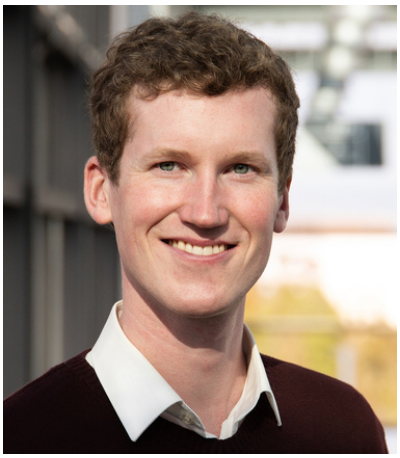

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DOKTORAND

Bewerbung
Energie-Campus 2023
Stiftung
Energie & Klimaschutz

ARBEITSTITEL

Large-scale electrochemical adipic acid derivative production: Electrifying technical organic synthesis.

Large-scale electrochemical adipic acid derivative production: Electrifying technical organic synthesis.

Worldwide adipic acid production causes up to 300 Mt of CO_2 equivalent emissions annually – up to 1/3 of the German total emissions in 2022. On industrial scale, no green process to synthesize adipic acid is utilized, yet. Therefore, for example, nylon 6,6 still relies on a fossil feedstock and a polluting production. In my PhD project, I worked on closing this gap by using an alternative climate friendly and waste-free synthesis route using electro-organic synthesis. The designed continuous flow reactor uses electricity instead of nitric acid, lignin-derived 4-alkylcyclohexanols instead of crude oil as a feedstock and reusable Ni-foams instead of toxic catalysts. Additionally, it allows for an efficient scale-up.

Drastic changes in the global climate system have caused an unprecedented scientific interest - foremost, in the energy sector.[1] Primary energy has to undergo a rapid transition towards 100% renewables.[2] This is a challenging task, not only for the electricity, heating and mobility sectors, but also for the chemical industry.[3] In addition to the energy to run the reactions, also the required raw materials used as substrates, catalyzers or for other purposes, need to be reconsidered. Circular economy from cradle-to-cradle, using **biobased feedstocks** up till the end-of-life use of products, is becoming an important benchmark for future processes. Obviously, such large-scale changes in production processes are an extremely complex task and bear high risks. Therefore, they need scaled-up demonstrations of environmentally as well as economically mature concepts to kick-start the process of change.

Electro-organic synthesis fits this need:[4,5] Once organic synthesis meets electrochemistry, a waste-free, safe, green and often more efficient alternative to conventional syntheses is facilitated. A few general remarks regarding electro-organic synthesis: Electricity-driven, a redox reaction occurs simultaneously at two conductive electrodes, which are separated by an electrolyte. I would like to refer the interested reader to an article by the Baran group that explains fundamental concepts in an appealing way.[6] Industrial relevant electro-organic applications include the Baizer process to adiponitrile (300.000 t/a, Monsanto / BASF / Ascend), fragrance “lily of the valley” (BASF) and maltol flavor (Otsuka).[7,8]

The focus of my project was to achieve a more sustainable synthesis of monomers for polyamides like nylon 6,6. More than **3 Mt of conventional adipic acid** are produced annually;[9] in particular, for the polycondensation to nylon 6,6. Here, the source is crude oil, and the conversion is empowered by nitric acid at elevated temperature. Both need to be replaced for climate as well as environmental reasons. Not only crude oil causes severe CO_2-emissions. Commonly, the oxidation of cyclohexanol and cyclohexanone (KA oil) with nitric acid produces 300 kg nitrous oxide (N_2O) per ton of adipic acid. A global annual production of more than 3 Mt leads to approximately 1 Mt of N_2O being produced – and, still too often, emitted.[10] It’s climate-polluting effect on a 100-year scale corresponds to 296 CO_2 equivalents;[11] accumulating to annually max. 300 Mt CO_2 equivalents, if exhausted.[12] Nowadays, catalytic N_2O cleavage to N_2 and O_2 at up to 1000 °C is often used, while 10%[9] of the global N_2O emissions[11] still result from the adipic acid synthesis. Noteworthy, the catalytic degradation of N_2O requires significant energy as well. This corresponds to 20–300 Mt of CO_2 equivalents, annually.[11,12] For comparison, Germany emitted about 750 Mt CO_2 equivalents in 2022.[13] Green electrification of this process would **fully avoid these climate-damaging process emissions**.[14] While temperatures of close to 100 °C are needed for the conventional process, the electrooxidation can be **performed at room temperature**.

Motivated by replacing the fossil-based feedstock by a regenerative, biobased one, this project shed light on monomeric derivatives carrying an alkyl substituent in their backbone. Lignin resembles the world’s largest source of aromatics, especially phenols, which can be hydrogenated to

4-alkylcyclohexanols.[15] Such outstanding potential of biogenic resourced prompted this research to start from 4-methyl-, 4-ethyl- and 4-propylcyclohexanols and -nones (Figure 1).

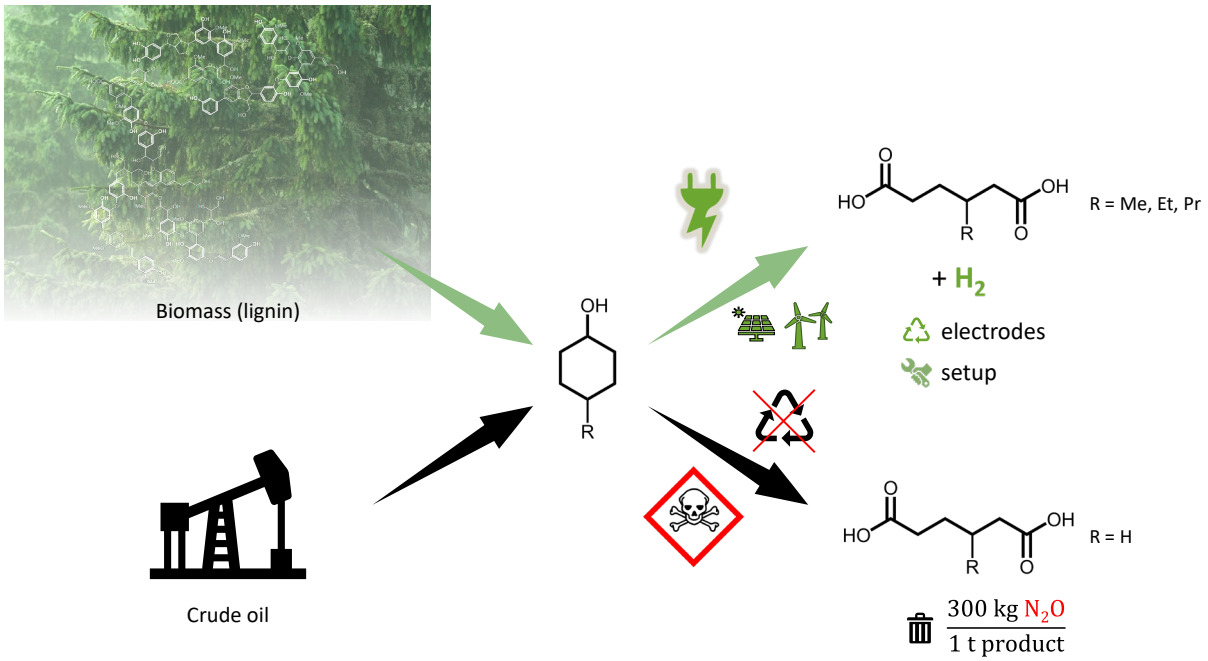

Figure 1: Schematic, summarizing the ideas of this project: The feedstock of cyclohexanol was to be changed from fossil- to biobased. The conversion to adipic acid (derivatives) shall no longer rely on toxic catalysts, nitric acid and the production of climate-polluting nitrous oxide, but on reusable setups, fueled by green electricity in a flexible consumption; contributing to stabilizing the grid in the future.

With these substrates in hand, the Waldvogel group showed good results on a mmol scale.[16] Key to this successful electrooxidation were an aqueous electrolyte and an activated nickel anode. Schäfer et al. published a review in the 80s, highlighting crucial parameters in the electrooxidation of alcohols and ketones in aqueous electrolytes.[17] With this information in hand, my project contained three puzzle parts: Firstly, the middle electrification step in the value chain from lignin to polyamides / polyesters was improved, compared to an earlier study in the Waldvogel group. Secondly, the challenges of **reusing the nickel foam anode** for the oxidation of monomeric species were solved.[19] In more detail, an activation and cleaning procedure was found, to almost fully diminish waste generation. Lastly, methods to **efficiently and inexpensively scale-up** this process for technical polycondensations of the isolated products, were a very important milestone.[14]

During my PhD, at first, a procedure to gain active nickel oxyhydroxides surface at foam anodes, could successfully be optimized, even reusing the foam several times. As a first scaled setup, electrooxidations of alcohols and ketones at these active nickel foams were performed in a large flow electrolyzer (geometrical anode surface area of 108 cm²) and semi-flow oxidations at an even 12-fold stacked electrode area in an electrochemical continuously stirred tank reactor (e-CSTR). Thereby, **mol-scale electro-conversion** of the 4-alkylcyclohexanone was performed in moderate yields.

Why are scaled electrochemical setups desirable?

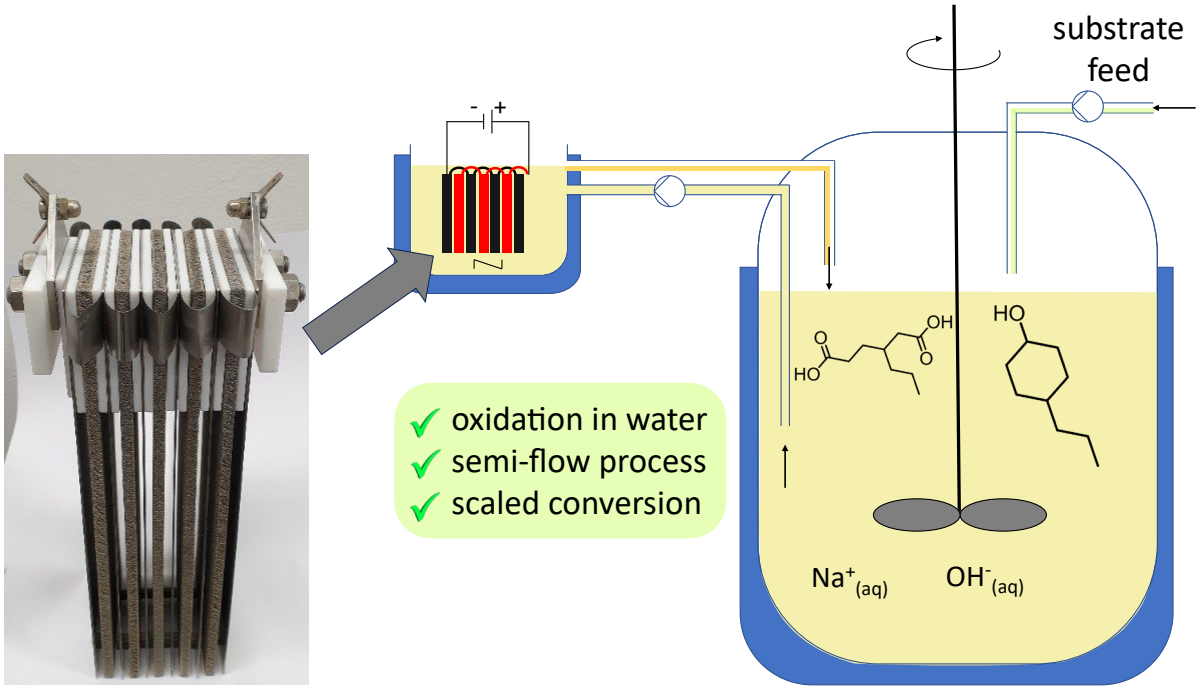

Figure 2: Left: Image of the reaction stack with nickel foam anodes and stainless-steel cathodes. The immersed total geometrical anode surface area is >1200 cm^2. Right: Schematic of the scaled electrochemical continuously stirred tank reactor (e-CSTR).

Electrooxidations to carboxylic acids are limited to low current densities due to possible Kolbe electrolysis for higher values (ca. >50 mA/cm^2).[20] Consequently, low space-time-yields are achieved using small cells. Scaling the cells was key to enhance the productivity and get insights into relevant parameters for technical scale production. We screened conditions utilizing a flow electrolyzer, reaching a quantitative NMR yield of 58% of 3-ethyladipic acid. Another approach was the design of an **easy-to-build stacked electrode setup**, combined with a **continuously stirred tank reactor** (Figure 2). Here, 3-propyladipic acid was synthesized with 48% qNMR yield. For both large-scale reactors, mixing was very important. Two mixing techniques were used, producing semi-stable emulsions. Moreover, these setups showed better yields for higher concentrations of substrate, diminishing the amount of aqueous electrolyte.

What's new about this activation procedure?

Earlier studies, which investigated the electrooxidation of alcohols and ketones at nickel oxy hydroxide anodes in aqueous electrolytes didn't aim to reuse the electrode or didn't present a reproducible cleaning and reactivation protocol for nickel foams.[17,21] Moreover, all recent publications relied on surface activations using frequently changing electrode polarity of two nickel electrodes, leading to only a single of them to be used for the reaction. Both produced waste, which is neither sustainable nor economically viable. We suggested a two-step activation process with short wetting of a single foam anode in 1 M caustic soda and subsequent direct current activation. Furthermore, SEM images revealed a highly porous fiber-like structure of the active surface layer. Those insights shed light on the **double to triple yield of the described oxidation at nickel oxyhydroxide anodes compared to oxidations at inactivated nickel** – even at multifold cleaned and reused foams (Figure 3). A patent application was filed together with an industrial collaborator.[22]

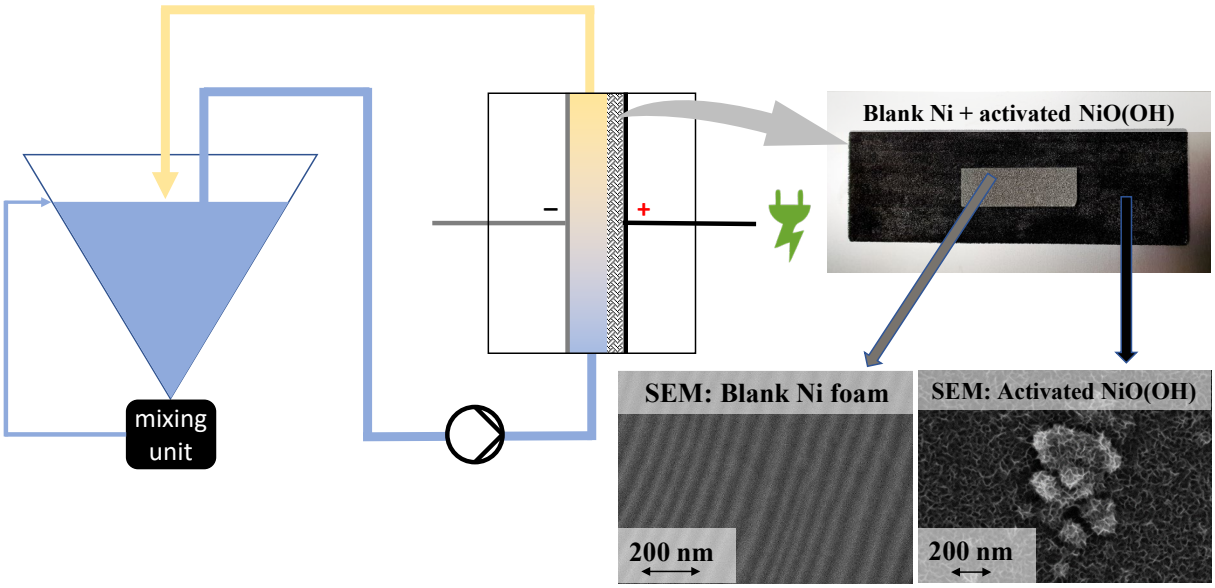

Figure 3: Left: Schematic of flow electrolyzer setup. Top right: Image of blank nickel foam located on top of larger activated nickel foam. Bottom right: Scanning electron microscope (SEM) images of blank nickel foam and its activated surface with close network of fibers.

How can these results contribute to grid stability?

Adding on the overarching goal of 100% renewable primary energy supply, a relevant question arises: How can the grid be stabilized, when fluctuating renewable current is the primary source (besides low amounts of biomass, hydro- or geothermal energy)? The answer has to be a variety of processes which are capable of converting fluctuating renewable electricity to chemical energy, simultaneously with the electricity production.

Taking advantage of a range of current densities, at very little yield losses, has a huge potential for renewable energy coupling. The **relevance of coupling electrified technical organic synthesis to the availability of renewable energy** is reflected in the fact of negative energy price of -0.60 €/kWh this summer.[23] Thus, envisioning a fully electrified chemical industry, coupled to renewable electricity, provides an outstanding support for future grid stability. This concept has the potential to advance a fast energy transition.

To summarize my results on a green electro-organic synthesis of 3-alkyladipic acids, I successfully tackled the following challenges: A large-scale electrochemically stirred tank reactor was designed and validated. An activation protocol was implemented to significantly reduce waste, e. g. by reusing and reactivating nickel foam anodes. Noteworthy, in all reactions, hydrogen was synthesized as by-product. No N_2O or other climate gases were released. Especially, the coupling of technical electro-organic synthesis to renewable energy contributes to solving the long-term challenges of grid stability in line with 100% renewable primary energy.

Acknowledgements

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References

(1) Seidler, J. et al. *MRS Energy Sustain.* **2020**, *7* (1), 42.
(2) Vollmer, D. et al. *Nat. Phys.* **2022**, *18* (12), 1383–1384.
(3) Biber, A. et al. *Electr. J.* **2022**, *35* (8), 107188.
(4) Biddinger, E. J. et al. *Electrochem. Soc. Interface* **2020**, *29* (3), 43–47.
(5) Bednarz, R. J.-R. et al. *GIT Lab. J.* **2021**. Online only. Bednarz, R. J.-R. et al. *GIT Labor-Fachz.*, **2021**. Online only.
(6) Kingston, C. et al. *Acc. Chem. Res.* **2020**, *53* (1), 72–83.
(7) Pletcher, D. et al. *Industrial Electrochemistry*; Bla*ckie Academic & Professional, London, New York, 2nd edn,* **1993**.
(8) Pollok, D. et al. *Chem. Sci.* **2020**, *11* (46), 12386–12400.
(9) Rios, J. et al. *Green Chem.* **2021**, *23* (9), 3172–3190.
(10) Mainhardt, H. et al. *IPCC Good Pract. Guid. Uncertain. Manag. Natl. Greenh. Gas Invent.* **2001**.
(11) Ehhalt, D. et al. *IPCC* **2018**, 244.
(12) Shimizu, A. et al. *Chemosphere - Glob. Change Sci.* **2000**, *2* (3–4), 425–434.
(13) Umweltbundesamt, Nationale Treibhausgas-Inventare 1990 bis 2021. *Indikator: Emissionen von Treibhausgasen*; **2023**.
(14) Bednarz, R. J.-R. et al. *ChemCatChem* **2023**, *15* (17), e202300606.
(15) Schutyser, W. et al. *ACS Sustain. Chem. Eng.* **2016**, *4* (10), 5336–5346.
(16) Rauen, A. L. et al. *Green Chem.* **2020**, *22*, 5956–5960.
(17) Schäfer, H.-J. *Top. Curr. Chem.* **1987**, *142*, 101–129.
(19) Bednarz, R. J.-R. et al. *Org. Process Res. Dev.* **2023**, acs.oprd.3c00146.
(20) Kolbe, H. *J. Für Prakt. Chem.* **1847**, *41* (1), 137–139.
(21) Jud, W. et al. *Org. Process Res. Dev.* **2022**, *26* (5), 1486–1495.
(22) Roemer, E.; Weinelt, F.; Bednarz, R. J.-R.; Waldvogel, S. R. Herstellung einer aktivierten Nickeloxidhydroxid-Schaum-Elektrode mit verbesserter Stabilität / Standzeit unter den Reaktionsbedingungen. 2023E00058DE.
(23) aWATTar Deutschland GmbH. Tarif Hourly, 22.07.2023, 2 pm. https://www.awattar.de/tariffs/hourly (accessed 05.10.2023).

Großskalige elektrochemische Produktion von Adipinsäure-Derivaten: Elektrifizierung technischer organischer Synthese

Large-scale electrochemical adipic acid derivative production: Electrifying technical organic synthesis

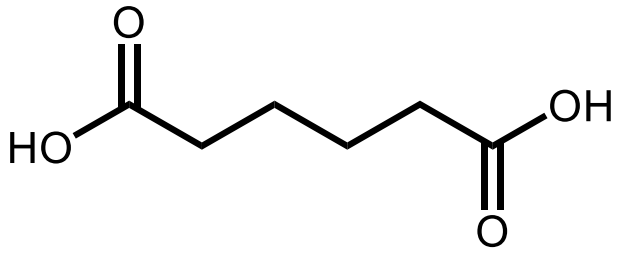
Roland Bednarz, Universität Mainz

Klimaschutz -
Katastrophe oder Chance?
SCIENTISTS FOR FUTURE
MAINZ / WIESBADEN

- 100% Erneuerbare Energien
- Netzstabilität
- Verstromte Synthese

X X X X

-X-Z-X-Z-X-Z-X-Z-Nylon



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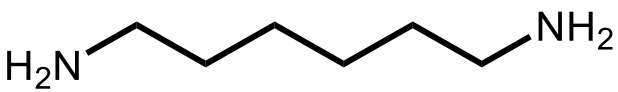

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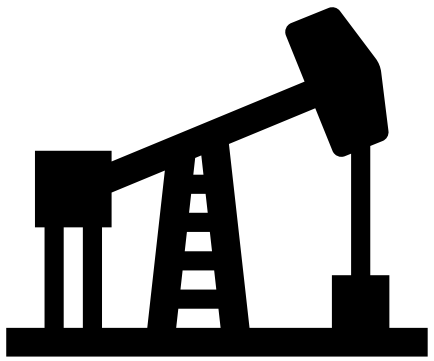

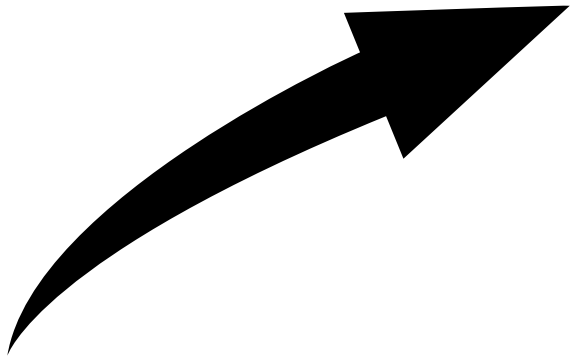

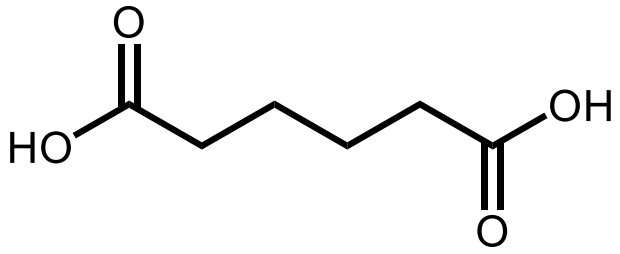

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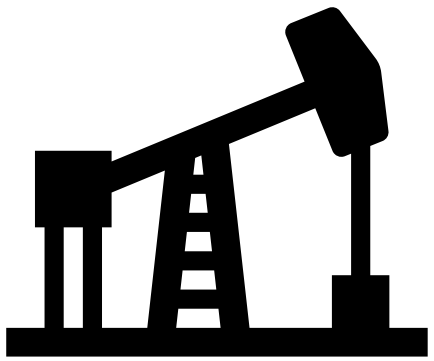

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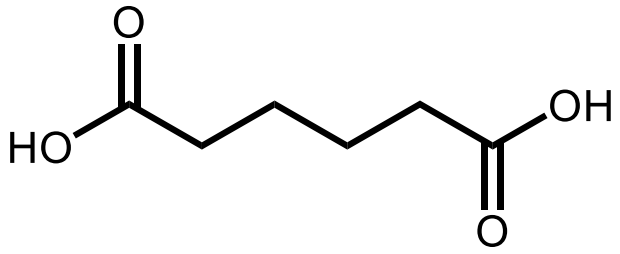

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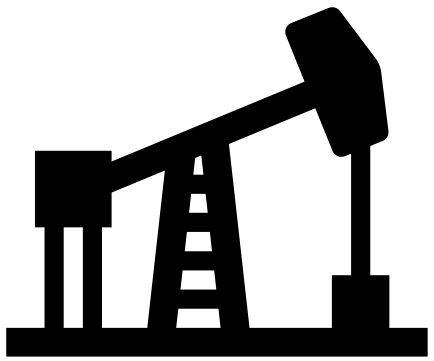

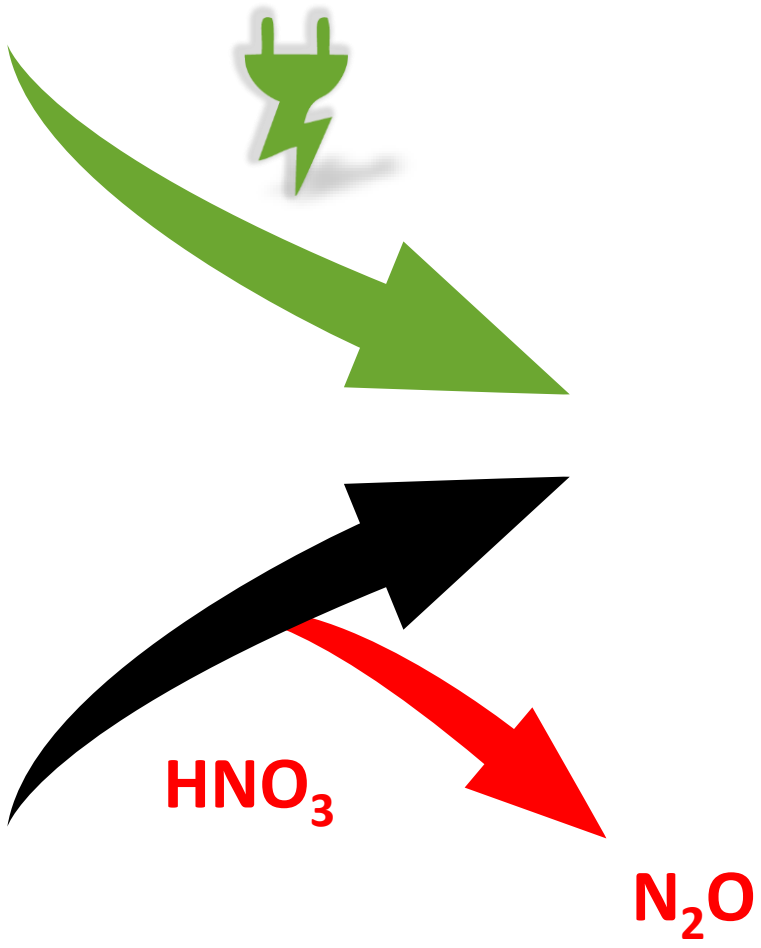

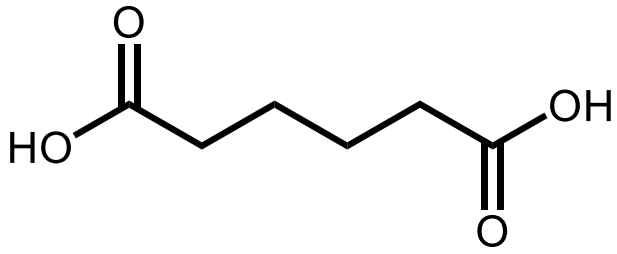

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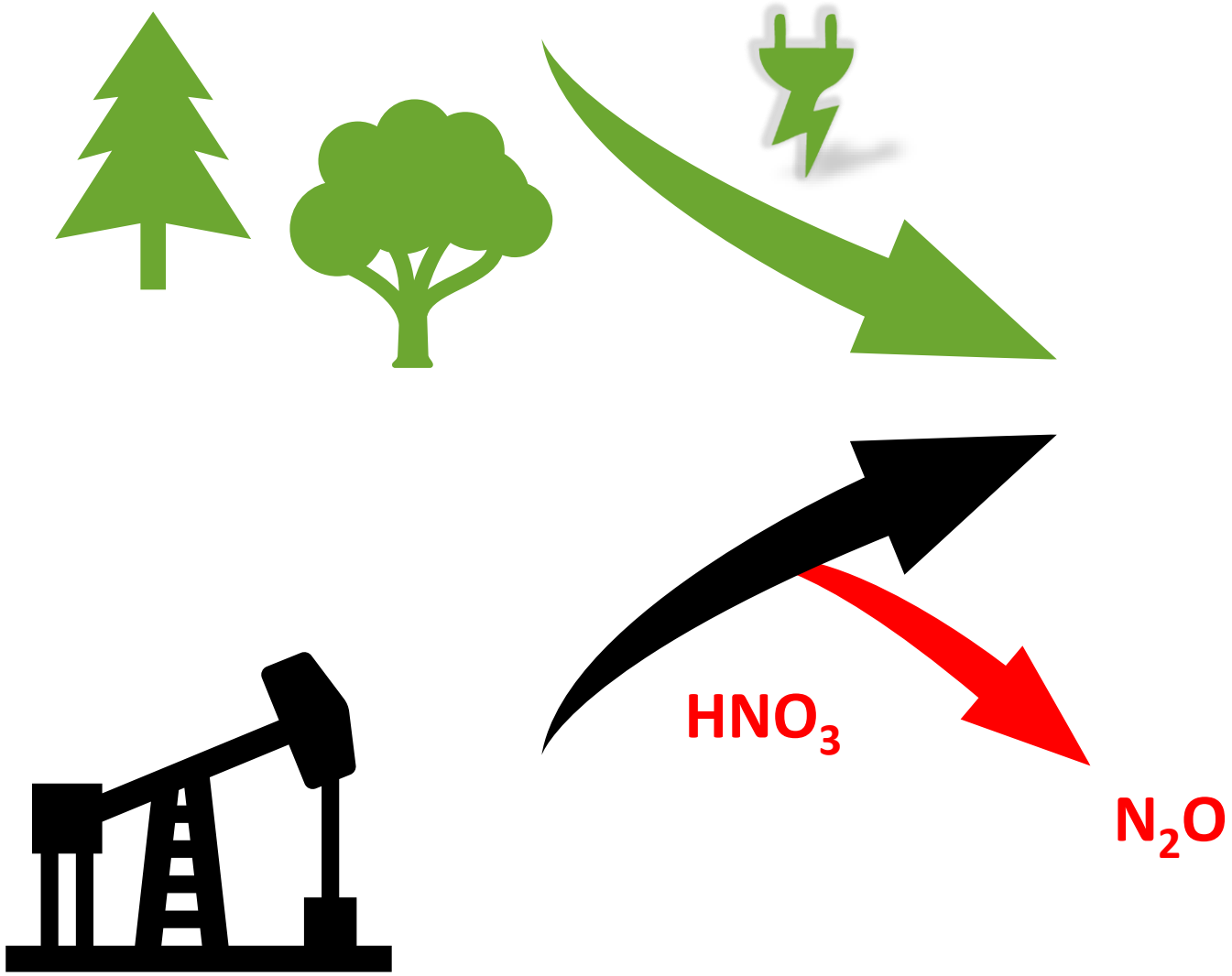

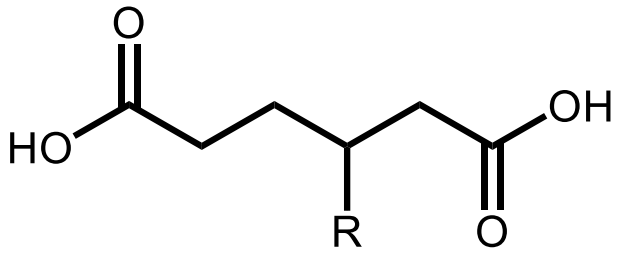

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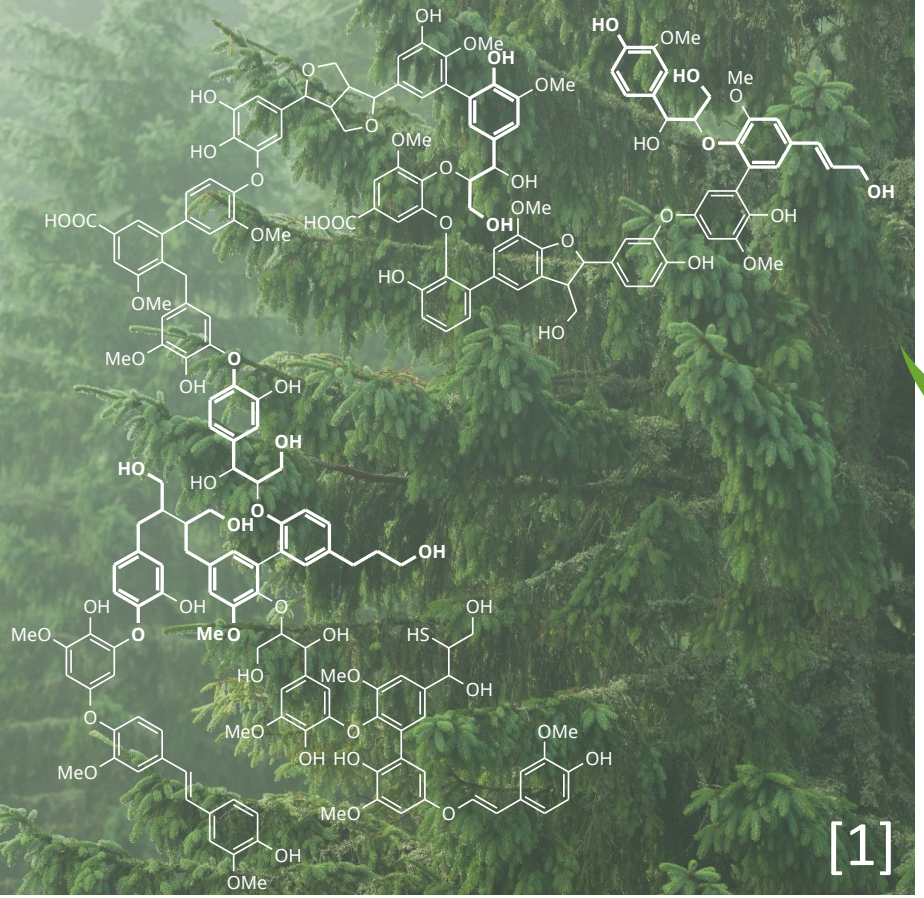

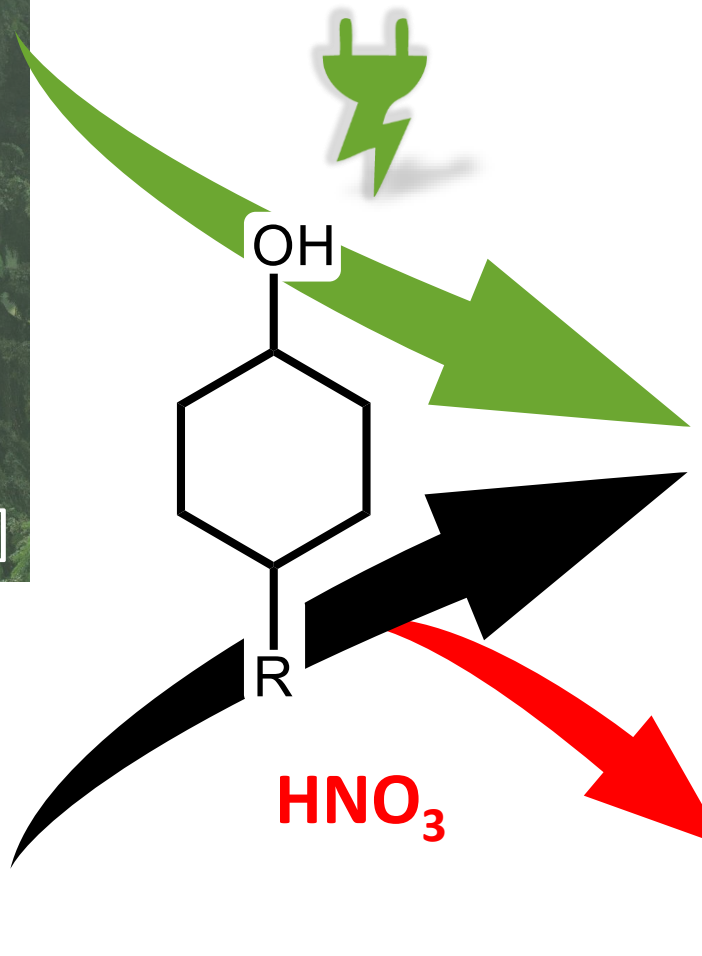

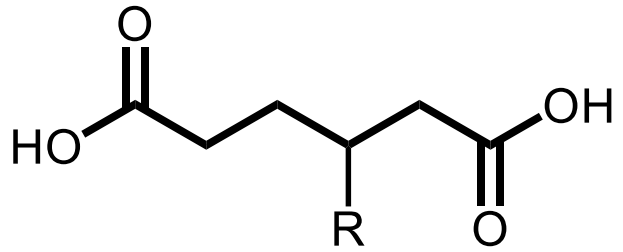

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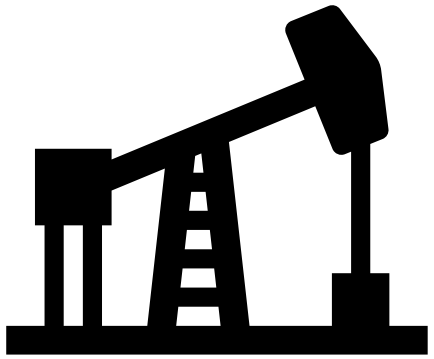

[1] Adapted from Zirbes, M. et al., *ACS Sustainable Chem. Eng.* **2020**, 8, 19, 7300–7307.

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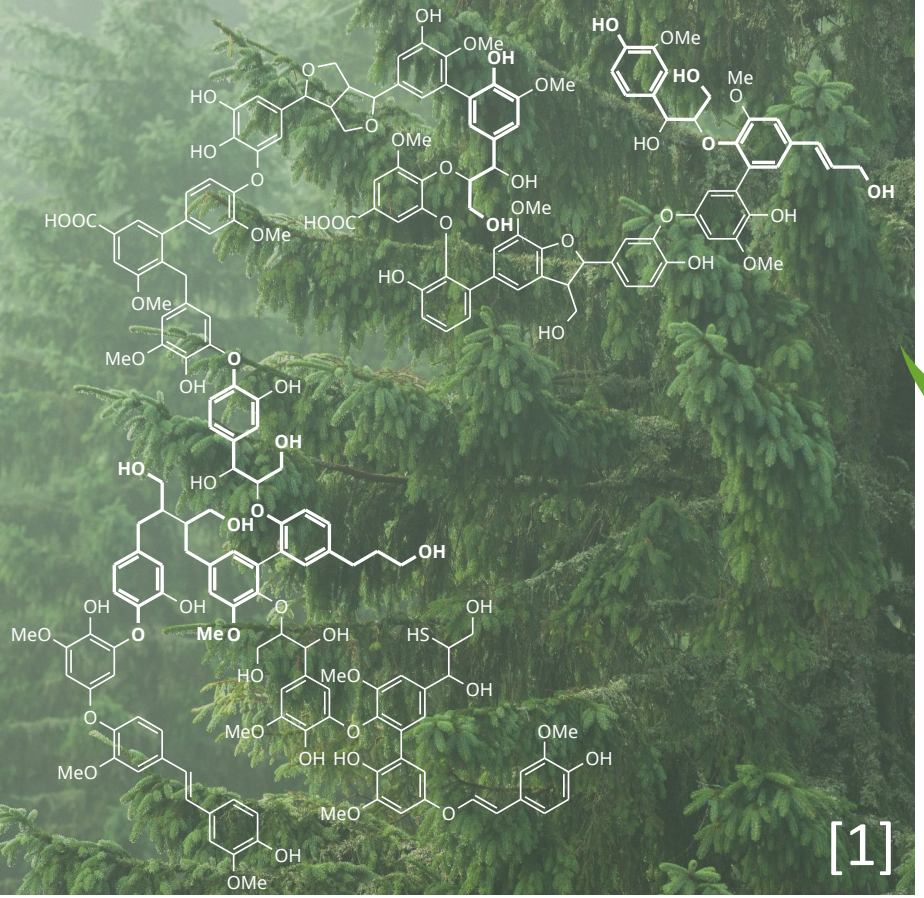

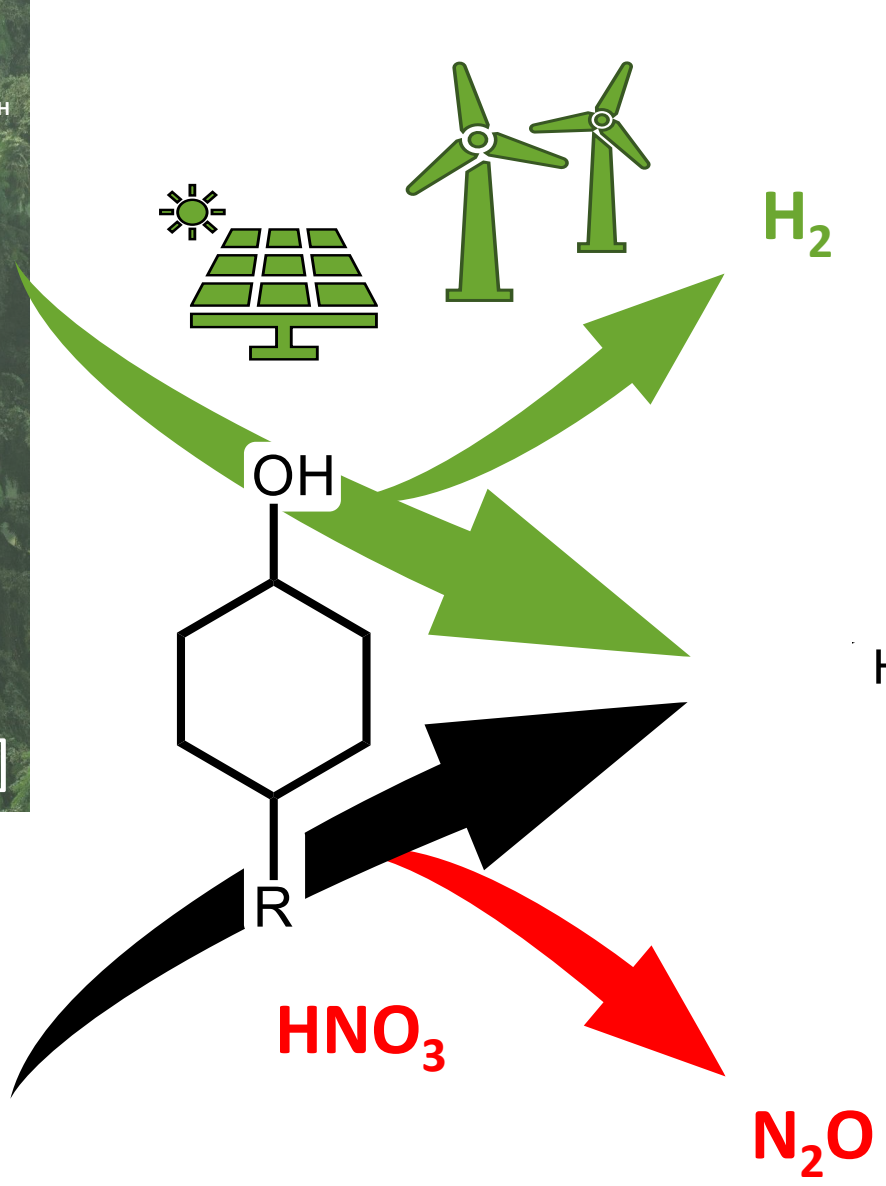

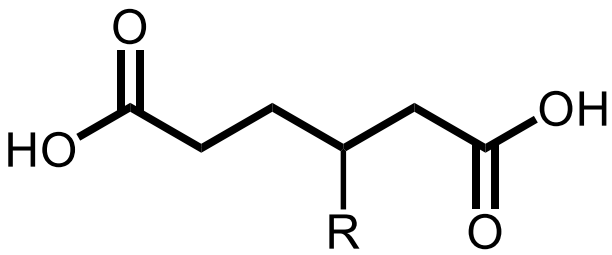

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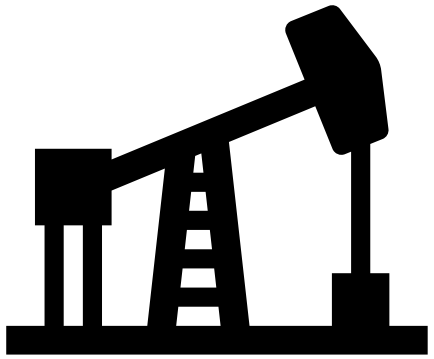

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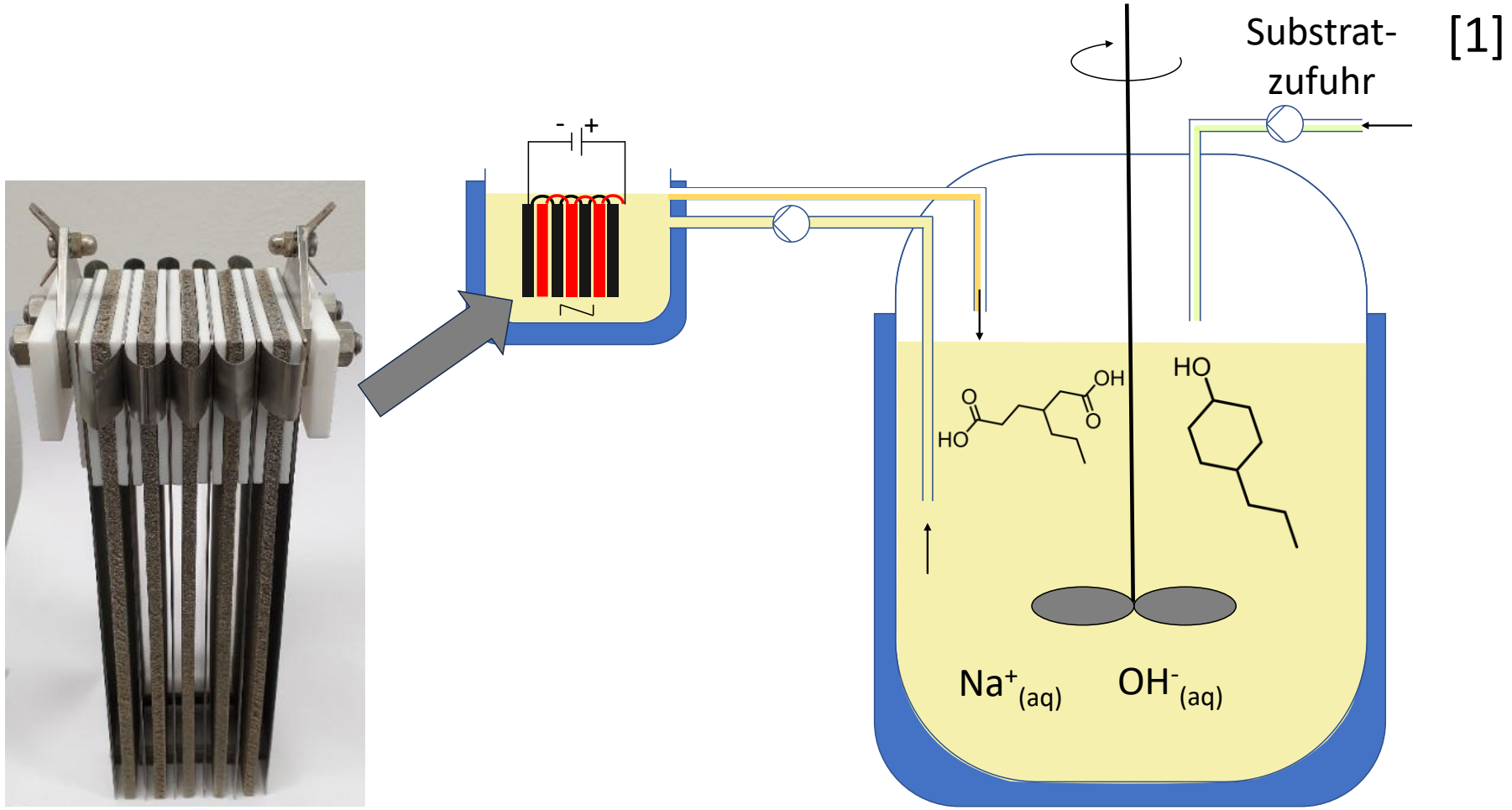
Stapelelektroden-Reaktor: Hochskalierung – modular und simpel



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[1] Angepasst von Bednarz, R. J.-R. et al., *ChemCatChem* **2023**, e202300606.

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1) **Preiswert**

2) **Klimafreundlich**

3) **Netzstabilisierend**

Vielen Dank für Ihre Aufmerksamkeit!

Forschungsgruppe Siegfried R. Waldvogel

Bednarz, R. J.-R. et al., *GIT Labor-Fachz.,* **2021**, online.
Bednarz, R. J.-R. et al., *GIT Laboratory Journal,* **2021**, online.
Kisukuri, C. M.[+], **Bednarz, R. J.-R.**[+] et al., *ChemSusChem* **2022**, 15, e2022008.
Vollmer, D., **Bednarz, R. J.-R.** et al., *Nature Physics* **2022**, 18, 1383–1384.
Bednarz, R. J.-R. et al., *Org. Process Res. Dev.* **2023**, https://doi.org/10.1021/acs.oprd.3c00146
Bednarz, R. J.-R. et al., *ChemCatChem* **2023**, e202300606.
Jiménez-Meneses, P.[+], **Bednarz, R. J.-R.**[+] et al., *ACS Sustain. Chem. Eng.* **2023**, eingereicht.

Drei Patente wurden eingereicht.