Catalytic Conversion of Renewable Resources into Bulk and Fine Chemicals

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Most countries have signed the Paris Agreement, in which they pledge to do everything in their power to reduce global warming to just 2 degrees by taking measures before 2050. The best way to do this is by a complete ban on the use of fossil fuels, not only for energy and transportation, but also for the production of chemicals. The most important renewable resource for the production of chemicals is lignocellulose as well as its constituents, cellulose, hemicellulose, the carbohydrates they are made from and lignin. Indeed, the first factories for the production of a number of important monomers made from sugars are being built at this very moment.¹ In the lecture a short introduction will be given on methods to convert lignocellulose into chemicals. We will then focus on the most promising venue, the use of platform chemicals, such as levulinic acid and 5-hydroxymethylfurfural (HMF), that can be made via dehydration of sugars. We will show that these platform chemicals can be used for the economic production of nylon intermediates, such as caprolactam and adipic acid.² More recently, we have focused on the conversion of 1-hydroxy-2,5-hexanedione (HHD), which can be prepared by aqueous hydrogenation of HMF, into aliphatic and aromatic chemicals.³ Copper-catalysed oxidation of HHD gave 2,5-dioxo-hexanal in excellent yield.⁴ This compound could be cyclized to form dialkylaminophenol, bis-(dialkylamino)benzene as well as hydroquinone.⁵ Reaction in the presence of amines gave 3hydroxy-pyridinium compounds.⁶

¹ Industrial implementation of chemical biomass conversion. J. G. de Vries, *Curr. Opin. Green Sustain. Chem.***2023**, *39*,100715.

² a) Caprolactam from Renewable Resources: Catalytic Conversion of 5-Hydroxymethylfurfural into Caprolactone. T. Buntara, S. Noel, P. H. Phua, I. Melián-Cabrera, J. G. de Vries and H. J. Heeres, *Angew. Chem. Int. Ed.* 2011, *50*, 7083-7087. b) Catalytic Conversion of Renewable Resources into Bulk and Fine Chemicals. J. G. de Vries, *Chem. Rec.* 2016, *16*, 2787–2800. c) Nylon intermediates from bio-based levulinic acid. A. Marckwordt, F. El Ouahabi, H. Amani, S. Tin, N. V. Kalevaru, P. C. J. Kamer, S. Wohlrab, J. G. de Vries, *Angew. Chem. Int. Ed.*, 2019, *58*, 3486–3490.

³³ Bio-based building blocks from 5-hydroxymethylfurfural via 1-hydroxyhexane-2,5-dione as intermediate. B. Wozniak, S. Tin and J. G. de Vries, *Chem. Sci.*, **2019**, *10*, 6024–6034.

⁴ Synthesis of a-keto aldehydes via selective Cu(I)-catalyzed oxidation of a-hydroxy ketones. S. Zheng, W. Smit, A. Spannenberg, S. Tin, J. G. de Vries, *Chem. Commun.*, **2022**, *58*, 4639–4642.

⁵ A New Strategy for the Synthesis of Valuable Benzenoid Aromatics from Bioderived Feedstock. S. Zheng, Z. Wei, B. Wozniak, F. Kallmeier, E. Baráth, H. Jiao, S. Tin, J. G. de Vries, *Nat. Sustain.* Under review. For a preprint see: https://doi.org/10.21203/rs.3.rs-2129703/v1

⁶ Synthesis of N-Substituted 3-Hydroxypyridinium Salts from Bioderived 5-Hydroxymethylfurfural in Water. S. Zheng, S. Chakrabortty, E. Baráth, S. Tin, and J. G. de Vries, *ACS Sustainable Chem. Eng.* **2022**, *10*, 15642–15647.