

Biofuels from Waste Biomass: A Cascade Strategy for the Sustainable Production of 2-Methyl-Tetrahydrofuran and 2-Butanol

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Abstract

In recent years, the replacement of fossil resources with renewable ones has focused great interest, especially as regards the production of biofuels and valuable products. In particular, 2-methyl-tetrahydrofuran (MeTHF) and 2-butanol (2-BuOH) are compounds of surplus value, which can be obtained from biomass. MeTHF can be readily used in blends with gasoline without major engine changes and it has been also thoroughly investigated as additive for the preparation of alternative fuel transportation mixtures called *p-series fuels* approved by the United States Department of Energy [1]. On the other hand, 2-BuOH is mainly used for the synthesis of methylethylketone, but recently it has found other applications both as solvent and fuel additive due to its high octane number [2]. Both these molecules, MeTHF and 2-BuOH, can be obtained from a series of hydrogenation-dehydration or decarboxylation-hydrogenation steps respectively of levulinic acid (LA) which is another promising platform chemical derived from biomass. Here, a cascade strategy for the production of MeTHF and 2-BuOH from waste biomass has been investigated, thus encouraging the valorization of waste biomasses into added-value bio-chemicals, instead of their traditional combustion for energy recovery or, even worse, of their landfill disposal. In this context, in the first step the acid-catalysed hydrothermal conversion of the exhausted cellulose powder, waste from the tissue paper production, into LA has been optimized, achieving LA yield up to about 33-40 wt% at 180°C for 20 minutes in the presence of HCl 1.68 wt% under microwave irradiation adopting a cellulose powder loading in water of 7 wt%. Then, in the subsequent step, the obtained biomass-derived LA-rich acid reaction aqueous slurry after neutralization was directly subjected to hydrogenation in the presence of commercial catalytic systems. Ru and Ru/Re catalysts were adopted and the selectivity of the process was significantly influenced by the reaction conditions as well as by the nature of an eventual heterogeneous acid co-catalyst, such as niobium phosphate (NBP) and zeolite HY. In particular, in the presence of 5 wt% Ru/C and 5 wt% Re/C, MeTHF molar yield calculated respect to the initial LA moles present in the slurry, up to 25 mol% was ascertained working at 200°C and 9.5 MPa of H₂ employing NBP as acid co-catalyst. On the other hand, in the presence of 5 wt% of Ru/C, 2-BuOH molar yield calculated respect to the initial LA moles present in the slurry, up to 65 mol% was reached adopting 200°C and 3 MPa of H₂ using zeolite HY as acid co-catalyst. In conclusion, the optimization of both the reaction conditions and the composition of the catalytic system allows us to obtain different target products such as MeTHF and 2-BuOH, opening the way to the direct production of biofuels from waste biomasses.

[1] M.A. Eldeeb, B. Akih-Kumgeh, *Energies* 11 (2018) 512.

[2] Y. Ying, D. Liu, *Fuel* 205 (2017) 109.