A library of lignocellulose-derived monomers from 5-(chloromethyl)furfural

Davide Dalla Torre,[a] Giacomo Trapasso,[a] Fabio Aricò[a,]*

[a] Department of Environmental Sciences, Informatics and Statistics, Ca' Foscari University of Venice, Scientific Campus Via Torino 155, 30170 Venezia Mestre, Italy.

Davide Dalla Torre: davide.dallatorre@unive.it

Abstract

The ultimate goal of the Biorefinery is to move away from a fossil-based business towards a more sustainable industry centered on the use of renewable feedstocks, capable of respecting the principle of the circular economy [1]. Among the various furan-derived compounds obtained from carbohydrate-rich feedstocks, 5-(chloromethyl)furfural (CMF) has recently attracted increasing attention.[2] CMF has largely been regarded as an impurity and has consequently been removed during downstream purification or discarded in side streams without further valorization.[3] Only in recent years this molecule has gained recognition as a valuable Bio-Based platform chemical due to its stability, hydrophobicity, and easier extractability compared to 5-hydroxymethylfurfural (HMF).[4] In this work, CMF was successfully employed as a versatile biomass-derived platform molecule for the synthesis of a library of lignocellulosic (LC) monomers. The optimal conditions involved the reaction of CMF and vanillin in a 1.0:1.0 molar ratio in the presence of K_2CO_3 (1.0 eq. mol) in acetonitrile, affording the desired product (Fur-Van monomer) in only 2 h. These conditions were subsequently extended to a range of lignin-derived monomers bearing aldehyde, ketone, ester, and allyl functionalities, demonstrating the broad applicability of the methodology. The protocol was successfully scaled up to 5.0 g of CMF while maintaining high isolated yields. Furthermore, the LC monomers were readily converted into the corresponding (di)ol derivatives through a straightforward reduction, affording a complementary library of LC diol monomers in high yields. All compounds were comprehensively characterized by spectroscopic and thermal analyses, including DSC and TGA, demonstrating their suitability as monomers for polycondensation processes leading to high-molecular-weight polymeric materials.

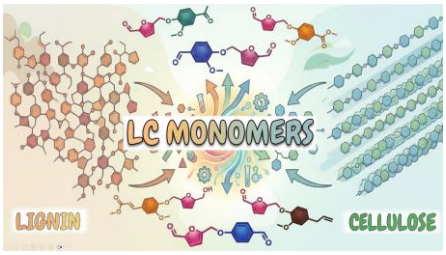

Figure 1. CMF: a gateway to a library of lignocellulose-derived monomers

Keywords

Bio-Based platform chemicals, 5-(chloromethyl)furfural (CMF), lignin-derived monomers, lignocellulosic monomers, waste valorization.

Acknowledgements

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

References

[1] E.Loiseau, L.Saikku, R.Antikainen, N. Droste, B.Hansjürgens, K.Pitkänen, P.Leskinen, P.Kuikman, M.Thomsen, *Journal of Cleaner Prod.*, 2016, **15**, 361– 37.

[2] J. Bueno Morón, F. Arbore, G. P. M. van Klink, M. Mascal and G. M. Gruter, *ChemSusChem*, 2024, **17**, e202400495

[3] D. Soukup-Carne, F. S. Bragagnolo, C. Soleo Funari and J. Esteban, *Catalysts*, 2024, **14**, 117.

[4] M. Mascal, *ChemSusChem*, 2015, **8**, 3391–3395.