PhD project proposals to the Einstein Center of Catalysis (EC^2) <u>for a PhD start in Oct. 2023</u>

Abstract:

Title of Project: Reductive catalytic fractionation of waste cellulosic-biomass to functional chemicals and subsequently to green polymers

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Intensive utilization of fossil resources for the production of energy, fuels, and chemicals led to the current environmental challenges. Therefore, a shift to renewable carbon resources is greatly needed. This transition will decouple chemical production from fossil resources and the resulting greenhouse emissions. To establish competitive biorefinery processes, efficient utilization of the whole lignocellulosic biomass (cellulosic and lignin fractions) waste streams is required. In this regard, a significant potential of the widely available side/waste stream of cellulosic biomass (forming ~80% of lignocellulosic biomass) in the chemical industry is underexploited. Therefore, this project aims to use non-edible side/waster carbohydrate-rich streams for the production of functional chemicals and subsequentially biobased materials that are biodegradable or recyclable. Primary, the cellulosic biomass, will be treated via reductive catalytic fractionation (RCF) in continuous-flow reactors to functional building blocks, e.g., carboxylic acids, sugar alcohols, and diols, using supported metal catalysts. These synthesized functional chemicals will be transformed into biodegradable polymers using the biocatalysis concept.

Extended description version of the project:

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1. Overall goal of the project

This project is intended to design an efficient process for converting waste cellulosic-biomass fractions to fine chemicals that subsequently can be converted to biopolymers. This project will be devoted to developing a flow-through process using reductive catalytic fractionation (RCF) of cellulosic-biomass-derived compounds, as well as real cellulosic biomass waste streams to functional chemicals (**WP1**), *cf.* **Figure 1**. For this purpose, suitable catalysts will be identified based on intensive literature research, synthesized, and thoroughly characterized via classical and advanced techniques to understand the structure-performance relationship in this process (**WP2**). Detailed product analysis (GC-MS, GC-FID, HPLC, and 1D and 2D NMR) for deep understanding of the complex RCF reaction mechanism (**WP3+4**), kinetic investigations of the established reductive catalytic fractionation of cellulosic biomass (**WP5**).
The functional chemicals that are synthesized via the RCF step will be subjected to polymerization steps using biocatalysts, as well as hybrid catalysts, i.e., immobilized different biocatalysts on inorganic support materials or porous carbon (**WP6+7**). The possible biopolymers that can be synthesized via the biocatalytic route are shown in **Figure 2**. The synthesized biopolymer will be thoroughly characterized to understand its properties and potential application platform (**WP8**).

2. State of the art

Biorefinery is the process of direct and efficient chemical or biorefining of whole fraction biomass to a wide range of products. Last two decades, biorefinery has been performed in a lab batch system, which is a finite internal volume with a longer contact time between reactant and catalyst that leads to catalyst deactivation, as well as batch process requires high operation costs.[1] Seeking for more sustainable, efficient, and economically competitive green processes, the use of heterogeneous catalysts in continuous-flow systems presents advantages over batch counterparts, such as minimization of downstream costs, higher thermal efficiency, and less hazardous nature.[2] Moreover, flow regimes allow novel chemical transformations not achievable in a batch system. Additionally, most of these processes focus on the valorization of lignin fraction to monoaromatics via the lignin-first approach.[3] The lignin-first approach uses a reaction temperature of 200-230°C to efficiently extract and fragment the lignin, but this leads to hydrothermal caramelization of highly valuable hemicellulosic fraction (40-50% of waste biomass) to humins, which has low value and cannot be used and caused technical problems. All these will render the utilization of all studies beyond labscale understanding. Rarely fragmentation and upgrading of real cellulosic biomass waste stream were investigated.[4] Alternatively, the valorization of the single sugars-derived compound, *e.g.*, glucose, xylose, sorbitol, 1,2,6-hexantriols, via hydrogenation, hydrodeoxygenation, and oxidation are investigated mostly in a batch system.[2] Furthermore, most of the used catalysts are not sustainable for large-scale operations, *i.e.*, noble metal-based catalysts. Finally, most of the available studies for the synthesis of functional chemicals from cellulosic fractions do not show the utilization of the synthesized compounds in different applications.

New technologies for the conversion of biomass into high-value chemicals, including polymers and plastics, are a must and a challenge. The development of green processes in the last decade involved a continuous increase in the interest toward the synthesis of polymers using in vitro biocatalysis. Among the remarkable diversity of new bio-based polymeric products meeting the criteria of sustainability, biocompatibility, and eco-friendliness, a wide range of polyesters with shorter chain lengths were obtained and characterized, targeting biomedical, and cosmetic applications.[4]

The utilization of biocatalysts in industrial processes is gaining increased recognition due to their potential for eco-friendliness and cost-effectiveness.[4] Biocatalytic processes align with sustainability objectives by promoting safer and more environmentally friendly chemistry while considering economic competitiveness and societal concerns. Additionally, they offer the opportunity to design a new generation of polymers.[5] Consequently, the application of lipases as catalysts for polymerization reactions has garnered attention over the past two decades, as evident from the growing number of publications and the subject being extensively reviewed by experts such as Kobayashi and colleagues.[6] Biocatalytic strategies utilizing lipases have emerged as promising alternatives to conventional polymerization methods, overcoming challenges associated with metal catalyst traces, toxicity, and high temperatures.[5-6] Furthermore, lipases enable the functionalization of polymers like polylactic acid or polycaprolactone, enhancing their drug delivery properties in systems requiring greater hydrophilicity.[4]

[1] Brandi et al., Green Chem. 2020, 22, 2755.

[2] Brandi et al., ACS Sustainable Chem. Eng. 2021, 2, 927.

[3] Pandalone et al., RSC Sustainability 2023, DOI: 10.1039/d2su00076h.

[4] Tripathi et al., Curr. Sustain. Renew. Energy Rep. 2020, 7, 66.

[5] Todea et al., Processes 2021, 9, 646.

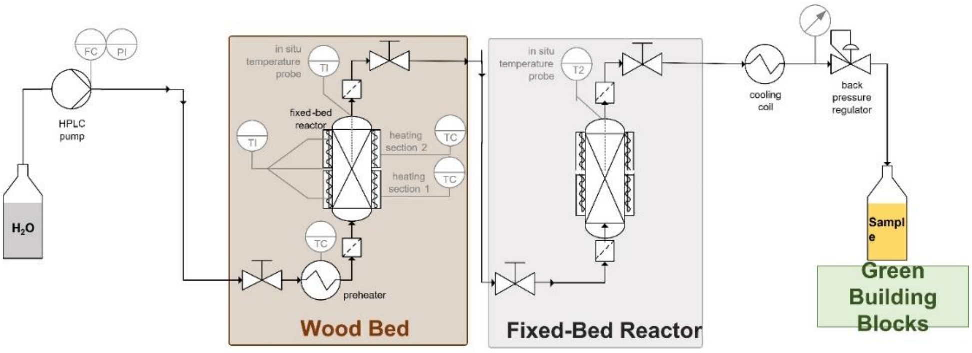
[6] Kobayashi et al., Chem. Rev. 2001, 101, 3793.

3. Specific aims and how they may be reached:

1. Objectives
    - Preparation and characterization of solid catalysts for RCF of cellulosic-biomass in flow-through processes
    - Establishing the RCF of cellulosic-biomass in flow-through processes
        - Understanding the mechanism of RCF of cellulosic-biomass

    - kinetic investigations of the established reductive catalytic fractionation of cellulosic biomass
- Preparation and characterization of biocatalysts and hybrid catalysts for biopolymer synthesis

2. Sketch potential experimental strategies



➢ **Figure 1**: a proposed experimental strategy for the intended RCF of cellulosic biomass fraction.

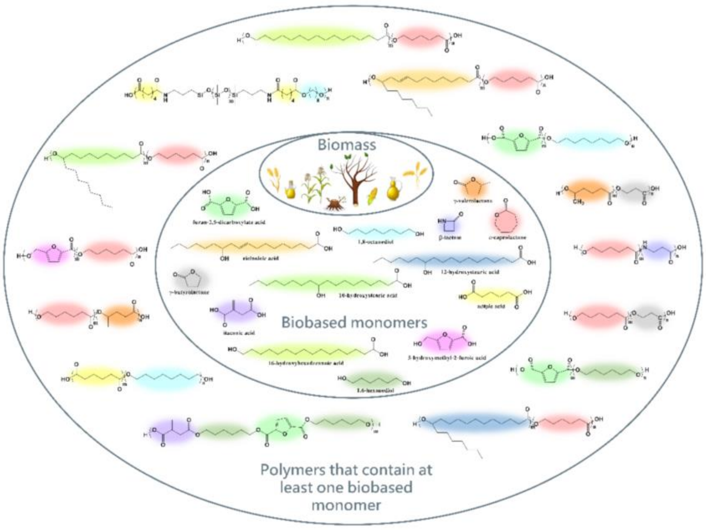


Figure 2. Potential bio-based polymers that can be synthesized from cellulosic biomass waste stream.[4]

3 work packages

WP1: Design and construction of the flow-through setup
WP2: Synthesis and characterization of the catalysts
WP3: RCF of cellulosic biomass-derived compounds and real cellulosic biomass waste stream
WP4: Unravelling the reaction mechanism based on a detailed analysis of the reaction products
WP5: Kinetic investigations of the established RCF
WP6: synthesis and characterization of biocatalysts and hybrid catalyst for polymerization of the synthesized functional chemicals
WP7: Polymerization of the synthesized functional chemicals using biocatalysis
WP8: Detailed characterization of the synthesized green polymers

2. relevant specific references if necessary (not more than five)

3. short statement on facilities / specific equipment / other resources available if applicable

   Since 2012, the UniCat BASF JointLab BasCat has been established at the Technische Universität Berlin, serving as an interface between academic and application-oriented research through a multidisciplinary approach involving physical, technical, inorganic, and organometallic chemistry, physics, as well as materials and engineering Sciences. In addition to fundamental research and knowledge-based development of new catalysts, the transferability of findings to industrial processes is also a focal point. BasCat possesses extensive methodological expertise relevant to the project, including:

   - Design and construction of facilities for evaluating catalytic reactions (including high pressure and high temperature)
   - Reactivity studies on heterogeneous catalysts in the gas phase
   - Parameter field studies, kinetic studies, and kinetic modeling
   - Controlled synthesis of catalyst materials

   In collaboration with the Excellence Cluster "Unifying Systems in Catalysis" (UniSysCat) in the field of renewables, current work focuses on the utilization of lignocellulosic biomass through the development of a flow process for the catalytic fractionation of beech sawdust (RSC Sustainability 2023, DOI: 10.1039/d2su00076h, and Chem. Ing. Tech. 2022, 11, 1611). Furthermore, Dr. Majd Al-Naji has developed catalytic flow processes in the liquid phase for the conversion of cellulose biomass into bio-based chemicals (ChemSusChem 2022, 15, e202102525, ACS Sustainable Chem. Eng. 2021, 2, 927, Green Chem. 2020, 22, 2755, and Green Chem. 2020, 22, 7398). Additionally, Dr. Majd Al-Naji from BasCat has developed metal-free carbocatalysts for various sustainable processes involving cellulose-derived compounds and polyethylene waste (ChemCatChem, 2023, 15, e202201095, and ChemSusChem (2023), e202201991).

4. Indicate possible further collaborations

   Several potential collaborations within the academic network in Berlin/Btandenburg can be established. For instance, the advance characterization of the catalyst could be performed in collaboration with Fritz-Haber-Institute (FHI). Moreover, the scope of this project is in line with chemical invention factory (CIF) GreenCHEM project that recently funded via BMBF. Moreover, the close partnership between Technische Universität Berlin and BASF SE could be promoting further collaboration in the field of biorenewable synthsis and catalyst development.