Complete Exploitation of *Eucalyptus nitens*: optimization of hydrothermal conversion of its cellulose fraction to levulinic acid and butyl levulinate

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The fractionation of the structural components of lignocellulosic biomass (cellulose, hemicellulose and lignin) and the valorization of each resulting fraction for specific purposes enable the development of sustainable processes for biomass utilization, according to the perspective of an integrated biorefinery. The purpose of the present work is the complete sustainable exploitation of *Eucalyptus nitens* biomass in the perspective of a circular economy. In this work, *Eucalyptus nitens* ADW (autohydrolysed-delignified sample) wood, obtained from a first autohydrolysis treatment of the starting biomass to remove and exploit hemicellulose and water-soluble extractives, followed by a second step of delignification on the resulting solid through the HCl-catalyzed acetic acid Acetosolv method, was employed. This cellulose-rich feedstock was used for the production of levulinic acid in water and butyl levulinate in *n*-butanol, in both cases by reaction in diluted acid medium. Among biomass-derived products, levulinic acid and butyl levulinate have been identified as important versatile bio-molecules employed for the preparation of fuel additives, fragrances, solvents, pharmaceuticals, plasticizers, polymers, perfumes and flavoring formulations. In the specific case of butyl levulinate, due to its high boiling properties, it finds advantageous applications for blends in diesel-type combustion systems, allowing, as oxygenated diesel alternative, a reduction of soot particle emissions. Starting from *Eucalyptus nitens*, a cheap biomass, in the first part of our research the possibility of levulinic acid production has been evaluated employing microwave heating and diluted HCl as homogeneous acid catalysts. In the second part, the one-pot synthesis of butyl levulinate has been studied and optimized under microwave heating starting from the same *Eucalyptus* species, adopting *n*-butanol as green solvent and diluted H_2SO_4 as homogeneous catalyst. Lastly, the optimized butyl levulinate synthesis has been repeated adopting traditional heating, in order to demonstrate the potential of butyl levulinate production on a larger scale. The effects of the main reaction parameters, temperature, reaction time and acid concentration were investigated and optimized. Under the best reaction conditions, employing microwave irradiation, both target products were obtained with very promising yields: in water, at 180°C after 20 minutes in the presence of HCl, levulinic acid yield accounted for 65 mol%, value higher than those reported in the literature for similar types of ADW biomasses, whereas, in *n*-butanol, at 190°C after 15 minutes in the presence of H_2SO_4, butyl levulinate yield up to 30 mol% together with concentration of 54 g/L were reached, starting from an initial biomass loading of 20 wt%, values never ascertained in the case of butyl levulinate, opening the way towards its real applications.