Catalytic hydrogenation of crude hexanoic acid, easily obtained by anaerobic fermentation of grape pomace

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Abstract

According to European climate law 2021, the progressive transition from traditional fossil sources to renewable ones represents, more than even, an urgent need. In this regard, biomasses can be exploited, not only adopting the already developed thermochemical treatments, but also through novel bio-catalytic pathways, including the production of carboxylic acids via acidogenic fermentation [1]. Besides, the combination of a bio-chemical approach with a traditional chemical one could make possible to achieve a better exploitation of the biomass, aimed at the sustainable and selective production of value-added bio-products. Remarkably, carboxylic acids can be further chemically converted into more value-added bio-products, which can be advantageously proposed within the pharmaceutical, polymer, and fuel industries [2]. In this context, a strategic conversion path is the hydrogenation of the carboxylic acids to the corresponding alcohols and/or esters [3]. In this work, the optimization of the catalytic hydrogenation of hexanoic acid to 1-hexanol and hexyl hexanoate, as the main products of interest, has been first investigated. For this purpose, different rhenium-supported catalysts have been tested in the hydrogenation of commercial hexanoic acid, evaluating the synergistic effects of the metal loading and support acidity on the conversion and selectivity to 1-hexanol and hexyl hexanoate. The choice of rhenium as the hydrogenation metal is appropriate for economic reasons and for its resistance to poisoning [4]. Rhenium catalysts resulted very active, the adoption of acid supports influencing the selectivity towards hexyl hexanoate formation. Instead, 5 wt% Re on neutral carbon resulted more selective towards 1-hexanol production and, for this purpose, this catalyst was tested for the hydrogenation of a crude hexanoic acid, easily obtained by fermentation of grape pomace and simple insolubilization step. This agri-food waste biomass, whose worldwide generation is about 9 Mt/year, represents a clean source of carbohydrates, that can be exploited by catalytic conversion, instead of being landfilled or used for low-value applications. It is noteworthy that the obtained hexanoic acid-rich liquor has been hydrogenated without any further purification treatment, making the entire proposed bio-chemical process simpler and more sustainable. Hydrogenation of crude hexanoic acid has confirmed the promising performances of 5 wt% Re/C, achieving an almost complete conversion of the substrate (~98 mol%) and prevailing selectivity in 1-hexanol (~58 mol%), rather than hexyl hexanoate (~30 mol%), under the previously optimized reaction conditions. According to these results, the novel exploitation of grape pomace for the combined production of 1-hexanol/hexyl hexanoate mixtures to be used as bio-fuels or bio-solvents appears a promising route.

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