Lignin as Potential Sustainble and Renewable Feedstock for Aromatic Fine Chemicals and Fuels

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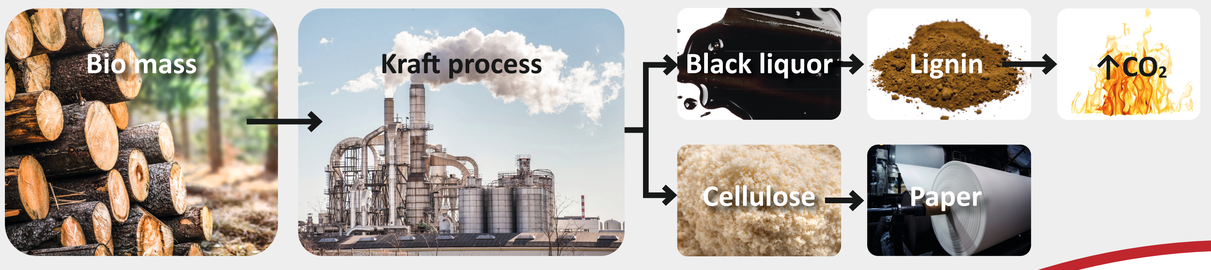
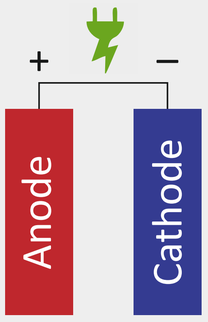
Lignin as Renewable Biomass

Structure and extraction of lignin

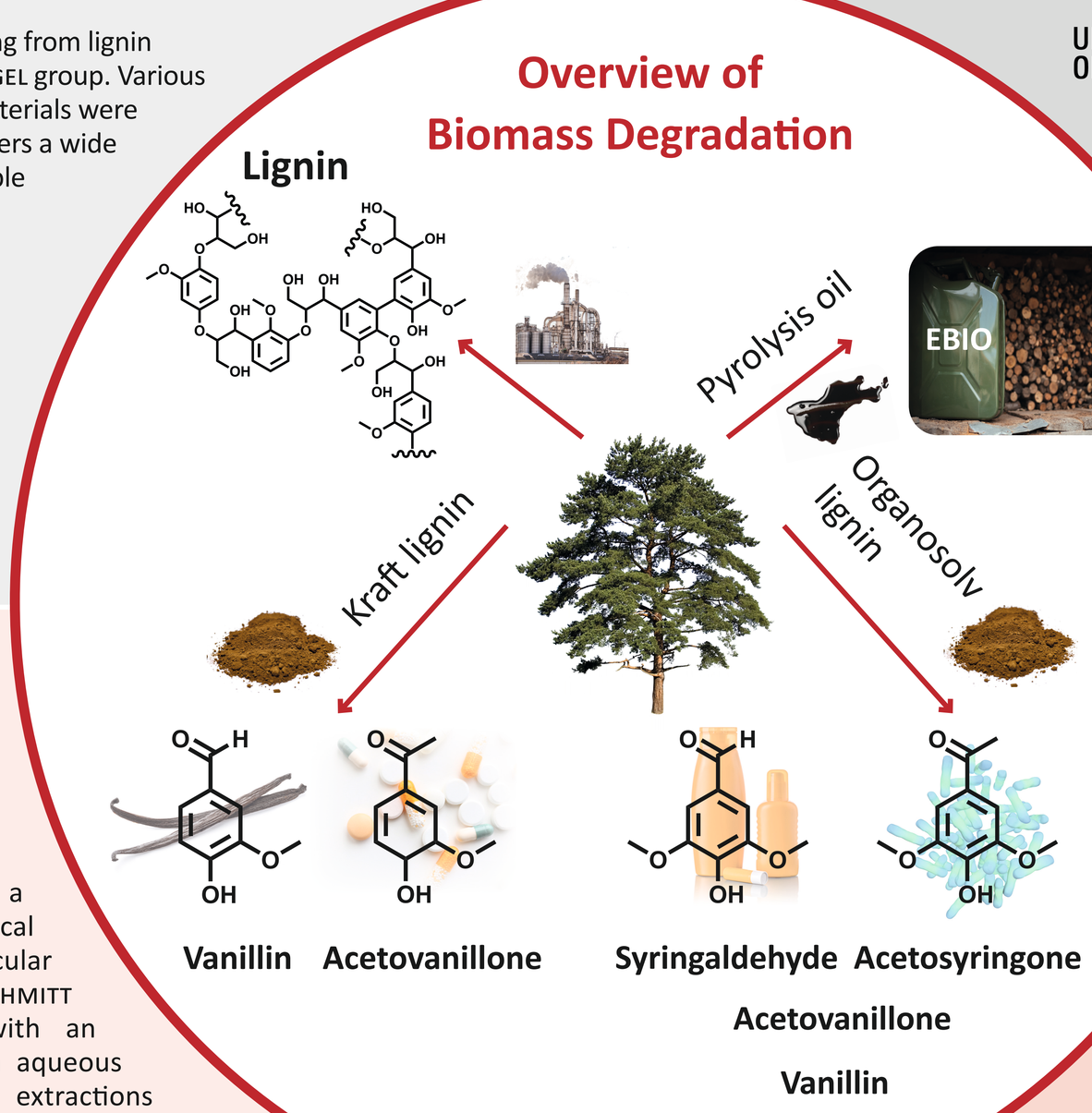
Lignin is a renewable biopolymer with a polyphenolic structure that represents a major proportion of plant-derived biomass. In nature, lignin gives plants compressive strength and is part of the cell wall. The combustion of lignin produces large amounts of carbon dioxide, which is why the selective degradation to high-value monomers that can be used for other applications should be pursued. There are several ways to remove lignin from wood, e. g. Kraft process.[1]



The aforementioned feed stocks originating from lignin were used in the research of the WALDVOGEL group. Various pathways for the conversion of raw biomaterials were explored using electrochemistry which offers a wide range of advantages leading to a sustainable reaction pathway.



- Inexpensive electric current
- Inherently safe
- Sustainable reaction pathway
- Technical application due to easy scale up



Introducing EBIO Horizon 2020

Implementation of EBIO technologies

(considering only pyrolysis oil and Black liquor)

Decrease of 190 Mt/ year of CO_2

Increase of 61 Mt/year biofuel

In the EBIO project the goal is to develop an economically, environmentally, and socially friendly process for transport fuel production from biomass. It targets the electrochemical conversion of two low-valued and industrially available bio-liquids (pyrolysis oil and black liquor) into green fuels, platform chemicals, and high-value compounds. This project benefits all participants in the manufacturing process, the electrochemical development and electrochemical system optimization, and co-processing from refineries.

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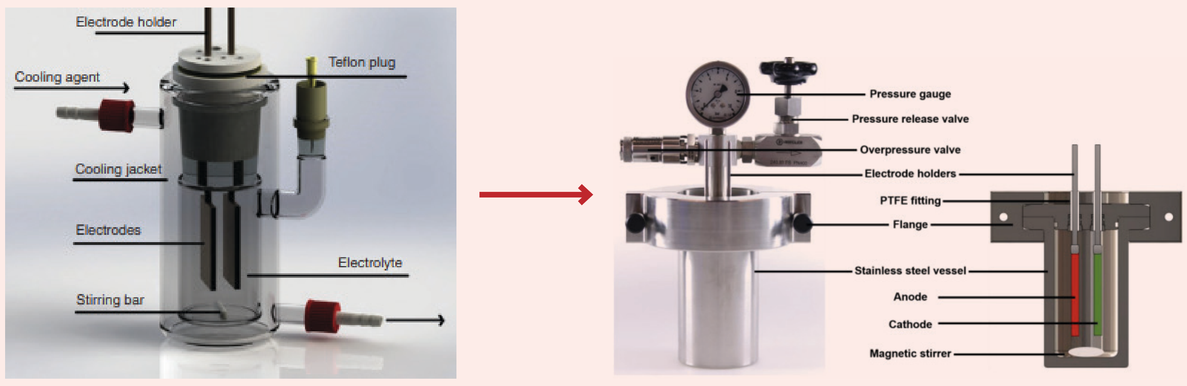
The electrochemical research focuses on oxidative and thermal degradation of lignin as well as the electrochemical hydrogenation by the WALDVOGEL group. It offers a promising route towards the sustainable production of biofuels that will have industrial application in the future.

Electrochemical degradation of Kraft lignin to high-value chemicals

The WALDVOGEL group developed a sustainable method for the electrochemical degradation of lignin into low molecular weight phenolic compounds. SCHMITT published an anodic degradation with an activated nickel foam electrode in an aqueous caustic soda solution with successful extractions of up to 1.8 wt% vanillin. The experiment was performed using a divided cell with a current density of 38 mA/cm² at 80 °C to avoid a pressurized system.[2]

ZIRBES managed to avoid the issue of pressurization by designing an electrochemical set up which made pressures up to 8 bar, and therefore high temperatures (160 °C), possible. Using linear screening it was shown that the optimal current density lay between 10.0 – 12.5 mA/cm² with 2.7 C/mg_{lignin} as the favorable amount of charge. The vanillin yield from Indulin AT Kraft lignin was 4.2 wt% which is 60% of the possible amount relative to the nitrobenzene oxidation standard. Acetovanillone was also obtained as a by-product in 0.8 wt%.[3]



Electrochemical degradation of organosolv lignin to high-value chemicals

BREINER applied the established system on a different feedstock called organosolv lignin and extended the scope of phenolics from vanillin and acetovanillone to syringaldehyde and acetosyringone. For syringaldehyde up to 2.1 wt% and acetosyringone up to 1.5 wt% were obtained from BEC-2-TNO (beech) and WHS-2-TNO (wheat straw) lignin respectively. The characterization of the aldehydes and ketones was done with FT-IR spectroscopy to compare the characteristic bands of syringyl and guaiacyl units of the crude (black curve) and oxidized (green curve) lignin as well as NMR spectroscopy (Figure 1).[4]

In addition, current density, lignin quantity, base concentration and temperature were investigated by linear screening in order to find optimal conditions for the degradation of organosolv lignin (SPR-1-TNO). The results of the temperature screening are shown below (Figure 2). The optimal conditions in relation to highest vanillin yield are 12.5 – 15 mA/cm² and 750 mg organosolv lignin in 85 g of 3 M $NaOH_{(aq.)}$.

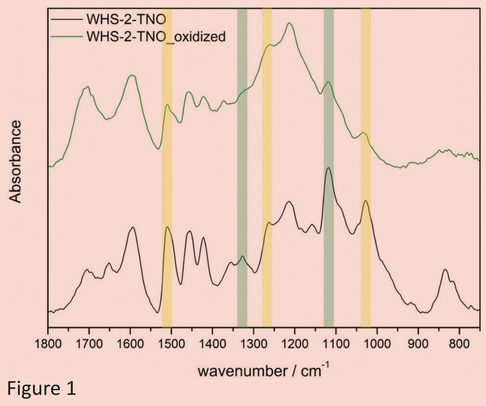


Figure 1

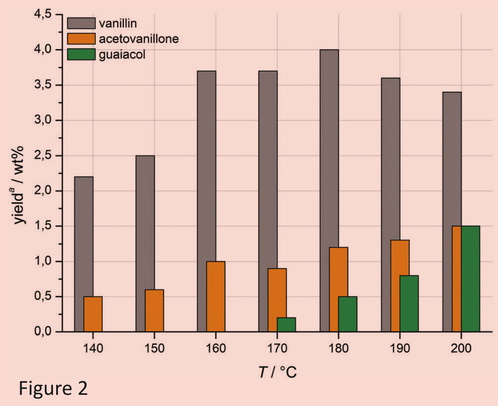


Figure 2

References

[1] M. Zirbes, S. R. Waldvogel, Current Opinion in Green and Sustainable Chemistry 2018, 14, 19–25.
[2] D. Schmitt, C. Regenbrecht, M. Hartmer, F. Stecker, S. R. Waldvogel, Beilstein J. Org. Chem. 2015, 11, 473–48.
[3] M. Zirbes, L. L. Quadri, M. Breiner, A. Stenglein, A. Bomm, W. Schade, S. R. Waldvogel, ACS Sustainable Chem. Eng. 2020, 8, 7300–7307.
[4] M. Breiner, M. Zirbes, S. R. Waldvogel, Green Chem. 2021, 23, 6449–6455.

EBIO BIOFUELS THROUGH ELECTROCHEMICAL TRANSFORMATION OF INTERMEDIATE BIO-LIQUIDS

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