5,5'(Oxy-bis(methylene)bis-2-furfural (OBMF) from 5-hydroxymethyl-2-furfural (HMF): a systematic study for the synthesis of a new platform molecule from renewable substances

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The continued exploitation and depletion of fossil fuels has prompted the scientific community to search for more sustainable and environmentally friendly alternatives. In the last decade, the synthesis of biomass-derived chemicals has become a priority to boost the transition from refinery to biorefinery.[1] Sugars are an extremely abundant bio-resource in nature; even today, one of the most studied reactions is the synthesis of 5-hydroxymethyl-2-furfural (HMF). This compound is considered extremely important for biorefinery because of its wide range of possible applications (pharmaceutical, biofuels, polymer precursors, surfactants).[2] However, it has been observed, during the spontaneous degenerative process of HMF, the formation of a compound that could be equally important 5,5'-[oxybis(methylene)]bis-2-furfural (OBMF).
The synthesis of OBMF is scarcely reported in the literature, only in recent years interest in this dimer of HMF has emerged for its possible applications in industry.[3] Good yield values of OBMF are reported in the literature from HMF (Figure 1) in the presence of an acid catalyst; however, the solvents used are the most common halogenated and/or aromatic solvents, known to be toxic. The objective of this work was to find a viable synthetic route to access OBMF without having to resort to the use of such solvents and, in addition, utilize already commercially available and inexpensive acid catalysts. Through small-scale optimizations, the best solvent was found to be dimethyl carbonate;[4] In addition, two heterogeneous acid catalysts - Purolite 269 and ferric sulfate (Fe2(SO4)3) - showed excellent efficiency in promoting the HMF etherification reaction with quantitative yields (> 90%). Subsequently, a scale-up of the reaction was carried out, obtaining OBMF with an isolated yield of 81%. Given the excellent results obtained, this work can be a starting point to undertake the study of new synthetic methodologies for this molecule such as continuous flow reactions of which the literature is lacking.

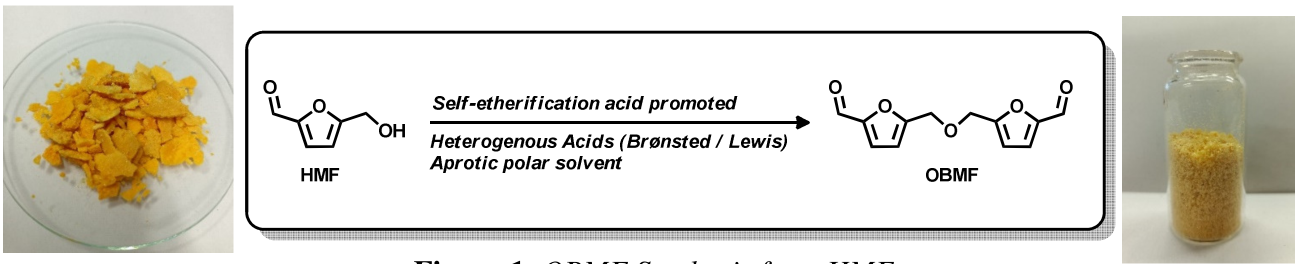

Figure 1. *OBMF Synthesis from HMF.*

References

[1] a) Y. Zhao *et al.*, *Bioresour. Technol.*, **2012**, *114*, 740–744; b) D.B. Bevilaqua *et al.*, *J. Clean. Prod.,* **2013**, *47*, 96–101.
[2] a) J.J. Bozell *et al.*, *Green. Chem.,* **2010**, *12*, 539−554; b) L.V. Romashov *et al.*, *Chem. Asian J.*, **2017**, *12*, 2652–2655; c) A. Bohre *et al.*, *ACS Sustainable Chem. Eng.,* **2015**, *3*, 1263–1277 d) Z. Xu *et al.*, *ChemSusChem,* **2016**, *9*, 1255–1258.
[3] a) J.M. Timko *et al.*, *J. Am. Chem. Soc.*, **1974**, *96*, 7159–7160.
[4] P. Tundo *et al.*, *Green Chem.*, **2018**, *20*, 28–85