Electrocatalytic conversion of Kraft lignin and industrial black liquor

1st June 2023

RRB Riga

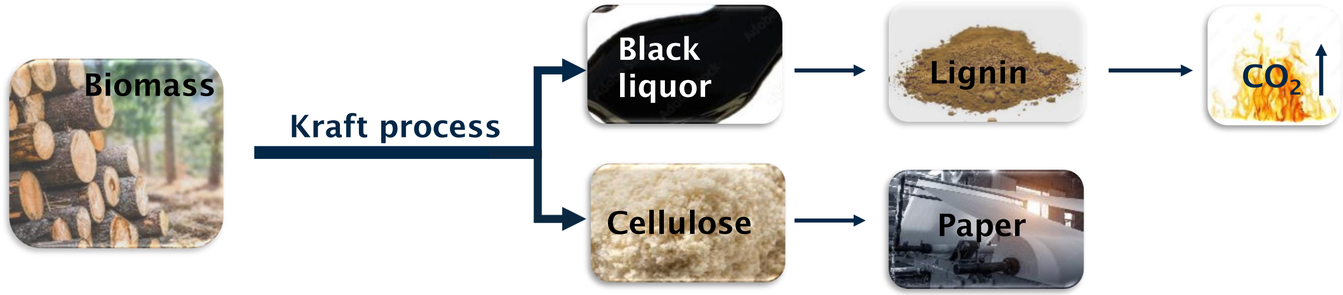
Presenter: Elisabeth K. Oehl[1]
Further contributors: Roman Tschentscher[2], Audrey Minnard[2], Francisco Pereira[2], Niclas Schupp[1], Carl-Johan Hjerpe[3], Jonas Kihlman[3], Bernd Wittgens[2], Siegfried R. Waldvogel[1]

[1] Department of Chemistry, Johannes Gutenberg-University, Mainz, Germany
2 Process Technology, SINTEF Industry, Oslo, Norway
3 ÅF-Industry AB, Karlstad, Sweden

This project has received funding from the European Union's Horizon 2020 Research and Innovation Programme under Grant Agreement No. 101006612.

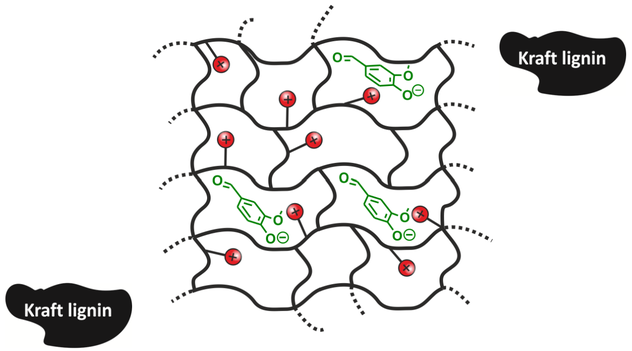
Overview - Lignin and Black Liquor

- Motivation: Biomass utilisation for a sustainable, second life cycle and reduced CO_2 emisson

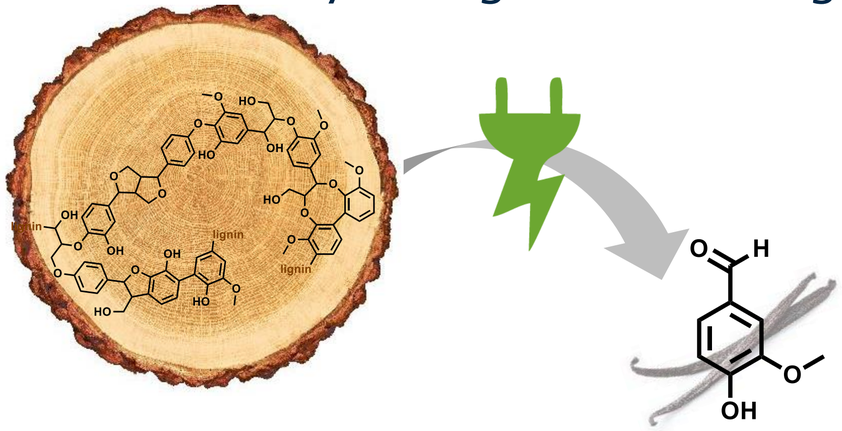


- Acquisition of phenolics from industrial lignin and black liquor

1. Adsorption of phenolics onto anionic IE resins



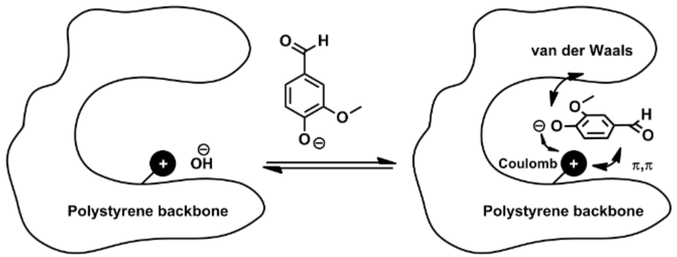
2. Electrocatalytic degradation of lignin



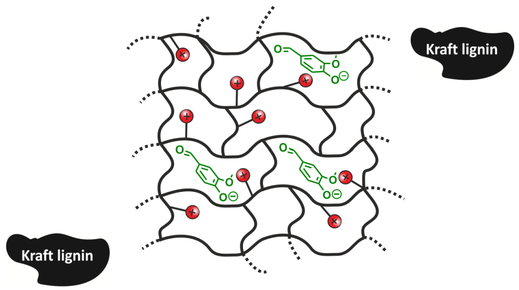
Adsorption of Phenolics in Black Liquor

- Isolation of phenolics using highly alkaline ion-exchange resins[a] avoiding inefficient acidification followed by liquid-liquid extraction processes
- **Reversible adsorption** due to:

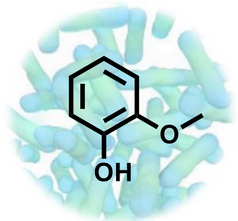
Coulomb and Van-der-Waals interactions

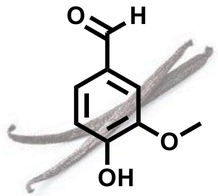


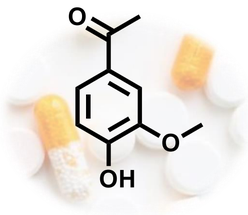
Size exclusion



- Continuous adsorption/desorption process offers eco-friendly removal of 1.2 wt%/mL black liquor





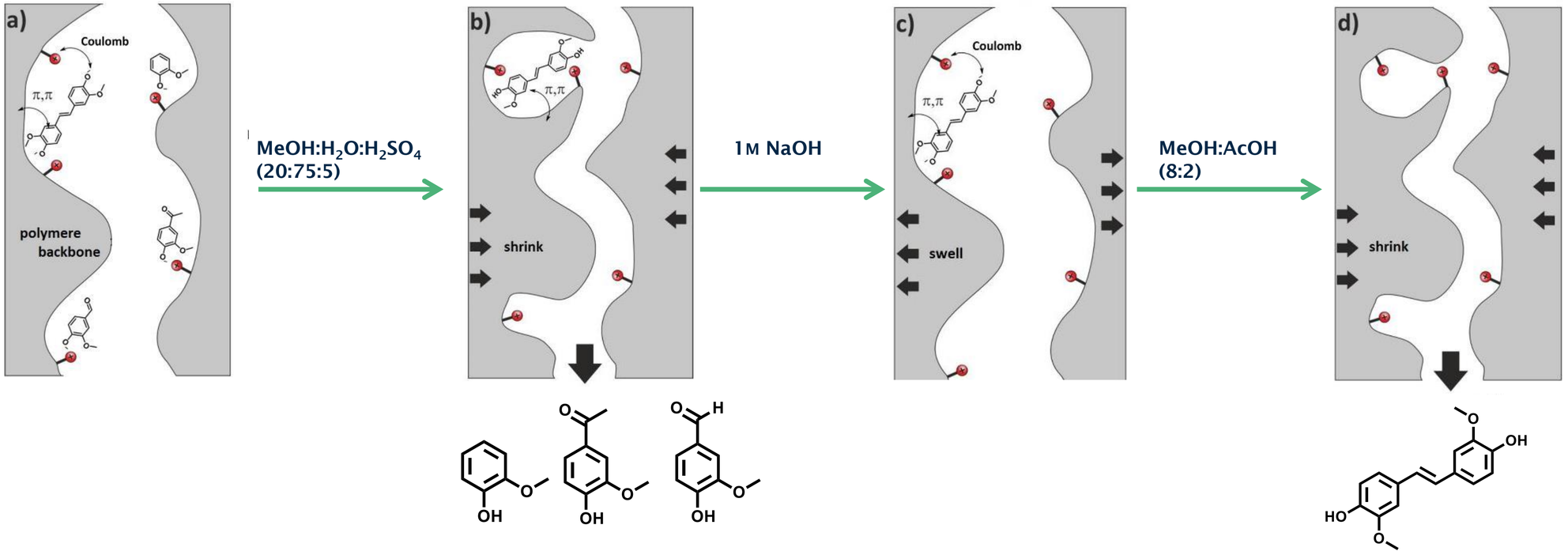


D. Schmitt, C. Regenbrecht, D. Schollmeyer, S. R. Waldvogel, *Beilstein J. Org. Chem.* **2015**, 11, 473–480.

[a] Dowex Monosphere 550a OH, diameter of 0.5 – 0.6 mm, exchange capacity of 1.10 meq/mL.

Adsorption and Separation of Phenolics in Black Liquor

- Separation of phenolics based on different pKa values
- Two-steps desorption: Utilize differences in interaction strength for stepwise desorption of compound groups

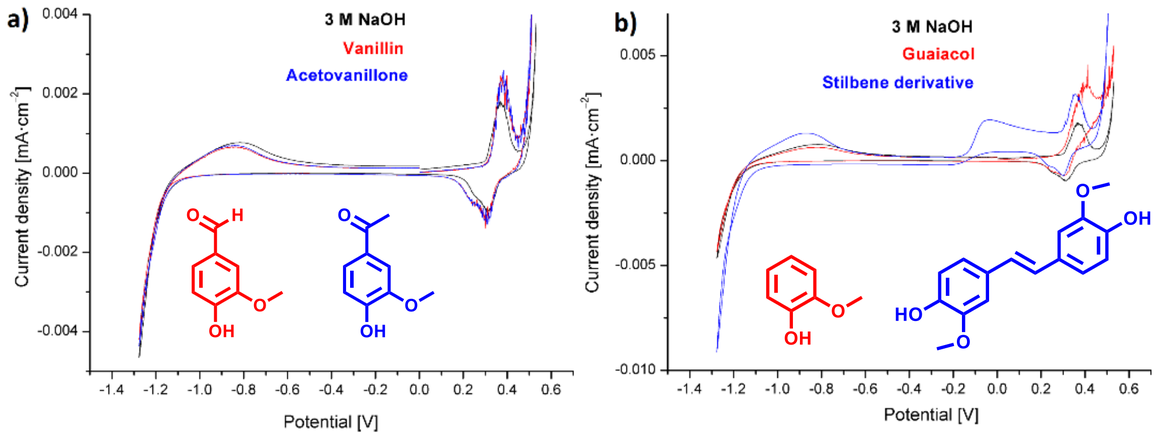


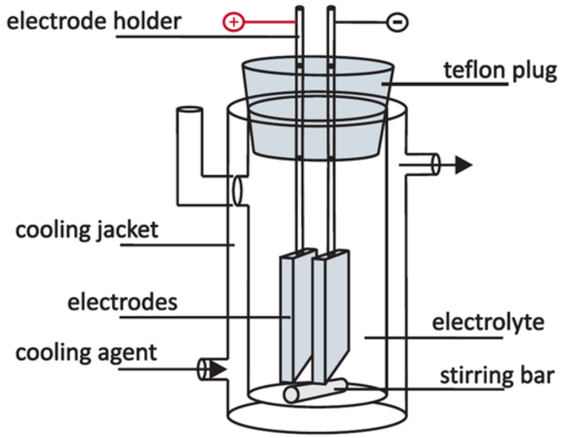
D. Schmitt, C. Regenbrecht, D. Schollmeyer, S. R. Waldvogel, *Beilstein J. Org. Chem.* **2015,** 11, 473–480.

Highly Selective Anodic Degradation of Lignin

- Development of an electrochemical degradation of lignin at low pressure and low temperature
- Consideration of target molecule, set-up and electrode material
- Investigation of the current density, temperature, and basicity for process optimisation

Identification and quantifaction:
Gas chromatography with internal standard (dodecylbenzene) in a one-point calibration



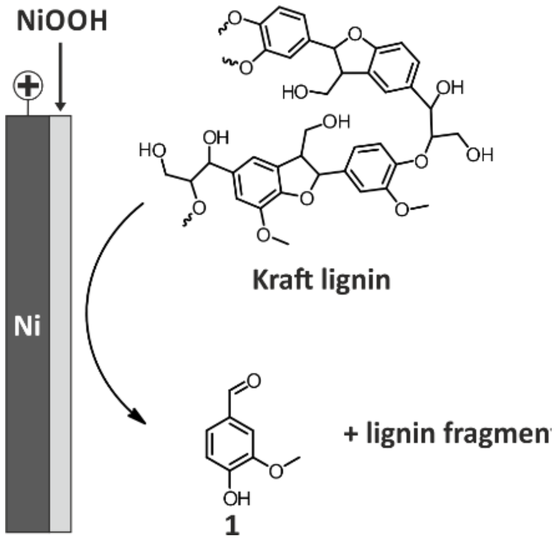


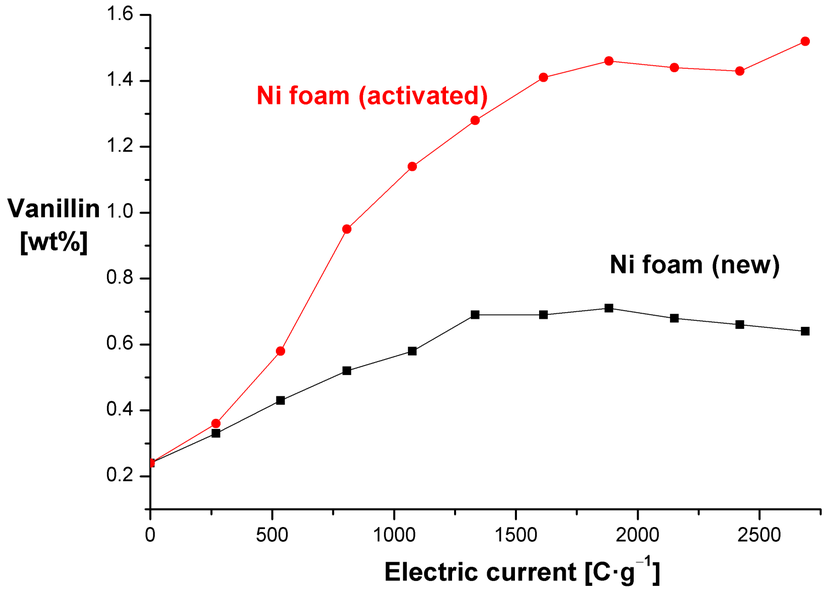
a) CV of vanillin and acetovanillone, suitable for electrolysis; **b)** CV of guaiacol and 4,4'-dihydroxyl-3,3'-dimethoxystilbene, unsuitable for electrolysis; **Conditions:** Ni (WE), glassy carbon (CE), Ag/AgCl (RE), analyte conc. 10 mmol/L in 3 M NaOH.

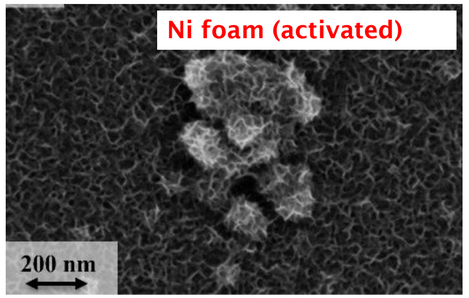
D. Schmitt, C. Regenbrecht, D. Schollmeyer, S. R. Waldvogel, *Beilstein J. Org. Chem.* **2015,** 11, 473–480.

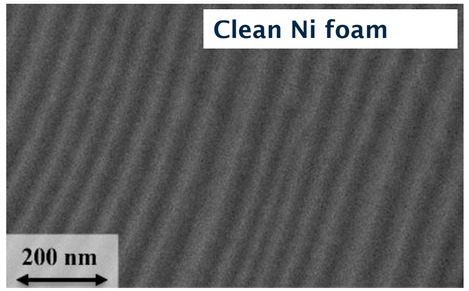
Electrocatalytic Behaviour and Activation of Ni Electrodes

- Similar electrocatalytic behaviour of Ni and Co → Co (alloys) showed corrosion
- Ni foam showed corrosion stability, enabled yields of vanillin up to 1.0 wt% and an improved space-time yield
- Growth of electrocatalytically active NiO(OH) species at the anodic surface significantly increases vanillin yield









Activation of Ni electrodes:
80 mL depleted black liquor 80 °C,
38 mA/cm², 120 C/cm² →rinse with H_2O

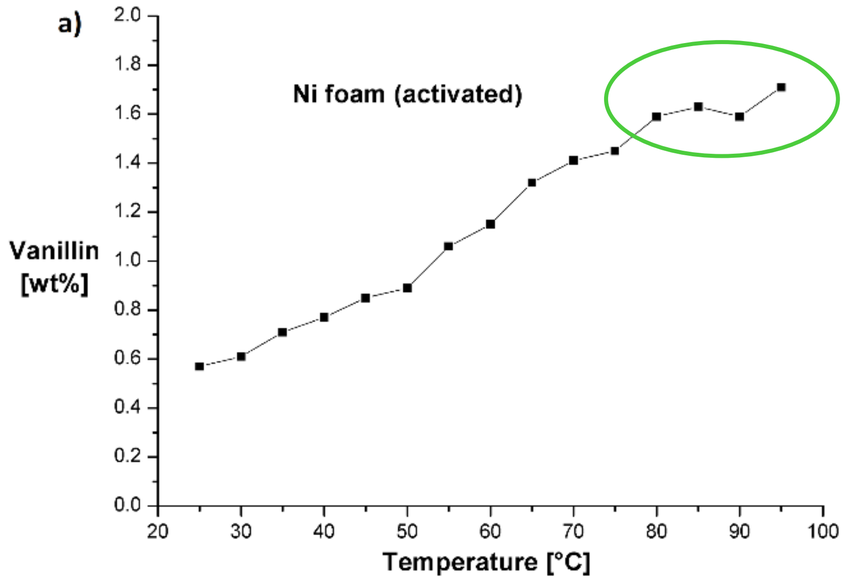
D. Schmitt, C. Regenbrecht, D. Schollmeyer, S. R. Waldvogel, *Beilstein J. Org. Chem.* **2015,** 11, 473–480.

M. Zirbes, D. Schmitt, N. Beiser, D. Pitton, T. Hoffmann, S. R. Waldvogel, *Chem. Electro. Chem.* **2019**, 6, 155–161.

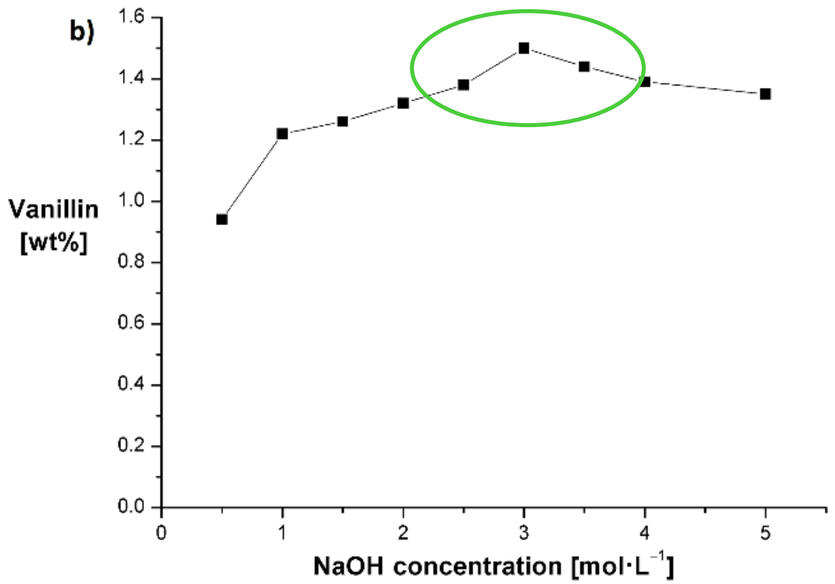
R. J.-R. Bednarz, S. R. Waldvogel, *Org. Process Res. Dev.* **2023** [submitted].

Highly Selective Degradation of Lignin to Vanillin

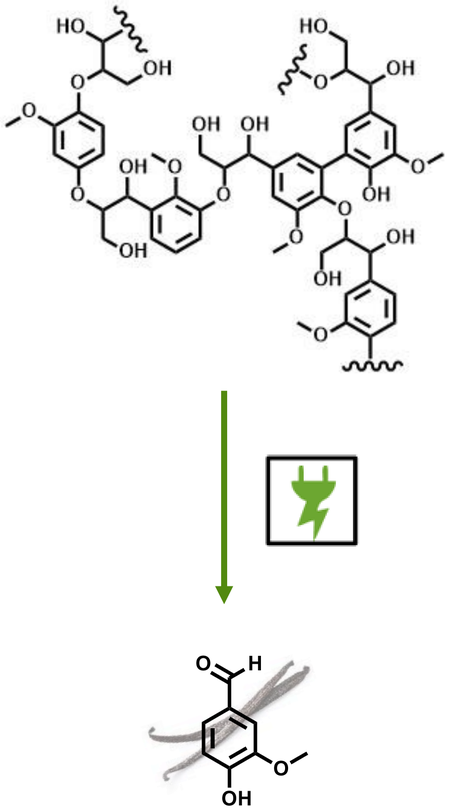
- Linear screening led to optimised reaction conditions
  - 80 ˚C, 3 M NaOH, 2500 C/g
- High selectivity, reduced reagent waste, and cost efficient



a) Influence of reaction temperature.



b) Influence of basicity on the electrochemical degradation of lignin using Ni foam electrodes.

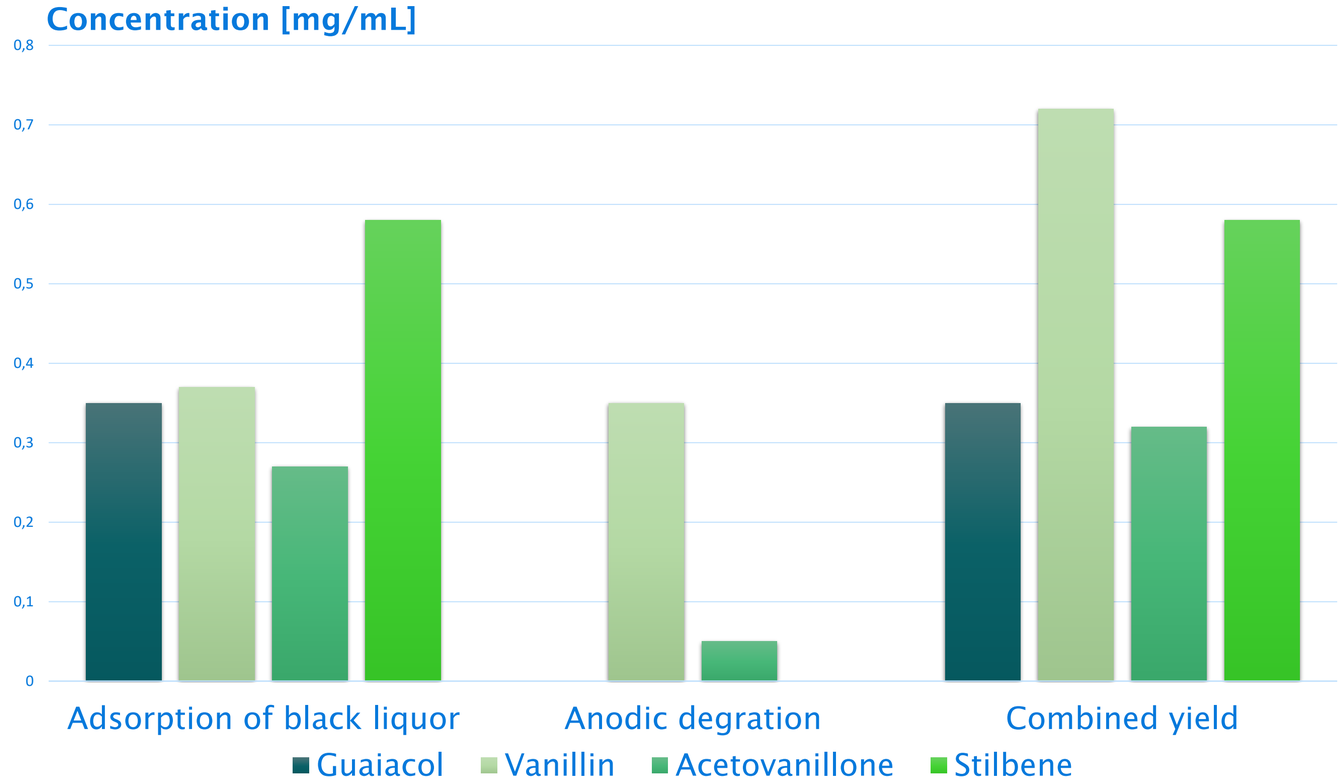


1.6 wt%

M. Zirbes, D. Schmitt, N. Beiser, D. Pitton, T. Hoffmann, S. R. Waldvogel, *Chem. Electro. Chem.* **2019**, 6, 155–161.

Selective accumulation of Vanillin by Anodic Degradation of Lignin in Black liquor

- Maximising yield of vanillin through combination of adsorption and electrochemical degradation of depleted Black liquor

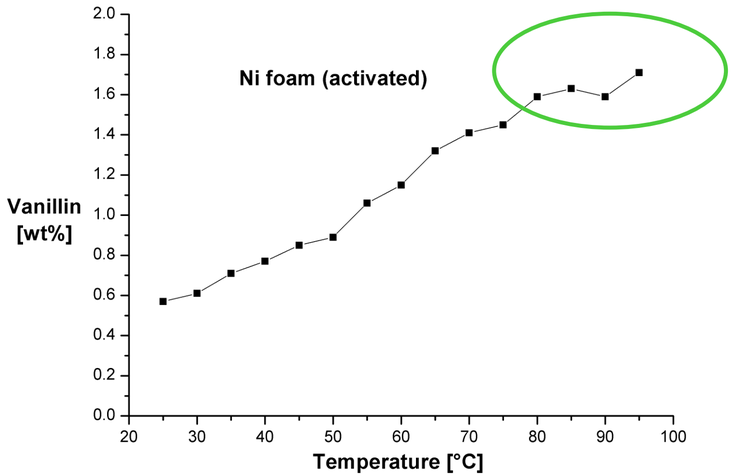


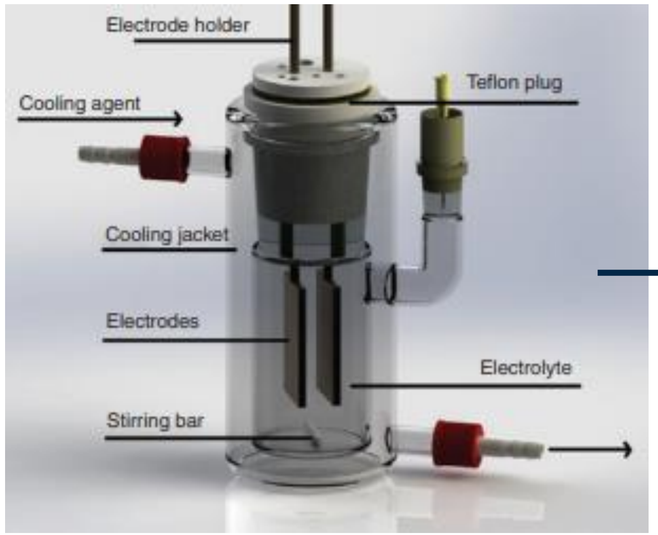
Reaction conditions:
40 mL depleted black liquor 80 °C,
38 mA/cm², 35 C/mL

D. Schmitt, C. Regenbrecht, D. Schollmeyer, S. R. Waldvogel, *Beilstein J. Org. Chem.* **2015,** 11, 473–480.

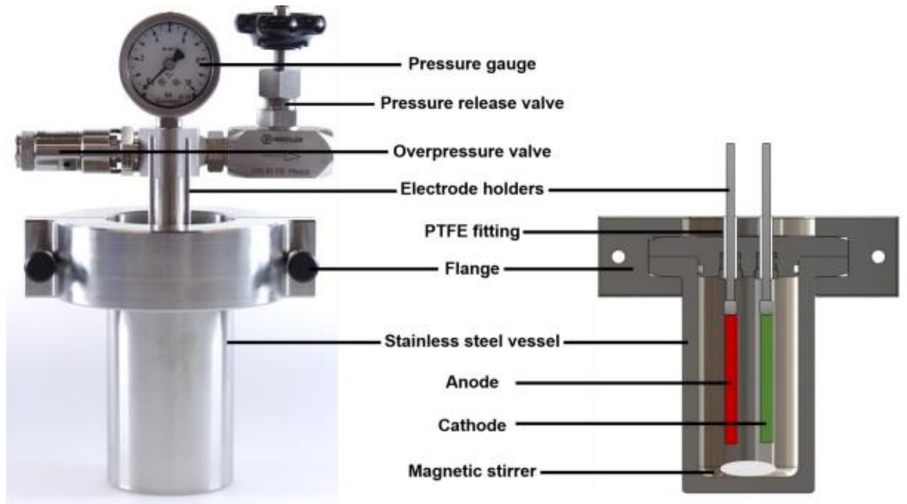
Lignin Degradation Relative to Temperature

- Yields improved linearly with increasing temperature
- Development of a pressurised system (up to 8 bar) enables higher temperatures (200 °C)
- First experiments on low-quality Kraft lignin[a]





Undivided beaker electrolysis cell



Undivided high-temperature electrolysis cell

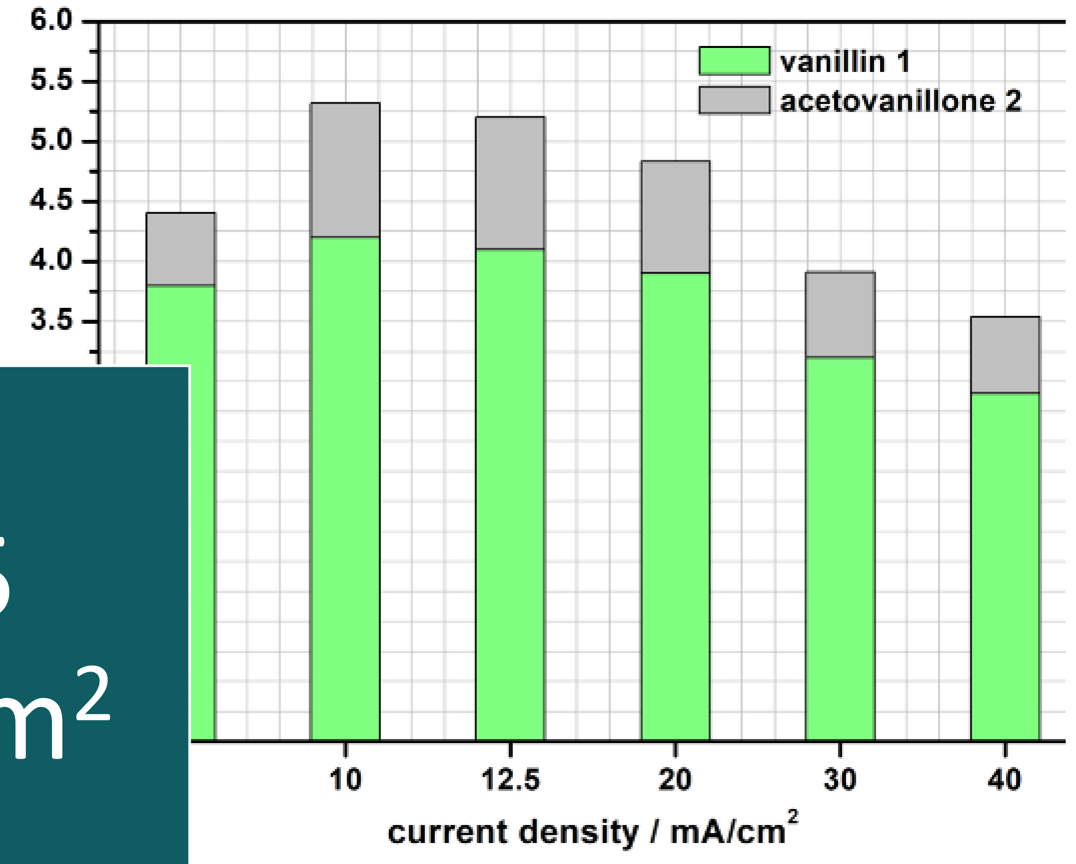
[a] low-quality lignin and high quality lignin Indulin AT lignin both purchased from WestRock

M. Zirbes, D. Schmitt, N. Beiser, D. Pitton, T. Hoffmann, S. R. Waldvogel, *Chem. Electro. Chem.* **2019**, 6, 155–161.

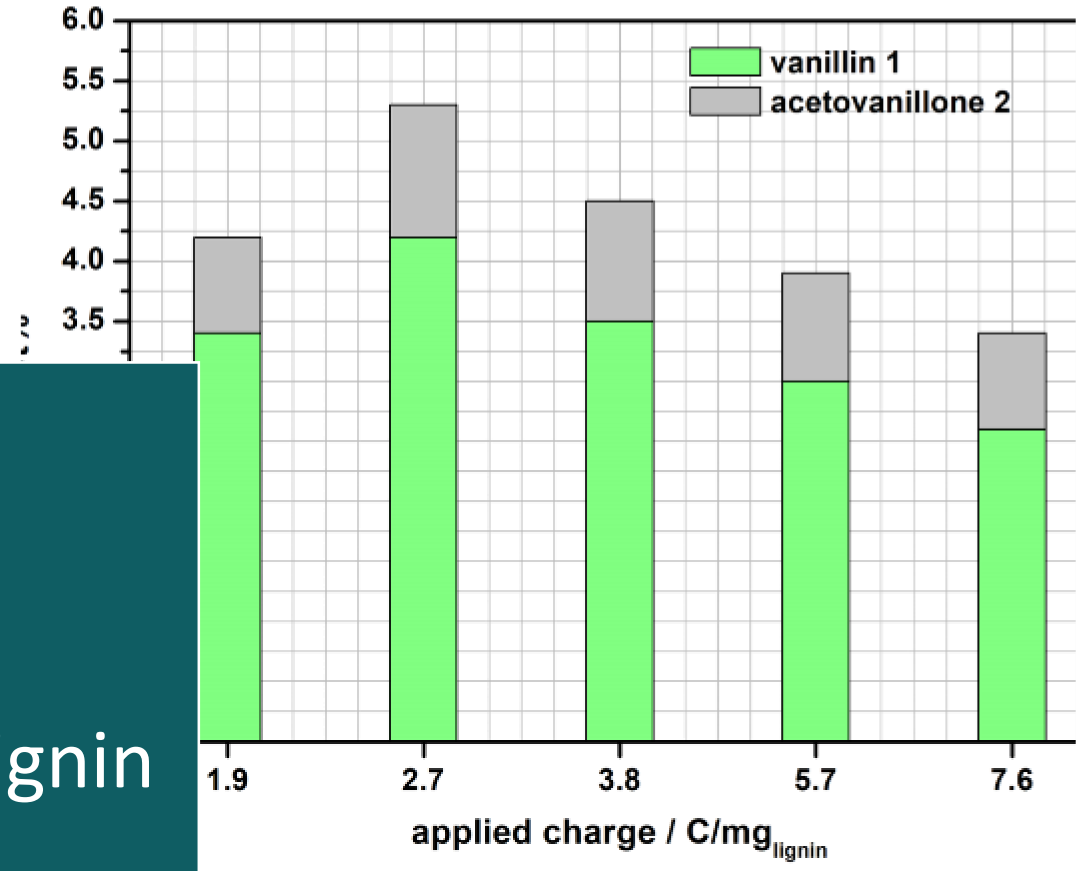
M. Zirbes, D. Schmitt, L. L. Quadri, M. Breiner, A. Stenglein, A. Bomm, W. Schade, S. R. Waldvogel, *ACS Sustainable Chem. Eng.* **2020**, 8, 7300−7307

Optimisation of Anodic Lignin Degradation of High-quality Lignin

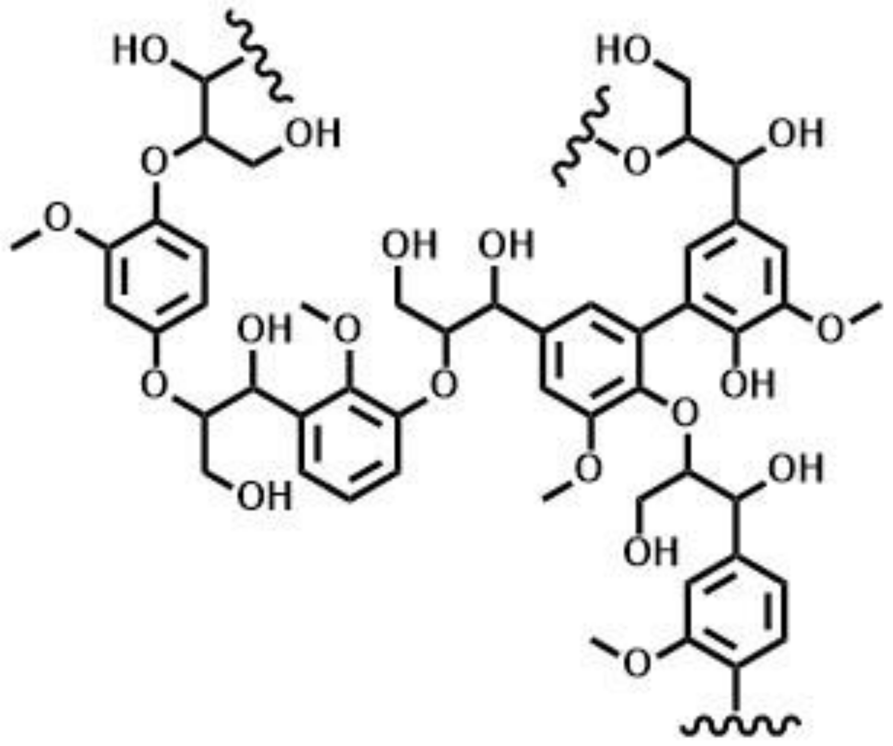
- Change of feedstock to high-quality Indulin AT lignin

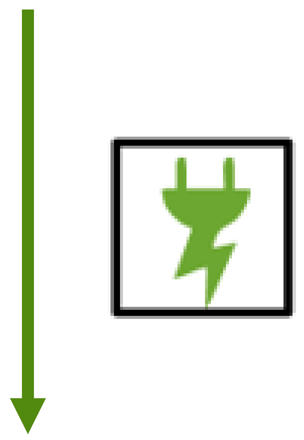


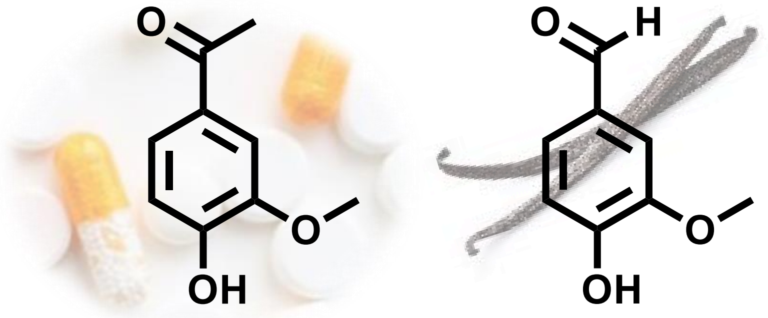
12.5
mA/cm²



2.7
C/mg$_{Lignin}$







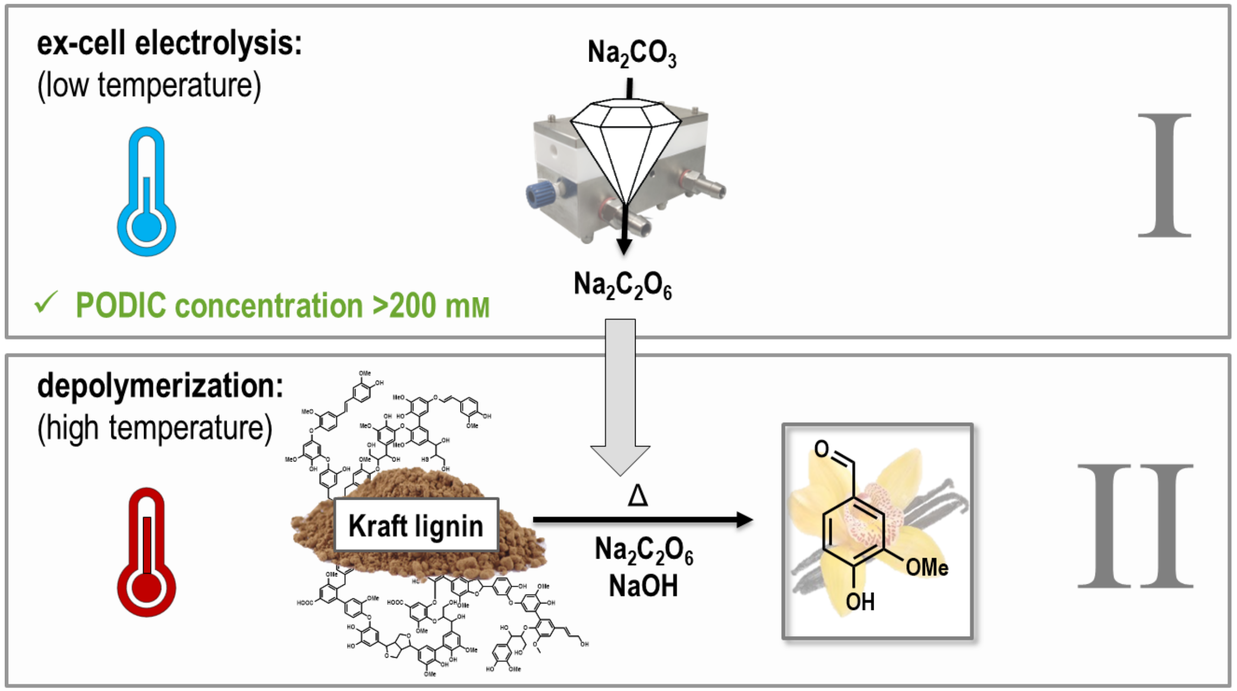
1.1 wt% 4.2 wt%

- Activation and geometry of the Ni electrodes showed minor influence on yield → planar nickel as electrode material and *in situ* activation
- 4.2 wt% vanillin after optimization →60% of the maximum possible value (Reference: NBO - nitrobenzene oxidation)

M. Zirbes, D. Schmitt, L. L. Quadri, M. Breiner, A. Stenglein, A. Bomm, W. Schade, S. R. Waldvogel, *ACS Sustainable Chem. Eng.* **2020**, 8, 7300−7307

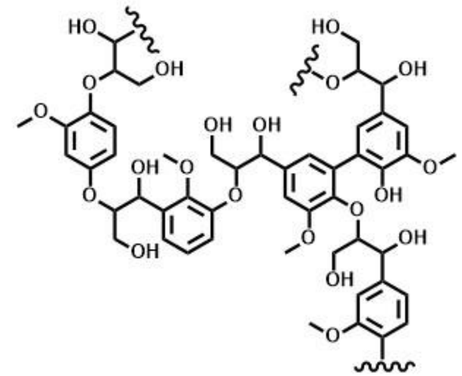
Electrochemical Degradation with high performance oxidiser

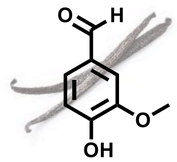
- Two steps: electrochemical formation of peroxodicarbonat (oxidiser) followed by thermal degradation



Electrolytic conditions: 1 M Na_2CO_3 (aq), BDD (+) stainless steel (-), 0.24 A/cm², 12 cm², 2.88 A, 2 F, undivided, constant current, v = 100 mL/min, E = 5-6 V.

Reaction conditions: 3 M NaOH (aq), 200 mg Kraft lignin, 17-35 mL PODIC solution, added at 50 °C, 6-12 h heating at 175°C





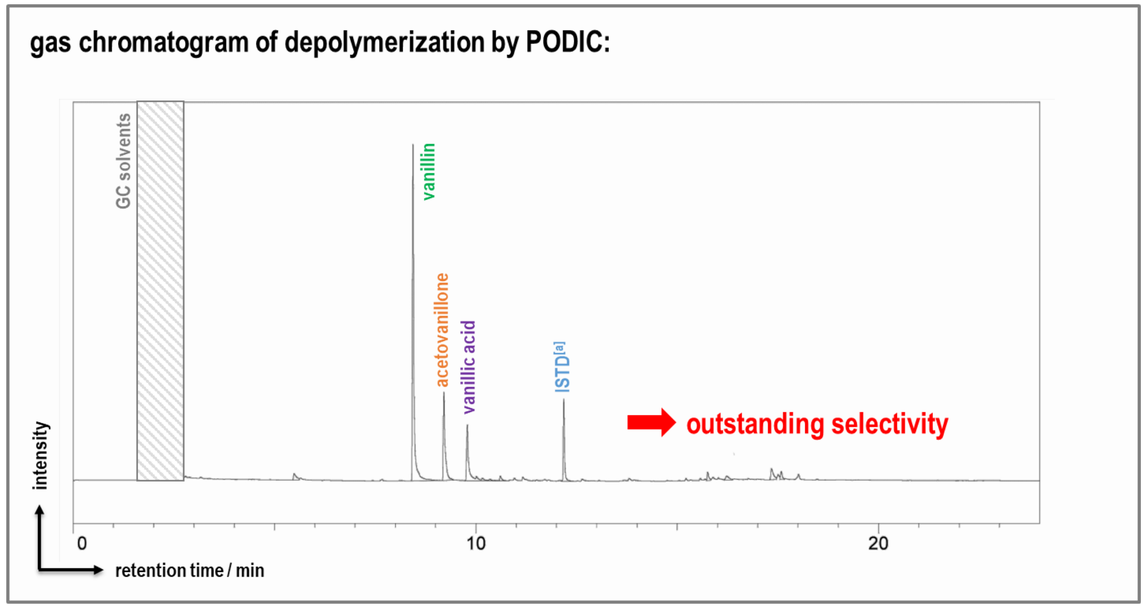
5.7 wt%

- 5.7 wt% vanillin →90% of the maximum possible value (Reference: NBO - nitrobenzene oxidation)

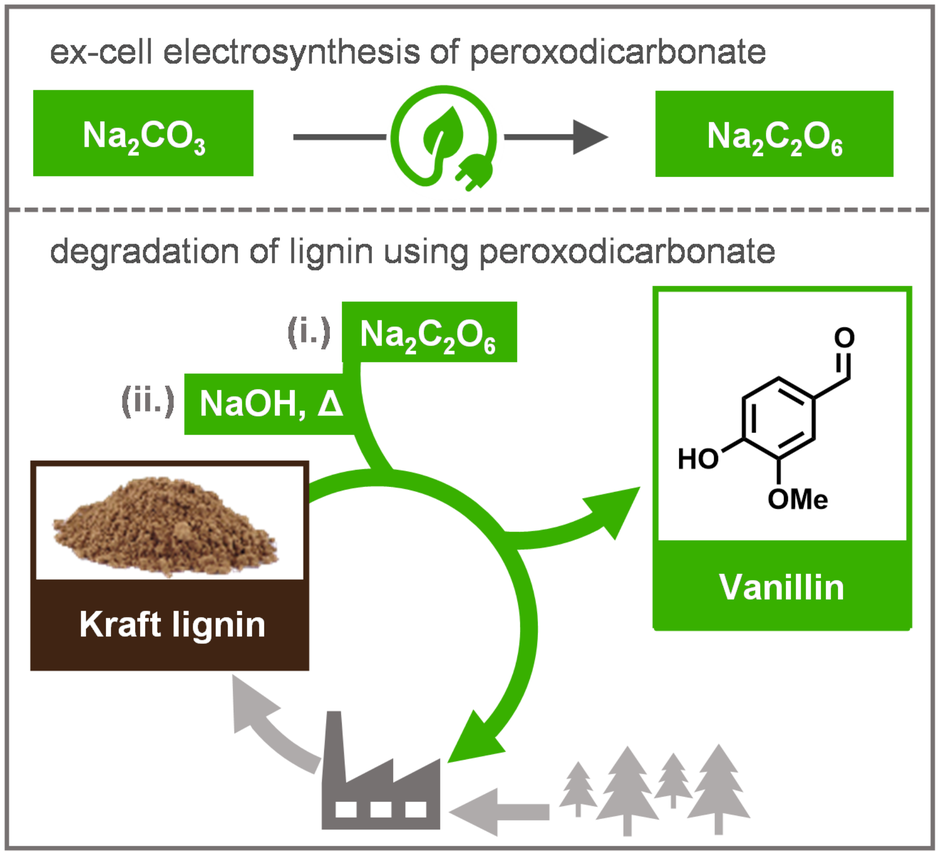
WO 2020099350 A1 20200522, **2020**.

High selectivity and industrial application of lignin degradation

- **Pilot plant** in Trondheim, NO (SINTEF) by Horizon 2020 project LIBERATE (7 wt% vanillin)



[a] ISTD: *n*-dodecylbenzene, 2 µL .

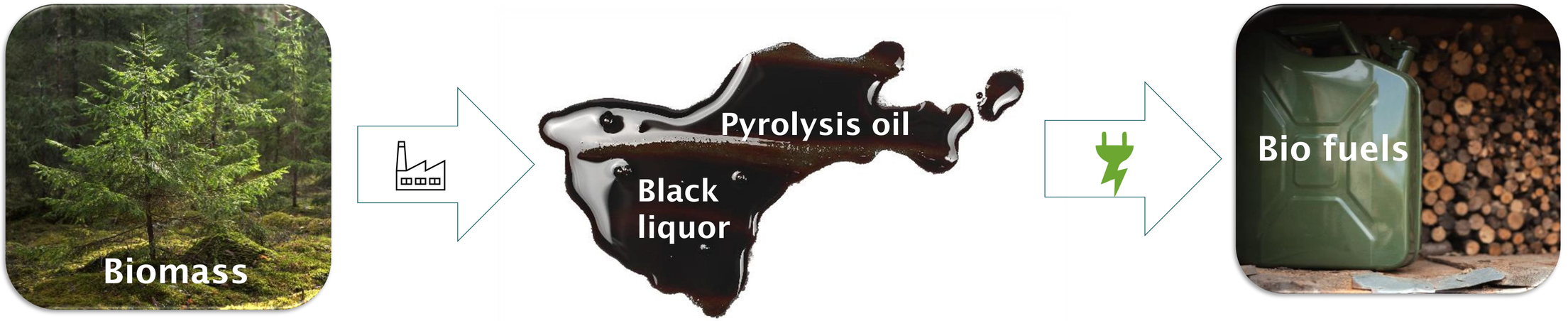


WO 2020099350 A1 20200522, **2020**.
Angew. Chem. Int. Ed. **2023**, e202219217, highlighted in ChemistryViews Feb. 23rd, 2023.

Introduction of EBIO

Goal: Development of an economically, environmentally, and socially friendly process for transport fuel production from biomass.

Process: Electrochemical conversion of low-value bio-liquids (pyrolysis oil and black liquor) into green fuels, platform chemicals, and high-value compounds.

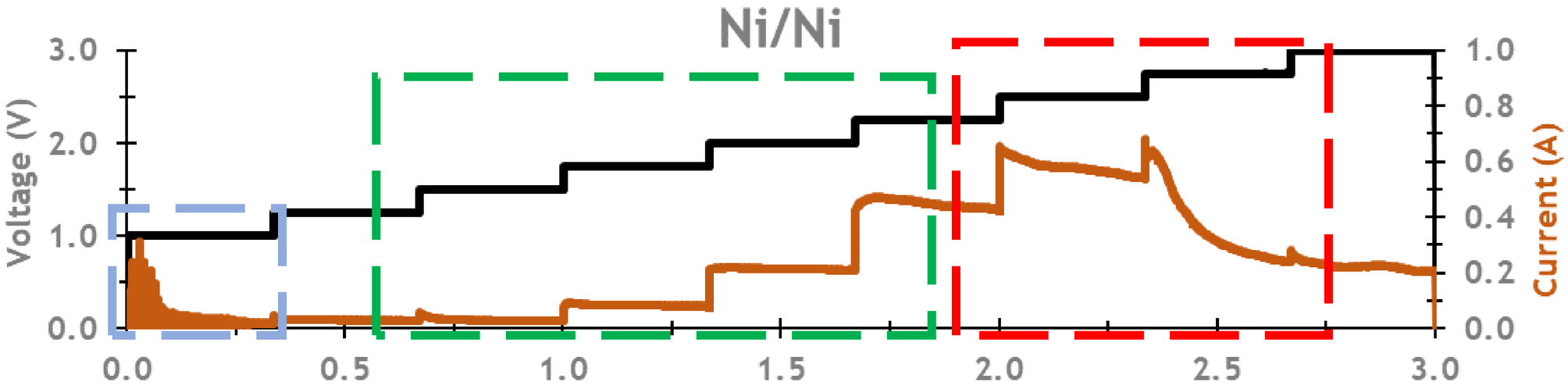


Partners:

SINTEF, btg biomass technology group, Johannes Gutenberg Universität Mainz, CONDIAS Conductive Diamond Products, University of Twente., Tüpraş, AFRY, etaflorence renewable energies

Degradation of Lignin in Black liquor

- Black liquor shows excellent electrolyte due to its high inorganic content
- Important parameters: Liquid flow rate and viscosity
- Chrono-amperometry: current densities up to 500 A/m^2 without deposit formation on the electrode (2.2 V)



Faradaic efficiencies towards lignin oxidation > 90%

- Extent of undesired repolymerisation was quantified and correlated both to the black liquor composition, electrode materials and applied cell voltage

Prof. Dr. Siegfried R. Waldvogel

JOHANNES GUTENBERG UNIVERSITÄT MAINZ

Thank you!

Dr. Roman Tschentscher

SINTEF

Dr. D. Schmitt
M. Zirbes

Waldvogel Lab

This project has received funding from the European Union's Horizon 2020 Research and Innovation Programme under Grant Agreement No. 101006612.

ebio-h2020.eu
@Ebio_h2020
ebio-h2020-project
info@ebio-h2020.eu