Levulinic acid production from lignocellulosic biomass using lignin-catalyst

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Developing technologies for converting lignocellulosic biomass to energy, fuels, and value-added chemicals is an important step in making biorefineries a feasible alternative to the current oil-based productive system. In this context, the development of technologies to enable the use of biomass's economic and energy potential is a strategic approach for achieving the sustainability of productive chains, which must undergo a careful evaluation of the environmental, economic, and social impacts. However, various challenges, such as fractionation and separation of lignocellulosic materials, still hamper small- and large-scale biorefineries (Cantero et al., 2019; Mika, Cséfalvay and Németh, 2018). The use of lignocellulosic biomass to produce bioproducts, such as cellulosic ethanol, xylitol, furfural, levulinic acid, lactic acid, butanol, butyric acid, isobutene, biomethane, biohydrogen, among others, will improve the agroindustry sector portfolio and the spread of biorefineries to the rural areas (Bozell et al., 2010; Deutschann and Dekker, 2012; Ravindran and Jaiswal, 2016). Despite advances in research to improve pre-treatment techniques, the recalcitrance of lignocellulosic biomass is how cellulose, hemicellulose, and lignin are strongly associated in the lignocellulosic matrix, still represents a significant challenge for the implementation of biorefineries that are, in fact, economically competitive. Homogeneous systems with mineral acids, although efficient, suffer from problems of product and catalyst separation, reactor corrosion, acid recycling, and wastewater treatment, limiting the sale of levulinic acid and other chemical compounds derived from biomass sugars, when this system is adopted (Alonso et al., 2013; Huang and Fu, 2013). In this context, acidic solid catalysts enter, which are pointed out as suitable alternatives to mineral liquid acids. Its main advantages over homogeneous acid catalysis systems are the absence of corrosion damage, easy separation, and recyclability of the catalysts (Hu et al., 2015; Huang and Fu, 2013). The present work developed a solid carbonaceous acid catalyst based on lignin-based. It is used to convert cellulose to levulinic acid, with the particularity that both reagent and catalyst came from the same raw material – a mixture of straw and sugarcane bagasse in a 1:1 ratio. Sugarcane straw and bagasse are important sources of renewable carbon produced on a large scale in Brazil, and levulinic acid is an important synthetic precursor in the chemical sector that can be obtained through acid catalysis of cellulose. The process described in this work covered the following steps: getting cellulose and lignin by chemical fractionation of the biomass comprised of straw and sugarcane bagasse; incomplete carbonization of the recovered lignin and its subsequent sulphonation with concentrated sulfuric acid to synthesize an acidic solid catalyst and direct conversion of cellulose to levulinic acid via simultaneous hydrolysis and dehydration reactions catalyzed by the solid carbonaceous acid synthesized from lignin. Straw and sugarcane bagasse mixtures (mass ratio 1:1) were pretreated in dry block reactors. The solid/liquid ratio for all tests was 1:20 at 110°C. The optimization of cellulose extraction was made using a 2^2 rotational central composite design varying NaOH concentration (0.2 to 5 % w/v) and reaction time (3 to 117 min). The lignin precipitation was carried out using a 2^2 rotational central composite design testing different pH values (3 to 10) and residence time (6 to 69 min) of the acidified liquor to reach a more quantity of lignin. The solid acid catalysts were synthesized through a step of incomplete carbonization of the lignin followed by a step of sulphonation of the carbonized solid. The 600 ºC and 800 ºC were studied as carbonization temperatures (Tc) in the synthesis of these catalysts. For heterogeneous cellulose catalysis, an amount in grams of the best catalyst obtained was used, equivalent to the normality (N) of the H_2SO_4 solution (2% v/v).

Therefore, 1g of cellulosic pulp, 0.8430 g of catalyst, and 8 mL of distilled water were reacted at 140 °C and solid/liquid ratio of 1:8. Yield calculations were performed based on the equations described in Chen et al. (2019) and Pyo et al. (2020). The chemical characterization of the mixture of biomasses revealed a composition of approximately 42 % cellulose, 26 % hemicellulose, and 28 % lignin. The experimental design for cellulose recovery and lignin removal showed that under relatively mild reaction conditions of 110 °C, 117 min, and solid/NaOH (4.4 % w/v) ratio of 1:20, more than 91 % of the lignin was dissolved into the black liquor, recovering a solid with a cellulose content higher than 78 %. Furthermore, lignin was also fully recovered in the form of the precipitate by simply reducing the pH of the black liquor to 3 (under this condition, 11 g of precipitate were recovered per liter of liquor). With the recovered lignin, it was then possible to synthesize a solid carbonaceous catalyst with a total acid site density of 7.3 mmol/g, which was able to convert up to 17.11 % of the cellulose and obtain yields of up to 38.55 % of levulinic acid when a catalyst/cellulose ratio of only 8:10 (w/w) was applied. Therefore, the process proposed here has the potential to enable the inclusion of levulinic acid, a high-value chemical compound, among the by-products of the national sugar-energy sector, increasing the competitive potential of that sector.

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