

Editorial

Novel Catalytic Strategies for the Synthesis of Furans and Their Derivatives

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The depletion of fossil resources and their environmental issues make the transition toward alternative feedstock even more urgent. Under this perspective, as a renewable and carbon neutral resource, lignocellulosic biomass looks promising for the chemical industry. In recent years, research has focused on the development of a feasible biorefinery, proposing several strategies for the conversion of biomass and its structural components. Among them, hemicellulose and cellulose are currently the most investigated ones, and their conversion to platform chemicals surely represents a hot topic. Furans, such as furfural and 5-hydroxymethylfurfural (HMF), are strategic platform chemicals derived from hemicellulose and cellulose, respectively. They can be involved in several reactions (hydrogenation, hydrogenolysis, hydrogen transfer, oxidation, etherification, etc.), leading to the production of renewable biofuels and biochemicals, such as monomers, surfactants, solvents, adhesives, pharmaceuticals, and agrochemicals. However, the great reactivity of furans also leads to the formation of significant by-products; thus, properly tuning the properties of the catalyst applied in both furan synthesis and their utilizations, as well as the optimization of the process conditions, still represent a challenge facing the development of a sustainable and feasible process that involves furans as platform chemicals. For these reasons, continuous investigations are undoubtedly necessary. This Special Issue presents the most recent and significant advances in both furan synthesis and utilization, focusing on the proposed catalytic systems, the applied process conditions, and the kinetic and mechanistic aspects.

The synthesis of furans can be performed starting from model compounds, such as monosaccharides and polysaccharides, or, more advantageously, from waste biomasses. However, as highlighted in the review of Fulignati et al. (Contribution 1), the synthesis of HMF from biomasses, analogously to that of furfural, is much more challenging. In this study, the authors analysed all the possible process variables (type of feedstock, catalyst, solvent, heating system, and pretreatment step) in a holistic manner, concluding that a feasible process should involve the employment of biomasses rich in C6 sugars as a feedstock, inorganic salts as the catalyst, and a biphasic system as the reaction medium. Regarding the heating system, the microwave method shows promise, but as of now, its employment on the industrial scale is not feasible due to scale-up technical issues. On the other hand, the necessity of adopting a pretreatment step strongly depends on the characteristics of the feedstock, and it is really only advantageous if it allows the valorisation of each biomass component.

A furanic compound alternative to HMF that has been scarcely investigated up to this point is 5-chloromethylfurfural (CMF). The synthesis and exploitation of this compound have been commented on in the review of Soukup-Carne et al. (Contribution 2). It is worth noting that CMF presents some advantages with respect to HMF, such as its production, which takes place under milder reaction conditions; its lower polarity, which makes it easier to separate with an organic solvent; and the presence of chlorine in its chemical structure that, being a better leaving group, gives rise to the production of several valuable compounds through the reactions of rehydration, hydrogenation, oxidation, esterification,



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etherification, and amination. However, CMF synthesis still has some limitations, such as the adoption of halogenated solvents in the extraction phase, mainly 1,2-dichloroethane, thus making it necessary to find a greener alternative. Lastly, the kinetic information regarding CMF synthesis is lacking despite it being fundamental for reactor and process designs and, consequently, for its scalability.

Among the derivatives of HMF, 2,5-furandicarboxylic acid (FDCA) is the most relevant one. It is a green alternative to terephthalic acid, since it leads to the production of PEF instead of PET, with the former having more advantageous mechanical and thermal properties. The most investigated route for the synthesis of FDCA involves HMF oxidation; the employed catalyst, oxidant agent, and reaction conditions are the main variables of this process. Liuzzi et al. (Contribution 3) prepared different Au on carbon catalysts via a sol-immobilization route and investigated the role of polymeric stabilizers such as polyvinylpyrrolidone (PVP), polyethylene glycol (PEG), and polyvinyl alcohol (PVA), on the catalyst's activity and stability. The obtained results proved that PVA allowed the formation of smaller and more active Au nanoparticles, while PEG and PVP both led to the formation of bigger and less active nanoparticles. Through computational studies, the authors justified these experimental observations, demonstrating that the monomer of PVA had the lowest adsorption energy on the Au nanoparticles, thus the polymer can be easily removed from the Au surface increasing the number of active sites. Moreover, the recyclability tests conducted on the catalysts highlighted some deactivation for all the prepared systems; however, high amounts of polymer were found to increase catalyst stability, despite lower reactivity also being observed.

The FDCA esters have been investigated less with respect to FDCA, despite their higher solubility in organic media, a property that potentially makes them easier to be isolated and adopted as monomers for the synthesis of PEF. On this basis, Trapasso et al. (Contribution 4) proposed an innovative synthetic route for the synthesis of FDCA methyl ester (FDME) starting from galactaric acid, employing dimethyl carbonate (DMC) as a solvent, and using $\text{Fe}_2(\text{SO}_4)_3$ as a Lewis catalyst. Under the optimized reaction conditions, an FDME yield of 70 mol% was reached when the reaction was performed at gram scale (5.0 g of galactaric acid). The authors attributed the high efficiency of $\text{Fe}_2(\text{SO}_4)_3$ to its synergistic effect with DMC in the cyclization and aromatization steps, but deeper investigations are necessary to better understand the mechanism of this reaction.

Similarly to the exploitation of HMF, the conversion of furfural also leads to the production of valuable compounds such as 2-methylfuran (2-MF), which is obtained through a hydrogenation reaction, as investigated by Smirnov et al. (Contribution 5). These authors prepared Ni-doped Mo carbide with Ni/Mo atomic ratio of 0.1 (Ni_{0.1}MoC) supported with SiO_2 , Al_2O_3 and carbon, and adopted them as the catalysts for the batch hydrogenation of furfural to 2-MF. Several physical–chemical analyses revealed that the Mo carbides and metallic nickel, formed during the thermal treatment of the catalyst, were the main active sites. The carbon-supported catalyst was shown to be the most active and selective, leading to complete furfural conversion and a 2-MF yield of 61 mol% under the best reaction conditions. Thus, the same catalyst was also adopted for the solvent-free hydrogenation of furfural in a fixed-bed reactor, reaching complete furfural conversion and an 86 mol% 2-MF yield.

γ -Valerolactone (GVL) is another useful derivative of furanic compounds that can be obtained via different reaction pathways from both HMF and furfural. In the work of Tolek et al. (Contribution 6), the one-pot conversion of furfural to GVL was performed employing Co- and Pt-doped/ZSM-5 as the catalyst in the absence of liquid acids and molecular H_2 , but taking advantage of the use of a hydrogen donor, such as isopropyl alcohol. The authors found that the Co- and Pt-doped/ZSM-5 catalyst achieved a higher GVL yield (85.4 mol%) in comparison to the non-modified H-ZSM-5 zeolite (35.4 mol%) under the same reaction conditions, thanks to its different acidic properties. In fact, the presence of Co and Pt increased the Lewis and weak acid sites, thus facilitating the reduction of furfural to GVL through a hydrogen transfer mechanism.

In the last article of this Special Issue, via in situ NMR analysis, Warthegau et al. (Contribution 7) investigated the mechanism and kinetics of the reaction between naturally abundant aldoses (glucose, xylose, mannose, and galactose) and CH-acidic nitrile-containing nucleophiles working at low temperatures in aqueous solutions of diluted base catalysts without metal catalysts. The final product was a bicyclic species mainly consisting of two fused furanic rings which formed with high stereoselectivity. Its mechanism was articulated through the three following steps: (i) conversion of aldose to cyclized Knoevenagel adduct; (ii) formation of bicyclic intermediates via concerted Knoevenagel condensation and oxa-Michael addition; and (iii) amine-, nitrile-, and polyol-bearing furan product.

In conclusion, these seven papers highlight the relevance of the synthesis of furanic compounds and their derivatives for the development of biorefineries, under the perspective of a sustainable energy transition.

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List of Contributions

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