Simultaneous extraction and controlled chemical functionalization of hardwood lignin for improved phenolation

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Supplementary Information

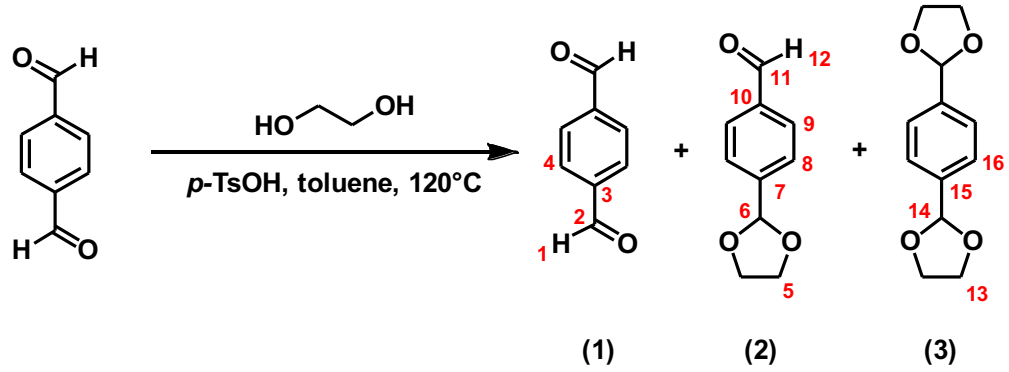
S1 Chemicals and materials

All commercial chemicals were of analytical grade and were used without further purification. 2-Chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane 95% (TMDP), Terephthalic aldehyde 99% (TALD), 5% ruthenium on carbon, dichloromethane >99%, Dimethylsulfoxide >99% (DMSO), ethylene glycol >99%, ethyl acetate >99.5%, potassium bromide, p-Toluenesulfonic acid monohydrate >98.5% (*p*-TsOH), sodium hydroxide were purchased from Sigma Aldrich. 1,4-Dioxane and sodium hydrogen carbonate were purchased from Carl Roth. Chromium (III) acetylacetonate, 97%, Pyridine 99.5% were purchased from Acros Organics. Chloroform-d_3 99,8% ($CDCl_3$) and Dimethylsulfoxide-d_6 (DMSO-d_6) were purchased from Cambridge Isotope Laboratories. Hydrochloric acid 37% w/w (HCl) and tetrahydrofuran (THF) stabilized with 0.025% w/w of BHT were purchased from Fisher Chemical. Diethyl ether was purchased from Carlo Erba. Decane was purchased from TCI Europe NV. Toluene was purchased from VWR. Phenol 99%, *N*-Hydroxy-5-norbornene-2,3-dicarboximide, 97% were purchased from Alfa Aesar. The Kraft Lignin (KL) used in this work (UPM's BioPiva™ 100) was chosen as a benchmark for the phenolation reaction because it is currently being explored as replacement for phenol in plywood production. The Kraft lignin was dried in a vacuum oven at 45°C for 24h prior to its use. Birch wood (Betula Pendula) was procured by Prof. Michael Studer from the Bern University of Applied Sciences. The tree was harvested in in May of 2018 in Solothurn, Switzerland. It was first debarked, the trunk was cut in wood chips and dried at 40°C for 24 hours. The wood chips were subsequently transported to EPFL and cleaned from residual leaves and bark. The wood chips were then milled with a 6mm screen and sieved with a 0.45 mm mesh.

S.2 Experimental Methods

S2.1 Synthesis of Model compounds

Synthesis of a mixture of Terephthalic Aldehyde, 4-(1,3-Dioxolan-2-yl)benzaldehyde, and 1,4-bis(1,3-dioxolan-2-yl)benzene



Terephthalic Aldehyde (2.04 g, 15.2 mmol) and *p*-Toluensulfonic acid (0.7 g, 4.08mmol) were dissolved in 40mL of toluene in a 100mL round bottom flask. Ethylene glycol (1.5g, 24.1mmol) was then added to this solution. The reaction was equipped with a Dean-Stark apparatus and was first heated at 120°C for 3h, then cooled to room temperature. Following cool down, the solvents were evaporated in vacuo. The residue was then redissolved in 50mL of dichloromethane and extracted with a saturated aqueous solution of $NaHCO_3$ (2x50 mL) and brine (1x50 mL). The organic phase was dried over anhydrous Na_2SO_4, filtered and dried in a rotary evaporator to obtain a yellow syrup (2.8 g, 2,8% w/w compound 1, 64,5% w/w compound 2, 32,7 % w/w compound 3 calculated by ^{1}H NMR) which was used without further purification. ^{1}H NMR ($CDCl_3$): δ4.00-4.12 (m, H_5, H_{13}), 5.81 (s, H_{14}), 5.85 (s, H_6), 7.47 (s, H_{16}), 7.62 (d, J=8.2, H_8), (7.85, d=8.2, H_9), 8.02 (s, H_4), 10.01 (s, H_{12}), 10.11 (s, H_1). ^{13}C NMR ($CDCl_3$): δ65.2 (C_{13}), 65.4 (C_5), 102.8 (C_6), 103.4 (C_{14}), 126.5 (C_{16}), 127.1 (C_8), 129.8 (C_9), 130.1 (C_4), 136.9 (C_{10}), 139.0 (C_{15}), 139.9(C_3), 144.4 (C_7), 191.5 (C_2), 191.9 (C_{11})

S2.2 Extraction of terephthalic aldehyde protected lignin

5g of birch wood chips, terephthalic aldehyde (see ratios in table S1) and 25mL of dioxane were introduced into a 100mL round bottom flask with a magnetic stirrer and stirred until the aldehyde was fully dissolved. When the aldehyde was fully dissolved, 0.8 mL of hydrochloric acid 37% w/w were added to the mixture. The round bottom flask was equipped with a condenser and a gas bubbler to create an air lock. The mixture was then heated at 85°C for 3h under vigorous stirring. The system was then cooled to room temperature, following which 1.15g of $NaHCO_3$ were slowly added to the mixture and stirred for 45 minutes. The reaction mixture was then filtered and the retentate was washed with dioxane. The filtrate was evaporated in a rotary evaporator. The solid residue was inserted in a 100mL round bottom flask and washed with distilled water for one hour, filtered again and dried overnight in a vacuum oven at 45°C to obtain a cellulose-rich solid.

The evaporated dioxane-filtrate was redissolved in 15mL of fresh dioxane, precipitated in 400mL of diethyl ether and stirred for 1h to dissolve most of the carbohydrates and unreacted terephthalic aldehyde. The mixture was then filtered and purified overnight with a Soxhlet extractor using diethyl ether as a solvent to remove all impurities. The washed solid was then dried overnight in a vacuum oven at 45°C to obtain terephthalic aldehyde protected lignin.

Table S1. Biomass/terephthalic aldehyde ratios used during of lignin extractions

Sample	Dry birch wood chips [g]	Terephthalic Aldehyde [g]	mmol TALD/g dry biomass
1	4.729	8.004	12.62
2	4.714	7.125	11.27
3	4.751	6.102	9.58
4	4.716	5.018	7.93
5	4.701	4.023	6.38
6	4.760	3.017	4.73
7	4.722	2.030	3.20
8	4.754	1.029	1.61
9	4.722	0.538	0.85

S2.2.1 Mass Balance of terephthalic aldehyde protected lignins

The yields of cellulose rich solids, lignin and carbohydrate derivatives shown in **Table S2** are calculated based on the composition of birch biomass previously published by Amiri et al.[1] shown in **figure S1.**

The yield of effective lignin is calculated according to the following equations:

$$\begin{aligned}\textbf{Effective isolated lignin} &= g_{\text{isolated lignin}} - n_{\text{bound TALD}} \times 118.04\text{g/mol} \\ &\quad - n_{\text{residual TALD}} \times 134.13\text{g/mol}\end{aligned} \qquad \text{(Equation S1)}$$

$$\textbf{Lignin Extraction Yield}_{\,Klason}\,[\textbf{wt.}\,\%] = \frac{\text{Effective isolated lignin}}{\text{Original Klason Lignin Content}}\text{x}100 \qquad \text{(Equation S2)}$$

Where in the equations:

$g_{\text{isolated lignin}}$: mass of isolated lignin

$n_{\text{bound TALD}}$: mmol of TALD covalently bound to the isolated lignin (measured by ^{1}H NMR according to **section S3.1**)

118.04 g/mol: Molecular weight of a TALD molecule when covalently bound to the lignin

$n_{\text{residual TALD}}$: mmol of residual TALD impurities in the isolated lignin (Calculated by ^{1}H NMR according to **section S3.1**)

134.13g/mol: Molecular weight of residual free terephthalic aldehyde

Table S2. Yields of cellulose rich solids, isolated lignin and carbohydrate derivatives after pretreatment

Sample	Cellulose rich solid [%][a]	Lignin [%][b]	Furfural [%][c]	HMF [%][c]	TALDX [%][c]
1	53.08%	90.62%	0.21%	1.10%	4.29%
2	52.16%	103.32%	0.38%	1.20%	5.43%
3	59.88%	84.38%	0.15%	0.98%	4.13%
4	56.62%	99.44%	0.19%	1.05%	4.93%
5	60.02%	87.83%	0.15%	0.92%	4.76%
6	57.42%	99.66%	0.21%	1.18%	4.67%
7	63.95%	85.08%	0.14%	0.85%	3.74%
8	58.22%	87.96%	0.12%	1.98%	3.55%
9	60.30%	80.59%	0.10%	1.12%	2.51%

[a] calculated based on the initial weight of dry biomass, [b] based on the initial Klason Lignin content, [c] based on the initial xylan content.

A graphical representation for Sample 1 is presented as an example in **figure S1.**

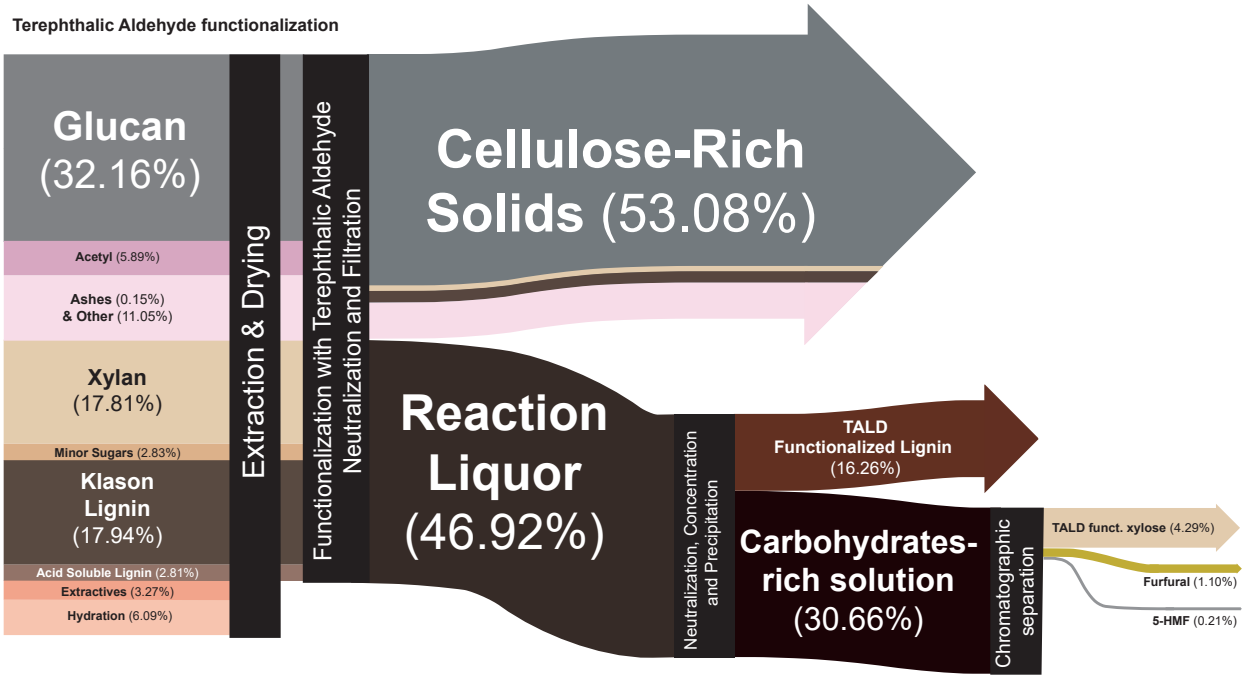


Figure S1. Mass balance of the terephthalic aldehyde-facilitated fractionation of lignocellulosic biomass for sample 1

S2.3 Extraction of Mild Organosolv Lignin (OSL)

10 g of birch wood was introduced in a 250mL round bottom flask with 80 mL of an 80:20 Ethanol:H_2O solution. 1.6mL of HCl 37% in H_2O w/w were then added to this solution. The extraction was refluxed under vigorous stirring for 5 hours. The solid residue was filtered, washed with ethanol and dried under reduced pressure. 15mL of acetone were subsequently added to dissolve the lignin, which was then precipitated in 300 mL of deionized water. This lignin was filtered and dried. For a further purification lignin was then dissolved in dioxane and precipitated in diethyl ether. The precipitate was then filtered and dried overnight in a vacuum oven at 45°C. OSL was obtained with a yield of 28 wt.% on an initial Klason lignin content basis.

S2.4 Phenolation of lignins

S2.4.1 Acid catalysed phenolation

Phenol was put in a 10mL Reacti-Vial™ equipped with a magnetic stir bar. The reagent was melted and 0.5g of lignin were added. Then, 0.108 mL of concentrated H_2SO_4 were added dropwise and the reaction was run for 30 minutes at 110°C. The reaction was then cooled to room temperature and 5mL of DMSO were added to the vial. The resulting solution was added dropwise to 300 mL of deionized water previously adjusted to pH 1 with H_2SO_4. After the precipitation, the phenolated lignin was filtered and washed with water until the filtrate's pH was measured as neutral with pH indicator strips. The collected lignin was then dried overnight in a vacuum oven at 45°C.

S2.4.2 Basic catalysed phenolation

Phenol was put in a 10mL Reacti-Vial™ equipped with a magnetic stir bar. The reagent was melted and then 0.5g of lignin were added. Then, 0.2 mL of a 30% w/w NaOH solution in water were added dropwise and the reaction was run for 24 h at 130°C. The reaction was then cooled to room temperature and 5mL of DMSO were added to the vial. The resulting solution was added dropwise to 300 mL of deionized water previously adjusted to pH 1 with H_2SO_4. After precipitation, the lignin was filtered and washed with water until the filtrate's pH was measured as neutral with pH indicator strips. The collected lignin was then dried overnight in a vacuum oven at 45°C.

S2.5 Hydrogenolysis of lignin into aromatic monomers

100mg of isolated lignin were added to a 50ml high-pressure Parr reactor equipped with a magnetic stirrer together with 100mg of 5 wt% Ru/C and 20 mL of tetrahydrofuran. The reactor was then closed and was first purged with N_2, then twice with H_2 and finally pressurized with 40 bar of H_2 before starting the reaction. The reactor was heated with high-temperature heating tape (Omega) connected to a variable power supply which was controlled by a PID temperature controller (Omega). The reaction was stirred at 600 rpm for 3h at 250°C. Afterward, the reactor was cooled down to room temperature with a flow of compressed air and H_2 was evacuated from the reactor.

S2.6 Characterization of lignins

S2.6.1 Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectroscopy

DRIFT spectroscopy was performed on a PerkinElmer Frontier IR instrument. Samples were prepared by mixing approximately 15mg of lignin and 0.5g of KBr in a mortar until obtaining a homogeneous solid powder. Spectra were collected at room temperature from 500 to 4000cm^{-1} with a scan number of 32. The background was recorded using solid KBr finely ground in a mortar.

S2.6.2 Gel Permeation Chromatography (GPC)

The number average (Mn) and weight average (Mw) molecular weight of lignin samples, as well as their polydispersity index (PD) were determined by gel permeation chromatography (GPC) using an Agilent 1260 15 infinity equipped with a refractive index detector and 2x Agilent PL-Gel Mixed C+ guard column set. GPC analyses were conducted in tetrahydrofuran (1 ml/min @40 °C) and the calibration was performed with polystyrene standards (**Table S3**).

Table S3. Molecular weight of isolated TALD lignin and propionaldehyde stabilized lignin determined by GPC.

Sample	Mn [g/mol]	Mw [g/mol]	PD
1	2500	5700	2.3
2	2400	6300	2.6
3	2600	6800	2.6
4	2500	6500	2.6
5	2500	6400	2.6
6	2400	6300	2.6
7	2500	5800	2.4
8	2400	5700	2.4
9	2500	5400	2.2
Propionaldehyde-stabilized lignin	3100	7400	2.4

Table S4. Molecular weight of various isolated lignins determined by GPC

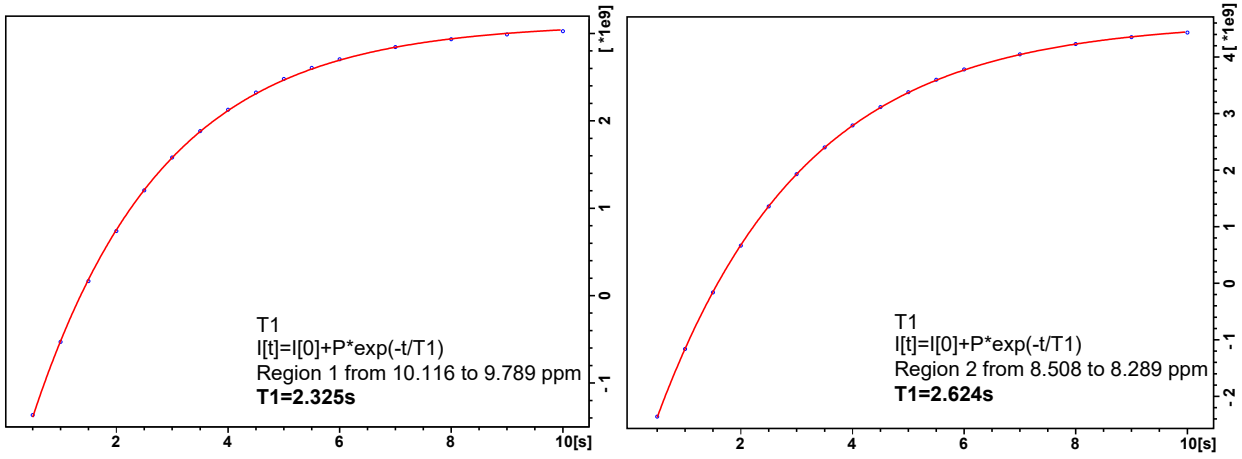
Sample	Mn [g/mol]	Mw [g/mol]	PD
TALD	2600	6900	2.6
TALD-APH	600	900	1.5
TALD-BPH	2900	3900	1.4
OSL	2800	9000	3.2
OSL-APH	500	800	1.5
OSL-BPH	1100	2300	2.1
Kraft	900	1800	2.0
Kraft-APH	1100	1700	1.5
Kraft-BPH	1000	2100	2.1

S2.6.3 Nuclear Magnetic Resonance (NMR)

The NMR characterization of the model compounds was performed on a Bruker Avance III 400 MHz spectrometer equipped with a BBFO-Plus probe. The ^{1}H and ^{13}C spectra of the model compounds were recorded using the standard pulse sequences from Bruker. The NMR characterization of lignin samples were performed on Bruker Avance 600 or 800 MHz spectrometers equipped with a 5 mm BBO and TCI cryoprobe respectively. The spectra were processed using the software Bruker TopSpin 3.6.1.

Quantitative ^{1}H, ^{13}C and HSQC (Heteronuclear Single Quantum Coherence) spectra of functionalized lignins were recorded using standard pulse sequences with some modifications: D1=10s, NS=8, P1=8us, TD=65536, O1P (F2, F1)=6.175ppm, 125ppm, SW (F2, F1)=13.0186ppm, 150ppm.

The central peak of the solvent peaks was systematically used as reference ($CDCl_3$: δH/δC 7.24/77.23, DMSO-d6 δH/δC 2.50/39.50). Inversion Recovery experiments were performed to determine the relaxation time of the signals relative to the terephthalic aldehyde functionalization and the internal standard (**Figure S2**).



FigureS2. T1 relaxation time estimates for the NMRs of TALD-functionalized lignin and the internal standard (1,4 DNB)

The Bruker DOSY (Diffusion Ordered SpectroscopY) pulse sequence (ledbpgp2s) was used to investigate the diffusion of molecular systems in solution. The DOSY diffusion time interval (d20) and gradient pulse length (p30) were set at 0.1 s and 2000 ms, respectively, with a recycle delay

(d1) of 2 s. Each 1D free induction decay had 4K complex points with 8 scans averaged. The diffusion gradients were ramped from 2% to 98% at linear increments to generate 16 increments in the diffusion dimension. All experiments were performed at a temperature of 298K. DOSY spectra for TALD lignin (sample 1), KL-BPH and OSL-BPH are shown in **Figure S3**.

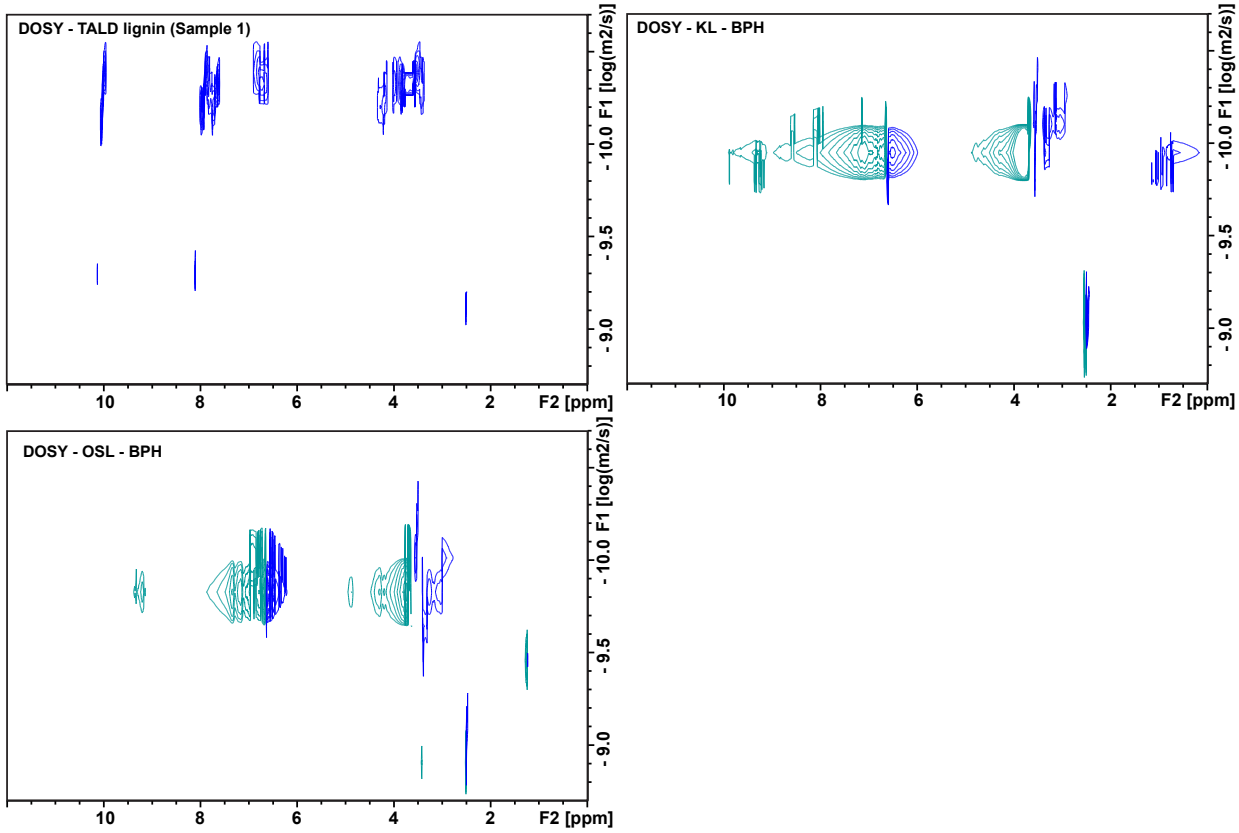


Figure S3. DOSY spectra of TALD lignin (sample 1), KL-BPH and OSL-BPH.

^{31}P NMR and hydroxyl group quantification was performed following a protocol published by Meng et al. by working under inert athmosphere[2] (**Table S5**). Lignin samples were dried overnight at 45°C under vacuum. Approximately 30 mg of lignin were massed in a glass vial, to which was added 0.1 ml of a solution of deuterated pyridine and chloroform (1.6:1, v/v) containing chromium (III) acetylacetonate solution (~5.0 mg/mL,) and *N*-Hydroxy-5-norbornene-2,3-dicarboximide (NHND) as an internal standard (~18.0 mg/mL). Subsequently, 0.5mL of a solution of deuterated pyridine and chloroform (1.6:1, v/v) was added and stirred until full dissolution of the lignin. Once the solution was clear, 0.1mL of 2-chloro-4,4,5,5-tetramethyl-1,3-2-dioxaphospholane (TMDP) were carefully added to the solution. The mixture was stirred for 1h and then transferred to an

NMR tube and analysed within 3h. The NMR spectra were recorded on a Bruker Avance 600 MHz spectrometer equipped with a 5 mm BBO cryoprobe The experimental NMR parameters used were: Pulse program= Inverse gated decoupling pulse (zgig), SW=100 ppm, O1P=140 ppm, AQ=0.8 s, D1=10 s, NS=128.

Table S5. Quantification of aliphatic, phenolic and carboxylic hydroxyl groups on various lignins via ^{31}P NMR. The results are reported in mmol/g of effective lignin. *Aliph-OH* refers to the aliphatic hydroxyl groups, *5-Subst.-OH* refers to phenolic groups on aromatic rings substituted at the position 5 (such as Syringol units), *G-OH* refers to phenolic groups of Guaiacol units, *H-OH* refers to phenolic groups of Hydroxyphenylpropane units and *COOH* refers to carboxylic acid groups.

Sample	Aliph-OH [mmol/g]	5-Subst.-OH [mmol/g]	G-OH [mmol/g]	H-OH [mmol/g]	COOH [mmol/g]
TALD	3.21	0.70	0.27	0.02	0.07
TALD-APH	0.13	0.10	0.34	6.45	0.04
TALD-BPH	1.55	0.62	0.23	4.34	0.20
OSL	3.10	0.56	0.64	0.14	0.06
OSL-APH	0.16	1.09	0.40	3.91	0.09
OSL-BPH	1.80	0.75	0.50	1.94	0.27
Kraft	1.55	1.37	1.69	0.15	0.39
Kraft-APH	0.50	1.90	1.77	3.45	0.33
Kraft-BPH	1.32	1.36	1.45	1.23	0.43

S3 Analytical Methods

S3.1 Quantification of free aldehyde in terephthalic aldehyde protected lignin by ^{1}H NMR

40-60mg of Terephthalic aldehyde protected lignin were massed in an NMR tube. 50 µL of a solution of 1,4-dinitrobenzene (1,4-DNB) in DMSO-d6 (89.7g/L) were then introduced in the NMR tube, to which, 500 µL of additional DMSO-d6 were added. If needed, the sample was briefly sonicated until full dissolution of the lignin sample. The exact quantities used in this

preparation are shown in **Table S4**. ^{1}H NMR spectra were recorded with a long D1 (at least 10s) to allow for the lignin signals and internal standard to fully recover.

The spectrum was then processed, phased and the baseline was corrected by using the command ABS in the Bruker TopSpin software. The spectrum was then integrated. The peak of 1,4-dinitrobenzene (1,4-DNB, the internal standard) at 8.43 ppm was calibrated to 4 protons. The integral of the peak assigned to the free terephthalic aldehyde group (TALD) bound to the lignin at 10.01 ppm and the integral the peak assigned to the unbound terephthalic aldehyde at 10.14 ppm were then estimated.

The quantification of bound and residual terephthalic aldehyde were then calculated using the equations detailed below.

The integrals of the peaks assigned to 1,4-dinitrobenzene and bound terephthalic aldehyde were normalized by the number of protons generating the signals according to Equations S3 and S4.

Normalized 1,4-DNB integral = (measured I.S. integral)/4 (Equation S3)

Normalized aldehyde integral = (measured aldehyde integral)/1 (Equation S4)

The number of moles of 1,4-dinitrobenzene generating the integral could then be calculated with Equation S5 by knowing the quantity and purity of the internal standard introduced into the NMR tube.

mmol 1,4-DNB in NMR sample= (mg 1,4-DNB in NMR tube*0.98)/(168.11 mg⁄mmol) (Equation S5)

Where 168.11 mg/mmol is the molecular weight of 1,4-dinitrobenzene and 0.98 is the purity of the internal standard used for these analyses.

The number of moles of free aldehyde generating the signal of TALD bound to the lignin was then calculated with Equation S6.

mmol aldehyde in NMR sample= (Normalized aldehyde integral)/(Normalized 1,4-DNB integral)*(mmol 1,4-DNB in NMR sample) (Equation S6)

Finally, the number of moles of free aldehyde bound to the lignin per gram of isolated lignin could be calculated according to the Equation S7.

mmol of free aldehyde in 1g of lignin = (mmol aldehyde in NMR sample)/(mg of lignin in NMR tube)*1000 (Equation S7)

Table S6: Detailed quantities used for ^{1}H NMR quantification of the functionalized lignins and quantification results

Sample	mg lignin	mL I.S solution	mL DMSO-d6	mmol bound TALD/g lignin	mmol residual TALD/g lignin
1	52.7	0.05	0.5	1.88	0.060
2	50.5	0.05	0.5	1.99	0.053
3	45.4	0.05	0.5	1.72	0.049
4	54.9	0.05	0.5	1.68	0.037
5	50.4	0.05	0.5	1.64	0.040
6	49.0	0.05	0.5	1.51	0.022
7	45.8	0.05	0.5	1.16	0.036
8	50.5	0.05	0.5	0.83	0.003
9	49.2	0.05	0.5	0.47	0.002

S3.2 Quantification of aromatic monomers from hydrogenolysis of isolated lignin by GC (Gas Chromatography)

After the hydrogenolysis reaction was complete and cooled to room temperature, the reactor was brought to atmospheric pressure by purging the H_2 and then opened. 0.5 mL of internal standard solution (decane in 1,4-dioxane 10g/Kg) were added to the reaction mixture and stirred with a

spatula until homogeneous. The mixture was then transferred with a Pasteur pipette to a syringe equipped with a Chromafil Xtra H-PTFE 20/25 syringe filter and filtered. 1mL of the filtrate was transferred to a GC vial and analysed with a GC (Agilent 7890B series) equipped with an HP5-column and a flame ionization detector (FID). The injection temperature was 300 °C. The column temperature program was: 40 °C (3 min), 30 °C/min to 100 °C, 40 °C/min to 300 °C and 300 °C (5 min). The detection temperature was 300 °C. The monomer yield on Klason lignin basis was calculated according to recent published guidelines which are based on the area of the monomer and the area of decane in the GC chromatogram[3]. The detailed calculation is presented here below:

$$n_{decane} = \frac{W_{decane\ in\ sample}}{MW_{decane}} \quad \text{(Equation S8)}$$

$$n_{monomer} = \frac{A_{monomer\ in\ sample}}{A_{decane\ in\ sample}} \times n_{decane} \times \frac{ECN_{decane}}{ECN_{monomer}} \quad \text{(Equation S9)}$$

To compare the results between samples with different monomeric composition and products with different degrees of hydrodeoxygenation and side truncation, the monomer yield was calculated by using the native molecular weight (**Table S7**) of guaiacyl or syringyl β-O-4 units generating the different monomers after hydrogenolysis (**Figure S5**).

$$\text{Monomer yield [wt\%]} = \frac{\sum(n_{monomer} MW_{native})}{\text{Effective isolated lignin}} \times \text{Lignin extraction yield}_{klason} \quad \text{(Equation S10)}$$

The monomer yields of the isolated yields are shown in **Figure S4**.

In the equations,

$W_{decane\ in\ sample}$ (mg): the mass of decane used as an internal standard in each analysed sample;

MW_{decane} (mg mmol^{-1}): the molecular weight of decane (142 mg mmol^{-1});

n_{decane} (mmol): the molar amount of decane in each analysed sample;

$n_{monomer}$ (mmol): the molar amount of monomer in each analysed sample;

$A_{monomer\ in\ sample}$: the peak area of monomer in the GC-FID chromatogram;

$A_{decane\ in\ sample}$: the peak area of decane in the GC-FID chromatogram;

ECN_{decane}: the effective carbon number (10) of decane;

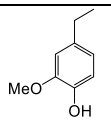
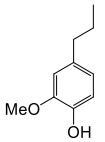
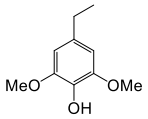
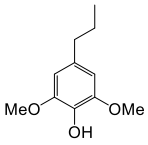
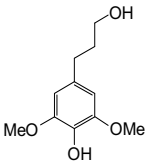
$ECN_{monomer}$: the effective carbon number of the lignin monomer molecule (**Table S7**);

$MW_{native\ repeating\ unit}$ (mg $mmol^{-1}$): the molecular weight of native guaiacyl and syringyl β-O-4 units (see Figure S5).

Lignin extraction $yield_{klason}$: Extraction yield based on Klason lignin contend as defined in Equation S2.

Effective Isolated lignin: Mass of lignin corrected per amount of covalently bound TALD as defined in Equation S1 and Section S3.1.

Table S7. Structure, name and effective carbon number used (ECN) of lignin monomers obtained using THF as the GC solvent[4].

Lignin monomer structure	Name	Effective carbon number in THF ($ECN_{monomer}$)	MW monomer after hydrogenolysis [g/mol]	MW of native repeating unit [g/mol]
	4-Ethyl-guaiacol	7	152.19	196.20
	4-Propyl-guaiacol	8	166.22	196.20
	4-Ethyl-syringol	7	182.22	226.23
	4-Propyl-syringol	8	192.25	226.23
	4-Propanol-syringol	7.4	212.25	226.23

The monomer yields of isolated lignins based on these calculations are represented in **Figure S4**.

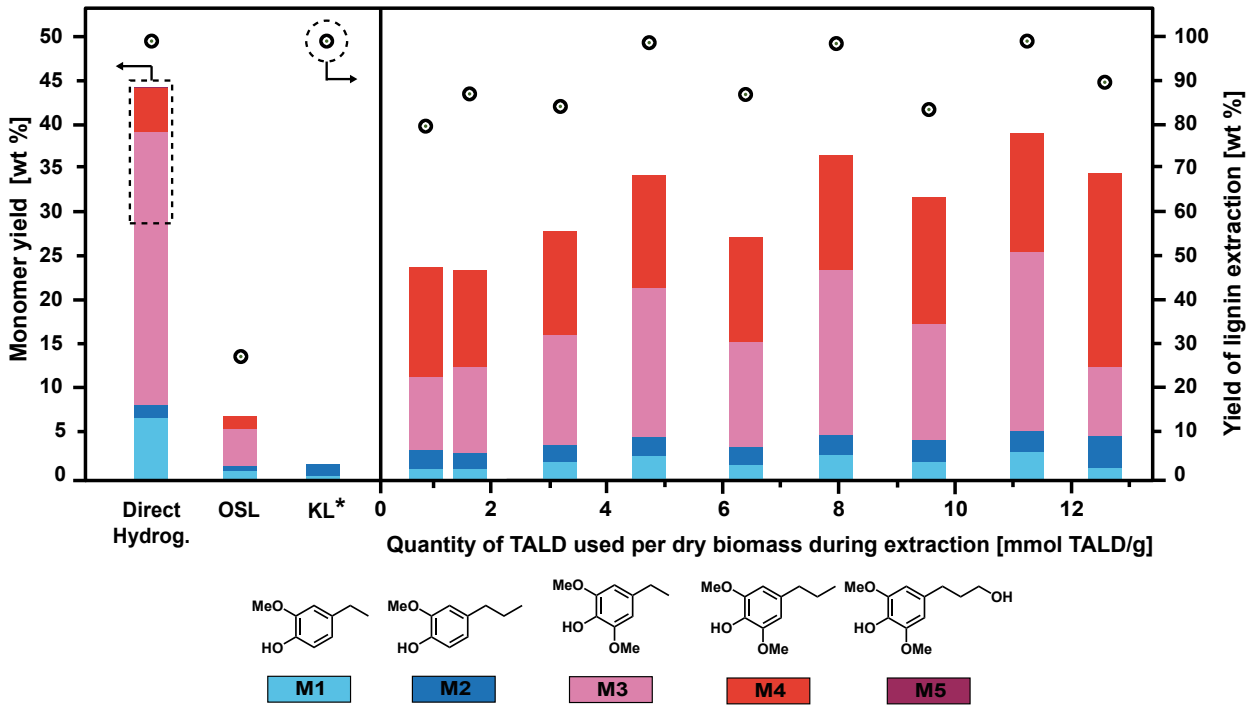


Figure S4. Depolymerization and extraction yields of TALD-functionalized lignins, OSL and KL. *For Kraft Lignin, we assumed (1) that the Klason lignin of the original biomass used to produce Kraft lignin (which we did not have access to) was the same as that of the biomass used for the other experiments and (2) that the lignin extraction yield (which was unknown) to produce this Kraft lignin was 100%. In this way, we likely overestimate yields from Klason lignin but avoid any unfair comparison with our results.

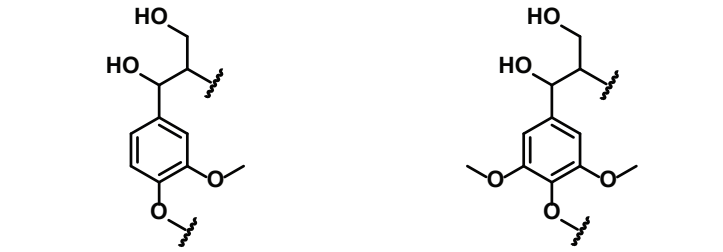


Figure S5. Structure of the native guaiacyl and syringyl repeating units and their molecular weight.

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