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SUSTAINABLE GRAM-SCALE SYNTHESES OF FURANICS

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Among the numerous bio-based platform chemicals - key molecules of the Biorefinery research field - a series of furan-based compounds easily synthetised from D-fructose has captured the scientists' attention in consideration of their potential market applications. An archetype of these molecules is 5-hydroxymethylfurfural (HMF), a building block that has found numerous applications in the synthesis of chemicals, materials, bio-based polymers and fuels.[1] The most common synthetic route to HMF is based on D-fructose dehydration. This acid-catalyzed triple dehydration has been conducted in the presence of numerous catalysts ranging from mineral and Lewis acids, metal chlorides, metal oxides, heteropolyacids, ion-exchange resins, zeolites, ionic liquids (ILs), functionalized carbon materials, mesoporous silica materials and solid metal phosphate.[2] Although all these catalysts led to an efficient conversion of D-fructose into HMF, typical reaction drawbacks include harsh reaction conditions, such as the use of strong acids, high temperatures and difficult isolation of the target molecule from the reaction media. In fact, despite the large number of publications reported in the literature, only limited attention has been paid to the separation of HMF from the reaction mixture. As a result, most of syntheses leading to HMF and furanics are based on small scale reactions where separation and isolation strategies are rarely addressed. Thus, with a few exceptions, the products yield always refers to an HPLC-based evaluation.[3]

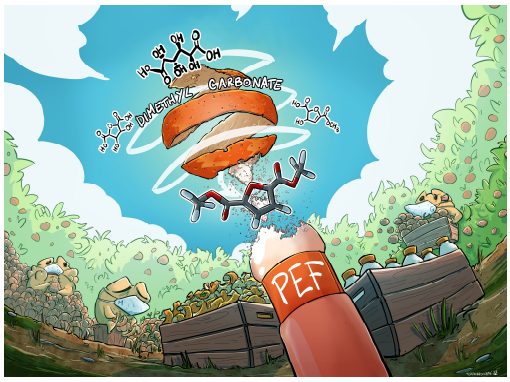

Figure 1. FDME synthesis from mucic acid.

On the other hand, our interest into furanics exploitation is i) to develop simple synthetic approaches and ii) to exploit their application as monomers for biopolymer, additives for biofuels or synthons for industrially relevant compounds.
As a result, in recent years we have investigated the multi-grams scale syntheses of HMF,[4] 5-bis(hydroxymethyl)furan (BHMF), 2,5-bis[(alkoxycarbonyl) oxymethyl]furan (BAMF),[5] 2,5-Bis[(alkoxycarbonyl)oxymethyl] furan (BCMF)[6] and more recently to 2,5-furandicarboxylic acid dimethyl ester (FDME, Figure 1).[7] On-going investigations also include the preparation of HMF dimer, namely, 5,5 '(oxy-bis(methylene)bis-2-furfural (OBMF) and its derivatives. Most of the abovementioned compounds have been achieved employing commercially available catalysts, green solvents, mild reaction conditions and the products were isolated as pure employing simple purification procedures.

References

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