dissolution selectivity in rice husk pre-treatment.

	Untreated Rice Husk	BDES 1-6 Treated			TDES 1-6-1 Treated			TDES 1-6-2 Treated			TDES 1-6-3 Treated		
		1	2	3	1	2	3	1	2	3	1	2	3
Hemicellulose (%)	23.4	59.1	35.0	37.5	51.5	34.6	30.2	42.1	44.1	38.2	45.4	41.5	20.5
Cellulose (%)	36.5	29.1	49.2	45.4	32.9	50.8	48.0	36.0	41.4	42.9	34.8	42.6	57.7
Lignin (%)	27.1	11.2	10.1	11.2	5.6	9.1	14.4	7.8	10.0	12.7	6.7	10.9	13.2
Ash (%)	13.0	0.6	5.7	5.9	10.0	5.5	7.4	14.1	4.5	6.2	13.1	5.0	8.6

[a] DES was recycled for two more cycles of pretreatment of new rice husks samples

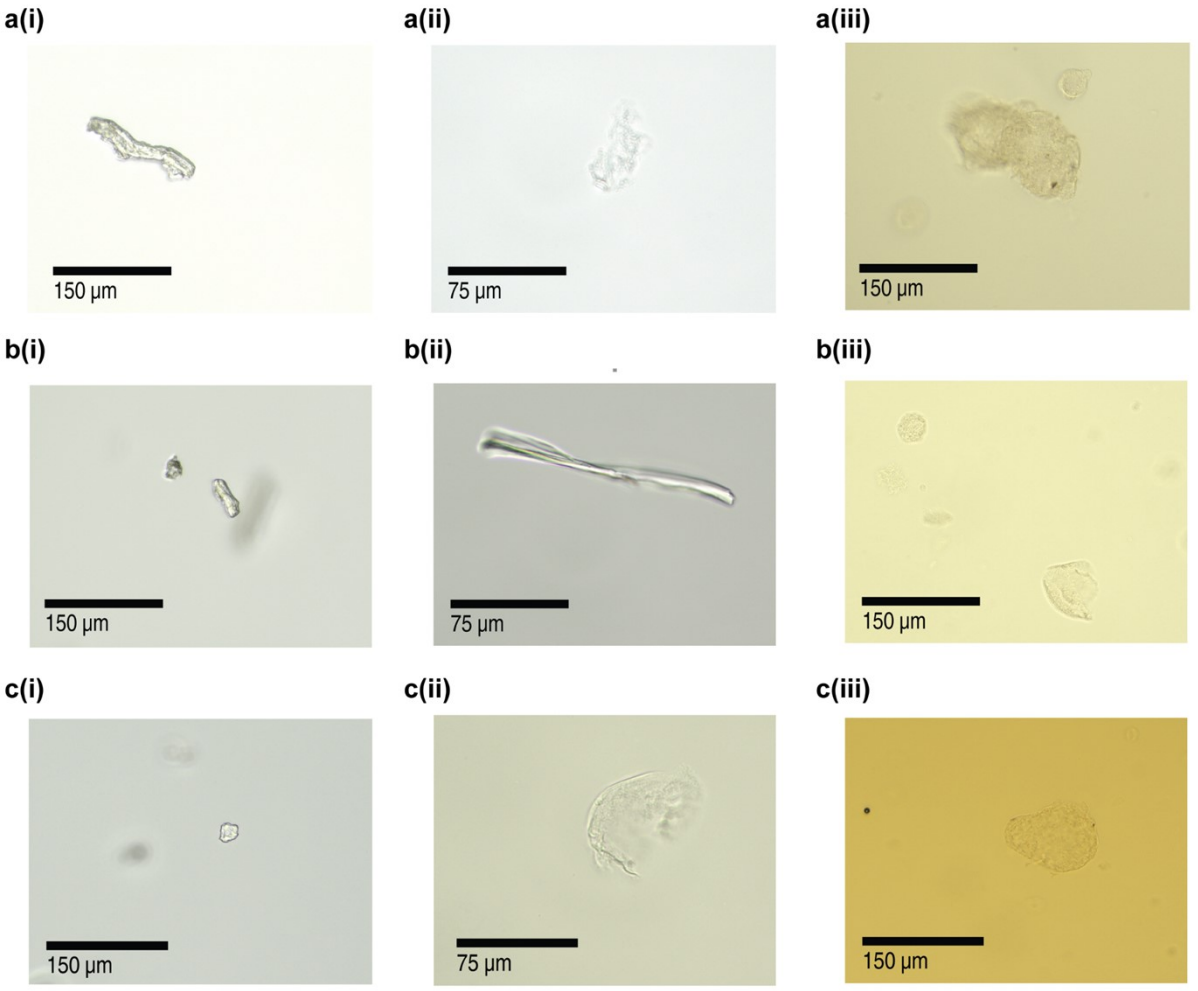

Fig. S7: Optical microscopic images of cellulose, hemicellulose, and lignin from **a(i) – a(iii).** alkali-pretreatment, **b(i) – b(iii).** BDES-pretreatment, and **c(i) – c(iii).** TDES-pretreatment of rice husks.

Table S3: ^{13}C qNMR assignment of precipitated lignin samples.

δ (ppm)	Assignment	Binary DES Lignin (mmol g^{-1})	Ternary DES Lignin (mmol g^{-1})	Alkali Lignin (mmol g^{-1})
50.0 – 48.1	C–β in G type β–5, β–β units	-	-	0.02
58.4 – 54.5	$-OCH_3$	9.3	4.1	0.3
61.0 – 58.5	C–γ in G type β–O–4 units	1.4	0.6	-
62.6 – 61.6	C–γ in G type β–5, β–1 units	3.2	4.9	-
67.0 – 64.8	C–γ in G type β–O–4 units with α–C=O	20.2	38.5	-
68.0 – 66.6	C–α in G type β–O–4 units (threo), C–γ in G type β–β	3.6	7.4	-
72.6 – 68.0	C–α in G type β–O–4 units (erythro)	183.3	172.2	-
117.9 – 111.5	C-5 in G type	-	-	0.2
150.5 – 146.0	C-3/C-5 of S type, C-3 in G type β–O–4 units	-	-	0.2
171.0 – 167.5	C=O in ϕ–COOH, Ester C=O in ϕ–C(=O)OR	177.6	192.7	-
173.4 – 167.5	Ester C=O in R–C(=O)OCH3	38.5	29.2	-
175.7 – 173.2	C=O in ϕ–CHO	24.3	47.4	-
178.2 – 176.0	C=O in ϕ–CH=CH–CHO, C=O in ϕ–C(=O)CH(–O ϕ)–C–	4.9	1.4	-

3. Precipitation and characterization of lignin samples

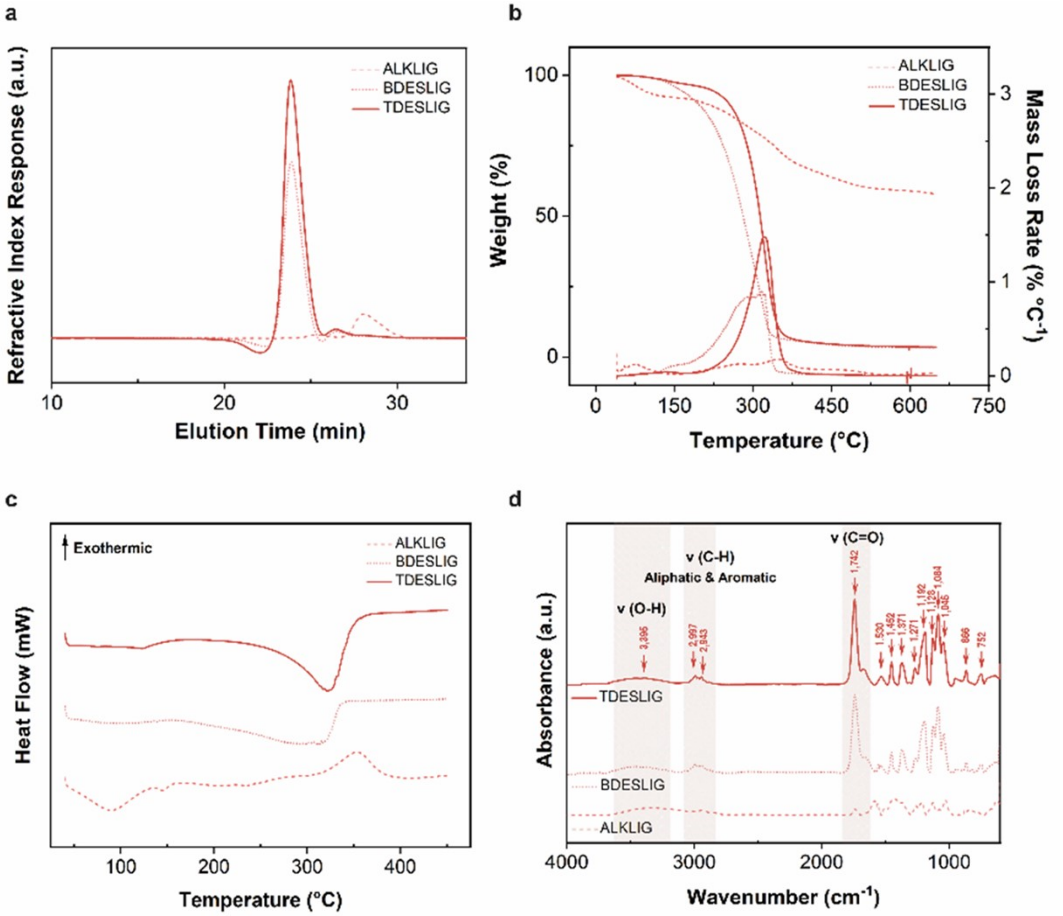

Fig. S8: a. Gel-permeation chromatograms, **b.** TGA and derivative profile, **c.** DSC thermogram, and **d.** ATR FT-IR spectra of precipitated lignin samples from alkali-, BDES-, and TDES-pretreatments.

Table S4: GPC analysis results of precipitated lignin samples.

	Retention Time (min)	M_n	M_w	M_p	M_z	M_{z+1}
ALK LIG	20.4	6,324	6,584	6,453	6,845	7,101
	22.9	1,817	1,890	1,688	1,967	2,049
	25.2	341	355	336	371	388
BDES LIG	22.4	2,785	3,066	2,313	3,413	3,807
	23.9	721	795	862	865	930
TDES LIG	22.1	3,127	3,538	2,750	4,088	4,765
	23.8	718	794	881	865	929

Table S5: DSC & TGA analysis results of precipitated lignin samples.

Sample	DSC Analysis		TGA Analysis		
	Degradation Peak (°C)	$\Delta H_{enthalpy}$ (J g^{-1})	Onset Temperature (°C)	Peak Degradation Temperature (°C)	Total mass change (%)
ALK LIG	353.5	111.4	230.8	349.5	41.7
BDES LIG	312.1	-418.8	236.0	315.9	96.7
TDES LIG	324.2	-322.2	284.1	323.0	96.5

Table S6: ^{1}H-^{13}C 2D HSQC NMR assignment of precipitated lignin samples.

δ_H/δ_C (ppm)	Assignment
5.2/ 67.3	Hibbert's Ketone
5.0/ 70.0	Cα-Hα in β-O-4' linkages to free hydroxyl
4.9/ 62.2	Cγ-Hγ in cinnamyl alcohol end-groups
4.4/ 59.6	Cγ-Hγ in β-O-4' linkages to acetylated hydroxyl
4.1/ 72.9	Cγ-Hγ of resinol substructure
3.8/ 55.6	Methoxy-
3.7/ 62.5	Cγ-Hγ of phenylcoumaran substructure
3.6/ 53.8	Cβ-Hβ of phenylcoumaran substructure
3.4/ 55.7	Cβ-Hβ of resinol substructure
7.6/ 141.7	C2-H2/C6-H6 of pBA substructure
7.5/ 130.0	C2-H2/C6-H6 of p-coumarate substructure
6.8/ 118.7	C6–H6 in guaiacyl units
6.7/ 115.1	C5–H5 in guaiacyl units
6.4/ 110.3	C2–H2 in guaiacyl units
6.2/ 106.4	C2-H2/C6-H6 in syringyl units