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Bypassing Reppe Chemistry: A Green Valorization Chain for the Production of N-Vinyl-2-Pyrrolidones from Biogenic Acids

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PURPOSE OF THE ABSTRACT

Carboxylic acids, such as succinic and itaconic acid, have been proposed as promising platform chemicals of future bio-refineries.[1] However, further upgrading of these chemicals into valuable products requires specific processes that handle oxygen-containing, highly functionalized feedstocks efficiently - a trait that is absent in current oil based technologies. In this context, the manufacture of pyrrolidones from carboxylic acids has been described in several articles, dealing mostly with the production of pharmaceutical intermediates from easily reducible levulinic acid.[2]
In contrast, our research focuses on the production of polyvinylpyrrolidones, with a plethora of applications in the food, cosmetic and pharmaceutical industries. Due to their favorable properties, these polymers and the respective monomer (N-vinyl-2-pyrrolidone = NVP) are in steadily increasing demand.[3] The resulting opportunities for new producers and production strategies, lend economic merit to our envisioned, green valorization chain (see Figure 1).

While we are also working on the production of N-unsubstituted pyrrolidones, which may be fed into the classical Reppe vinylation,[4] the current contribution focuses on an eco-friendly pathway to NVP via N-(2-hydroxyethyl)-2-pyrrolidones (HEP). The latter, which are obtained through the reductive amidation of carboxylic acids with monoethanolamine, are easily dehydrated, thus avoiding the difficult handling of pressurized acetylene, while reducing process waste at the same time.[5] With succinic acid as the main model compound, an extensive screening of catalysts and process conditions for the reductive amidation will be shown. As a consequence, the production of HEP in high yields with subsequent purification can be realized under optimized conditions. Finally, the dehydration of HEP is achieved over mild solid acids in a continuous gas phase reactor. Optimized acid properties and process conditions are implemented to avoid cleavage of the hydroxyethyl substituent. Purification by distillation ultimately yields the desired monomer, thus completing a process chain characterized by efficient catalytic conversions and simple purification operations.

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FIGURES

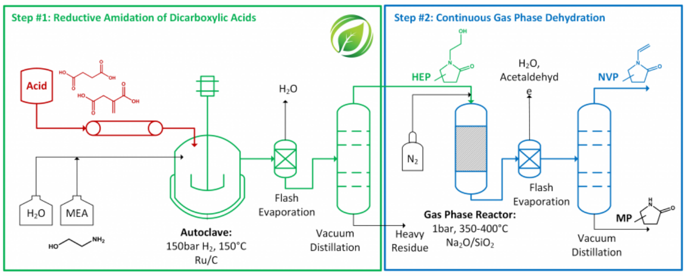

FIGURE 1

Schematic process for the two-staged transformation of dicarboxylic acids to sustainable vinyl-2-pyrrolidone monomers;

(MEA = monoethanolamine, HEP = N-(2-hydroxyethyl)-2-pyrrolidone, NVP = N-vinyl-2-pyrrolidone, MP = methyl-2-pyrrolidone)

FIGURE 2

KEYWORDS

biomass conversion | green chemistry | heterogeneous catalysis | carboxylic acids

BIBLIOGRAPHY

Literature

[1] T. A. Werpy, J. E. Holladay, J. F. White, Top Value Added Chemicals From Biomass. I. Results of Screening for Potential Candidates from Sugars and Synthesis Gas, 2004.

[2] X.-L. Du, L. He, S. Zhao, Y.-M. Liu, Y. Cao, H.-Y. He, K.-N. Fan, Angew. Chem. 2011, 123, 7961.

[3] Grand View Research Inc., Polyvinylpyrrolidone (PVP) Market Worth $2.75 Billion by 2024, PR Newswire 2016. Visited 15.10.2017.

[4] Y. Louven, K. Schute, R. Palkovits, ChemCatChem (accepted) [DOI: 1002/cctc.201801751].

[5] a) Y. Shimasaki, H. Yano, K. Ariyoshi und H. Kambe, Journal of Molecular Catalysis A: Chemical 2005, 239, 125–129. b) Y. Shimasaki and H. Yano, Nippon Shokubai Co., Process for production of tertiary n-alkenyl carboxylic acid amide, EP 0701998 B1 1998.

Image Sources

[1] Imbedded images designed by mudassir101 and Freepik - Freepik.com