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Biomass-derived catalysts: synthesis and characterization of hydrochars and pyrochars

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Abstract

Lignocellulosic biomass is one of the more important renewable sources and it will play a strategic role in many future markets, taking into consideration that a renewable energy share of 32% is binding at the European level by 2030 [1]. Deconstruction of lignocellulosic biomass can be carried out via hydrothermal processes and, among them, hydrothermal carbonization (HTC) represents a versatile process, which promotes the progressively deoxygenation of the biomass, under relatively mild reaction conditions (T up to about 250 °C for 48 h) [2]. This is an environmentally and low-cost treatment, thus resulting suitable for any type of biomass, including wet and waste ones. The obtained solid-rich product, called hydrochar, can be used in a wide range of applications, such as adsorption, energy storage, CO_2 sequestration, catalysis etc. In this last field, within the project PRIN 2020 LEVANTE "LEvulinic acid Valorization through Advanced Novel Technologies" (2020CZCJN7), different hydrochars have been synthesized starting from cellulose and the effects of the main reaction parameters, such as reaction time, temperature and substrate loading, have been investigated employing statistical modelling. The adopted central composite design has allowed us to identify the best reaction conditions (220°C for 5h, with 20 wt% of cellulose loading), in order to maximize both the hydrochar yields and its reactive functionalities. For this purpose, the synthesized hydrochars have been characterized by elemental analysis, SEM, EDS, FT-IR, TGA, whereas the recovered liquid phase has been analyzed by HPLC. Under the selected set of processing parameters, the yield of hydrochars was in the range 38-48 wt%, with a carbon content of 60-70 wt% and corresponding higher heating values amounting to 17-27 MJ/kg, confirming the successful conversion of cellulose into a carbonaceous material. Moreover, Boehm titration has been applied to quantify acidic functional groups, in particular carboxylic, lactonic and phenolic ones, whose amounts increase under more severe reaction conditions. For comparison, the best reaction parameters have been also adopted for the synthesis of hydrochars starting from glucose and xylose as reference model compounds. Finally, on the basis of final applications, also pyrochars have been prepared starting from the optimal hydrochars, working at 600°C with a heating rate of 10°C/min, in order to increase the aromatization degree and the surface areas. All the synthesized hydrochars and pyrochars will be further functionalized and employed, as acid catalysts, for the valorization of levulinic acid, in particular for its conversion to diphenolic acid, in agreement with the objectives of the project LEVANTE.
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Keywords: *hydrochars, pyrochars, levulinic acid*

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