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Novel approaches towards industrial bulk and specialty chemicals through chemoenzymatic cascades

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PURPOSE OF THE ABSTRACT

Enzyme catalysis has emerged towards a key technology in the chemical industry, in particular for the production of chiral fine chemicals and pharmaceuticals. In contrast, applications of enzyme catalysis in the field of bulk chemicals and specialty chemicals are still rare. In general, among current challenges in enzyme catalysis related to production of products in these high-volume low-cost product segments are the realization of production processes running at high substrate loading (being in a multi-100 g/L range) together with economic work-up steps as well as the efficient combination of biotransformations with chemocatalytic reactions towards multi-step synthetic sequences. The development of chemoenzymatic one-pot cascades, being a young but emerging field of research,[1] avoids the need for tedious work-up steps such as isolation and purification of intermediates, thus offering a perspective for decreasing the overall number of unit operation steps, needed amount of solvent (used for extraction) and consequently lowering the amount of formed waste.

In this presentation, examples from our recent research collaborations with academic and industrial project partners to develop technically feasible biocatalytic and chemoenzymatic processes for applications in the field of specialty and bulk chemicals starting from biorenewable feedstocks will be given.

One case-study is related to the development of a new technology platform for chiral and achiral nitriles.[2-6] By means of aldoxime dehydratases as a biocatalyst, a cyanide-free approach to nitriles starting from readily available aldehydes was established and a broad substrate scope was demonstrated. This process technology can be used for synthesizing the polymer building block adiponitrile, benzonitriles as specialty chemicals as well as fatty nitriles as precursors for detergents and lubricants,[4-6] The enzymatic process for fatty nitriles, which was developed jointly with Klüber Lubrication, runs at a high substrate loading of up to 1.4 Kg per L of aqueous reaction medium, thus representing one of the highest substrate loadings in enzyme catalysis with hydrophobic substrates in aqueous media.[6] Furthermore, a chemoenzymatic process consisting of an initial metal-catalyzed hydroformylation of an alkene as high pressure reaction under formation of the corresponding aldehyde, which was then converted into the desired nitrile by means of enzyme catalysis, has been developed.[7]

A second case-study is the development of a chemoenzymatic process to produce the polymer-building block caprolacton starting from biorenewable raw materials. Polycaprolacton is of interest as a polymer also due to its favorable biodegradability properties, but is today produced from fossil feedstocks. A chemoenzymatic process has been developed based on metal-catalyzed hydrogenation of phenol (which is available in bio-based form on large scale today), followed by a biocatalytic "double oxidation" of cyclohexanol with molecular oxygen as only reagent.[8] Currently, the further development of this process concept is done within a joint research project with BYK-Chemie/ALTANA.

In a third case study, preliminary results on the combination of metal-catalyzed syngas high pressure chemistry, hydrogenation and enzymatic esterification within a chemoenzymatic process for producing tailor-made lubricants is presented. Within a joint project with OQ Chemicals (previously OXEA) and Klüber Lubrication, oligomeric esters are accessible based on enzymatic esterification within a solvent-free process under neat conditions, which enables a fine-tuning of the performance properties of the lubricant molecules and resulted in the formation of a new generation of bio-based lubricants with proven biodegradability.[9]

FIGURES

FIGURE 1

FIGURE 2

KEYWORDS
Industrial applications | Aldoxime dehydratases | Chemoenzymatic synthesis | Nitriles

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