Metrics for green syntheses: two case studies in biorefinery

Giacomo Trapasso [a),*] Mattia Annatelli, [a)] Beatriz Chìcharo [a)] and Fabio Aricò [a)]

a) Department of Environmental Science Informatic and Statistics, Ca' Foscari University of Venice, Scientific Campus
Via Torino 155, 30170 Venezia Mestre, Italy
**Email: giacomo.trapasso@unive.it*

Green metrics is a relatively new concept in Green Chemistry. The application of rigorous green metrics must go along with the experimental validation of synthetic procedures; this is necessary to give precise guidelines so to define a green synthetic approach and avoid misunderstanding and pretentious claims originating from subjective rather than objective evaluations.

5-(hydroxymethyl)furfural (HMF) has been labelled as the "sleeping giant" of the bio-based platform-chemicals realm, due to its versatility and being the starting point for endless chemical transformations into novel monomers for producing bio-based polymers. Among HMF derivatives, 2,5-Furandicarboxylic acid (FDCA) has been extensively studied as monomer for the production of polyesters such as polyethylene furanoate (PEF), considered as one of the most valuable bio-based substitute of the petroleum-derived polyethylene terephthalate (PET). However, the sustainability of the synthetic procedures leading to HMF and its derivatives represent a key aspect that must be addressed in order to foster their entrance into the bio-based plastic market. In this scenario, green metrics such as the environmental factor (E-factor) and the process mass intensity (PMI) represent an useful tool towards this goal.[1]

From these premises, the present study reports an alternative synthetic procedure for the production of 2,5-furandicarboxylic acid dimethyl ester (FDME) starting from galactaric acid via dimethyl carbonate (DMC) chemistry. Both sulfonic resins and an iron-based Lewis acid showed to promote the one-pot formation of FDME. The pure product was retrieved as a white crystalline solid with an isolated yield of up to 70%. Based on the different intermediates identified, a possible reaction mechanism was proposed, which highlights the essential contribute of DMC in the product formation.[2] This presentation is also focussing on some key points inherent to the IUPAC project 2017-030-2-041: Metrics for Green synthesis. Thus, the greenness of the herein discussed synthetic procedure was evaluated using the most common green metrics and compared with other available synthetic pathways.

References:

[1] M. Annatelli, J. E. Sánchez-Velandia, G. Mazzi, S. V. Pandeirada, D. Giannakoudakis, S. Rautiainen, A. Esposito, S. Thiyagarajan, A. Richel, K. S. Triantafyllidis, T. Robert, N. Guigo, A. F. Sousa, E. García-Verdugo, F. Aricò, Green Chem., 2024, Advance Article.
[2] G. Trapasso, M. Annatelli, D. Dalla Torre, F. Aricò, Green Chem., 2022,24, 2766-2771; G. Trapasso, B. Chícharo, T. Gherardi, D. Redolfi-Bristol, F. Aricò, Catalysts 2023, 13(7), 1114.

Acknowledgements:

This work was supported by the DoE 2023-2027 (MUR, AIS.DIP.ECCELLENZA2023_27.FF project).