Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting information to the research paper "Overcoming lignin heterogeneity: Reliably characterizing the cleavage of technical lignin"

Run list

In order to prevent systematic errors influencing the experimental data, the different experimental runs are conducted in a randomized order. Table SI 1 shows the specific parameters of the different runs as well as the sequence in which they were conducted. The standardized order makes it easier to see the clustering according to the specific reaction parameters, whereas the run number is the actual sequence of the experiments.

Table SI 1 Detailed listing of the reaction parameters and run order for the conducted experiments

Run	Standardized Order	Temperature [°C]	Current density [A/cm²]	C_{Lignin} [mol/l]	C_{NaOH} [mol/l]	Electrode material
1	1	30	0.0021	5	1	Pt
2	12	80	0.0383	5	4	Ni
3	13	30	0.0021	20	4	Pt
4	9	30	0.0021	5	4	Ni
5	2	80	0.0021	5	1	Ni
6	16	80	0.0383	20	4	Pt
7	15	30	0.0383	20	4	Ni
8	4	80	0.0383	5	1	Pt
9	10	80	0.0021	5	4	Pt
10	3	30	0.0383	5	1	Ni
11	7	30	0.0383	20	1	Pt
12	6	80	0.0021	20	1	Pt
13	14	80	0.0021	20	4	Ni
14	11	30	0.0383	5	4	Pt
15	5	30	0.0021	20	1	Ni
16	8	80	0.0383	20	1	Ni

Model significancies concerning the different investigated signals

Model significancies show how statistically reliable the conclusions drawn from the DoE are. The number signifies how probable the observed result is, if no statistical correlation between the factors and the signals exist. A number of 0.0019 means that the observed behavior of the system only occurs in 0.19% of all cases, if there is no underlying correlation between factor and signal as interpreted. Table SI 2 shows the significancies of the evaluated signals.

Table SI 2 Model significancies for the evaluated signals. Values lower than 0.05 signal significancy, lower 0.001 signal high significancy

evaluated signal	significancy
UV absorbance	0.0019
Vanillin yield	<0.0001
Monomer yield	0.0011
Acid insoluble lignin	<0.0001
Molecular weight	0.0039

Vanillic acid fraction	<0.0001

Transformations

Following data transformation has been conducted before evaluating the data statistically:

Table SI 3 Transformation of specific data sets

transformed signal	transformation
vanillic acid fraction	y'=1/y
acid insoluble lignin	y'=y^0.5

Standard Error of Measurement (SEM)

Table SI 4 Typical Standard Error of Measurement for the applied analysis methods

Analytical technique	Average SEM
Lignin acid solubility	0.005%
UV-absorbance	0.528%
Monomer concentration	0.728%
Molecular weight	0.371%

Electrochemical reactor

Fig. SI 1 shows the scheme of the utilized electrochemical reactor and its most important characteristics.

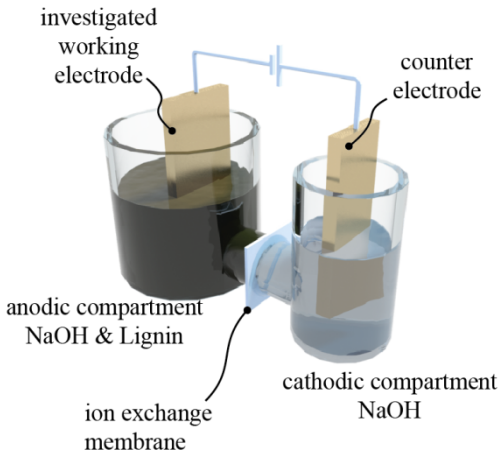

Fig. SI 1 Scheme of the utilized electrochemical reactor

Substances investigated by LC-MS

As already mentioned, liquid chromatography coupled with an ion trap mass spectrometer has been used to investigate and quantify a certain set of lignin-derived products. The chosen components all have an aromatic hydrocarbon group with the phenol-characteristic OH-group. However, they all have different functional groups. Fig. SI 2 shows the chemical structures of the quantified phenols and additional information can be found in Table SI 5.

.

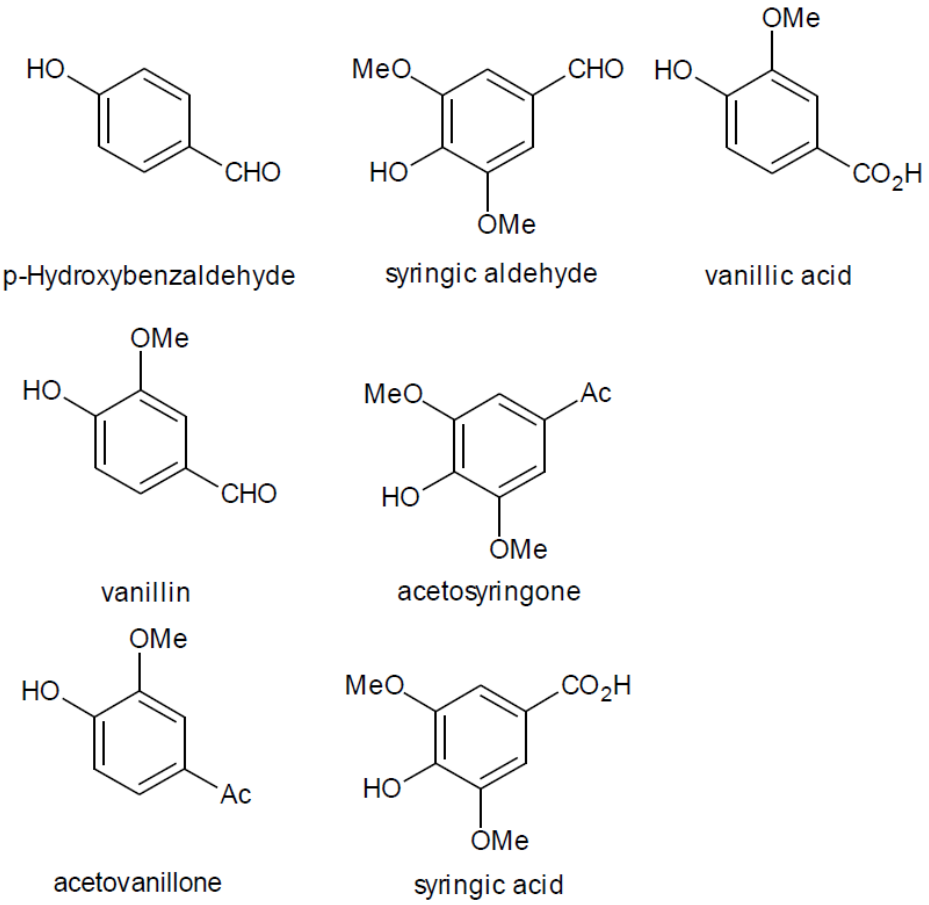

Fig. SI 2 Chemical structures of the investigated lignin-derived products

Table SI 5 Characteristics of the quantified phenolic components

Name	p-hydroxy-benzaldehyde	vanillic acid	syringic acid	vanillin	syringic aldehyde	aceto-vanillone	aceto-syringone
CAS number	123-08-0	121-34-6	530-57-4	121-33-5	134-96-3	498-02-2	2478-38-8
Abbreviation	P1	P2	P3	P4	P5	P6	P7
Formula	$C_7H_6O_2$	$C_8H_8O_4$	$C_9H_{10}O_5$	$C_8H_8O_3$	$C_9H_{10}O_4$	$C_9H_{10}O_3$	$C_{10}H_{12}O_4$
MW [g/mole]	122.12	168.15	198.17	152.15	182.17	166.17	196.2

SPE Recovery

Prior to the evaluation with LC-MS a solid phase extraction (SPE) was done to accumulate the phenols to be detected from the sample and transfer them from the reaction medium to a medium suitable for LC-MS measurements. As no complete and loss-free transfer of the investigated molecules is possible, recovery rates had to be investigated beforehand. These recovery rates are taken into account when calculating the monomer concentration of the samples. Table SI 6 shows the recovery rates for the different phenols.

Table SI 6 Recovery rates of investigated phenols after SPE

	P1	P2	P3	P4	P5	P6	P7
Mean [wt%]	99	97	86	89	72	85	74
Std. dev. [%]	1.72	1.81	2.84	2.45	3.29	2.45	3

Sample preparation

Fig. SI 3 shows the scheme of the sampling and sample preparation, as described in the analysis paragraph.

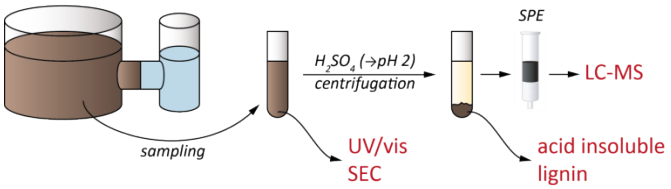

Fig. SI 3 Sampling and treatment of the samples as preparation for the different analysis techniques

Monomer distribution of selected experimental runs

Table SI 7 shows the product distribution of two exemplary runs. As expected from lignin derived from beech wood, vanillin, vanillic acid and acetovanillone make up the majority of the recovered monomers. The syringic type of monomers can only be found in very small amounts.

Table SI 7 Distribution of the investigated products for the experimental runs with the highest and lowest total monomer yield (10 and 11 respectively) in %

Run	Hy	VAc	Sac	V	S	VO	SO
10	3.02	23.46	0.19	67.63	0.31	5.31	0.08
11	3.65	29.91	0.31	61.36	0.31	4.40	0.07

Overoxidation of vanillin to vanillic acid

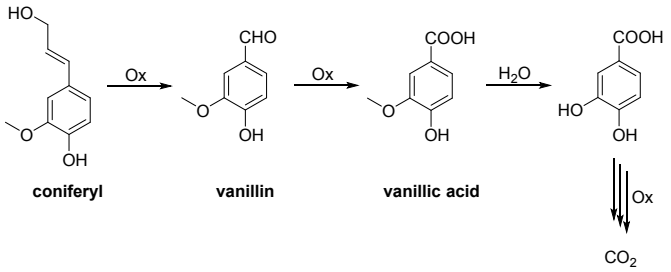

Fig. SI 4 Overoxidation of vanillin to vanillic acid and mineralization to CO_2.

Parity plots for relative MW vs. UV absorbance and relative MW vs. target monomer yield

Fig. SI 5 and Fig. SI 6 show the parity plots for the comparison of relative molecular weight with the UV absorbance and the relative molecular weight with the product yield, respectively. As already mentioned in the research paper, there is no correlation between the compared signals.

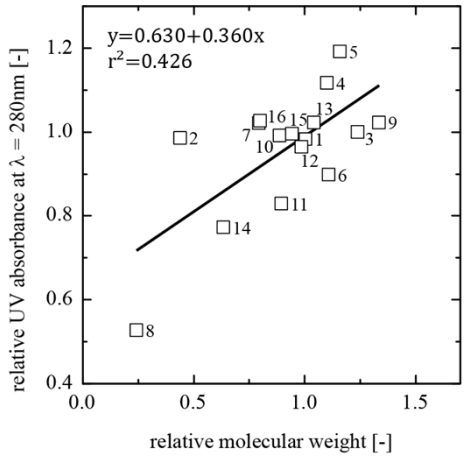

Fig. SI 5 Parity plot of the relative molecular weight in comparison to the relative UV absorbance of the experimental runs 1 to 16 after 4 hours of electrochemical reactions at different reaction parameters. The numbers next to the points depict the run number. The equation for the linear correlation as well as the r² of the correlation can be found in the top left corner.

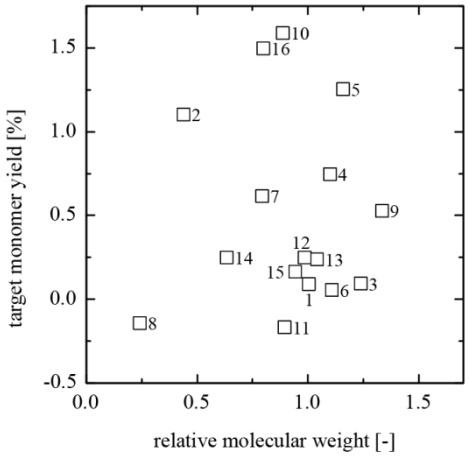

Fig. SI 6 Parity plot of the relative molecular weight in comparison to the target monomer yield of the experimental runs 1 to 16 after 4 hours of electrochemical reactions at different reaction parameters. The numbers next to the points depict the run number.

Parity plots for the comparison between the acid solubility and the relative molecular weight at different reaction times

Fig. SI 7 shows the correlation between the relative molecular weight and the relative acid insolubility at different times during the electrochemical treatment for all the experiments conducted in this study. The data has been plotted for all occasions where samples for acid solubility and molecular weight were taken simultaneously (30, 60 and 90 minutes of reaction time). It is interesting to note, that the correlation between the molecular weight and the acid solubility grows stronger over the reaction duration. After 30 minutes, an r^2 of -0.076 shows no linear correlation. At 60 minutes reaction time, a pattern emerges with an appreciable correlation between the MW and the acid solubility (r^2=0.564). After 90 minutes, the r^2 of 0.701 approaches the value after 240 minutes of reaction (r^2=0.739).

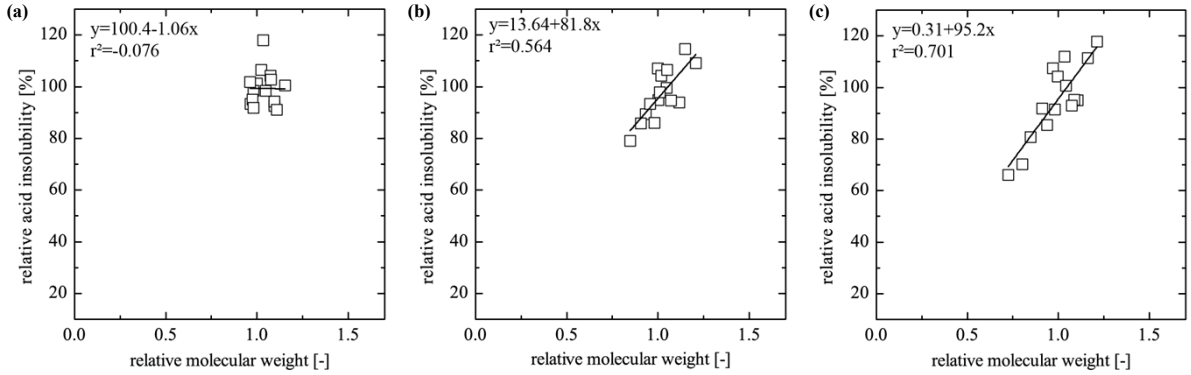

Fig. SI 7 Parity plot of the relative molecular weight in comparison to the relative acid insolubility of the experimental runs 1 to 16 after 30 (a), 60 (b) and 90 (c) minutes of electrochemical reactions at different reaction parameters. The equation for the linear correlation as well as the r^2 of the correlation can be found in the top left corner.

Initial concentration of monomers in the untreated Kraft lignin

Due to the harsh conditions of the Kraft pulping process, low amounts of monomers are already present in the untreated Kraft lignin. The initial amount of monomers has been determined for all samples used in the experiments and the results were corrected accordingly. Table SI 8 shows the initial distribution of the quantified components.

Table SI 8 Typical product distribution before the electrochemical treatment of Kraft lignin (data from run 2)

Hy	VAc	Sac	V	S	VO	SO
3.02	23.46	0.19	67.63	0.31	5.31	0.08

Elemental Analysis

Elemental analysis of the Kraft lignin was conducted with a vario EL cube elemental analyzer in order to determine the elemental composition of the utilized Kraft lignin. A representative distribution is shown in Table SI 9.

Table SI 9 Elemental composition of the utilized Kraft lignin (the oxygen amount is calculated to form a total sum of 100%).

N [%]	C [%]	H [%]	$O_{calculated}$ [%]	S [%]

0.36	61.57	5.79	31.28	1.00

t-Value Pareto Charts

Due to the nature of the statistical framework of DoE, numbers for the insignificant effects cannot be given without altering the numbers of the significant effects. In order to illustrate that only the significant effects were chosen, the following figures show the pareto charts of the t-values of the investigated effects.

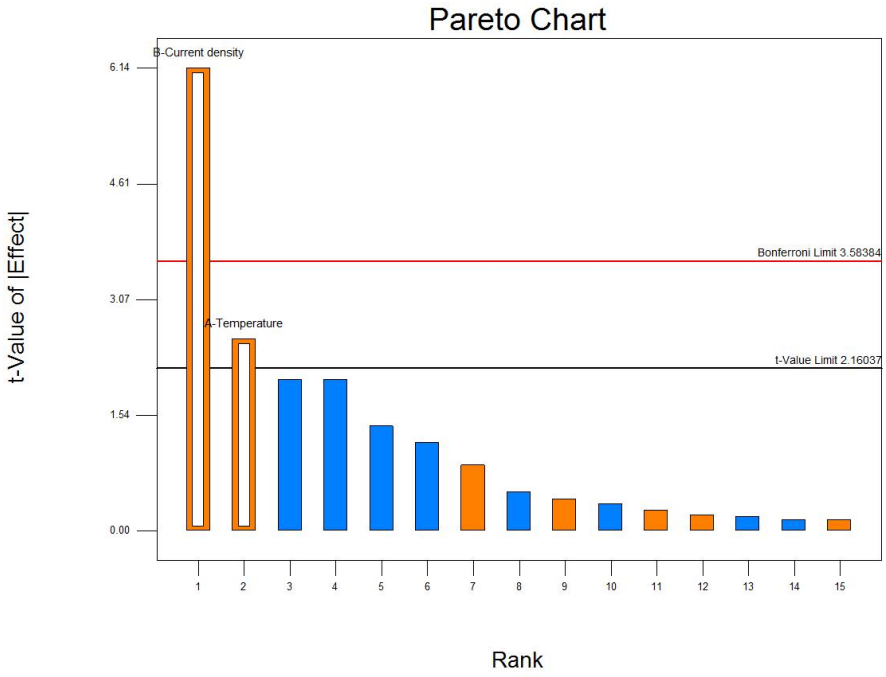

Fig. SI 8 Pareto chart of the t-value of investigated effects on acid solubility

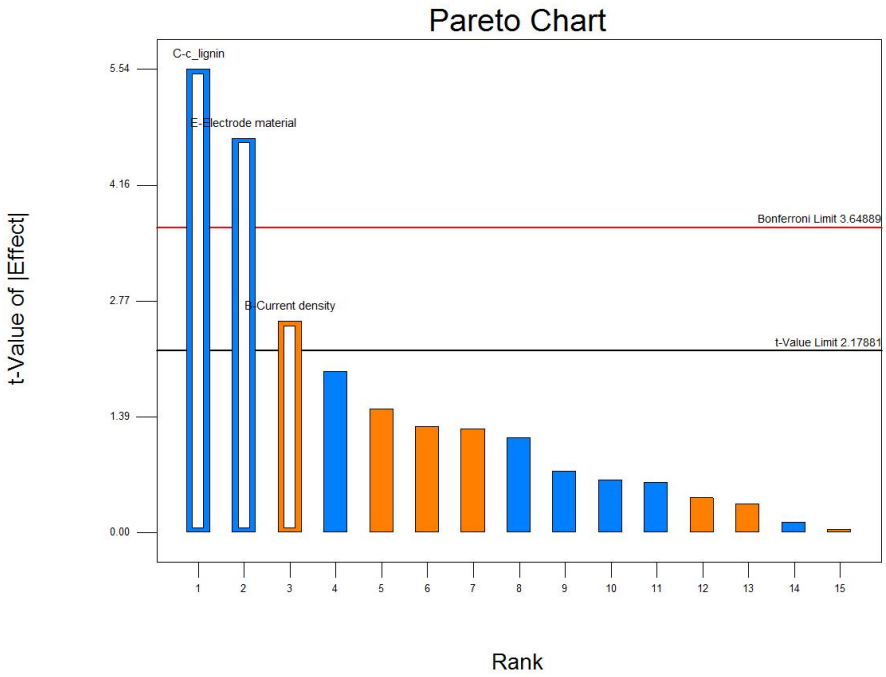

Fig. SI 9 Pareto chart of the t-value of investigated effects on monomer yield

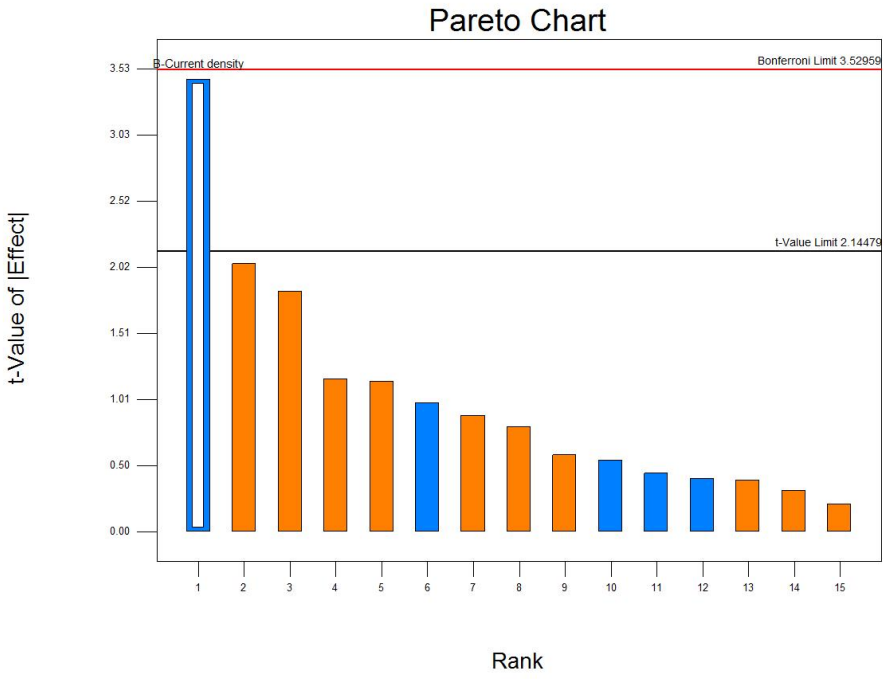

Fig. SI 10 Pareto chart of the t-value of investigated effects on relative molecular weight

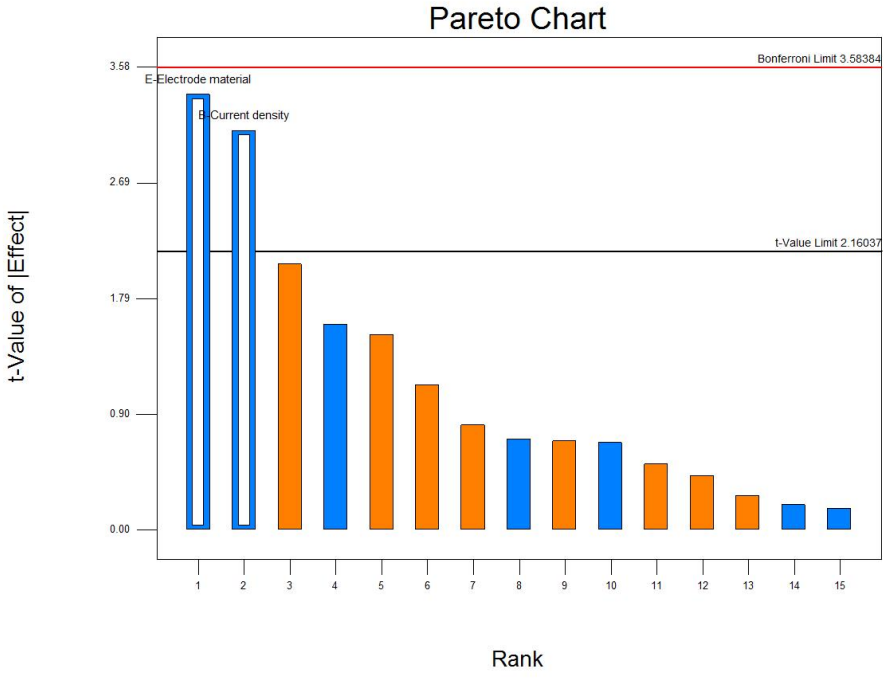

Fig. SI 11 Pareto chart of the t-value of investigated effects on UV absorbance