

# Selective Electrochemical Degradation of Lignosulfonate to Bio-Based Aldehydes

Jana Klein<sup>[a]</sup> and Siegfried R. Waldvogel<sup>1\* [a, b]</sup>

A sustainable electrochemical pathway for degradation and thermal treatment of technical lignosulfonate is presented. This approach is an opportunity to produce remarkable quantities of low molecular weight compounds, such as vanillin and acetovanillone. For the electrochemical degradation, a simple two-electrode arrangement in aqueous media is used, which is also easily scalable. The oxidation of the biopolymer occurs at the anode whereas hydrogen is evolved at the cathode. The subsequent thermal treatment supports the degradation of the

robust chemical structure of lignosulfonates. With optimized electrolytic conditions, vanillin could be obtained in 9.7 wt% relative to the dry mass of lignosulfonate used. Aside from vanillin, by-products such as acetovanillone or vanillic acid were observed in lower yields. A new and reliable one-pot, two-step degradation of different technically relevant lignosulfonates is established with the advantages of using electrons as an oxidizing agent, which results in low quantities of reagent waste.

## Introduction

In times of climate change, the use of fossil resources should be reconsidered.<sup>[1–4]</sup> Their use has major disadvantages regarding sustainability and their long-term availability.<sup>[3,5]</sup> In addition, their application results in a carbon imbalance in our ecosystem.<sup>[3]</sup> Due to the increasing development of environmental protections, protocols, and resource utilization, an environmentally friendly alternative to fossil fuels and chemicals is required.<sup>[4,6,7]</sup> This presents a new path for neutral and renewable biomass, as the most abundant biopolymer besides cellulose and hemicellulose is lignin.<sup>[8–10]</sup> Due to industrial processes and harsh conditions the native structure of lignin changes and technical lignin is received. Technical lignosulfonate represents a side-stream in the pulp and paper industry,<sup>[11,12]</sup> and its production accounts for approximately 10% of the total lignin output.<sup>[13]</sup> As it has chemically challenging properties (multiple substructures and behaviors), the industry uses only a small fraction (up to 2%) for further production such as animal feed, surfactants, binders, fine chemicals, and pesticides.<sup>[12–14]</sup> The remaining 98% is incinerated to recoup energy costs.<sup>[11,15]</sup>

The complexity and diversity of lignosulfonate is in the three-dimensional structure, which comprises of three aromatic

monomer subunits including *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol connected via carbon-carbon and ether linkages.<sup>[10,16–18]</sup> The composition and the linkages differ depending on the plant source.<sup>[9,19]</sup> In comparison to Kraft lignin, lignosulfonate has very hydrophilic groups such as sulfonates, which remarkably increases its solubility in water.<sup>[20,21]</sup> Due to the high sulfur content, lignosulfonate has a higher molecular weight than Kraft lignin.<sup>[20]</sup> The arene-containing backbone of lignin and lignosulfonate elicits a high potential to be broken down into their aromatic subunits to produce value-added chemicals such as vanillin, acetovanillone, syringaldehyde, and acetosyringone.<sup>[22–26]</sup>

Currently, the major part of world's supply of vanillin is produced from petrochemical feedstock via the intermediate guaiacol.<sup>[27,28]</sup> The utilization of lignosulfonate as a source for platform chemicals and fuels would curb society's dependence on fossil carbon and in turn reduce the emission of greenhouse gases.<sup>[3,6,11,29]</sup> Vanillin is a major product of lignosulfonate degradation and has a plethora of uses in industry.<sup>[1,21,22,30]</sup> These include flavorings, food, and as a starting material for several pharmaceuticals and polymeric materials.<sup>[1,28,31]</sup> Currently, only one process using lignosulfonate for degradation on an industrial scale is described by Borregaard Industries.<sup>[32]</sup> Lignosulfonate is oxidized by molecular oxygen under strongly alkaline conditions using a Cu catalysts and elevated temperatures (up to 185 °C).<sup>[33]</sup> From the point of sustainability and strict limitations of copper content in the eluent, the resumption of vanillin degradation from biomass without a contaminating catalysts is a logical venture.<sup>[11]</sup>

Existing studies focuses on the degradation of lignin into value-added products. A promising approach is oxidative degradation to obtain bio-based aromatic products such as arenes,<sup>[23,34]</sup> quinones,<sup>[35]</sup> and carboxylic acids.<sup>[36]</sup> Oxidizing agents such as hydrogen peroxide,<sup>[37]</sup> nitrobenzene,<sup>[38]</sup> or transition metal catalysts<sup>[39]</sup> are often used. Unfortunately, the use of oxidizers often requires stoichiometric amounts, and toxic by-products are produced. The use of rare metals such as

[a] J. Klein, Prof. Dr. S. R. Waldvogel  
Department of Chemistry, Johannes Gutenberg University Mainz  
Duesbergweg 10–14, 55131 Mainz (Germany)  
E-mail: waldvogel@uni-mainz.de

[b] Prof. Dr. S. R. Waldvogel  
Institute of Biological and Chemical Systems – Functional Molecular Systems (IBCS-FMS)  
Hermann-von-Helmholtz-Platz 1  
76344 Eggenstein-Leopoldshafen (Germany)

Supporting information for this article is available on the WWW under <https://doi.org/10.1002/cssc.202202300>

© 2023 The Authors. ChemSusChem published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

ruthenium, palladium and platinum as catalysts is associated with high cost due to their limited availability.<sup>[40]</sup> Addressing these challenges with an electrochemical process opens the door to CO<sub>2</sub>-neutral plastics, green building blocks, flavors, and fragrances.<sup>[3,18]</sup>

Existing electrochemical approaches utilized various technical lignins (Kraft lignin and organosolv lignin)<sup>[22–24,26]</sup> and oxidized them using nickel electrodes during a thermal treatment at temperatures up to 160 °C. Vanillin was obtained as a target product in yields up to 4.2 wt% (Kraft lignin)<sup>[30]</sup> and 4.0 wt% (organosolv lignin),<sup>[22]</sup> respectively. Ni is a well-known electrode material for lignin degradation.<sup>[22,23,26,41–45]</sup> Previous studies have confirmed the superior performance of nickel compared to Pt or graphite.<sup>[44]</sup> Under the alkaline conditions used, nickel electrodes form an electrocatalytically active nickel oxide hydroxide layer, on which oxidation of the lignin takes place. NiOOH is very selective for the oxidation of alcohols and has the advantage of being an insoluble but conductive layer at the anodic surface.<sup>[46]</sup> During the process, NiOOH is continuously regenerated and ensures the reaction performance.<sup>[44,45]</sup> Moreover, the advantages of the electrochemical lignin degradation are the moderate reaction conditions, a wide range of applications, consistently good yields, and a robust system. Besides the anodic conversion, a reductive degradation is also described.<sup>[47]</sup> The electrochemical oxidative degradation of lignin is in accordance with the principles of green chemistry,<sup>[48,49]</sup> given the prevention of hazardous waste and the limited use of catalysts.

The new oxidative method described below shows a selective conversion of lignosulfonate into aromatic compounds with a tolerance to sulfur poisoning.<sup>[50]</sup> These monomers, such as vanillin (1) and acetovanillone (2), are obtained in good yields (2 to almost 10 wt%). The crucial step of this innovative method (Figure 1) is the separation of the oxidation process from the thermolysis. This process proves to be cost-effective and environmentally friendly, as degradation is possible in one-pot, and no separation or isolation steps are required in between. In comparison to previous work oxidation is

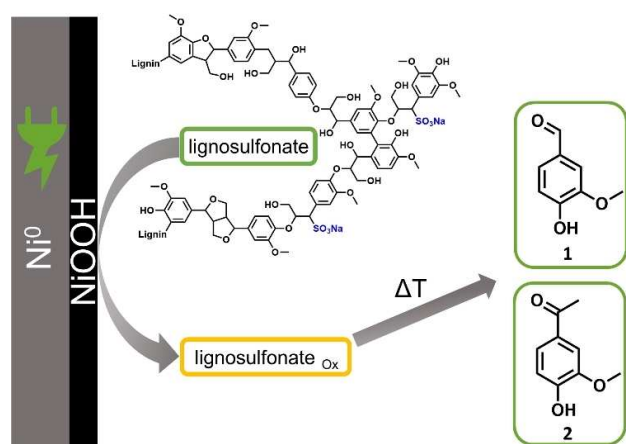
performed at room temperature and the energy consumed can be derived from renewable resources such as solar or wind. Compared to petroleum-based routes,<sup>[17]</sup> this could be a good alternative for the future.

## Results and Discussion

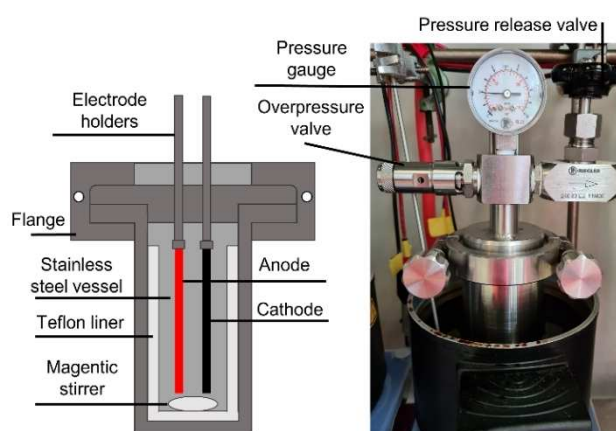
A two-step one-pot degradation for technically relevant lignosulfonates is developed for a sustainable access to vanillin (1) and acetovanillone (2). The reaction is performed in an undivided pressurized electrolysis cell (autoclave, Figure 2), which allows for working in aqueous media at temperatures above 100 °C.

Softwood lignins consist of about 90% of coniferyl alcohol (G units),<sup>[51]</sup> which has a vanillin-like substructure.<sup>[52]</sup> Using technical lignosulfonate (softwood) the formation of vanillin is expected. Because of the high stability of lignosulfonate for electrolysis under acidic conditions, all experiments were performed under alkaline conditions (1–5 M aq. NaOH). In alkaline media, the solubility of lignosulfonate is increased since sodium salts are formed.<sup>[53]</sup> First, thermal treatment under alkaline conditions without electricity was carried out to degrade lignosulfonate (Figure 3). The thermal degradation of lignosulfonate at 130 °C for 11 h in 3 M NaOH showed a maximum yield of 2.8 wt% for vanillin (1) and 0.8 wt% for acetovanillone (2; see GP1 in the Supporting Information).

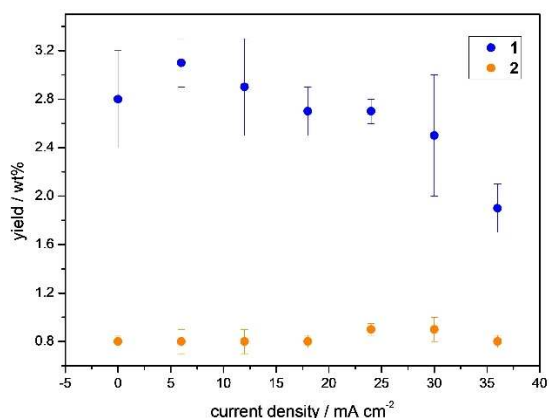
Various experiments were then performed to investigate the influence of electricity onto the monomer yield. Nickel was chosen as the preferred electrode material due to well-known inherent advantages for lignin degradation.<sup>[42,43,54]</sup> Lignin was treated simultaneously thermally at 130 °C and electrochemically. Performing the electrolysis and the thermal treatment simultaneously (one-step degradation, see GP2 in the Supporting Information) increased the vanillin yield to 3.1 wt%, a considerable improvement of 0.3 wt% (Figure 4). By increasing the current density from 6 to 36 mA cm<sup>-2</sup> a general decrease in the yield of vanillin was observed, whereas the yield of acetovanillone did not change significantly from 0.8 wt%. The



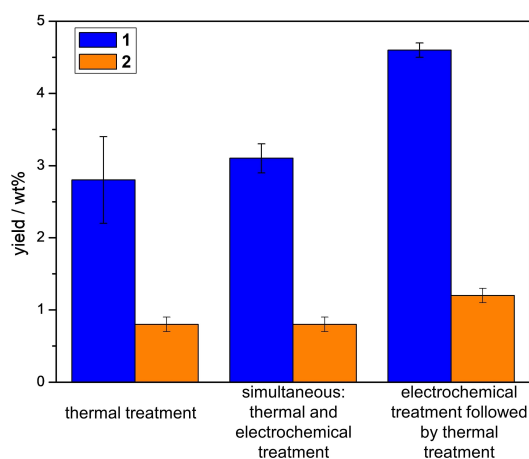
**Figure 1.** Conversion of technical lignosulfonate into monoaromatic compounds through anodic oxidation and subsequent thermal treatment.



**Figure 2.** Left: cross-section of autoclave, right: autoclave in operation.



**Figure 3.** Impact of the current density onto the yield of 1 and 2 at high-temperature electrolysis. Reaction conditions: 500 mg liginosulfonate, applied charge 2.8 C mg<sup>-1</sup>, 3 M NaOH, 130 °C, 11 h. The first point represents the thermal degradation without electricity.



**Figure 4.** Thermal degradation of liginosulfonate in comparison with simultaneous electrochemical and thermal treatment and in the two-step one-pot protocol.

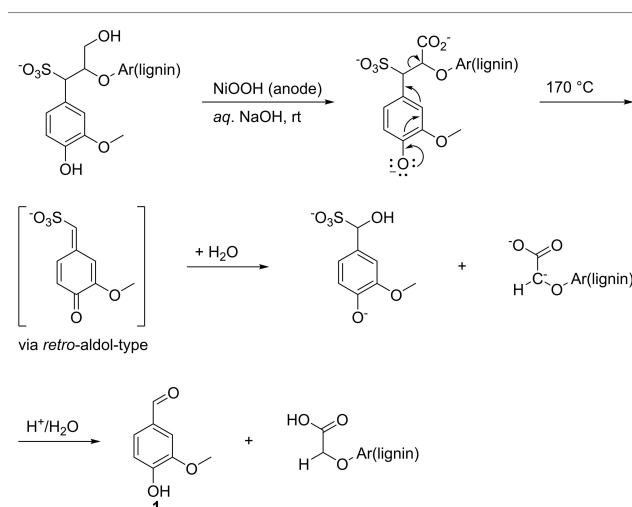
highest observed yield was obtained at the lowest tested current density of 6 mA cm<sup>-2</sup> (Figure 3). The observed drop in yield could be due to over-oxidation<sup>[55]</sup> or cross-coupling of vanillin.<sup>[33,56]</sup> Therefore, it is clear that current density has a pronounced influence on the achievable yield of vanillin (1). Due to the impact of current density observed during simultaneous thermal and electrochemical treatment, electrolysis was subsequently performed separately from the thermal treatment (two-step degradation).

Impressively, the two-step one-pot degradation with identical conditions to the simultaneous treatment increased the vanillin yield from 3.1 wt% to almost 4.6 wt% (see GP3 in the Supporting Information). Furthermore, the yield of acetovanillone increased from 0.8 wt% to 1.2 wt% (Figure 4). The key step for higher conversion was the separation of the electrochemical degradation and the thermal treatment. Increasing the temperature during the thermal degradation (up to 170 °C) resulted in higher conversion of the monomers.

In Scheme 1, a mechanistic rationale for the two-step one-pot degradation is postulated. By using NiOOH, primary alcohols are oxidized into carboxylic acids. In this step the oxidation requires low temperatures (rt). In terms of high alkaline conditions, the substructure of liginosulfonate has many negatively charged subunits, resulting in high columbic repulsion. High temperatures are needed to overcome this barrier. Therefore, subsequent thermal degradation would hypothetically support the liberation of the monomeric substructures from liginosulfonate. The sulfite adduct fulfills an additional important role as it protects the vanillin from over-oxidation. After acidification, this adduct is cleaved and 1 is liberated.

During the work-up, the aqueous alkaline solution was acidified with sulfuric acid, and remaining oxidized liginosulfonate precipitated from the aqueous layer. To determine the monomer yield, the crude product mixture from the degradation was extracted with ethyl acetate and an internal standard (*n*-dodecylbenzene) was added (see GP2 in the Supporting Information). Next, the sample was analyzed, and the yield determined through external calibration using GC (see Quantification in the Supporting Information). All yields are given in wt% based on the dry amount of liginosulfonate used. Organic oligomers were not analyzed, as the focus of this paper is on the monomeric fractions.

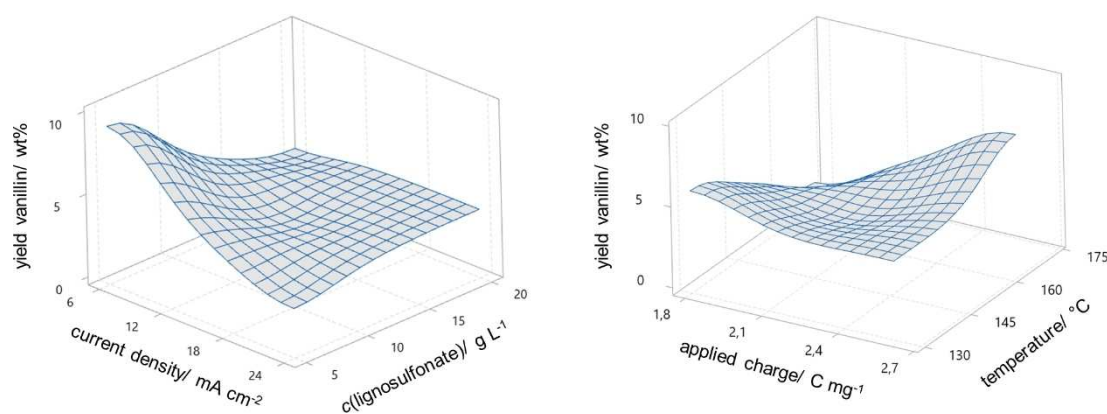
To further investigate the effect of anode material, several commercially available metallic and carbon-based electrodes were applied for the two-step one-pot degradation. The oxidation (2.7 C mg<sup>-1</sup>, 12.5 mA cm<sup>-2</sup>) was performed at room temperature, and the subsequent thermal treatment was run at 160 °C for 24 h (see GP3 in the Supporting Information). Their composition and performance are listed in Table 1. The best results were obtained with a vanillin (1) yield of 6.6 wt% and 1.2 wt% acetovanillone (2). Additionally, no destruction occurred at the NiOOH anode surface. Other nickel alloys showed lower monomer yields. T-400C suffered from electrode fouling,



**Scheme 1.** Postulated mechanism for the electrolysis and subsequent thermolysis of liginosulfonate.

Electrode	Electrode Compositions	Vanillin (1) yield <sup>[a]</sup>	Acetovanillone (2) yield <sup>[a]</sup>
Ni	Ni99.9	6.6 wt%	1.2 wt%
Inconel 625 (NiCr(2))	Ni61Cr22Mo9Fe5	2.6 wt%	0.6 wt%
DSC-8	Ni75Cr19Fe6	2.5 wt%	0.6 wt%
Waspaloy	Ni90 Ag10	5.1 wt%	1.1 wt%
Co	Ni58Cr19Co14	2.6 wt%	0.6 wt%
T-400C	Co99.9	2.4 wt%	0.6 wt%
DSA <sup>[b]</sup>	Co53.6Cr17Mo27Si2.4	corrosion	n.d.
Cuprosilver	TiRuO <sub>2</sub>	4.1 wt%	0.9 wt%
BDD	Ag62.5Cu37.5	1.9 wt%	0.6 wt%
Pt	boron-doped diamond	destruction	n.d.
Glassy carbon	Pt99	destruction	n.d.
	C100	destruction	n.d.

[a] The yield for 1 and 2 is related to the amount of starting material and was determined by GC with *n*-dodecylbenzene as internal standard. [b] For DSA anode: cathode was nickel. n.d.: none detected.



**Figure 5.** 3D-Plots of the Design of Experiments. Left: results showing the influence of current density, and lignosulfonate concentration; right: temperature, applied charge on the vanillin yield.

and both BDD and glassy carbon were destructed (see S5 in the Supporting Information). Pure cobalt suffered a loss in weight (16.4 mg) and in repeating the reaction twice with the same electrode, a loss of catalytic activity was observed as well. The vanillin yield decreased from 2.4 to 2.2 and 1.8 wt%. Aside from Co, all other yields were highly reproducible.

Based on the aforementioned results, Ni was used as the anode material for all further experiments. Under alkaline conditions, a Ni(OH)<sub>2</sub>/NiOOH system controls the oxidation potential of the reaction medium.<sup>[57]</sup> After defining the electrode material other electrolysis parameters such as stirring speed, lignosulfonate concentration, electrolysis temperature, thermal degradation temperature, NaOH concentration, current density, and applied charge were investigated (see Initial experimental design in the Supporting Information). In preliminary studies, the stirring speed (300–500 rpm) showed no influence on the selectivity or the yield (see GP3 in the Supporting Information). After the described findings, optimization of the two-step one-pot protocol was performed.

The transformation was optimized by a Design of Experiments (DoE) using a 2<sup>7-4</sup> and 2<sup>4-1</sup>-plan. A DoE was chosen to optimize the complex nature of the lignosulfonate degradation and to understand occurring cause-effect relationships and

multiparameter interactions.<sup>[58]</sup> Different oxidation temperatures did not affect the vanillin yield (see the Supporting Information, Table S6). Therefore, further experiments were conducted at room temperature (Table S7). Testing caustic soda concentrations between 5 M to 1 M indicated that the maximum yield could be improved with 3 M caustic soda (Table S6). Longer thermal degradation times (above 24 h) had a small impact on the monomer yields (Figure S7). Shorter thermal degradation times (12 h) showed a decrease in the monomer fraction yield, especially in vanillin (Table S6). The optimum degradation time was found to be 24 h. Three main factors were identified—the applied charge, the degradation temperature, and the lignosulfonate concentration—all of which had a high influence on the received yields (Figure 5).

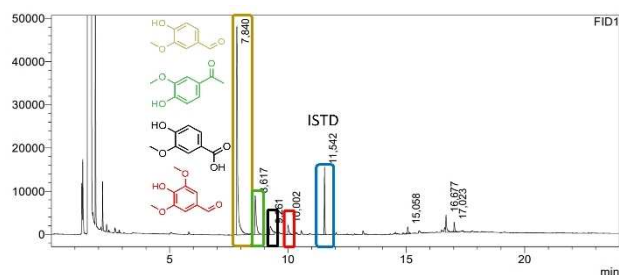
Increasing the lignosulfonate concentration decreased the vanillin yield, as did increasing the applied charge. By increasing the degradation temperature from 50 °C to 170 °C the vanillin yield could be improved (Figure S8). The optimized reaction conditions are summarized in Table 2.

The maximum yield of 9.7 wt% vanillin (1) and 2.4 wt% acetovanillone (2; Figure 6) was reached using technical lignosulfonate derived from spruce (softwood).

**Table 2.** Optimized reaction conditions for 250 mg liginosulfonate in 3 M NaOH after the Design of Experiments.

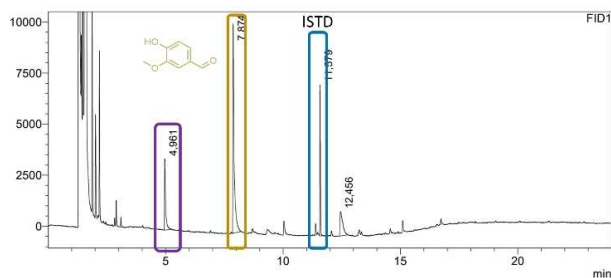
Parameters	Oxidation	Thermal treatment
degradation temperature	room temperature	170 °C
mass concentration LS	5 g L <sup>-1</sup>	5 g L <sup>-1</sup>
current density	6 mA cm <sup>-2</sup>	0 mA cm <sup>-2</sup>
applied charge	2.6 C mg <sup>-1</sup>	0 C mg <sup>-1</sup>
degradation time	5 h	24 h
stirring speed	300 rpm	300 rpm
pressure	0.5–5 bar	0.5–6 bar <sup>[a]</sup>

[a] Temperature dependent.

**Figure 6.** GC after electrolysis and subsequent thermal degradation. Yellow: vanillin, green: acetovanillone, black: vanillic acid, red: syringaldehyde. *n*-Dodecylbenzene was used as internal standard (ISTD blue).

To compare the received vanillin yield from the two-step one-pot protocol, nitrobenzene oxidation was used as a reference reaction to determine the maximum amount of vanillin (see GP4 in the Supporting Information). The nitrobenzene reaction is a selective reaction to degrade lignin into vanillin and is well-known as a benchmark reaction to evaluate the performance of lignin oxidation processes.<sup>[1,59]</sup> The same protocol has been used in previous studies to determine the maximum vanillin content of lignin.<sup>[30,60]</sup> Regarding the formation of vanillin by this method, no other aldehydes besides residues of unreacted nitrobenzene (purple) were visible in the GC (Figure 7).

The maximum yield of the nitrobenzene oxidation was 13.6 wt% vanillin. The vanillin yield from the two-step degradation achieved 71% in comparison to the nitrobenzene oxidation.

**Figure 7.** GC after nitrobenzene oxidation. Purple: nitrobenzene and yellow: vanillin. *n*-Dodecylbenzene was used as internal standard (ISTD blue).

## Conclusion

The electrochemical oxidative degradation of technically relevant liginosulfonates performed using Ni sheet electrodes, generating in situ a NiOOH layer, resulted in high selectivity of aromatic aldehydes such as vanillin and acetovanillone and was improved by separating the electrolysis and thermal step to liberate the target compounds. The method provides a new way for an energy-saving and low-cost protocol. This two-step one-pot protocol, when compared to the standard nitrobenzene oxidation, is nontoxic, cost-efficient, and environmentally friendly, as electrons are used as oxidizers. Using electrochemistry as a degradation path has the advantage of an inherently safe method, high sustainability, and can be considered green chemistry.<sup>[46,49,61]</sup> The presented method is a cost-effective, robust, and sustainable way to produce bio-based aldehydes from the poorly utilized renewable liginosulfonate. Another advantage is that vanillin is not over oxidized and yields almost 10 wt%, which is 71% of the vanillin yield of the laboratory scale standard (nitrobenzene oxidation).

Moreover, the method established operates in an aqueous system at temperatures below 170 °C. A simple two-electrode setup was investigated using electricity as oxidant, making the process significantly superior to existing methods in terms of selectivity and overall yield.

## Experimental Section

### Electrochemical reactor setup

High-temperature experiments were conducted in a simple undivided 0.05 L stainless steel cell with a Teflon liner (Figure 2). The cell is sealable with a flange and equipped with a manometer, a pressure release, and an over-pressure valve (8 bar). The reaction mixture is stirred by a magnetic stirrer. Heating was facilitated by a common oil bath using a standard electric heating plate. A glass pressure tube is also suitable for shorter reaction times (up to 2 h). However, after two hours, the caustic soda might attack the glass.

### Electrochemical degradation of liginosulfonate

For the electrolysis different electrode materials were tested. The electrodes are 2 × 6 cm, the active area is 6 cm<sup>2</sup>. 500 mg liginosulfonate was dissolved in aqueous caustic soda (3 M, 50 mL) under vigorous stirring. The solution was transferred into the autoclave; the electrodes are connected to electricity (6 mA cm<sup>-2</sup>, 2.6 C mg<sup>-1</sup>), and the cell was sealed and started at constant current mode by stirring at room temperature. Afterward, the reaction mixture was heated up to 170 °C and stirred for 24 h. The reactor was not pressurized externally. After the reaction was stopped, the reaction mixture was allowed to cool (room temperature), and the pH of the reaction mixture was adjusted to pH 1 by the addition of H<sub>2</sub>SO<sub>4</sub>. The aqueous layer was extracted with ethyl acetate (3 × 150 mL). The combined organic fractions were washed with saturated brine (30 mL) and dried over anhydrous magnesium sulfate followed by solvent removal under reduced pressure. The organic residue was dissolved in ethyl acetate (8 mL), 2 μL of the internal standard *n*-dodecylbenzene was added and the sample was analyzed by GC/MS.

## GC analysis

Gas chromatography was performed on a Shimadzu GC-2025 (Shimadzu, Japan) using a HP-5 column (Agilent Technologies, USA; length: 30 m, inner diameter: 0.25 mm, film: 0.25  $\mu$ m, 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 Zebtron ZB-5MSi column (Phenomenex, USA; length: 30 m, inner diameter: 0.25 mm, 5% phenyl 95% dimethylpolysiloxane, film: 0.25  $\mu$ m, pre-column: 5 m, carrier gas: helium) combined with a GC-MS-QP2010 with an ion source (EI) at 200 °C. Retention times of degradation products and the applied internal standard (ISTD): vanillin (1) 7.9 min, acetovanillone (2) 8.6 min, syringaldehyde (3) 10.0 min, acetosyringone (4) 10.5 min, *n*-dodecylbenzene (ISTD) 11.6 min. An internal standard calibration was performed.

## Acknowledgements

The project SElectiveLi has received funding from the Bio Based Industries Joint Undertaking under the European Union's Horizon 2020 research and innovation program under grant agreement No 837276. Finally, the authors thank Dr. Rosalie Hamill for proofreading the manuscript. Open Access funding enabled and organized by Projekt DEAL.

## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

**Keywords:** electrolysis · electrochemistry · lignin · lignosulfonate · oxidation

- [1] T. Hosoya, K. Yamamoto, H. Miyafuji, T. Yamada, *RSC Adv.* **2020**, *10*, 19199–19210.
- [2] B. E. Dale, *J. Chem. Technol. Biotechnol.* **2003**, *78*, 1093–1103.
- [3] C. O. Tuck, E. Pérez, I. T. Horváth, R. A. Sheldon, M. Poliakoff, *Sciences* **2012**, *337*, 695–699.
- [4] M. M. Abu-Omar, K. Barta, G. T. Beckham, J. S. Luterbacher, J. Ralph, R. Rinaldi, Y. Román-Leshkov, J. S. M. Samec, B. F. Sels, F. Wang, *Energy Environ. Sci.* **2021**, *14*, 262–292.
- [5] M. Garedew, C. H. Lam, L. Petitjean, S. Huang, B. Song, F. Lin, J. E. Jackson, C. M. Saffron, P. T. Anastas, *Green Chem.* **2021**, *23*, 2868–2899.
- [6] H. Wang, Y. Pu, A. Ragauskas, B. Yang, *Bioresour. Technol.* **2019**, *271*, 449–461.
- [7] a) A. Demirbas, *Energy Sources Part A* **2017**, *39*, 592–598; b) M. Klein, S. R. Waldvogel, *Angew. Chem. Int. Ed.* **2022**, *61*, e202204140; *Angew. Chem.* **2022**, *134*, e202204140; c) R. Rinaldi, R. Jastrzebski, M. T. Clough, J. Ralph, M. Kennema, P. C. A. Bruijninx, B. M. Weckhuysen, *Angew. Chem. Int. Ed.* **2016**, *55*, 8164–8215; *Angew. Chem.* **2016**, *128*, 8296–8354; d) C. Chio, M. Sain, W. Qin, *Renewable Sustainable Energy Rev.* **2019**, *107*, 232–249; e) C. Brandt, *Chem. Unserer Zeit* **2002**, *36*, 214–224.
- [8] a) S. Li, N. Li, G. Li, L. Li, A. Wang, Y. Cong, X. Wang, T. Zhang, *Green Chem.* **2015**, *17*, 3644–3652; b) R. Vanholme, B. Demedts, K. Morreel, J. Ralph, W. Boerjan, *Plant Physiol.* **2010**, *153*, 895–905.
- [9] A. Das, A. Rahimi, A. Ulbrich, M. Alherech, A. H. Motagamwala, A. Bhalla, L. da Costa Sousa, V. Balan, J. A. Dumesic, E. L. Hegg, B. E. Dale, J. Ralph, J. J. Coon, S. S. Stahl, *ACS Sustainable Chem. Eng.* **2018**, *6*, 3367–3374.
- [10] W. Boerjan, J. Ralph, M. Baucher, *Annu. Rev. Plant Biol.* **2003**, *54*, 519–546.
- [11] A. J. Ragauskas, G. T. Beckham, M. J. Bidy, R. Chandra, F. Chen, M. F. Davis, B. H. Davison, R. A. Dixon, P. Gilna, M. Keller, P. Langan, A. K. Naskar, J. N. Saddler, T. J. Tschaplinski, G. A. Tuskan, C. E. Wyman, *Sciences* **2014**, *344*, 1246843,1–8.
- [12] F. G. Calvo-Flores, J. A. Dobado, *ChemSusChem* **2010**, *3*, 1227–1235.
- [13] I. Sumerskii, P. Korntner, G. Zinoviyev, T. Rosenau, A. Potthast, *RSC Adv.* **2015**, *5*, 92732–92742.
- [14] S. Gillet, M. Aguedo, L. Petitjean, A. R. C. Morais, A. M. da Costa Lopes, R. M. Łukasik, P. T. Anastas, *Green Chem.* **2017**, *19*, 4200–4233.
- [15] T. Aro, P. Fatehi, *ChemSusChem* **2017**, *10*, 1861–1877.
- [16] S. Dutta, K. C.-W. Wu, B. Saha, *Catal. Sci. Technol.* **2014**, *4*, 3785–3799.
- [17] Q. Song, F. Wang, J. Xu, *Chem. Commun.* **2012**, *48*, 7019–7021.
- [18] Z. Sun, B. Fridrich, A. de Santi, S. Elangovan, K. Barta, *Chem. Rev.* **2018**, *118*, 614–678.
- [19] C. Crestini, H. Lange, M. Sette, D. S. Argyropoulos, *Green Chem.* **2017**, *19*, 4104–4121.
- [20] N.-E. E. Mansouri, J. Salvadó, *Ind. Crops Prod.* **2006**, *24*, 8–16.
- [21] J. Klein, K. Alt, S. R. Waldvogel, *Adv. Sustainable Syst.* **2022**, *130*, 2100391; 1–5.
- [22] M. Breiner, M. Zirbes, S. R. Waldvogel, *Green Chem.* **2021**, *23*, 6449–6455.
- [23] M. Zirbes, S. R. Waldvogel, *Curr. Opin. Green Sustain. Chem.* **2018**, *14*, 19–25.
- [24] D. Schmitt, C. Regenbrecht, M. Hartmer, F. Stecker, S. R. Waldvogel, *Beilstein J. Org. Chem.* **2015**, *11*, 473–480.
- [25] a) D. Schmitt, C. Regenbrecht, M. Schubert, D. Schollmeyer, S. R. Waldvogel, *Holzforschung* **2017**, *71*, 35–41; b) C. Yang, S. Maldonado, C. R. J. Stephenson, *ACS Catal.* **2021**, *11*, 10104–10114; c) X. Du, H. Zhang, K. P. Sullivan, P. Gogoi, Y. Deng, *ChemSusChem* **2020**, *13*, 4318–4343.
- [26] M. Zirbes, D. Schmitt, N. Beiser, D. Pitton, T. Hoffmann, S. R. Waldvogel, *ChemElectroChem* **2019**, *6*, 155–161.
- [27] A. Gavriilidis, A. Constantinou, K. Hellgardt, K. K. Hii, G. J. Hutchings, G. L. Brett, S. Kuhn, S. P. Marsden, *React. Chem. Eng.* **2016**, *1*, 595–612.
- [28] D. Havkin-Frenkel in *Kirk-Othmer Encyclopedia of Chemical Technology* (Hrsg.: J. W. & S. Inc), John Wiley & Sons, Inc, Hoboken, NJ, USA, **2000**, S. 1–12.
- [29] K. Chen, M. Cao, C. Ding, X. Zheng, *RSC Adv.* **2018**, *8*, 26782–26792.
- [30] M. Zirbes, L. L. Quadri, M. Breiner, A. Stenglein, A. Bomm, W. Schade, S. R. Waldvogel, *ACS Sustainable Chem. Eng.* **2020**, *8*, 7300–7307.
- [31] a) A. Jenkins, N. K. Erraguntla in *Encyclopedia of Toxicology*, Elsevier, **2014**, S. 912–914; b) *Encyclopedia of Toxicology*, Elsevier, **2005**; c) L. Yu in *Encyclopedia of Toxicology*, Elsevier, **2005**, S. 418–420.
- [32] a) T. Ren, W. Qi, R. Su, Z. He, *ChemCatChem* **2019**, *11*, 639–654; b) M. Fache, B. Boutevin, S. Caillol, *ACS Sustainable Chem. Eng.* **2016**, *4*, 35–46; c) G. Rødsrud, M. Lersch, A. Sjöde, *Biomass Bioenergy* **2012**, *46*, 46–59.
- [33] C. C. Bryan, *Manufacture of vanillin from lignin 1950*, US-2692291-A.
- [34] a) O. Y. Abdelaziz, D. P. Brink, J. Prothmann, K. Ravi, M. Sun, J. García-Hidalgo, M. Sandahl, C. P. Hultheberg, C. Turner, G. Lidén, M. F. Gorwa-Grauslund, *Biotechnol. Adv.* **2016**, *34*, 1318–1346; b) A. Rahimi, A. Ulbrich, J. J. Coon, S. S. Stahl, *Nature* **2014**, *515*, 249–252.
- [35] a) D. R. Dimmel, M. R. Karim, M. C. Savidakis, J. J. Bozell, *J. Wood Chem. Technol.* **1996**, *16*, 169–189; b) B. Biannic, J. J. Bozell, *Org. Lett.* **2013**, *15*, 2730–2733.
- [36] a) Z. Chen, C. Wan, *Renewable Sustainable Energy Rev.* **2017**, *73*, 610–621; b) A. Agarwal, M. Rana, J.-H. Park, *Fuel Process. Technol.* **2018**, *181*, 115–132; c) H. Zhu, L. Wang, Y. Chen, G. Li, H. Li, Y. Tang, P. Wan, *RSC Adv.* **2014**, *4*, 29917–29924.
- [37] a) J. A. Jennings, S. Parkin, E. Munson, S. P. Delaney, J. L. Calahan, M. Isaacs, K. Hong, M. Crocker, *RSC Adv.* **2017**, *7*, 25987–25997; b) Q. Xiang, Y. Y. Lee, *Appl. Biochem. Biotechnol.* **2000**, *84–86*, 153–162.
- [38] a) J. C. Villar, A. Caperos, F. García-Ochoa, *J. Wood Chem. Technol.* **1997**, *17*, 259–285; b) R. H. J. Creighton, R. D. Gibbs, H. Hibbert, *J. Am. Chem. Soc.* **1944**, *66*, 32–37.
- [39] a) M. Grilc, B. Likozar, J. Levec, *Appl. Catal. B* **2014**, *150–151*, 275–287; b) S. Li, W. Li, Q. Zhang, R. Shu, H. Wang, H. Xin, L. Ma, *RSC Adv.* **2018**, *8*, 1361–1370; c) Y. Zhai, C. Li, G. Xu, Y. Ma, X. Liu, Y. Zhang, *Green Chem.* **2017**, *19*, 1895–1903.
- [40] J. Zhang, J. Teo, X. Chen, H. Asakura, T. Tanaka, K. Teramura, N. Yan, *ACS Catal.* **2014**, *4*, 1574–1583.

- [41] a) C. Z. Smith, J. H. P. Utley, J. K. Hammond, *J. Appl. Electrochem.* **2011**, *41*, 363–375; b) D. Di Marino, T. Jestel, C. Marks, J. Viell, M. Blindert, S. M. A. Kriescher, A. C. Spiess, M. Wessling, *ChemElectroChem* **2019**, *6*, 1434–1442.
- [42] D. Di Marino, D. Stöckmann, S. Kriescher, S. Stiefel, M. Wessling, *Green Chem.* **2016**, *18*, 6021–6028.
- [43] S. Stiefel, A. Schmitz, J. Peters, D. Di Marino, M. Wessling, *Green Chem.* **2016**, *18*, 4999–5007.
- [44] N. Di Fidio, J. W. Timmermans, C. Antonetti, A. M. Raspolli Galletti, R. J. A. Gosselink, R. J. M. Bisselink, T. M. Slaghek, *New J. Chem.* **2021**, *45*, 9647–9657.
- [45] K. Yan, Y. Zhang, M. Tu, Y. Sun, *Energy Fuels* **2020**, *34*, 12703–12709.
- [46] H. J. Schäfer, *C. R. Chim.* **2011**, *14*, 745–765.
- [47] M. G. A. da Cruz, R. Gueret, J. Chen, J. Piątek, B. Beele, M. H. Sipponen, M. Frauscher, S. Budnyk, B. V. M. Rodrigues, A. Slabon, *ChemSusChem* **2022**, *15*, e202200718.
- [48] a) P. T. Anastas, J. B. Zimmerman, *Green Chem.* **2019**, *21*, 6545–6566; b) H. C. Erythropel, J. B. Zimmerman, T. M. de Winter, L. Petitjean, F. Melnikov, C. H. Lam, A. W. Lounsbury, K. E. Mellor, N. Z. Janković, Q. Tu, L. N. Pincus, M. M. Falinski, W. Shi, P. Coish, D. L. Plata, P. T. Anastas, *Green Chem.* **2018**, *20*, 1929–1961.
- [49] P. Anastas, N. Eghbali, *Chem. Soc. Rev.* **2010**, *39*, 301–312.
- [50] S. B. Beil, D. Pollok, S. R. Waldvogel, *Angew. Chem. Int. Ed.* **2021**, *60*, 14750–14759; *Angew. Chem.* **2021**, *133*, 14874–14883.
- [51] a) F. Fink, F. Emmerling, J. Falkenhagen, *Chemistry–Methods* **2021**, *1*, 354–361; b) R. M. Happs, B. Addison, C. Doepke, B. S. Donohoe, M. F. Davis, A. E. Harman-Ware, *Biotechnol. Biofuels* **2021**, *14*, 58–74.
- [52] a) R. Paliwal, K. Giri, J. P. N. Rai in *Advances in Environmental Engineering and Green Technologies* (Hrsg.: Y. Wang, S. Singh, K. Srivastava), IGI Global, **2015**, S. 120–144; b) E. M. Anderson, M. L. Stone, R. Katahira, M. Reed, W. Muchero, K. J. Ramirez, G. T. Beckham, Y. Román-Leshkov, *Nat. Commun.* **2019**, *10*, 2033–2043.
- [53] a) G. Wu, M. Heitz, *J. Wood Chem. Technol.* **1995**, *15*, 189–202; b) N. S. Abdelrahman, E. Galiwango, A. H. Al-Marzouqi, E. Mahmoud, *Biomass Conversion and Biorefinery* **2022**, *28*, 340–351.
- [54] a) S. Stiefel, C. Marks, T. Schmidt, S. Hanisch, G. Spalding, M. Wessling, *Green Chem.* **2016**, *18*, 531–540; b) B. Moodley, D. A. Mulholland, H. C. Brookes, *Water SA* **2011**, *37*, 33–40.
- [55] a) Y. Mathieu, J. D. Vidal, L. Arribas Martínez, N. Abad Fernández, S. Iborra, A. Corma, *ChemSusChem* **2020**, *13*, 4743–4758; b) Y. Hu, S. Li, X. Zhao, C. Wang, X. Zhang, J. Liu, L. Ma, L. Chen, Q. Zhang, *Catal. Commun.* **2022**, *172*, 106532–106540; c) J. Luo, P. Melissa, W. Zhao, Z. Wang, Y. Zhu, *ChemistrySelect* **2016**, *1*, 4596–4601.
- [56] a) K. Syrjänen, G. Brunow, *J. Chem. Soc. Perkin Trans. 1* **2000**, 183–187; b) L. V. Kayser, E. M. Hartigan, B. A. Arndtsen, *ACS Sustainable Chem. Eng.* **2016**, *4*, 6263–6267; c) J.-M. Bollag, S.-Y. Liu, R. D. Minard, *Soil Sci. Soc. Am. J.* **1980**, *44*, 52–56.
- [57] a) B. V. Lyalin, V. A. Petrosyan, *Russ. J. Electrochem.* **2010**, *46*, 1199–1214; b) B. Ash, V. S. Nalajala, A. K. Popuri, T. Subbaiah, M. Minakshi, *Nano-materials* **2020**, *10*, 1–22.
- [58] M. Dörr, M. M. Hielscher, J. Proppe, S. R. Waldvogel, *ChemElectroChem* **2021**, *8*, 2621–2629.
- [59] R. Sun, J. M. Lawther, W. B. Banks, *Ind. Crops Prod.* **1995**, *4*, 241–254.
- [60] a) K. Freudenberg, W. Lautsch, K. Engler, *Ber. Dtsch. Chem. Ges. A* **1940**, *73*, 167–171; b) T. P. Schultz, M. C. Templeton, *Holzforchung* **1986**, *40*, 93–97.
- [61] a) J. Seidler, J. Strugatchi, T. Gärtner, S. R. Waldvogel, *MRS Energy Sustainability* **2020**, *7*, 1–14; b) S. Möhle, M. Zirbes, E. Rodrigo, T. Gieshoff, A. Wiebe, S. R. Waldvogel, *Angew. Chem. Int. Ed.* **2018**, *57*, 6018–6041; *Angew. Chem.* **2018**, *130*, 6124–6149; c) M. Yan, Y. Kawamata, P. S. Baran, *Chem. Rev.* **2017**, *117*, 13230–13319; d) K. D. Moeller, *Chem. Rev.* **2018**, *118*, 4817–4833; e) D. Pollok, S. R. Waldvogel, *Chem. Sci.* **2020**, *11*, 12386–12400; f) B. A. Frontana-Urbe, R. D. Little, J. G. Ibanez, A. Palma, R. Vasquez-Medrano, *Green Chem.* **2010**, *12*, 2099; g) S. R. Waldvogel, B. Janza, *Angew. Chem. Int. Ed.* **2014**, *53*, 7122–7123; *Angew. Chem.* **2014**, *126*, 7248–7249.

Manuscript received: December 10, 2022

Revised manuscript received: January 17, 2023

Accepted manuscript online: January 18, 2023

Version of record online: March 9, 2023