Comprehensive valorisation of technically relevant organosolv lignins *via* anodic oxidation

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Electronic Supplementary Information

30 pages, 11 figures, 21 tables

Content

Materials

Lignin. The organosolv lignins used, the supplier and the corresponding pulping solvents are listed in table S1.

Table S1. Organosolv lignins for anodic oxidation.

lignin	source (wood type)	pulping solvent	supplier
SPR-1-TNO	spruce (softwood)	acetone/water/H_2SO_4 (FABIOLA™)	TNO, Netherlands
TNO-OS15100101	pine (softwood)	acetone/water/H_2SO_4 (FABIOLA™)	TNO, Netherlands
BEC-2-TNO	beech (hardwood)	acetone/water/H_2SO_4 (FABIOLA™)	TNO, Netherlands
WHS-2-TNO	wheat straw (straw)	acetone/water/H_2SO_4 (FABIOLA™)	TNO, Netherlands
Fichte KO 124	spruce (softwood)	ethanol/water	Fraunhofer CBP, Germany
Buche KO 168	beech (hardwood)	ethanol/water	Fraunhofer CBP, Germany
Clariant straw	cereal straw (straw)	enzymes/water (sunliquid®)	Clariant, Germany

Chemicals. Nitrobenzene was purchased from Janssen Chimica, Belgium. *n*-Dodecylbenzene was obtained from EGA-Chemie, Germany. Vanillin was purchased from Merck Millipore, Germany. Acetovanillone, acetosyringone and guaiacol were obtained from Sigma Aldrich, Germany. Syringaldehyde was purchased from TCI, Germany. Ethyl acetate (technical grade) was distilled prior to use. Dichloromethane (>99.8%, analytical grade) and methanol (≥99.9%, analytical grade) were obtained from Fisher Scientific, Germany. All chemicals and solvents were used as received, unless mentioned explicitly.

Electrodes. Nickel sheet electrodes were provided from IKA®-Werke GmbH & Co. Kg. Nickel foam (average pore size Ø1.4 mm) was obtained from Aqua Titan, Dortmund, Germany. Alloys used in electrolysis were bought from Goodfellow GmbH, Germany and Deloro Wear Solutions, Germany. The chemical composition of the respective alloy is given in table S2.

Table S2. Electrode materials with their respective chemical composition.

alloy	composition	alloy basis
Ni sheet	Ni99.9	Ni
Ni foam	Ni99.9	Ni
Hastelloy C276[a]	Ni57/Mo17/Cr15/Fe6/W4	Ni
Monel 400k[a]	Ni65/Cu33/Fe2	Ni
Waspalloy[a]	Ni59/Cr20/Co14 (traces:Mo/Ti/Al/Fe)	Ni
Ni/Cr 053250[a]	Ni75/Cr19/Fe5	Ni
Inconel 625[a]	Ni61/Cr22/Mo9/Fe5	Ni
Cobalt 99,9%[a]	Co99.9	-
Stellite™ 21[b]	Co64/Cr28/Mo5/Ni3	Co
Tribaloy™ T-400[b]	Co62/Mo28/Cr9/Fe1	Co
Stellite™ 4[b]	Co52/Cr30/W14/Fe2/Ni2	Co
Stellite™ 6[b]	Co61/Cr28/W5/Fe3/Ni3	Co
Tribaloy™ T-400C[b]	Co59/Mo27/Cr14	Co
Deloro™ 40[b]	Ni86/Cr12/Fe2	Ni
Ti/Al/V[a]	Ti90/Al6/V4	Ti

[a] purchased from Goodfellow GmbH, Germany; [b] purchased from Deloro Wear Solutions, Germany

Chromatography

For thin-layer chromatography (TLC), PSC plates silica gel 60 F254 of Merck KGaA, Darmstadt were used. The substances were detected under UV light (λ = 254 nm).

Preparative liquid chromatography for the separation of product mixtures was carried out using silica gel 60 M (0.040–0.063 mm) from Machery-Nagel GmbH & Co. KG, Düren at a maximum overpressure of 0.8 bar. All eluents used (ethyl acetate, technical grade; cyclohexane, technical grade) were purified by distillation under reduced pressure before use.

Gas Chromatographic Characterisation

Gas chromatography was performed on a Shimadzu GC-2025 (Shimadzu, Japan) using a ZB-5 column (Agilent Technologies, USA; length: 30 m, inner diameter: 0.25 mm, film: 0.25 µm, pre-column: 5 m, carrier gas: hydrogen) with a flame ionization detector (FID) at 310 °C. GC-MS measurements were carried out on a Shimadzu GC-2010 (Shimadzu, Japan) using a Zebron ZB-5MSi column (Phenomenex, USA; length: 30 m, inner diameter: 0.25 mm, 5% phenyl 95% dimethylpolysiloxane, film: 0.25 µm, pre-column: 5 m, carrier gas: helium) combined with a GCMS-QP2010 with an ion source (EI) at 200 °C. The method “hart” (50 °C starting temperature for 1 min, heating rate: 15 °C/min, 290 °C end temperature for 8 min) was applied in both cases.

Quantification of Vanillin. A precisely defined amount of vanillin (**1**) is weighed into a vial and dissolved in a mixture consisting of 6 mL methanol and 2 mL ethyl acetate. Afterwards, 2 µL *n*-dodecylbenzene is added as an internal standard (ISTD) using a 10 µL-Hamilton syringe. 0.8 mL of the resulting solution is filtered through silica gel (1.5 g, silica gel 60) with 2.5 mL of an ethyl acetate/methanol mixture (3:1) and analysed *via* gas chromatography. The resulting integral ratio between **1** and ISTD is graphically plotted against the corresponding sample weight (Figure S1). The quantities of **1** and the corresponding integral ratios obtained are given in Table S3.

Table S3. Calibration of GC *via* internal standard for vanillin (**1**).

entry / #	weight **1** / mg	integral **1**	integral ISTD	I(**1**) / I(ISTD)
1	3.059	13105	29010	0.452
2	6.048	36882	30214	1.221
3	9.065	61778	31856	1.939
4	12.009	85494	30716	2.783
5	15.959	123145	31924	3.857
6	20.030	165735	32708	5.067
7	24.990	203953	31995	6.375
8	30.060	247092	31417	7.865
9	35.008	292414	31704	9.223

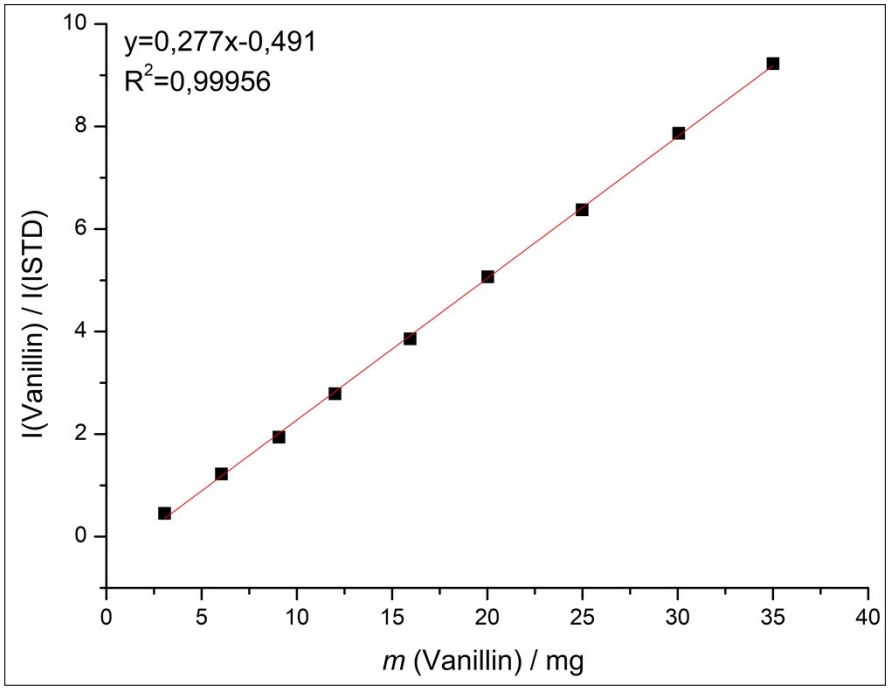

Figure S1. Plot of weight for vanillin (**1**) *vs*. integral ratio vanillin (**1**) and ISTD with linear fit.

After linear regression following equation is received:

$$I(\mathbf{1})/I(\text{ISTD}) = 0.277 \cdot m_1 - 0.491 \qquad \text{(S1)}$$

The fit line was not placed through the origin to consider potential product loss by the filtration process.

Quantification of Acetovanillone. A precisely defined amount of acetovanillone (**2**) is weighed into a vial and dissolved in a mixture consisting of 6 mL methanol and 2 mL ethyl acetate. Afterwards, 2 µL *n*-dodecylbenzene is added as an internal standard (ISTD) using a 10 µL-Hamilton syringe. 0.8 mL of the resulting solution is filtered through silica gel (1.5 g, silica gel 60) with 2.5 mL of an ethyl acetate/methanol mixture (3:1) and analysed *via* gas chromatography. The resulting integral ratio between **2** and ISTD is graphically plotted against the corresponding sample weight (Figure S2). The quantities of **2** and the corresponding integral ratios obtained are given in Table S4.

Table S4. Calibration of GC via internal standard for acetovanillone (**2**).

entry / #	weight **2** / mg	integral **2**	integral ISTD	I(**2**) / I(ISTD)
1	2.042	10845	33006	0.329
2	3.977	28313	33096	0.855
3	6.000	47849	32711	1.463
4	9.006	72903	31219	2.335
5	12.108	99018	29963	3.305
6	14.989	132052	30255	4.365
7	20.000	194492	32281	6.025
8	25.050	244257	31189	7.832

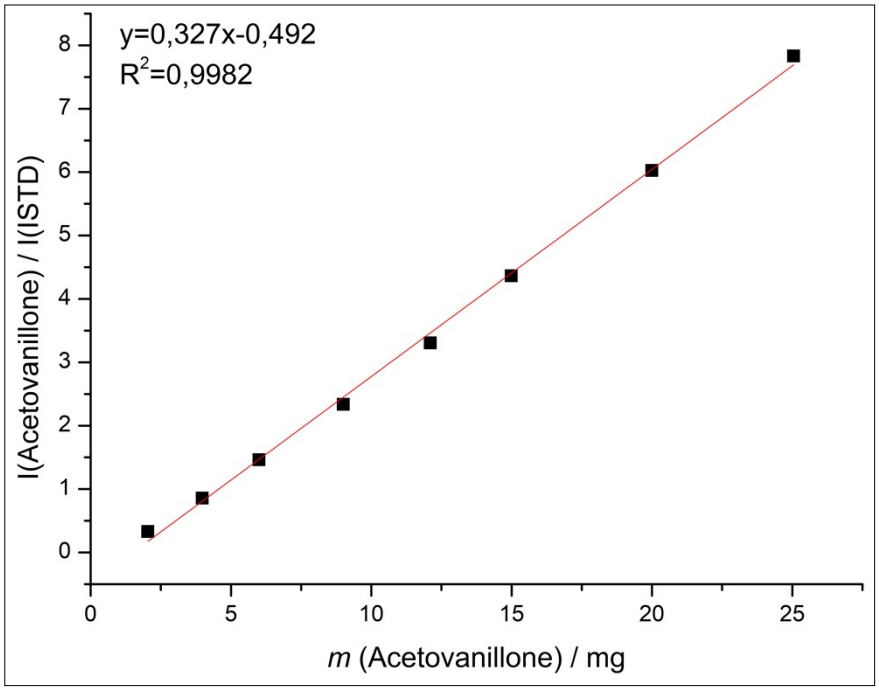

Figure S2. Plot of weight for acetovanillone (**2**) *vs*. integral ratio acetovanillone (**2**) and ISTD with linear fit.

After linear regression following equation is received:

$$I(\mathbf{2})/I(ISTD) = 0.327 \cdot m_{\mathbf{2}} - 0.492 \qquad (S2)$$

The fit line was not placed through the origin to consider potential product loss by the filtration process.

Quantification of Syringaldehyde. A precisely defined amount of syringaldehyde (**3**) is weighed into a vial and dissolved in a mixture consisting of 6 mL methanol and 2 mL ethyl acetate. Afterwards, 2 µL *n*-dodecylbenzene is added as an internal standard (ISTD) using a 10 µL-Hamilton syringe. 0.8 mL of the resulting solution is filtered through silica gel (1.5 g, silica gel 60) with 2.5 mL of an ethyl acetate/methanol mixture (3:1) and analysed *via* gas chromatography. The resulting integral ratio between **3** and ISTD is graphically plotted against the corresponding sample weight (Figure S3). The quantities of **3** and the corresponding integral ratios obtained are given in Table S5.

Table S5. Calibration of GC via internal standard for syringaldehyde (**3**).

entry / #	weight **3** / mg	integral **3**	integral ISTD	I(**3**) / I(ISTD)
1	2.096	3287	23415	0.140
2	3.983	12745	26517	0.481
3	6.009	25108	23890	1.051
4	9.016	40905	25065	1.632
5	11.974	58312	24361	2.394
6	15	81926	24320	3.369
7	19.981	121521	26608	4.567
8	24.969	164383	27568	5.963

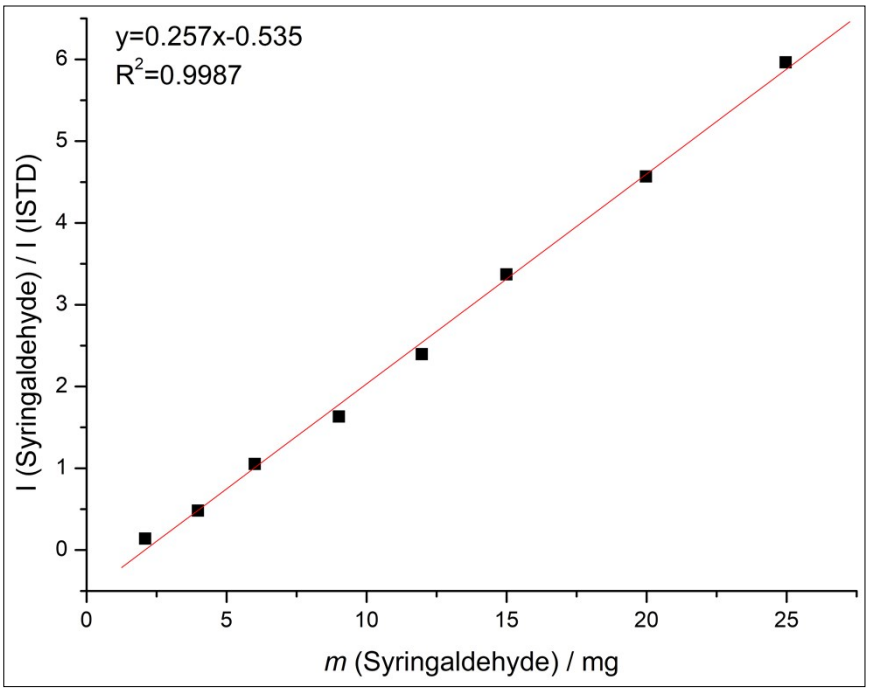

Figure S3. Plot of weight for syringaldehyde (**3**) *vs*. integral ratio syringaldehyde (**3**) and ISTD with linear fit.

After linear regression from entry 3 upwards, the following equation is received:

$$I(\mathbf{3})/I(\text{ISTD}) = 0.257 \cdot m_{\mathbf{3}} - 0.535 \qquad \text{(S3)}$$

The fit line was not placed through the origin to consider potential product loss by the filtration process.

Quantification of Acetosyringone. A precisely defined amount of acetosyringone (**4**) is weighed into a vial and dissolved in a mixture consisting of 6 mL methanol and 2 mL ethyl acetate. Afterwards, 2 µL *n*-dodecylbenzene is added as an internal standard (ISTD) using a 10 µL-Hamilton syringe. 0.8 mL of the resulting solution is filtered through silica gel (1.5 g, silica gel 60) with 2.5 mL of an ethyl acetate/methanol mixture (3:1) and analysed *via* gas chromatography. The resulting integral ratio between **4** and ISTD is graphically plotted against the corresponding sample weight (Figure S4). The quantities of **4** and the corresponding integral ratios obtained are given in Table S6.

Table S6. Calibration of GC via internal standard for syringaldehyde (**4**).

entry / #	weight **4** / mg	integral **4**	integral ISTD	I(**4**) / I(ISTD)
1	2.014	4040	20150	0.200
2	4.002	14332	22721	0.631
3	6.08	29973	26713	1.122
4	8.982	58206	27538	2.114
5	12.069	84238	27114	3.107
6	14.996	99764	24783	4.026
7	20.064	143751	24561	5.853
8	25.034	196749	26035	7.557

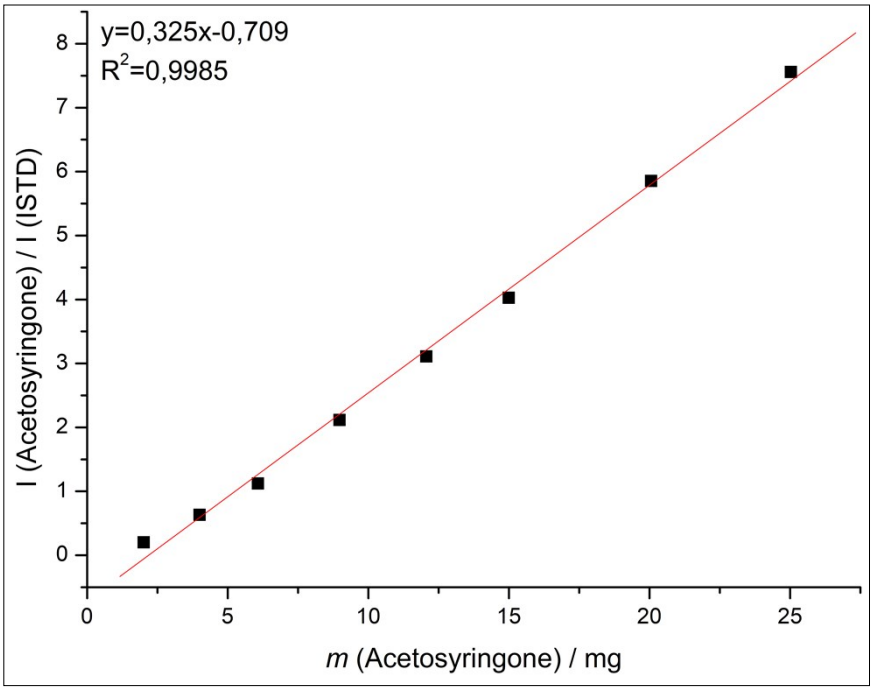

Figure S4. Plot of weight for acetosyringone (**4**) *vs*. integral ratio acetosyringone (**4**) and ISTD with linear fit.

After linear regression from entry 3 upwards, the following equation is received:

$$I(\mathbf{4})/I(\text{ISTD}) = 0.325 \cdot m_{\mathbf{4}} - 0.709 \qquad \text{(S4)}$$

The fit line was not placed through the origin to consider potential product loss by the filtration process.

Quantification of Guaiacol. A precisely defined volume of guaiacol (**5**) is given into a vial and dissolved in a mixture consisting of 6 mL methanol and 2 mL ethyl acetate. Afterwards, 2 µL *n*-dodecylbenzene is added as an internal standard (ISTD) using a 10 µL-Hamilton syringe. 0.8 mL of the resulting solution is filtered through silica gel (1.5 g, silica gel 60) with 2.5 mL of an ethyl acetate/methanol mixture (3:1) and analysed *via* gas chromatography. The resulting integral ratio between **5** and ISTD is graphically plotted against the corresponding sample weight (Figure S5). The quantities of **5** and the corresponding integral ratios obtained are given in Table S7.

Table S7. Calibration of GC via internal standard for guaiacol (**5**).

entry / #	weight **5** / mg	volume **5** / µL	integral **5**	integral ISTD	I(**5**) / I(ISTD)
1	2	1.8	17538	30029	0.584
2	4	3.6	27581	30793	0.897
3	6	5.4	61245	29229	2.095
4	9	8.0	96881	29667	3.266
5	12	10.7	134741	29729	4.532
6	15	13.4	171549	29969	5.724
7	20	17.9	233401	29707	7.857
8	25	22.3	304410	30191	10.083
9	30	26.8	379368	31099	12.199

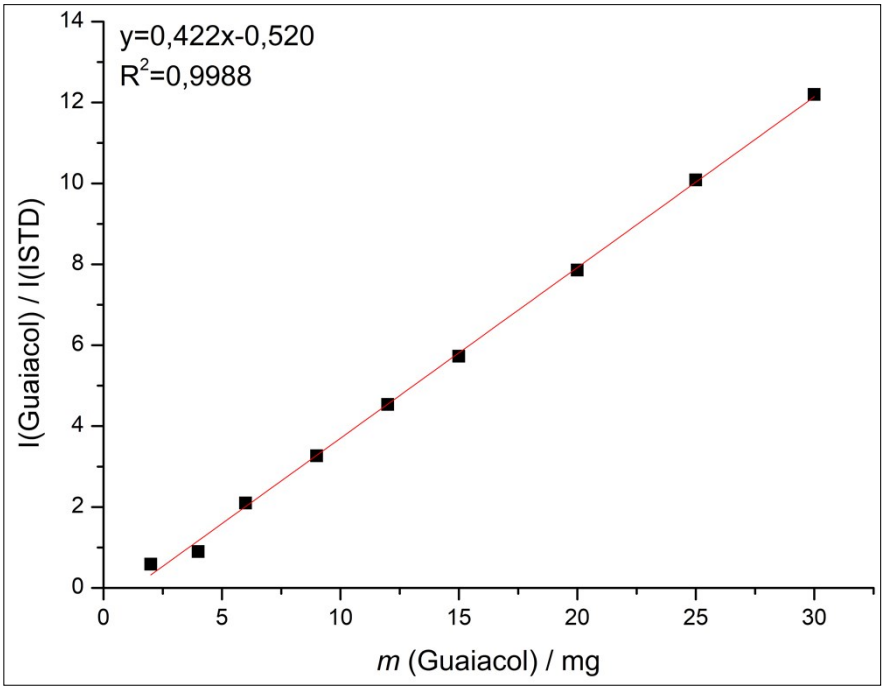

Figure S5. Plot of weight for guaiacol (**5**) *vs*. integral ratio guaiacol (**5**) and ISTD with linear fit.

After linear regression, the following equation is received:

$$I(\mathbf{5})/I(\text{ISTD}) = 0.422 \cdot m_{\mathbf{5}} - 0.520 \qquad \text{(S5)}$$

The fit line was not placed through the origin to consider potential product loss by filtration.

Quantification of organosolv lignin degradation. In general, to determine the yields of the products **1**–**5**, the crude product mixture from the lignin degradation is dissolved in a mixture consisting of 6 mL methanol and 2 mL ethyl acetate. Afterwards, 2 µL *n*-dodecylbenzene is added as an internal standard (ISTD) using a 10 µL-Hamilton syringe. 0.8 mL of the resulting solution is filtered through silica gel (1.5 g, silica gel 60) with 2.5 mL of an ethyl acetate/methanol mixture (3:1) and analysed *via* gas chromatography. The yields are provided using the equations S1–S5. The yields are given in wt%, based on the amount of lignin used. A typical Gas chromatogram is pictured below (Figure S6).

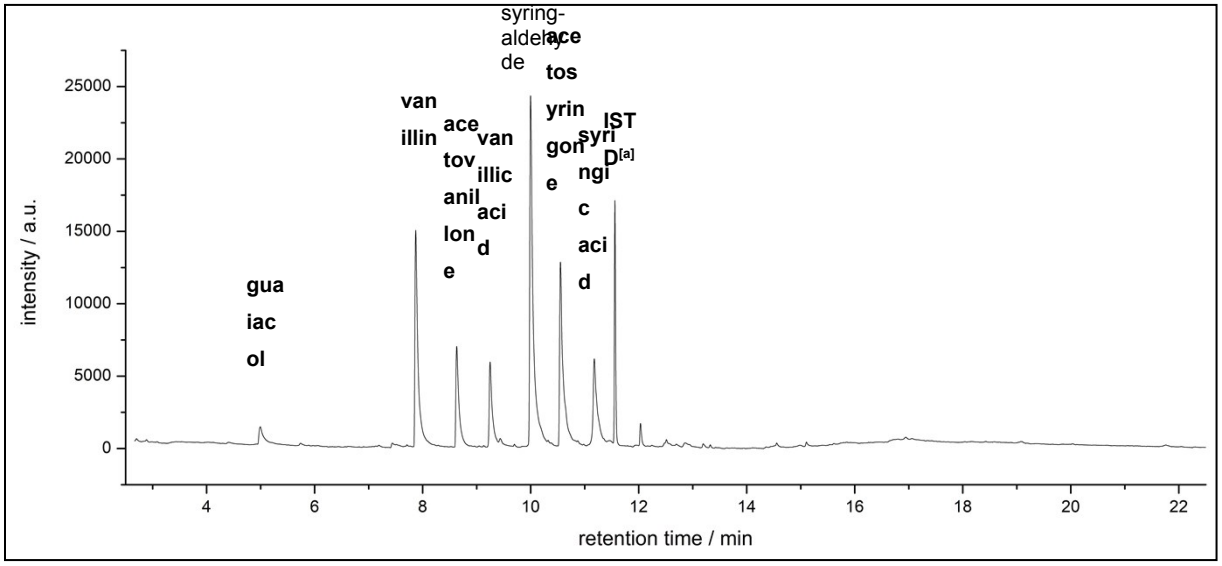

Figure S6. Gas chromatogram of crude product from high-temperature electrolysis of BEC-2-TNO lignin. [a]: *n*-dodecylbenzene as internal standard

Validity of the Calibration. The calibration for the products **1**–**5** was validated by isolating the resulting products from the electrolysis of BEC-2-TNO lignin under optimized reaction conditions. The usual workup by extraction with ethyl acetate (see Parameter Screening section, page S14) afforded 484 mg of crude product mixture. The remaining aqueous layer contained 102 mg of insoluble, oxidized lignin which was filtered off and dried for FT-IR and NMR analyses. The organic crude product mixture was separated *via* column chromatography on silica. A mixture of ethyl acetate and cyclohexane (1:1) was used as eluent. The obtained amount of product **1**–**5** is compared with the amount of product theoretically expected by calibration in table S8. The actual weight of the respective isolated compounds is given in parentheses. The relatively low percent recovery of 9% can be attributed to oligo- and polymers in the crude product that do not elute on the column. As these products were not of interest for this work, no further isolation or analytics were performed.

Table S8. Isolated yield compared with the yield determined *via* GC and internal calibration.

	1 yield / wt%	**2** yield / wt%	**3** yield / wt%	**4** yield / wt%	**5** yield / wt%
GC calibration	1.1	0.6	2.3	1.3	0.3
isolation	1.3 (9.9 mg)	0.7 (5.1 mg)	2.2 (16.7 mg)	1.2 (9.2 mg)	0.3 (2.5 mg)

Electrolytic conditions: 750 mg lignin; 85 g 3 M NaOH; nickel sheet electrodes; A = 6,2 cm^2; j = 15 mA/cm^2; Q = 2025 C (2.7 C per mg lignin); T = 180 °C; undivided cell; constant current mode.

Electrolysis Setup

High-temperature electrolysis cell (500 mL): High-temperature electrolysis experiments are conducted in a home-made undivided 0.5 L stainless steel cell (see Figure S7). The cell is sealable with a flange and equipped with a manometer, a pressure release- and an over-pressure valve (10 bar). The electrodes can be contacted to electricity from the outside. The inter-electrode gap is 18 mm. The electrolyte can be stirred with a magnetic stirrer. Heating is facilitated by a common oil bath with electric heating plate. A one-channel galvanostat (DC: 0–70 V; 0–1 A) with an external coulomb counter (both built by the mechanical shop of the *University of Bonn*) is used as power supply. For the electrochemical reaction, 2 x 6 cm electrodes of different materials are used. Terminal voltage in the cell following General Protocol A typically is in the range of 2–5 V.

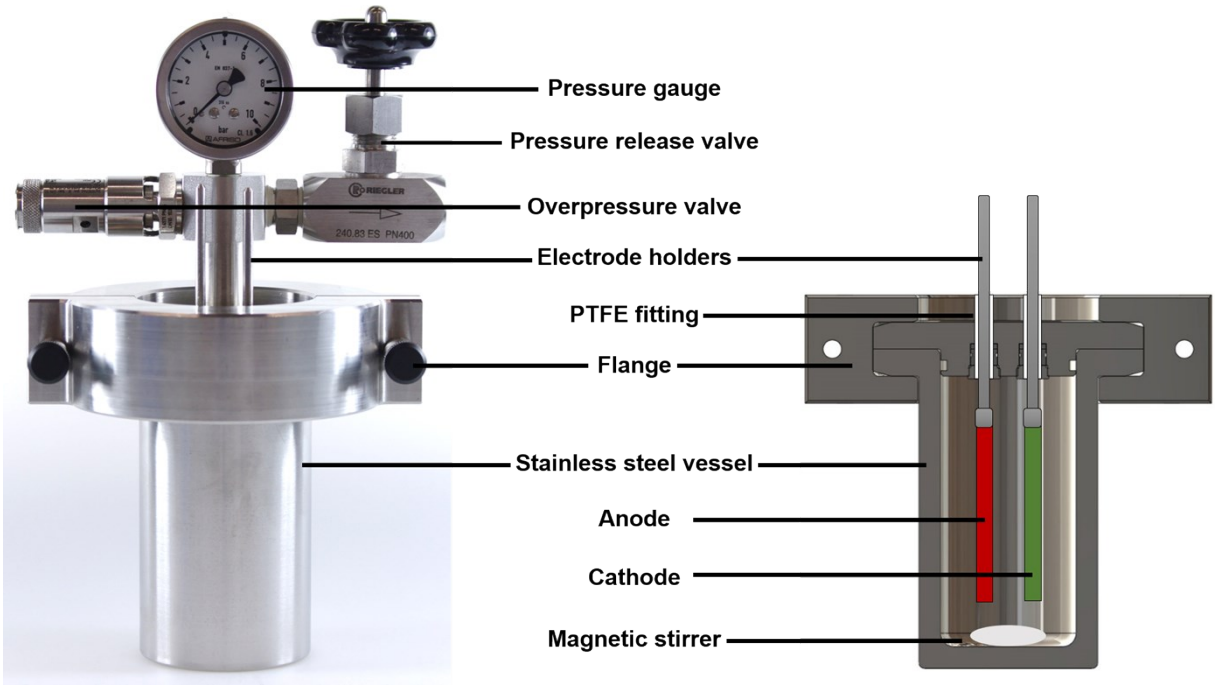

Figure S7. High-temperature electrolysis cell.

Parameter Screening

High-temperature electrolysis for the degradation of organosolv lignin (General Protocol A)

A solution of a defined amount of organosolv lignin in 85 g NaOH (various concentrations) is transferred into an undivided high-temperature electrolysis cell and the temperature is adjusted. After reaching the electrolysis temperature (approximated 25 min.), the corresponding electrodes are connected to electricity, and the electrolysis is started at constant current mode. The reactor was not pressurized externally. After complete application of the current, the mixture is allowed to come to room temperature (approx. 22 °C). The pH of the reaction mixture is adjusted by addition of conc. HCl (37%) to 1–2. The acidic mixture was extracted four times with ethyl acetate (approx. 150 mL each portion). During extraction, a brown precipitate formed in the separatory funnel, which was assigned to the aqueous phase and continuously extracted during the process to avoid product loss. The combined organic fractions are washed with a saturated NaCl solution (approx. 50 mL) and dried over anhydrous magnesium sulphate followed by solvent removal under reduced pressure. The crude product is dissolved in a mixture of 6 mL ethyl acetate and 2 mL of methanol, 2 µL of the ISTD (*n*-dodecylbenzene) is added, 0.8 mL of the resulting solution is filtered through silica gel (1.5 g, silica gel 60) with 2.5 mL of an ethyl acetate/methanol mixture (3:1) and analysed by GC/GC-MS. The yield of product **1**–**5** is determined with equation S1–S5. The yields are given in wt%, based on the amount of lignin used.

Precipitated, residual lignin in the aqueous phase is removed by filtration and dried in vacuum for further analysis *via* FT-IR and NMR spectroscopy.

All experiments were replicated to ensure the reproducibility and robustness of the electrolysis. The deviation in yield among individual experiments was never higher than 0.1 wt%. All following yields are concomitant with an error of ±0.1 wt%.

Initial test of various organosolv lignins from TNO (FABIOLA™ process)

According to General Protocol A, different organosolv lignins (provided by TNO) is electro-depolymerised using Ni sheet electrodes under non-optimized conditions (Table S9).

Table S9. High-temperature electrolysis of organosolv lignins (TNO) under non-optimized conditions.

entry / #	lignin	**1** yield / wt%[a]	**2** yield / wt%[a]	**3** yield / wt%[a]	**4** yield / wt%[a]
1	SPR-1-TNO	3.4	0.8	-	-
2	TNO-OS15100101	3.6	1.1	-	-
3	BEC-2-TNO	1.3	0.6	2.1	1.0
4	WHS-2-TNO	2.2	0.7	1.7	1.5

Electrolytic conditions: 525 mg lignin; 85 g 3 M NaOH; nickel sheet electrodes; A = 6.2 cm^2; j = 10 mA/cm^2; Q = 1418 C (2.7 C per mg lignin); T = 160 °C; undivided cell; constant current mode. [a] GC yields, 2 µL internal standard (*n*-dodecylbenzene), equation S1, S2, S3 and S4, yields are based on the amount of lignin used.

Optimization of current density for SPR-1-TNO lignin (spruce/softwood)

According to General Protocol A, SPR-1-TNO lignin is electro-depolymerised using Ni sheet electrodes by variation of the current density (Table S10).

Table S10. High-temperature electrolysis of SPR-1-TNO lignin under current density variation.

entry / #	j / mA/cm^2	**1** yield / wt%[a]	**2** yield / wt%[a]
1	5.0	3.5	1.1
2	7.5	2.7	0.8
3	10.0	3.4	0.9
4	12.5	3.7	1.0
5	15.0	3.7	1.0
6	20.0	3.4	0.9
7	25.0	3.1	0.8

Electrolytic conditions: 525 mg lignin; 85 g 3 M NaOH; nickel sheet electrodes; A = 6.2 cm^2; Q = 1418 C (2.7 C per mg lignin); T = 160 °C; undivided cell; constant current mode. [a] GC yields, 2 µL internal standard (*n*-dodecylbenzene), equation S1 and S2, yields are based on the amount of lignin used.

Optimization of lignin concentration for SPR-1-TNO lignin (spruce/softwood)

According to General Protocol A, SPR-1-TNO lignin is electro-depolymerised using Ni sheet electrodes by variation of the lignin concentration (Table S11).

Table S11. High-temperature electrolysis of SPR-1-TNO lignin under lignin concentration variation.

entry / #	lignin quantity / mg	**1** yield / wt%[a]	**2** yield / wt%[a]
1	525	3.7	1.0
2	600	3.6	0.9
3	675	3.7	1.0
4	725	3.7	1.0
5	750	3.7	1.0
6	800	3.5	0.9
7	850	3.4	0.9
8	1000	2.6	0.7
9	1500	2.7	0.8
10	2000	2.5	0.8

Electrolytic conditions: 85 g 3 M NaOH; nickel sheet electrodes; A = 6.2 cm^2; j = 15 mA/cm^2; Q = 2.7 C per mg lignin; T = 160 °C; undivided cell; constant current mode. [a] GC yields, 2 µL internal standard (*n*-dodecylbenzene), equation S1 and S2, yields are based on the amount of lignin used.

Optimization of base concentration for SPR-1-TNO lignin (spruce/softwood)

According to General Protocol A, SPR-1-TNO lignin is electro-depolymerised using Ni sheet electrodes by variation of the base concentration (Table S12).

Table S12. High-temperature electrolysis of SPR-1-TNO lignin under base concentration variation.

entry / #	c_{NaOH} / molL^{-1}	**1** yield / wt%[a]	**2** yield / wt%[a]
1	3.0	3.7	1.0
2	2.5	3.7	0.9
3	2.0	3.4	0.8
4	1.5	2.4	0.6
5	1.0	1.8	0.4
6	0.5	1.1	0.1

Electrolytic conditions: 750 mg lignin; 85 g NaOH; nickel sheet electrodes; A = 6.2 cm^2; j = 15 mA/cm^2; Q = 2025 C (2.7 C per mg lignin); T = 160 °C; undivided cell; constant current mode. [a] GC yields, 2 µL internal standard (*n*-dodecylbenzene), equation S1 and S2, yields are based on the amount of lignin used.

Optimization of applied amount of charge for SPR-1-TNO lignin (spruce/softwood)

According to General Protocol A, SPR-1-TNO lignin is electro-depolymerised using Ni sheet electrodes by variation of the applied amount of charge (Table S13).

Table S13. High-temperature electrolysis of SPR-1-TNO lignin under variation of the applied amount of charge.

entry / #	Q / C / mg(lignin)	**1** yield / wt%[a]	**2** yield / wt%[a]
1	2.0	3.3	0.8
2	2.7	3.7	1.0
3	3.0	3.7	0.9
4	3.5	3.7	0.9
5	5.0	3.0	1.0

Electrolytic conditions: 750 mg lignin; 85 g 3 M NaOH; nickel sheet electrodes; A = 6.2 cm^2; j = 15 mA/cm^2; T = 160 °C; undivided cell; constant current mode. [a] GC yields, 2 µL internal standard (*n*-dodecylbenzene), equation S1 and S2, yields are based on the amount of lignin used.

Optimization of reaction temperature for SPR-1-TNO lignin (spruce/softwood)

According to General Protocol A, SPR-1-TNO lignin is electro-depolymerised using Ni sheet electrodes by variation of the reaction temperature (Table S14).

Table S14. High-temperature electrolysis of SPR-1-TNO lignin under variation of the reaction temperature.

entry / #	*T* / °C	**1** yield / wt%[a]	**2** yield / wt%[a]	**5** yield / wt%[a]
1	140	2.2	0.5	-
2	150	2.5	0.6	-
3	160	3.7	1.0	-
4	170	3.7	0.9	0.2
5	180	4.0	1.2	0.5
6	190	3.6	1.3	0.8
7	200	3.4	1.5	1.5

Electrolytic conditions: 750 mg lignin; 85 g 3 M NaOH; nickel sheet electrodes; A = 6.2 cm^2; j = 15 mA/cm^2; Q = 2025 C (2.7 C per mg lignin); undivided cell; constant current mode. [a] GC yields, 2 µL internal standard (*n*-dodecylbenzene), equation S1, S2 and S5, yields are based on the amount of lignin used.

Optimization of electrode material for SPR-1-TNO lignin (spruce/softwood)

According to General Protocol A, SPR-1-TNO lignin is electro-depolymerised using different nickel- and cobalt-based electrodes (Table S15).

Table S15. High-temperature electrolysis of SPR-1-TNO lignin under variation of electrode material.

entry / #	electrode	**1** yield / wt%[a]	**2** yield / wt%[a]	**5** yield / wt%[a]
1	nickel sheet	4.0	1.2	0.5
2	nickel foam	3.5	0.4	0.5
3	Hastelloy C276	3.4	1.1	0.5
4	Monel 400k	3.7	1.3	0.4
5	Waspalloy	3.4	1.1	0.5
6	Ni/Cr 053250	3.6	1.1	0.4
7	Inconel 625	3.8	1.1	0.4
8	Cobalt 99,9%	1.3	0.6	0.5
9	Stellite™ 21	3.9	1.2	0.9
10	Tribaloy™ T-400	2.0	0.8	0.8
11	Stellite™ 4	2.9	0.9	0.8
12	Stellite™ 6	4.2	1.1	0.8
13	Tribaloy™ T-400C	1.9	0.8	0.8
14	Deloro™ 40	2.8	0.9	0.8
15	Ti/Al/V	2.7	1.0	0.5

Electrolytic conditions: 750 mg lignin; 85 g 3 M NaOH; j = 15 mA/cm^2 (based on the geometric shape); Q = 2025 C (2.7 C per mg lignin); T = 180 °C; undivided cell; constant current mode. [a] GC yields, 2 µL internal standard (*n*-dodecylbenzene), equation S1, S2 and S5, yields are based on the amount of lignin used.

High-temperature electrolysis of different organosolv lignins

According to General Protocol A, different organosolv lignins are electro-depolymerised with optimized conditions using nickel sheet electrodes (Table S16).

Table S16. High-temperature electrolysis of different organosolv lignins under optimized conditions.

entry / #	lignin	**1** yield / wt%[a]	**2** yield / wt%[a]	**3** yield / wt%[a]	**4** yield / wt%[a]	**5** yield / wt%[a]
1	SPR-1-TNO	4.0	1.2	-	-	0.5
2	TNO-OS15100101	4.0	1.2	-	-	0.5
3	BEC-2-TNO	1.4	0.7	2.4	1.2	0.3
4	WHS-2-TNO	2.5	1.0	1.8	2.5	-
5	Fichte KO 124	2.1	0.8	-	-	0.3
6	Buche KO 168	1.3	0.6	2.7	1.4	0.3
7	Clariant straw	1.3	0.7	0.9	1.3	-

Electrolytic conditions: 750 mg lignin; 85 g 3 M NaOH; nickel sheet electrodes; A = 6,2 cm^2; j = 15 mA/cm^2; Q = 2025 C (2.7 C per mg lignin); T = 180 °C; undivided cell; constant current mode. [a] GC yields, 2 µL internal standard (*n*-dodecylbenzene), equation S1–S5, yields are based on the amount of lignin used.

Thermal Lignin Degradation

A solution of 0.525 g of the respective organosolv lignin in 85 g 3 M NaOH is transferred into the undivided high-temperature electrolysis cell (with immersed nickel electrodes) and temperature is adjusted to 160 °C. After reaching the temperature (approximated 25 min.), the reaction is heated for additional 6.6 hours without applying electricity. The reactor was not pressurized externally. After 6.6 hours of heating at 160 °C, the mixture is allowed to cool to room temperature (approx. 22 °C). The pH of the reaction mixture is adjusted by addition of conc. HCl (37%) to 1–2. The acidic mixture was extracted four times with ethyl acetate (approx. 150 mL each portion). During extraction, a brown precipitate formed in the separatory funnel, which was assigned to the aqueous phase and continuously extracted during the process to avoid product loss. The combined organic fractions are washed with a saturated NaCl solution (approx. 50 mL) and dried over anhydrous magnesium sulphate followed by solvent removal under reduced pressure. The crude product is dissolved in a mixture of 6 mL ethyl acetate and

2 mL of methanol, 2 µL of the ISTD (*n*-dodecylbenzene) is added, 0.8 mL of the resulting solution is filtered through silica gel (1.5 g, silica gel 60) with 2.5 mL of an ethyl acetate/methanol mixture (3:1) and analysed by GC/GC-MS. The yield of the products **1**–**5** is determined with equation S1–S5. The yields are given in wt%, based on the amount of lignin used.

Table S17. Thermal degradation of organosolv lignin.

entry / #	lignin	**1** yield / wt%[a]	**2** yield / wt%[a]	**5** yield / wt%[a]
1	SPR-1-TNO	1.5	0.6	-
2	TNO-OS15100101	1.3	0.7	0.6

Reaction conditions: 525 mg lignin; 85 g 3 M NaOH; nickel electrodes; t = 6.6 h; T = 160 °C; undivided cell; [a] GC yields, 2 µL internal standard (*n*-dodecylbenzene), equation S1, S2 and S5, yields are based on the amount of lignin used.

Nitrobenzene Oxidation of Lignin (NBO)

The NBO experiment of lignin was conducted at 170 °C for 2.5 hours according to the literature.[1,2] 100 mg of the respective organosolv lignin was reacted in 14 mL 2 M NaOH with 0.8 mL nitrobenzene in a glass pressure tube at 170 °C for 2.5 h. Afterwards, the reaction mixture was allowed to come to room temperature. The alkaline solution was transferred to a separation funnel and extracted three times with dichloromethane (30 mL each) to remove unreacted nitrobenzene and its reaction products. The remaining aqueous alkaline mixture was acidified with conc. HCl (37%) to pH 2. The acidified solution was further extracted four times with ethyl acetate (25 mL each). After washing of the organic fraction with saturated aqueous NaCl solution, drying over magnesium sulphate and evaporation of the solvent a crude dark brownish solid was afforded. The crude product was dissolved in a mixture of 6 mL ethyl acetate and 2 mL of methanol, 2 µL of the ISTD (*n*-dodecylbenzene) was added. 0.8 mL of the resulting solution was filtered through silica gel (1.5 g, silica gel 60) with 2.5 mL of an ethyl acetate/methanol mixture (3:1) and analysed by GC/GC-MS. The yields of product **1** and product **3** were determined with equation 1 and 3. The yields are given in wt%, based on the amount of lignin used.

Table S18. Nitrobenzene oxidation of different organosolv lignins.

entry / #	lignin	**1** yield / wt%[a]	**3** yield / wt%[a]
1	SPR-1-TNO	5.8	-
2	TNO-OS15100101	7.0	-
3	BEC-2-TNO	3.8	5.3
4	WHS-2-TNO	5.5	5.4
5	Fichte KO 124	5.0	-
6	Buche KO 168	3.6	6.7
7	Clariant straw	3.5	4.3

[a] GC yields, 2 µL internal standard (*n*-dodecylbenzene), equation S1 and S5, yields are based on the amount of lignin used.

Stability test of monoaromatic compounds

A. A solution of 52 mg vanillin and 50.8 mg acetovanillone in 85 g 3M NaOH is transferred into an undivided high-temperature electrolysis cell with nickel electrodes and the temperature is adjusted to 180 °C. After reaching the electrolysis temperature (approximately 25 min.), the electrodes are connected to electricity, and the electrolysis is started at constant current mode with the following parameters: The electrode surface area was A=6.2 cm^2, the current density was j=15 mA/cm^2, the resulting current was I=93 mA and the amount of charge was 2025 C (resulting from the previously optimized conditions). The reactor was not pressurized externally. After complete application of the current (approximately 6 h 15 min), the mixture is allowed to come to room temperature (approx. 22 °C). The pH of the reaction mixture is adjusted by addition of conc. HCl (37%) to 1–2. The acidic mixture was extracted four times with ethyl acetate (approx. 150 mL each portion). The combined organic fractions are washed with a saturated NaCl solution (approx. 50 mL) and dried over anhydrous magnesium sulphate followed by solvent removal under reduced pressure, resulting in an organic fraction of 24 mg. The crude product is dissolved in a mixture of 6 mL ethyl acetate and 2 mL of methanol, 2 µL of the ISTD (*n*-dodecylbenzene) is added, 0.8 mL of the resulting solution is filtered through silica gel (1.5 g, silica gel 60) with 2.5 mL of an ethyl acetate/methanol mixture (3:1) and analysed by GC/GC-MS. No other signal than the standard could be detected via GC/GCMS. This indicates that during electrolysis, higher oligomers and polymers form that are either removed in the filtration process or can not be detected via GC/GC-MS. This theory is further

supported by a rusty red precipitate that formed on the anode surface which could only be removed with sandpaper.

B. A solution of 50.5 mg vanillin and 52.8 mg acetovanillone in 85 g 3 M NaOH is transferred into the undivided high-temperature electrolysis cell (with immersed nickel electrodes) and temperature is adjusted to 180 °C. After reaching the temperature (approximated 25 min.), the reaction is heated for additional 6 h 15 min without applying electricity. The reactor was not pressurized externally. After the heating period, the mixture is allowed to cool to room temperature (approx. 22 °C). The pH of the reaction mixture is adjusted by addition of conc. HCl (37%) to 1–2. The acidic mixture was extracted four times with ethyl acetate (approx. 150 mL each portion). The combined organic fractions are washed with a saturated NaCl solution (approx. 50 mL) and dried over anhydrous magnesium sulphate followed by solvent removal under reduced pressure, resulting in an organic fraction of 103 mg. The crude product is dissolved in a mixture of 6 mL ethyl acetate and 2 mL of methanol, 2 µL of the ISTD (*n*-dodecylbenzene) is added, 0.8 mL of the resulting solution is filtered through silica gel (1.5 g, silica gel 60) with 2.5 mL of an ethyl acetate/methanol mixture (3:1) and analysed by GC/GC-MS. The yield of the products **1** and **2** is determined with equation S1 and S2. The reaction afforded 39.2 mg (78% of the starting material) of vanillin and 35.4 mg (67% of the starting material) of acetovanillone. The gas chromatogram furthermore showed 2.0 mg of guaiacol that formed during the process, as well as traces of vanillic acid. The results show that the two compounds are much more stable if no electric current is applied, yet not inert to oxidation processes or Cannizzaro reaction.

FT-IR Spectroscopy

Fourier-transformed infrared (FT-IR) spectroscopy was performed at 20 °C on an ALPHA ATR spectrometer (Bruker Optik GmbH, Germany).

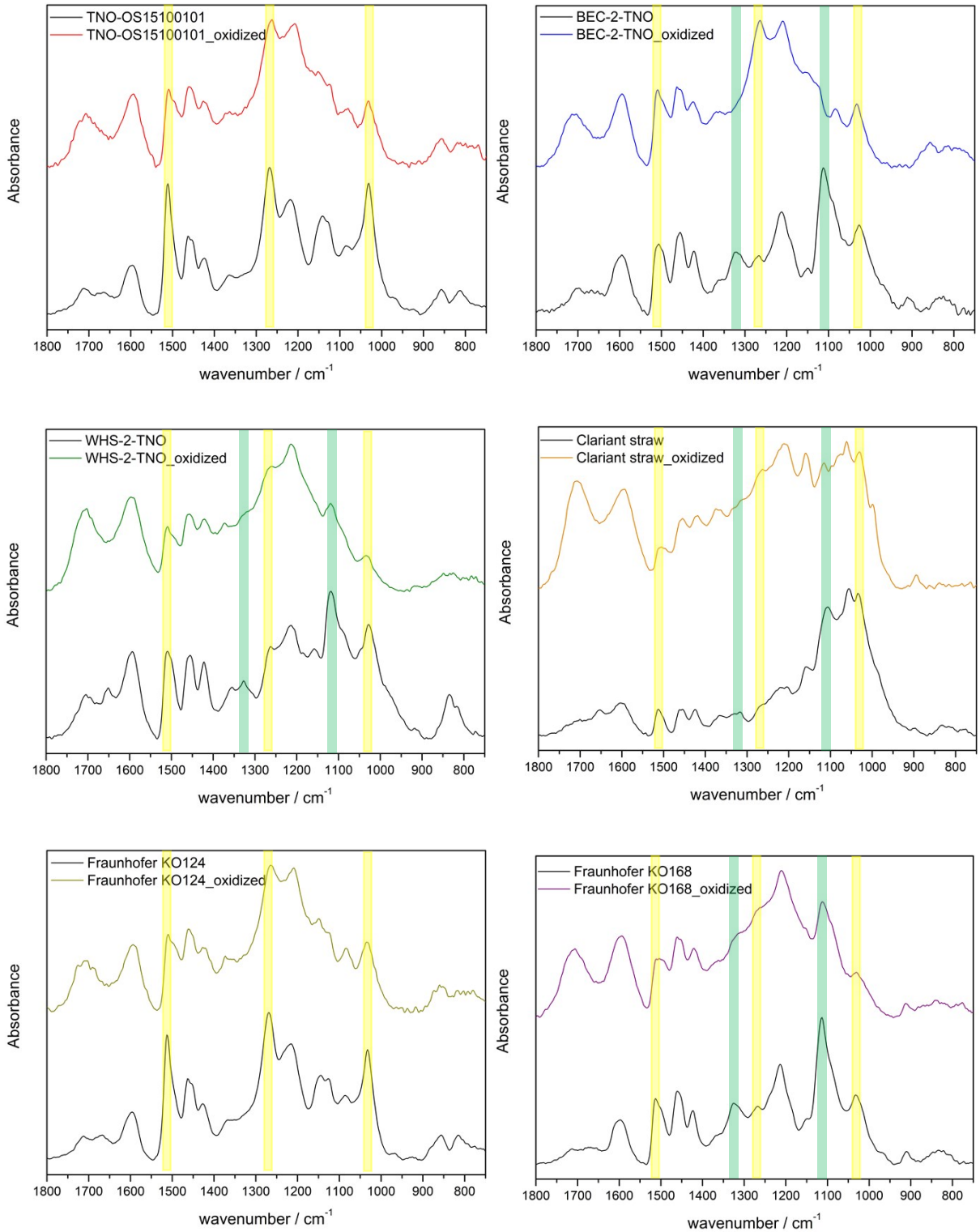

Figure S8. Spectra of different organosolv lignins before and after electrochemical treatment characterized via FT-IR (characteristic bands for *G*-units highlighted in yellow, characteristic bands for *S*-units highlighted in green).

NMR Spectroscopy

^{31}P NMR spectroscopy. To quantify hydroxyl functional groups in the respective organosolv lignins prior and after electrochemical depolymerisation, ^{31}P NMR spectroscopy was applied using a standard phosphitylating protocol.[3,4] 2-Chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP, purchased from Sigma Aldrich) was employed as phosphitylating agent. Lignin samples were dried under vacuum at RT for 24 hours. All solvents were dried and degassed prior to use. All further actions were carried out in a glovebox under argon atmosphere. Approximately 25 mg of the respective lignin was accurately weighed in a 5 mL vial. A solvent mixture of pyridine (Merck Millipore) and $CDCl_3$ (Deutero) (1.6/1 v/v) was prepared and 400 µL added to the lignin. A solution of chromium(III) acetylacetonate (Merck Millipore) (3.6 mg/mL) and cyclohexanol (Aldrich) (4.58 mg/mL) in pyridine/$CDCl_3$ was prepared and 150 µL added to the lignin solution. Chromium(III) acetylacetonate served as a spin relaxation agent and cyclohexanol as internal standard. The resulting solution was vigorously stirred until complete dissolving of the lignin. 50 µL of TMDP was added to the vial minutes before starting the NMR experiment and the solution was transferred to a 5-mm NMR tube. The ^{31}P NMR spectra were recorded at RT on a multi-nuclear resonance spectrometer type Avance III HD 400 from Bruker, Karlsruhe, Germany. The following acquisition parameters were used: inverse-gated pulse sequence, 25 s pulse delay, 200 acquisitions, 61.7 ppm sweep width (145 ppm used as centre), 30° pulse width. A 4 Hz line broadening was employed. The spectra were manually phased, using the signals of the internal standard and water as aids. Baseline correction was executed by the program. An integration file was generated and used for each spectrum. The integration regions for the respective functionalities are listed in table S19.

Table S 19. Integration regions used for the functional groups in quantitative ^{31}P NMR spectra of organosolv lignins phosphitylated with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane.

Structure or Functional group	Integration region / ppm
Cyclohexanol (internal standard)	145.30–144.90
aliphatic -OH	150.00–145.30
C_5 substituted phenolic -OH	144.50–140.75
Guaiacyl phenolic -OH	140.75–137.00
COOH	137.00–133.0

The signal area of cyclohexanol derivatized with TMDP, resulting from $6.87x10^{-4}$ of cyclohexanol, was integrated and calibrated to 1.0. As cyclohexanol contains one hydroxyl group and has a molecular weight of 100.16 $gmol^{-1}$, the number of moles of hydroxyl groups resulting from the standard in the sample was $6.859x10^{-6}$ mol. As a result, every unit area in the spectrum is equal to $6.859x10^{-6}$ mol of hydroxyl groups. By multiplying with the integration area of interest and dividing by the weight of the lignin sample, the number of moles of hydroxyl groups per g lignin was calculated. The results are shown in table S20.

Table S 20. Results for the quantitative analysis of the hydroxyl functionalisation of various organosolv lignins *via* ^{31}P NMR experiments (TMDP as phosphitylating agent).

lignin	Aliphatic OH / $mmol*g^{-1}$	C_5 subst. phenolic OH / $mmol*g^{-1}$	Guaiacyl phenolic OH / $mmol*g^{-1}$	COOH / $mmol*g^{-1}$
TNO-OS15100101	2.28	0.75	1.51	0.28
TNO-OS15100101 (oxidised)[a]	0.59	1.14	1.71	1.32
BEC-2-TNO	1.62	2.11	1.01	0.23
BEC-2-TNO (oxidised)[a]	0.35	1.66	1.14	1.51
WHS-2-TNO	2.15	1.07	1.31	0.65
WHS-2-TNO (oxidised)[a]	0.47	1.14	1.32	1.97

[a]Electrolytic conditions: 750 mg lignin; 85 g 3 M NaOH; nickel sheet electrodes; A = 6,2 cm^2; j = 15 mA/cm^2; Q = 2025 C (2.7 C per mg lignin); T = 180 °C; undivided cell; constant current mode.

The respective spectra are shown in figure S9.

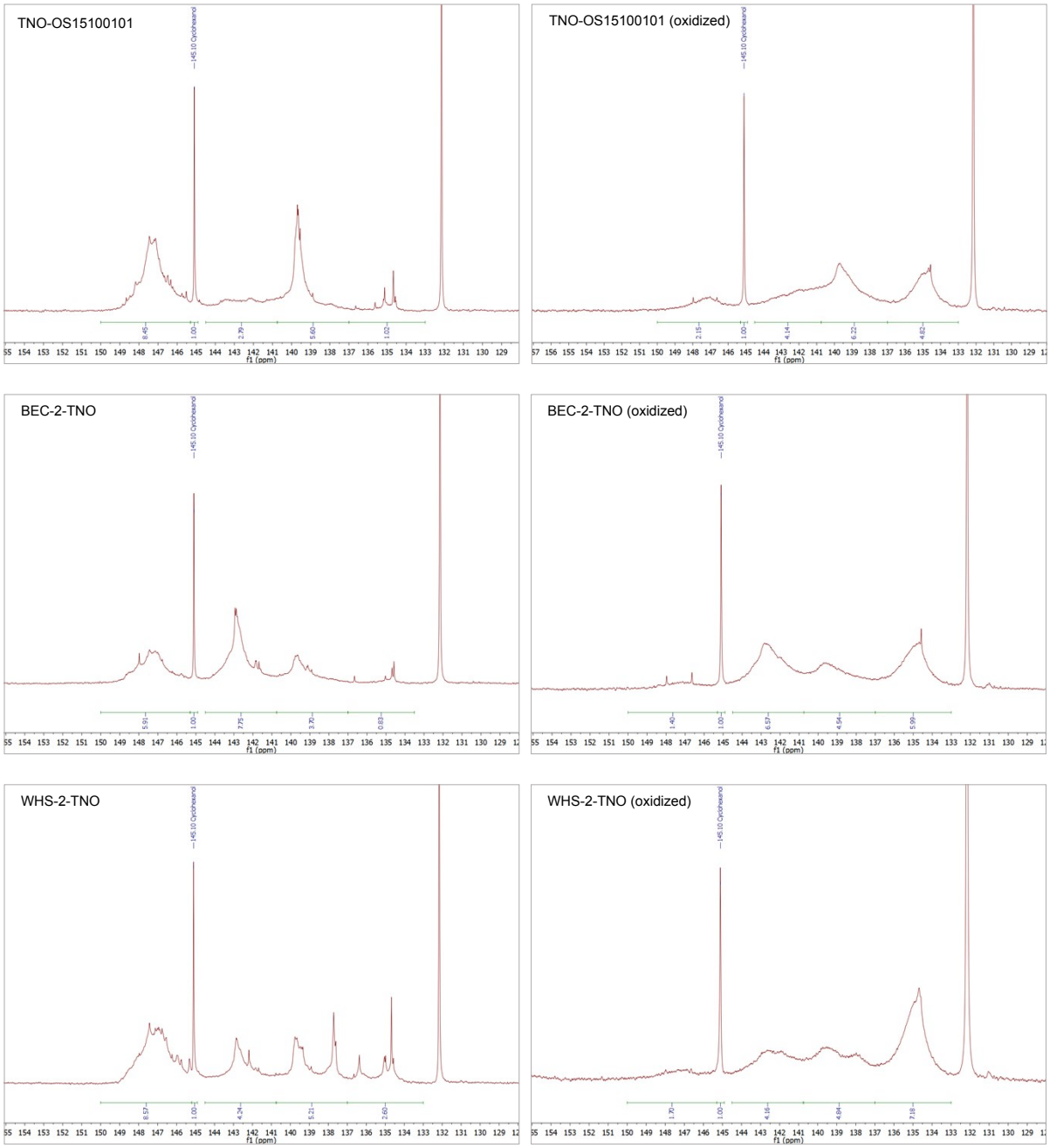

Figure S9. ^{31}P NMR spectra of various native and oxidized organosolv lignins with respective integration for hydroxyl quantification.

2D HSQC NMR spectroscopy. For heteronuclear single quantum coherence (HSQC) NMR spectroscopy of organosolv lignin, 200 mg of the respective lignin sample was dissolved in 0.6 mL DMSO-d_6 (Deutero) under vigorous stirring. The spectra were acquired at RT on a multi-nuclear resonance spectrometer type Avance III 600 from Bruker, Karlsruhe, Germany. A hsqcetgpsisp 2.2 pulse sequence was used. Matrices of 1024 data points in the ^{1}H-dimension and 256 data points in the ^{13}C-dimension were collected with a relaxation delay of 5 s and spectral widths from 10 to -1 ppm (^{1}H-dimension) and 160 to 0 ppm (^{13}C-dimension). The number of scans was 32. The spectra were processed with MestReNova. The spectra

were zero-filled up to 1024 points in the ^{13}C-dimension and automatic phase correction was applied. The central solvent peak (DMSO) was used as internal shift reference point (δ_C = 39.52 ppm, δ_H = 2.50 ppm). Assignment of the signals was carried out according to literature and is shown in table S21.[5,6]

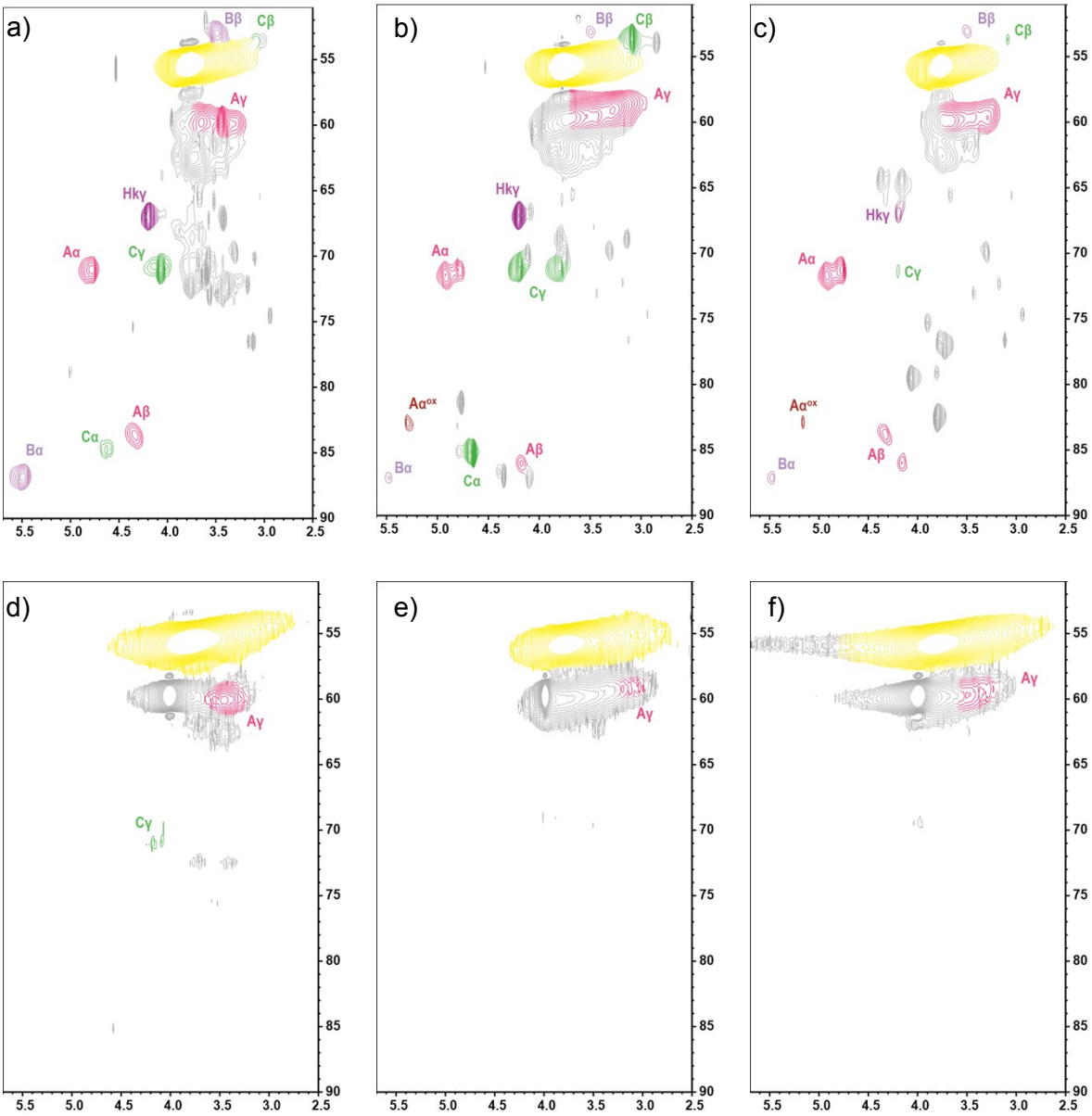

Figure S10. 2D HSQC NMR spectra of the aliphatic oxygenated region of a) TNO-OS15100101(pine), b) BEC-2-TNO (beech), c) WHS-2-TNO (wheatstraw), d) TNO-OS15100101(pine) after electrolysis, e) BEC-2-TNO (beech) after electrolysis, f) WHS-2-TNO (wheatstraw) after electrolysis and the main lignin structures identified (A) β-O-4, (B) β-5, (C) β-β, (Hk) Hibert's ketone, yellow peaks correspond to OMe groups.

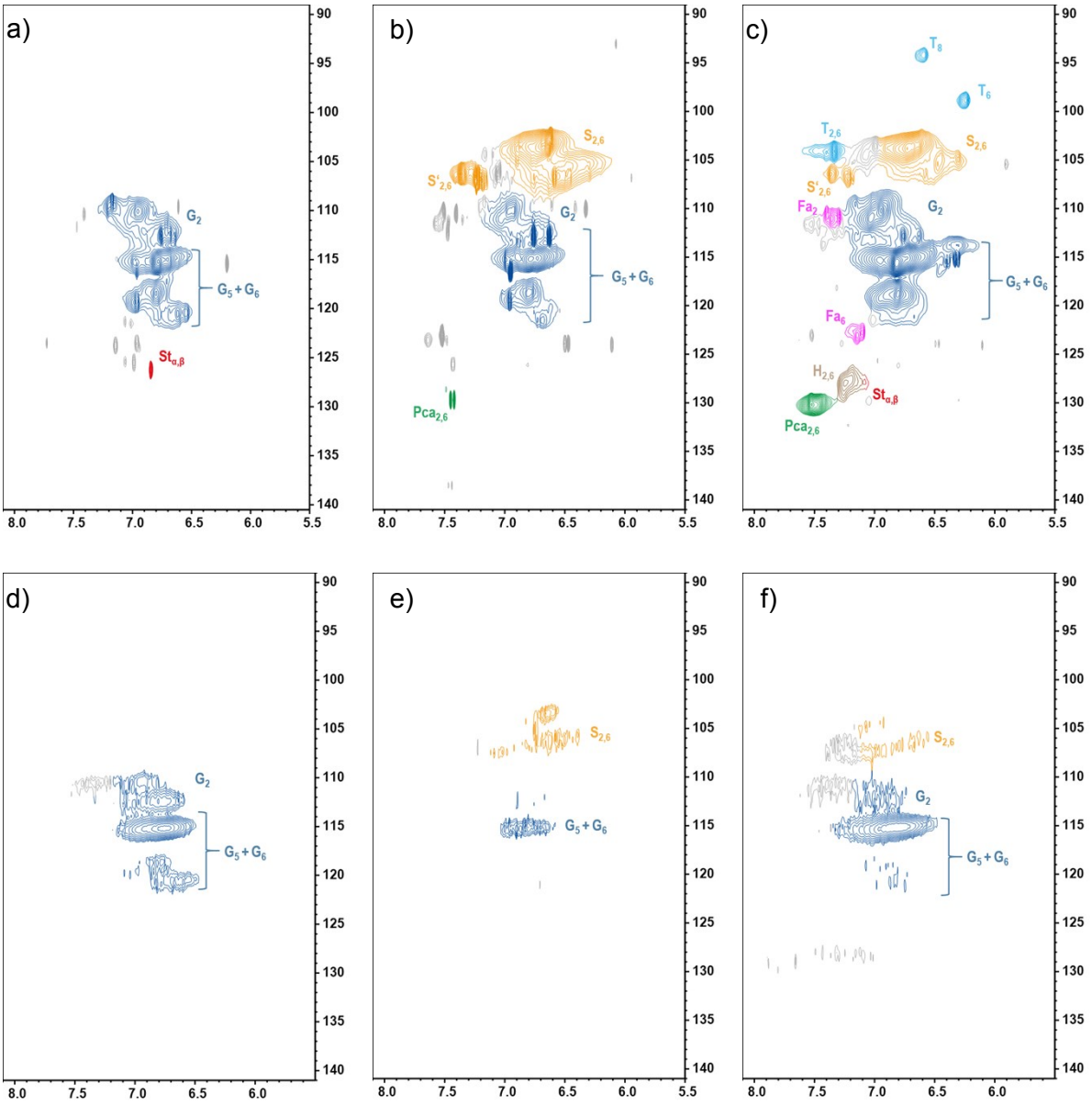

Figure S11. 2D HSQC NMR spectra of the aromatic region of a) TNO-OS15100101(pine), b) BEC-2-TNO (beech), c) WHS-2-TNO (wheatstraw), d) TNO-OS15100101(pine) after electrolysis, e) BEC-2-TNO (beech) after electrolysis, f) WHS-2-TNO (wheatstraw) after electrolysis and the main lignin structures identified (S) syringyl, (S'), *α*-oxidized syringyl, (G) guaiacyl, (H) p-hydroxyphenyl, (F) ferulate, (T) tricin, (Pca) p-coumarate and (St) stilbene.

All NMR spectra were analysed with MestReNova (version: 10.0.2 15465).

Table S21. ^{13}C and ^{1}H assignments of the lignin signals in 2D [^{13}C, ^{1}H] HSQC spectra[a]

label	δC/δH (ppm)						assignment
	pine	pine^{ox}	beech	beech^{ox}	straw	straw^{ox}	
B_β	53.0/3.5	n.d.	53.1/3.5	n.d.	53.0/3.5	n.d.	C_β−H_β in phenylcoumaran substructures (B)
C_β	53.6/3.1	n.d.	53.7/3.7	n.d.	53.7/3.1	n.d.	C_β−H_β in β−β′ resinol substructures (C)
-OMe	55.5/3.8	55.6/3.8	55.8/3.8	55.9/3.8	55.8/3.8	55.8/3.8	C−H in methoxyls
A_γ	60.0/3.7–3.3	60.1/3.6–3.4	59.4/3.7–3.3	59.3/3.4–3.1	59.6/3.7–3.3	59.7/3.6–3.3	C_γ−H_γ in γ−hydroxylated β-O-4′ substructures (A)
B_γ	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	C_γ−H_γ in phenylcoumaran substructures (B)
Hk_γ	67.0/4.2	n.d.	67.1/4.2	n.d.	67.1/4.2	n.d.	C_γ−H_γ in Hibbert ketone structures
C_γ	71.1/4.1 and 3.6	71.0/4.1	71.1/4.2 and 3.8	n.d.	71.3/4.2	n.d.	C_γ−H_γ in β−β′ resinol substructures (C)
A_α	71.0/4.8x	n.d.	71.2/4.8 and 71.6/4.9	n.d.	71.2/4.8 and 71.7/4.9	n.d.	C_α−H_α in β-O-4′ substructures (A
A_β	83.6/4.3	n.d.	86.0/4.2 (S)	n.d.	83.4/4.3 (G) and 86.0/4.2 (S)	n.d.	C_β−H_β in β-O-4’ substructures (A)
A_β^{ox}	n.d.	n.d.	83.0/5.3	n.d.	82.8/5.2	n.d.	C_β−H_β in α-oxidised β-O-4′ substructures (A^{ox})
C_α	85.8/4.6	n.d.	85.3/4.7	n.d.	n.d.	n.d.	C_α−H_α in β−β′ resinol substructures (C)
B_α	86.8/5.5	n.d.	87.1/5.5	n.d.	87.2/5.5	n.d.	C_α−H_α in phenylcoumaran substructures (B)
T_8	n.d.	n.d.	n.d.	n.d.	94.3/6.6	n.d.	C_8−H_8 in tricin units (T)
T_6	n.d.	n.d.	n.d.	n.d.	98.8/6.2	n.d.	C_6−H_6 in tricin units (T)
$T_{2,6}$	n.d.	n.d.	n.d.	n.d.	104.1/7.6	n.d.	C_2−H_2 and C_6-H_6 in tricin units (T)
$S_{2,6}$	n.d.	n.d.	103.4/6.6	103.5/6.7	103.8/6.7	104.4/6.9	C_2−H_2 and C_6−H_6 in syringyl units (S)
$S'_{2,6}$	n.d.	n.d.	106.4/7.4 and 106.9/7.2	n.d.	106.7/7.4 and 7.2	n.d.	C_2−H_2 and C_6−H_6 in syringyl units with α oxidisation(S’)
G_2	110.1/7.0	110.3/7.0	110.2/6.9	n.d.	110.2/7.0	112.0/7.0	C_2−H_2 in guaiacyl units (G)
Fa_2	n.d.	n.d.	n.d.	n.d.	111.0/7.4	n.d.	C2−H2 in ferulate (Fa)
$G_{5,6}$	115.2/6.8 and 119.3/7.0x	115.2/6.8	115.2/6.8 and 119.2/7.0	115.2/6	115.0/6.7 and 118.8/6.8	115.2/6.8	C5−H5 and C6−H6 in guaiacyl units (G)
Fa_6	n.d.	n.d.	n.d.	n.d.	123.0/7.1	n.d.	C6−H6 in ferulate (Fa)
$St_{\alpha,\beta}$	126.3/6.9	n.d.	n.d.	n.d.	127.9/7.1	n.d.	Cα−Hα and Cβ−Hβ in stilbene structures (St)
$H_{2,6}$	n.d.	n.d.	n.d.	n.d.	127.9/7.2	n.d.	C2,6−H2,6 in p-hydroxyphenyl units (H)
$Pca_{2,6}$	n.d.	n.d.	129.7/7.4	n.d.	130.2/7.5	n.d.	C2−H2 and C6−H6 in p-coumarate (Pca)

[a]Signals were assigned according to literature.[5,6,7]

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