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TOPIC(s) : Biocatalytic cascade reactions / (Chemo)enzymatic strategies

UPOs for the oxidative valorization of HMF

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PURPOSE OF THE ABSTRACT

2,5-Furandicarboxylic acid (FDCA) is a versatile platform chemical that has its main application in the polymer industry.[1] The enormous interest in this building block is largely due to the fact that it can be accessed via renewable starting materials. One of the most prominent strategies for the synthesis of FDCA is the catalytic oxidation of biomass derived 5-hydroxymethylfurfural (HMF).[2] The inclusion of FDCA in the list of the top 12 biobased chemicals by the U.S. Department of Energy (DOE) back in 2004[3] triggered a wave of research which resulted in a remarkable toolbox of catalytic oxidation methods towards FDCA. One of the most prominent strategies for the synthesis of FDCA is the catalytic oxidation of biomass derived HMF.[2] The main advantages of biocatalysts in this regard are their selectivity and benign reaction conditions, which are a prerequisite for a sustainable process. Yet, the challenge of enzymatic processes is to bring product titers to competitive levels. In this respect, unspecific peroxygenases (UPOs) have shown great potential as oxidation catalysts.[4] Despite the ever increasing interest in UPOs, up until now only AaeUPO has been used in cascades with oxidases for the oxidation of HMF.[5]

We screened 23 different UPOs and report that HspUPO[6] and UPOx8 are the first UPOs which are capable of performing three consecutive oxidation steps from HMF to FDCA on their own (Figure 1). We also observed that the chemoselectivity in the first oxidation step can be enhanced by the use of cosolvents, although accompanied by lower conversions. The combination of HspUPO with HMFO[7] and variants thereof[8] in a self-sufficient cascade leads to increased efficiency of the system.

Our results to date underscore the potential of UPOs for the synthesis of FDCA and thereby contribute to the development of sustainable and efficient methods for the production of value-added chemicals from biomass-derived feedstocks.

FIGURES

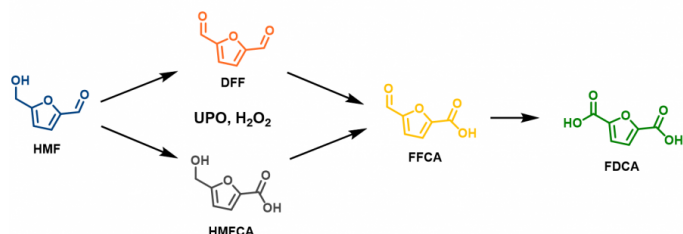


FIGURE 1

Oxidation of HMF to FDCA by UPO.

HMF = 5-Hydroxymethylfurfural, DFF =
2,5-Diformylfuran, HMFA =
5-Hydroxymethyl-2-furancarboxylic acid, FFCA =
5-Formyl-2-furancarboxylic acid, FDCA =
2,5-Furandicarboxylic acid

FIGURE 2

KEYWORDS

Unspecific Peroxygenases (UPOs) | 5-Hydroxymethylfurfural (HMF) | 2,5-Furandicarboxylic acid (FDCA) |
Enzymatic Cascades

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