How to promote a more sustainable industry: Revalorization of lignin

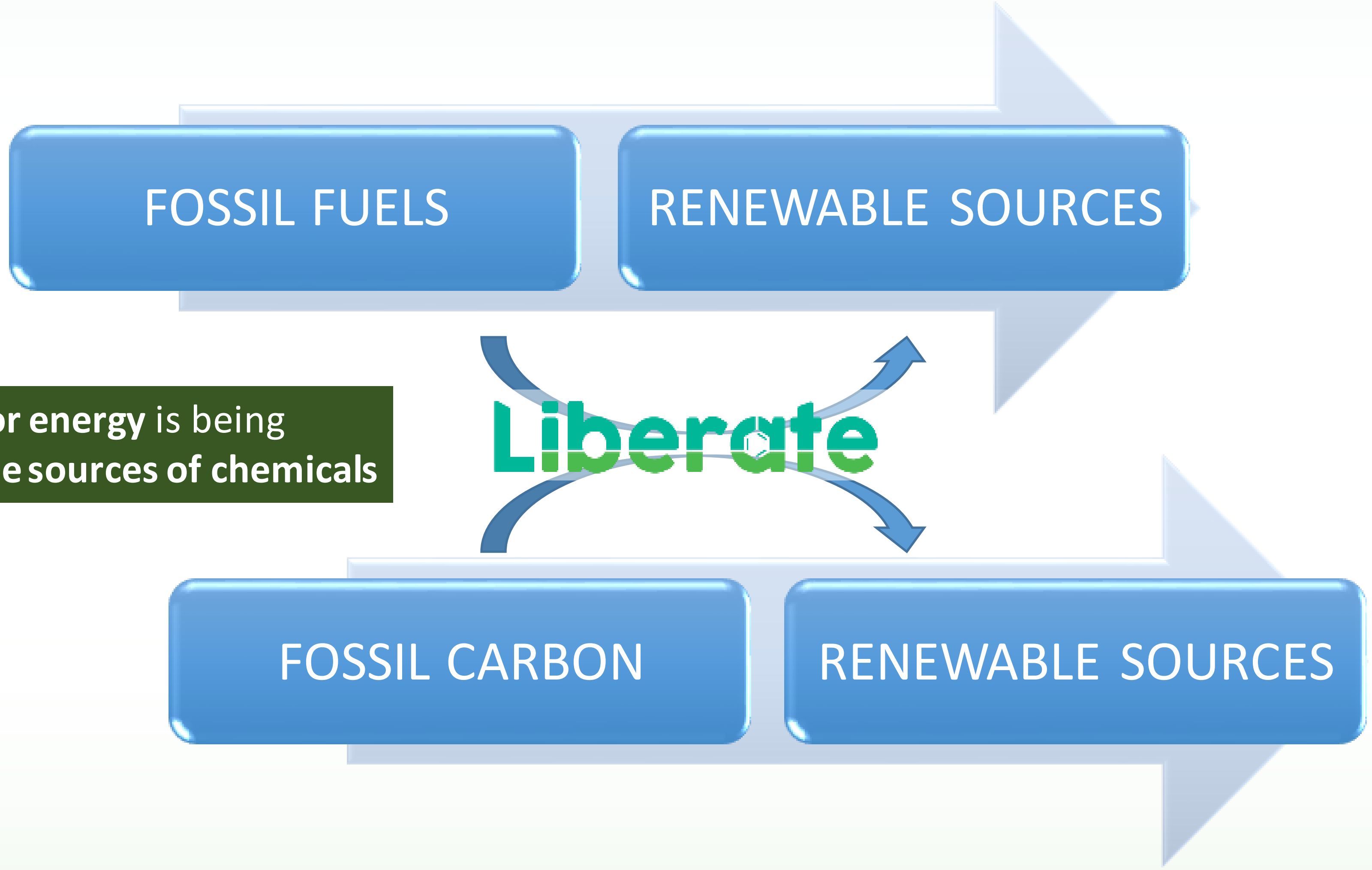
A presentation for undergraduate chemistry students and general public with interest in sustainable chemistry

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 820735.

SUSTAINABILITY: Chemicals vs Energy

ENERGY

CHEMICALS



The search of **renewables sources for energy** is being followed by the search for **renewable sources of chemicals**

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Liberate

Raw material

Plants, especially trees, consist of 3 components:

- **Cellulose** (main use: paper / pulping)
- **Hemi cellulose** (hydrolysed in pulping process)
- **Lignin** (main use: thermal energy for production in paper & pulping industry)

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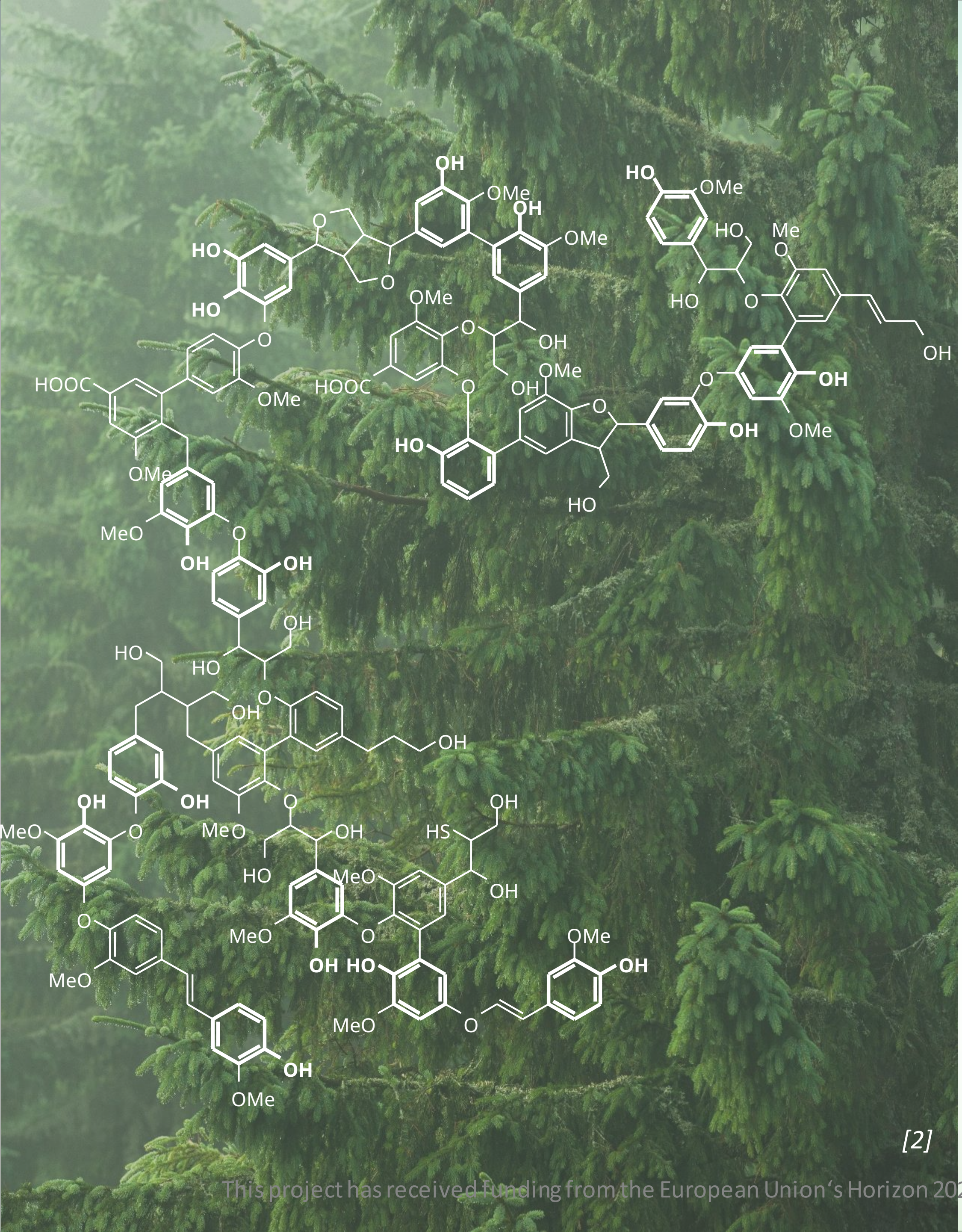

[2]

Liberate

Lignin

Lignin (main use: thermal energy production)

- Very complex structure of lignin
- Many aromatic structural motifs
- Contains phenolic structures[1]
- Renewable resource

➢ **World's largest aromatic feedstock – currently burned**

[1] Zirbes; Waldvogel, *Current Opinion in Green and Sustainable Chemistry* **2018**, *14*, 19–25.
[2] Zirbes et al., *ACS Sustainable Chem. Eng.* **2020**, *8, 19*, 7300–7307.

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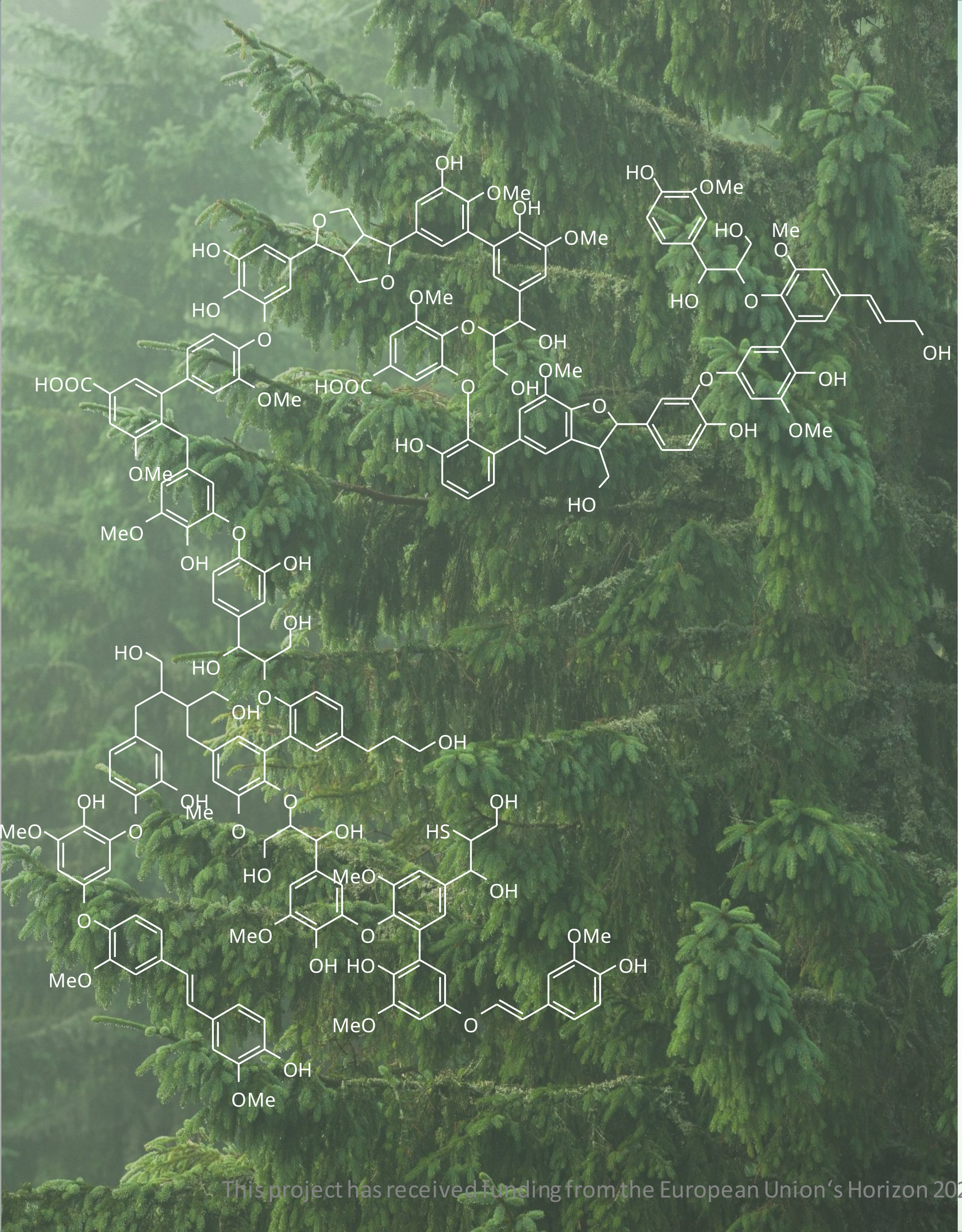
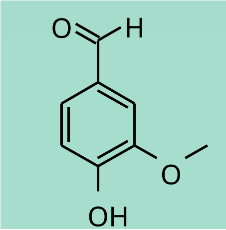


Lignin

3 ideas for better use of lignin:

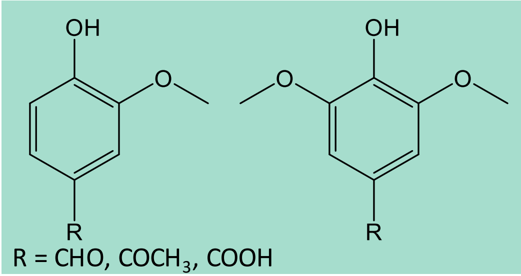
- ➢ Vanillin

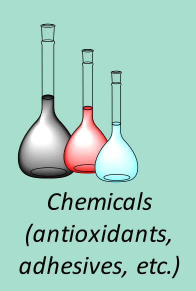


Vanillin

Vanilla pod [1]

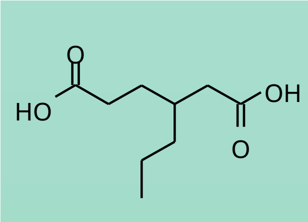
- ➢ Phenolic compounds





Guaiacyl and syringyl derivatives

- ➢ 3-Propyladipic acid



3-Propyadipic acid

Nylon [2]

[1] Foto: Ekrem Canli, [2] Foto: Michal Jarmoluk (PIXNIO)

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Why trying to use electrochemistry for by-product valorisation?

Advantages

- Lower number of experimental steps
- Electrons are cost-effective and amply available
- Green and safe character
- Good scalability
- Direct coupling to PV panels is possible

Disadvantages

- Complex mechanism involving frequently radicals
- Heterogeneous process that may lower productivity
- Specific equipment is needed
- Electrode corrosion and fouling is possible

➢ Advantages outweigh disadvantages, particularly regarding greenness

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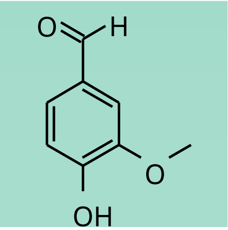
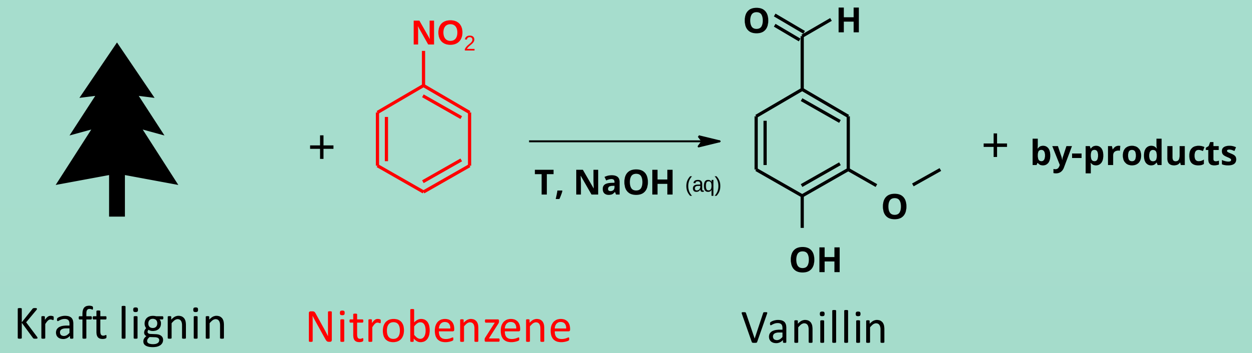
Lignin depolymerization to vanillin

- Vanillin commonly from crude oil (via benzene, 5–6 steps) → not sustainable
- First attempt to depolymerize lignin in 1939: via nitrobenzene oxidation (NBO) → not sustainable (toxic by-products)



Vanillin



[1] Freudenberg, K. "Lignin." *Fortschritte der Chemie Organischer Naturstoffe*. Springer, Vienna, **1939**. 1-26.

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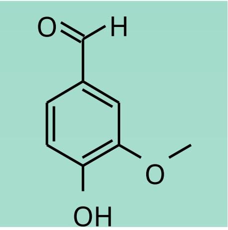
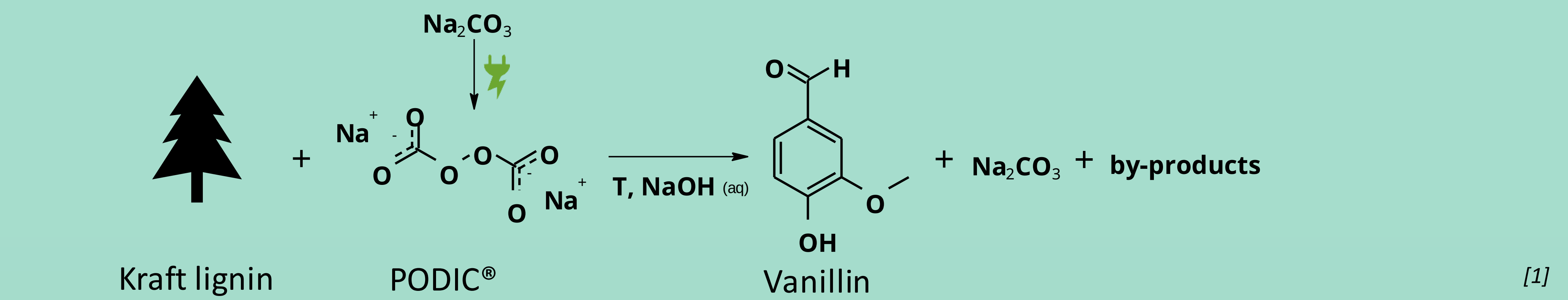
Lignin depolymerization to vanillin

- Vanillin commonly from crude oil (via benzene, 5–6 steps) → not sustainable
- First attempt to depolymerize lignin via NBO → not sustainable
- More climate friendly alternative:
  electrochemical oxidation via peroxodicarbonate (PODIC®)



Vanillin



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

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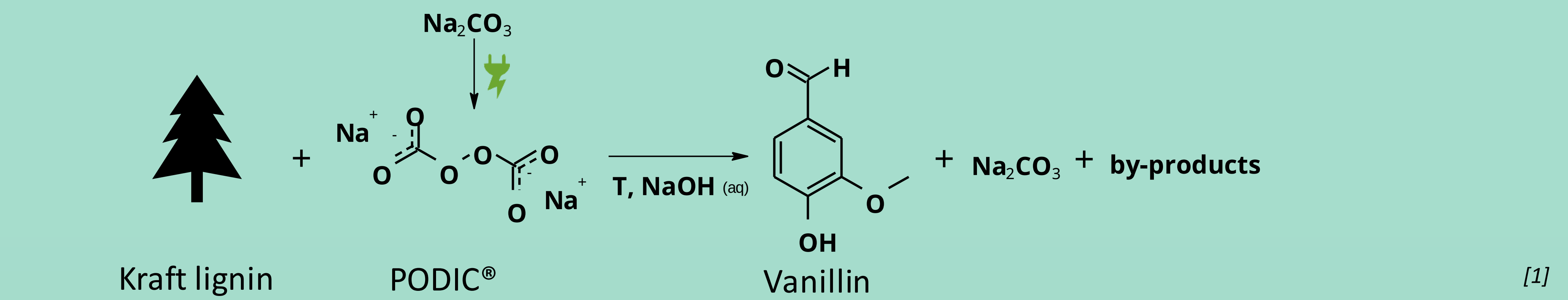
Lignin depolymerization to vanillin

- Vanillin commonly from crude oil
- First attempt to depolymerize lignin via NBO → yield: **7 wt. %**
- More climate friendly alternative:
  electrochemical oxidation via peroxodicarbonate (PODIC®) → yield: **6 wt. %**



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

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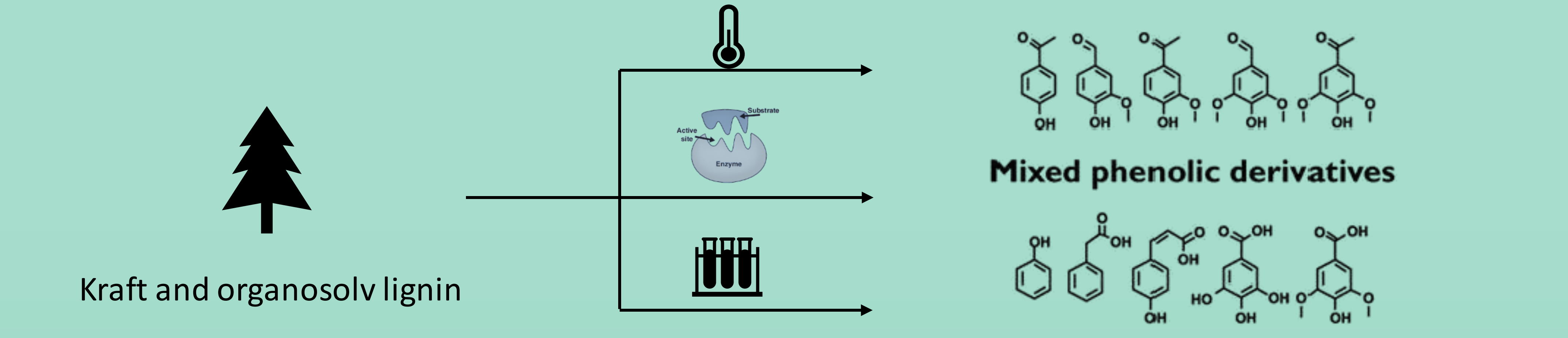
Lignin depolymerization to phenolic compounds

- Thermal depolymerization[1] → energetic demanding
- Biological depolymerization[1] → low-efficient
- Chemical depolymerization[1] → severe conditions

There is a need to improve the sustainability



[1] Zhou et al., *Energy Res*, **2022**, *9, 19*, 758744.

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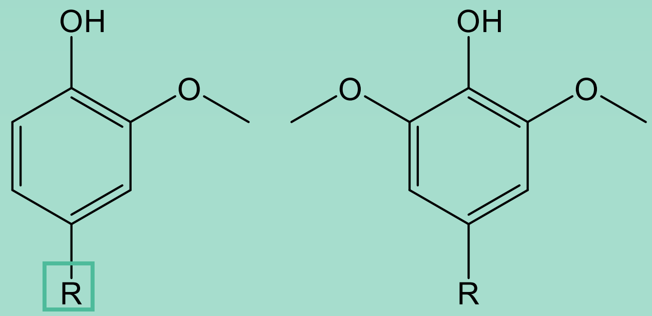
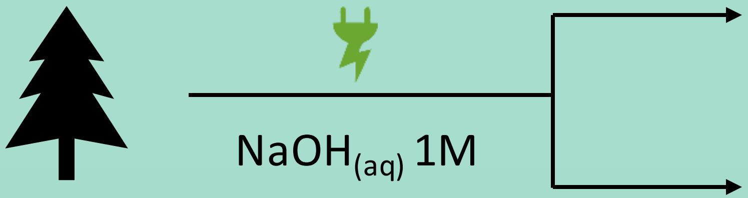
Lignin depolymerization to phenolic compounds



R = CHO, $COCH_3$, COOH

Syringyl and guaiacyl derivatives

- Direct electrochemical depolymerization
  - Mild conditions
  - Low energy costs
  - More sustainable process



Kraft and organosolv lignin

<u>Fraction of monomers and dimers with low polarity</u>

Syringyl and guaiacyl derivatives mainly

<u>Fraction of more polar higher molecular weight products</u>

Partially depolymerized and overoxidized

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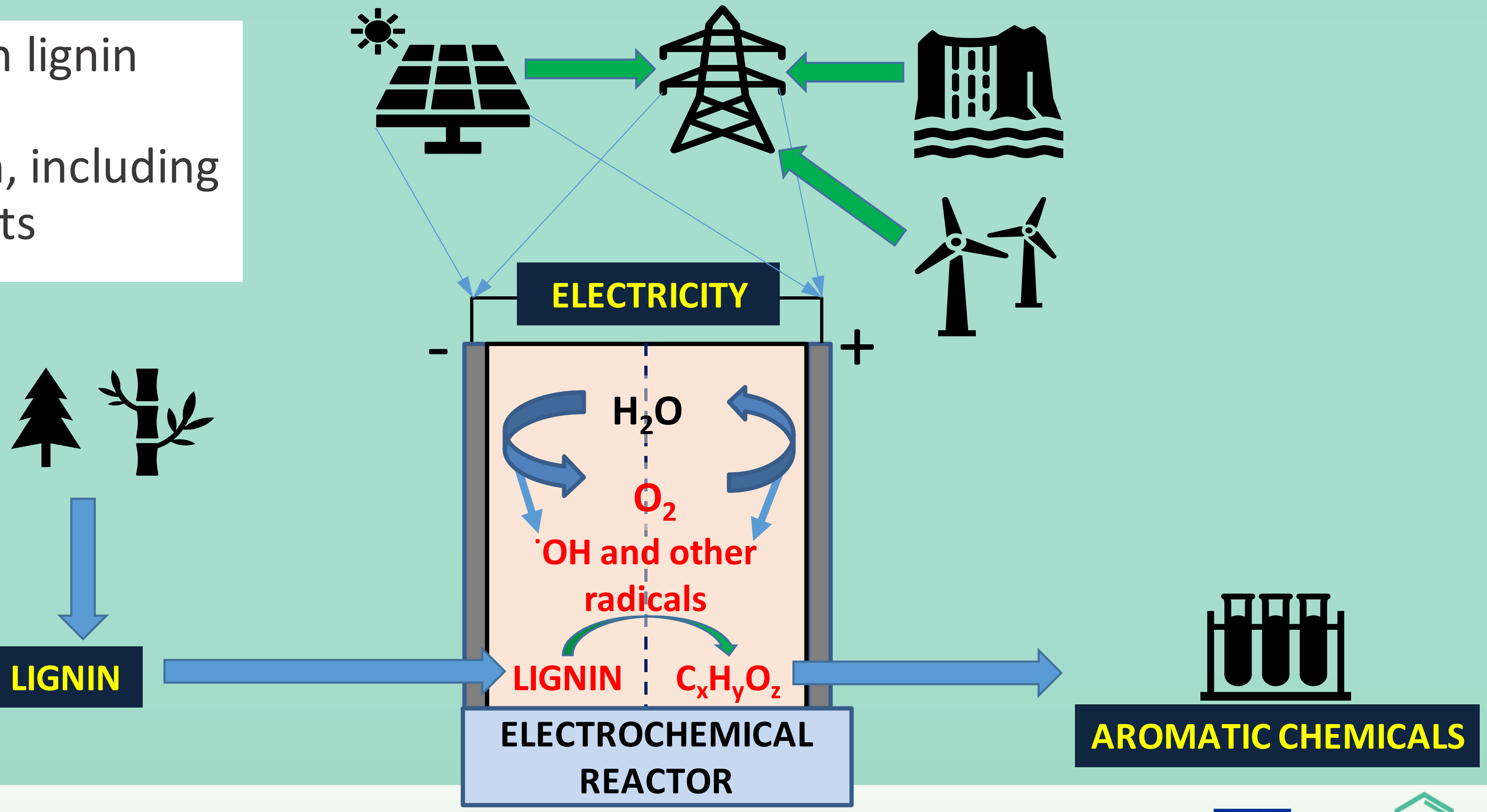
Lignin electrochemical depolymerization

Main processes in lignin electrochemical depolymerization, including inputs and outputs



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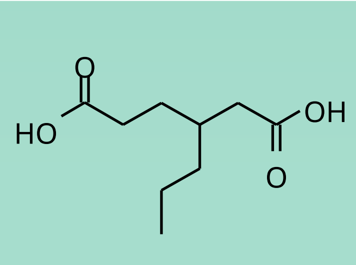
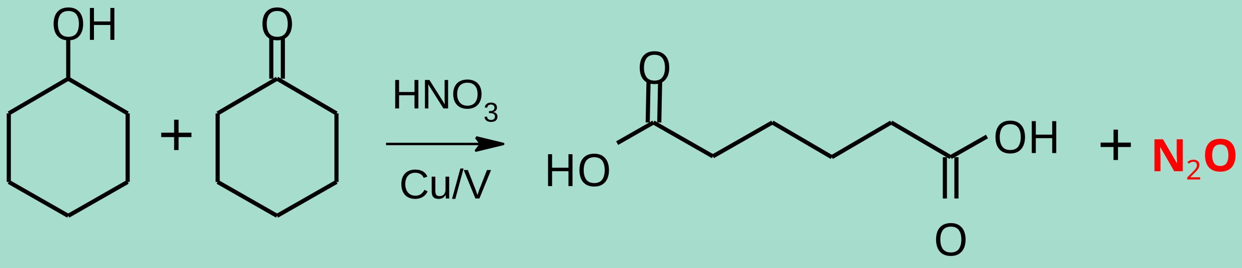
Lignin derived adipic acid

- Adipic acid is monomer for polyamide (nylon) polycondensation
- Conventional adipic acid synthesis:
  from cyclohexanol & cyclohexanone (KA oil)
  - 300 kg nitrous oxide (N_2O) are produced for 1 t of adipic acid[2]
  - Greenhouse gas potential of N_2O is 298 times higher than for CO_2[3] → not sustainable



3-Propyadipic acid

Nylon [1]



[1] Foto: Michal Jarmoluk (PIXNIO)
[2] Zhihong, W. et al., *IPCC Good Practice Guidance and Uncertainty Management in National Greenhouse Gas Inventories*, **2018**, 131.
[3] G. Myhre et al., Anthropogenic and Natural Radiative Forcing. IPCC AR5, table 8.7, **2013**.

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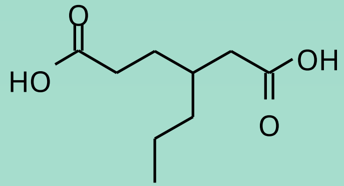
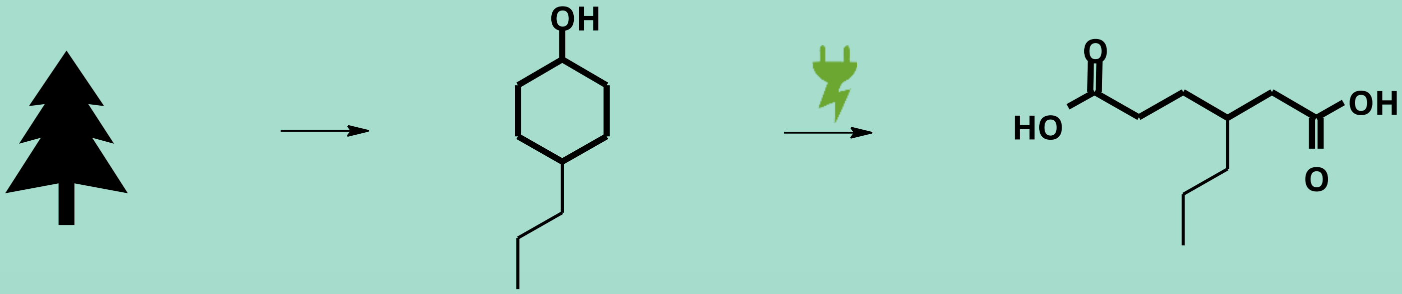
Lignin derived adipic acid



3-Propyadipic acid

- KA oil can be substituted by 4-propylcyclohexanol (4PCHol)
- 4-Propylcyclohexanol (4PCHol) via hydrogenation of lignin (yield: 85%)[1]
- From 4PCHol the side chain remains in 3-propyladipic acid (3PAA)



[1] W. Schutyser et al., *ACS Sustainable Chem. Eng.*, **2016**, *4*, 5336–5346.

[2] Foto: Michal Jarmoluk (PIXNIO)

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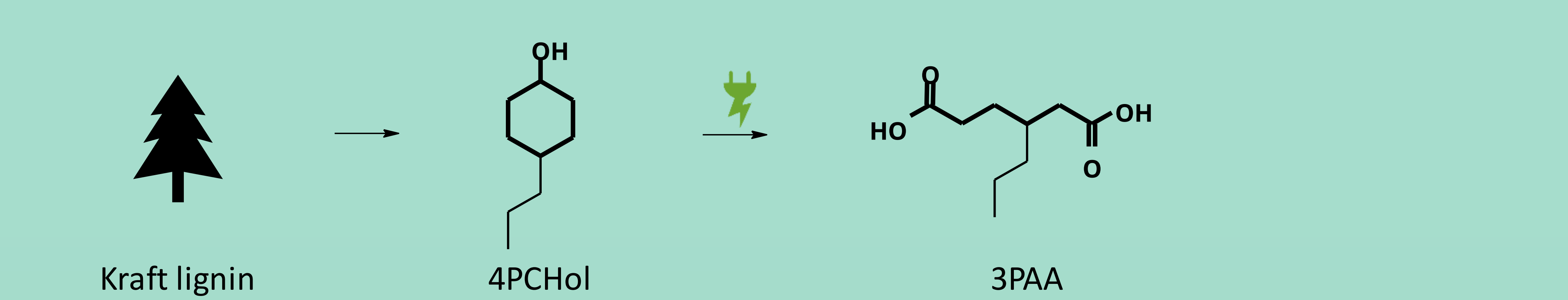
Lignin derived adipic acid

- Conventional adipic acid synthesis → yield: ≤ **96%**[1]
- Electrochemical 3-propyladipic acid synthesis → yield: **48%**[2]



[1] Castellan, A. et al., *Catalysis Today*, **1991**, *9*, 237–254.
[2] Bednarz, R. et al., Liberate results.

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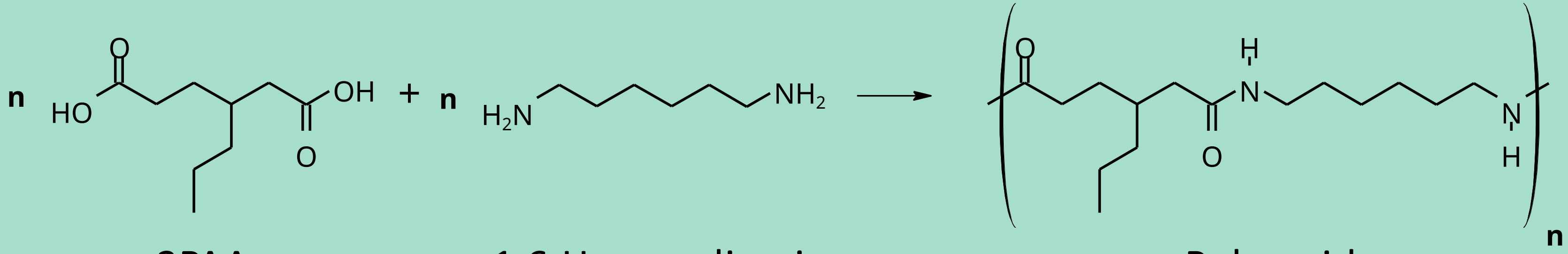
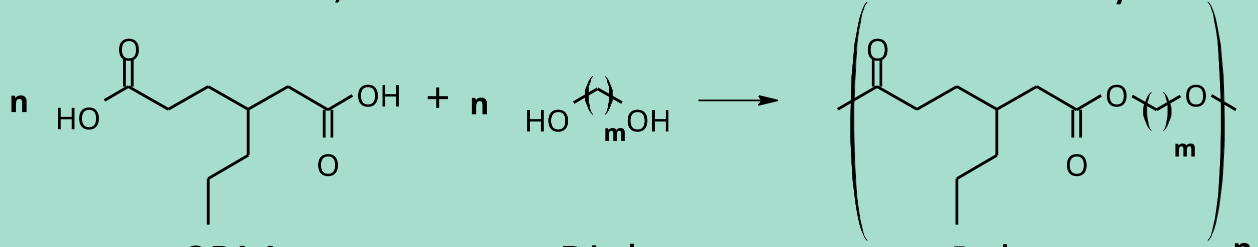
Lignin derived polymers

- Polymers from electrochemically generated 3-propyladipic acid





Nylon [1]

Fabric [2]

➢ Polymers with monomers from regenerative sources

[1] Foto: Michal Jarmoluk (PIXNIO)
[2] Foto: Bearas (Wikimedia Commons)

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Liberate

- EU project with partners from academia, industry & service sector
- Website: https://www.liberate-project.eu/

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