

## Synthesis and derivatization of 2,5-bis(hydroxymethyl)furan (BHMF)

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Biomass-derived C6-furanic platform chemicals are regarded as the most promising building blocks in biorefinery exploitation. 5-Hydroxymethylfurfural (HMF) is referred as a “sleeping giant” in consideration of its potential in bridging the gap from a fossil-based chemistry to a more sustainable one. HMF is a versatile substrate with enormous market potential as it can be easily converted into high value chemicals, materials and bio-based polymers.[1] However, there are some limitations in developing an efficient HMF-based chemistry, i.e., its preferred solubility in water rather than in organic solvents, the absence of a cost-efficient scale-up synthesis, and well know HMF stability issue partially solved by the addition of small amount of specific stabilizers.

In our laboratory we have developed a new approach to HMF from D-Fructose using dimethyl carbonate as an extracting solvent in the presence of an acidic heterogenous catalyst. This synthesis is easily scalable up to 20 grams of D-fructose and allows to recover HMF in 70% isolated yield.[2] Quick reduction of HMF to the related 2,5-bis(hydroxymethyl)furan (BHMF) was

also carried out using sodium borohydride as reducing agent. This latter approach led to prepare rapidly a rather large amount of BHMF. As a result, BHMF derivatization was also investigated. In particular we have focused on BHMF etherification reaction to achieve 2,5-bis(alkoxymethyl) furans (BAMFs) – well-known biofuel candidates. Several catalysts were investigated; (mild) reaction conditions were optimized and thus employed for the preparation of a library of BAMFs (10 compounds). Products isolation and purification were addressed for each BAMFs.[3] Two examples of etherification reactions were also conducted in gram-scale i.e. for the synthesis of 2,5-bis(methoxymethyl)furan and 2,5-bis(isopropoxymethyl) furan.

Ongoing research on BHMF includes studying its reactivity with dialkyl carbonates. The idea is to develop a library of easy accessible bio-based monomers for polycarbonate, polyurethanes as well as potentially interesting intermediates for surfactants and detergents production.[4]

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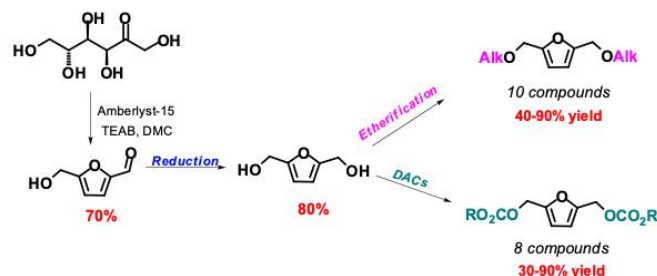


Figure 1. Synthesis of HMF from D-fructose and its conversions into BHMF and related monomers

### References

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