Towards Scalable Synthesis of Furanics: Products Purification and Comparative Environmental Assessment

Fabio Aricò
[1]*Ca' Foscari University of Venice, Department of Environmental Sciences, Informatics and Statistics, Via Torino 155, 30172 Venezia (Italy)*
**Fabio.arico@unive.it*

5-Hydroxymethylfurfural (HMF) is an archetype of bio-based platform chemicals, molecules derived by biomass that are the focus of Biorefinery research field.[1] HMF can be easily prepared from D-fructose via acid-catalyzed triple dehydration. This synthesis was carried out in the presence of numerous catalysts such as mineral and Lewis acids, metal chlorides, metal oxides, heteropolyacids and ion-exchange resins to mention just a few. [2] Although all these catalysts lead to an efficient conversion of D-fructose into HMF, typical reaction drawbacks include harsh reaction conditions and difficult isolation of the target molecule from the reaction media. Furthermore, despite the large number of publications reported in the literature, only limited attention has been focused on 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.

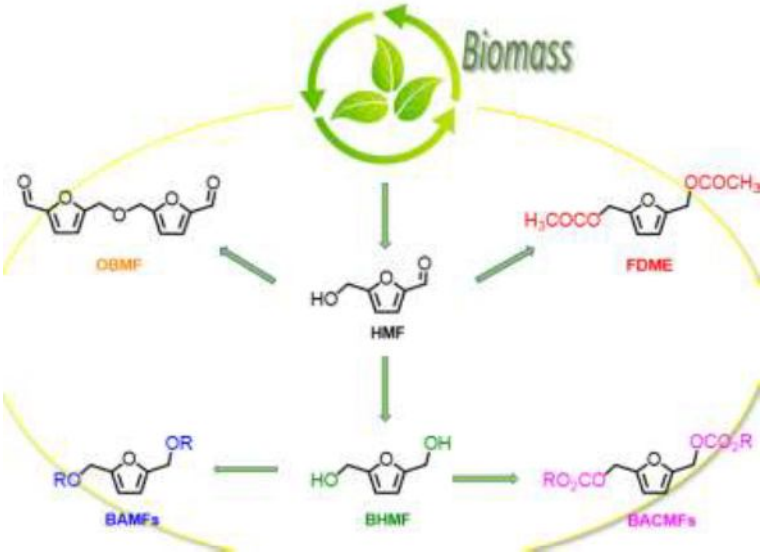

Figure 1. Furanics from biomass

Our interest into furanics is related to their upgrading into a variety of value-added derivatives, such as chemicals, materials, bio-based polymers and fuels. In this prospect it is pivotal to develop simple synthetic approaches addressing both isolation and purification of these compounds. In recent years we have investigated gram to multi-grams scale syntheses of HMF,[3] 5-bis(hydroxymethyl)furan (BHMF), 2,5-bis[(alkoxycarbonyl) oxymethyl]furan (BAMF),[4] 2,5-Bis[(alkoxycarbonyl)oxymethyl] furan (BCMF)[5], 2,5-furandicarboxylic acid dimethyl ester (FDME)[6] and more recently 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 via simple purification procedures. Furthermore, for specific examples green metrics and materials efficiency performance of the reported procedures have also been investigated taking into account E-factor and PMI green metrics.

Acknowledgements

We want to acknowledge the Organization for the Prohibition of Chemical Weapons (OPCW); Project Number L/ICA/ICB/218789/19 for funding part of this research. The presented work is also within the framework of COST Action FUR4Sustain (CA18220-European network of FURan based chemicals and materials FOR a Sustainable development), supported by COST.

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