University of Stuttgart
Institute of Biochemical Engineering (IBVT)

HIMMELFAHRTSTAGUNG on Bioprocess Engineering 2021

Bioplastic production from lignin

Development of a novel downstream processing for biotechnologically produced PET replacement

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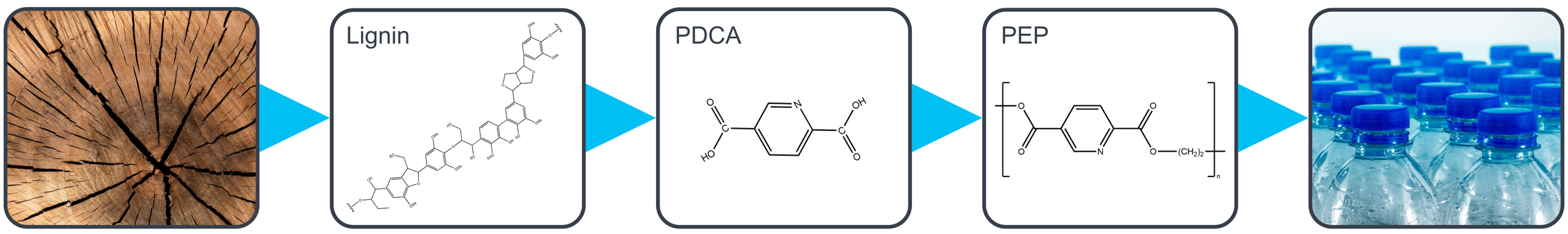
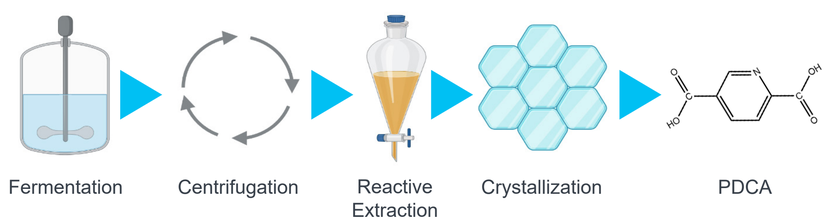


Introduction

The global demand for plastics is insatiable. Despite growing environmental awareness, bioplastics currently account for only 1 % of produced plastics. The cheap production of oil-based plastics often hampers their replacement. This makes low production costs essential for the success of a bioplastic. Lignin is a waste product of paper manufacturing and available in large quantities. Using lignin as a resource for plastics production is a cheap and sustainable alternative to oil. Engineered strains of *Rhodococcus jostii* and *Pseudomonas putida* degrade lignin and produce pyridinedicarboxylic acids (PDCAs), which can substitute terephthalic acid in PET. To keep production costs low, a highly efficient downstream processing is required.

Downstream

- PDCA is an extracellular product from lignin degradation by engineered strains[1]
- Biomass removal via centrifugation
- Reactive extraction is a common method for purification of carboxylic acids[2]
- Crystallization after reactive extraction yields solid PDCA



Reactive Extraction

- Complex formation of extractant and product[3]
- Extractants: trioctylamine (TOA) and Aliquat 336
- pH optimum: pH 2 TOA, pH 7 Aliquat 336
- Product concentrating by reduced volumes of acceptor phase

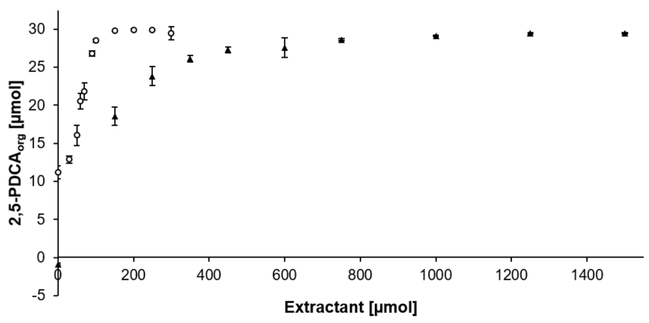
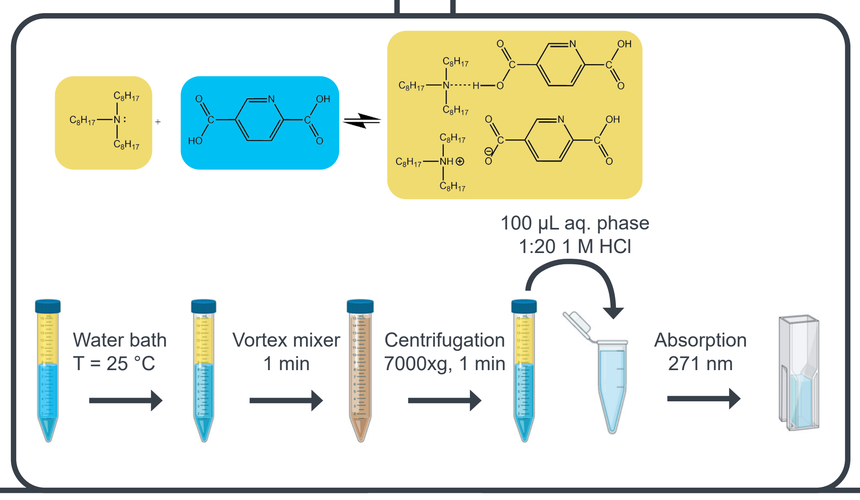


Figure 1: Molar amount of extractant for reactive extraction of 30 µmol 2,5-PDCA at pH 2 (TOA) and pH 7 (Aliquat 336). The amount of 2,5-PDCA in organic phase was calculated by mass balance from the amount of aqueous phase PDCA.

Re-Extraction

- Product recovery from organic phase after reactive extraction
- pH swing can disrupt the product-extractant complex
- Product concentrating by reduced volumes of acceptor phase



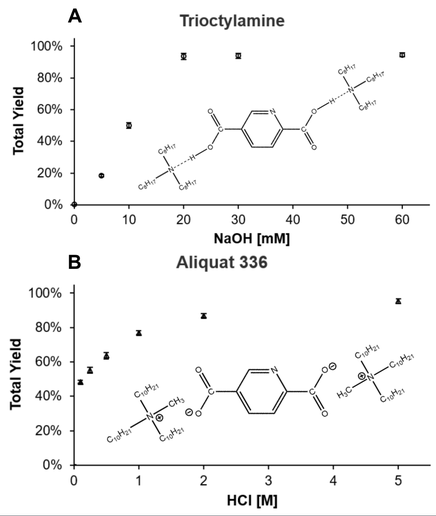


Figure 2: Re-extraction of 2,5-PDCA after reactive extraction with trioctylamine [A] or Aliquat 336 [B]. The yield was calculated by the amount of PDCA after re-extraction and the initial amount.

Crystallization

- After reactive extraction: PDCA is dissolved in water containing small amounts of ions
- Cooling crystallization (T < 30 °C) yields PDCA crystals, which can be purified from water
- pH plays an important role due to charge repulsion of negatively charged PDCA molecules
- Cooler temperatures accelerate crystallization
- Up to ~80 % crystallized PDCA after 14 days

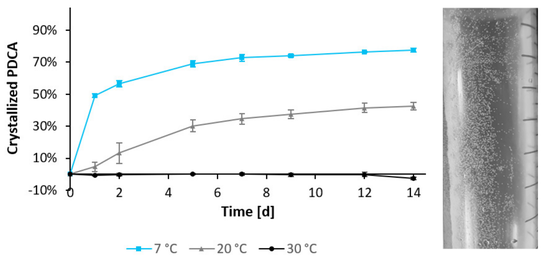


Figure 3: Crystallization of 2,5-PDCA (6 mM, pH 2) at 7, 20 and 30 °C. The amount of crystallized PDCA was calculated from the concentration of PDCA compared to the initial concentration.

Outlook

- Upscaling of reactive extraction in centrifugal extractor
- Multistage extraction from fermentation broth
- Optimization of cooling crystallization

Summary

- PDCA can replace terephthalic acid in PET plastics
- Reactive extraction removes complete PDCA from aqueous solution TOA and Aliquat 336 in 1-octanol
- Product recovery from organic phase through pH-swing
- PDCA is crystallized by cooling crystallization

[1] Mycroft, Zoe; Gomis, Maria; Mines, Paul; Law, Paul; Bugg, Timothy D. H. (2015): Biocatalytic conversion of lignin to aromatic dicarboxylic acids in Rhodococcus jostii RHA1 by re-routing aromatic degradation pathways. In Green Chem. 17 (11), pp. 4974–4979. DOI: 10.1039/C5GC01347J.
[2] Antony, F.M., Wasewar, K. Reactive extraction: a promising approach to separate protocatechuic acid. Environ Sci Pollut Res 27, 27345–27357 (2020). https://doi.org/10.1007/s11356-019- 06094-x
[3] Kumari, Anju; Gaur, Ankur; Wasewar, Kailas L.; Kumar, Sushil (2018): Modeling and Optimization of Reactive Extraction of Isonicotinic Acid Using Tri- n -octylamine in Biocompatible Diluents Mixture: Response Surface Methodology and Regeneration of Solvents. In Ind. Eng. Chem. Res. 57 (37), pp. 12485–12493. DOI: 10.1021/acs.iecr.8b01533

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