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Catalytic conversion of crude carboxylic acid-rich feedstocks into *n*-hexyl esters

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N-hexyl esters originating from short- and medium-chain carboxylic acid sources, are industrially exploitable as solvents, fragrances and food additives [1]. In some cases, the production of these carboxylic acids is still realized by a petroleum-based approach, whilst their production by implementation of new biotechnological routes is gaining ground, to favour their production on the industrial scale. In this context, grape pomace (GP) is an agro-industrial waste originating from the wine manufacturing process, resulting rich in ethanol, which can be advantageously converted into hexanoic acid (HexAc), through an innovative chain-elongation anaerobic fermentation [2, 3]. Remarkably, acid-catalyzed esterification of HexAc with *n*-hexanol (HexOH) provides hexyl hexanoate (HexHex), an ester which can be exploited as oxygenated additive for diesel vehicles [3]. In this work, HexHex synthesis has been optimized starting from commercial compounds (HexAc and HexOH) and sulfonic Amberlyst resin as the acid catalyst, varying temperature, catalyst loading, alcohol/carboxylic acid molar ratio, and including in-situ a drying agent (MgSO₄) to further promote the HexHex production. The optimal reaction conditions were identified (catalyst loading = 0.5 wt%, temperature = 120 °C, time = 4h, HexOH/HexAc molar ratio = 2, MgSO₄ = 5 wt%), achieving a maximum HexAc conversion of about 94 mol%, with a complete selectivity to the target HexHex. Afterwards, the same reaction conditions were applied to the esterification of a real HexAc-rich GP digested crude, which mainly included HexAc (84 wt%), butyric acid - ButAc (11 wt%), achieving a complete conversion to the corresponding *n*-hexyl esters after 4 h. In the second part of this study, the esterification of a crude originating from anaerobic digestion of Organic Fraction of Municipal Solid Waste (OFMSW), was proposed. This aqueous digested crude was more complex, including acetic acid (7 wt%), propionic acid (13 wt%), butyric acid (7 wt%). The esterification reaction between the involved carboxylic acids and HexOH was carried out, working at a constant loading of Amberlyst resin (0.5 wt%) and alcohol/ (sum of) carboxylic acids molar ratio (2 mol/mol). The best operating temperature was identified (110 °C), obtaining promising yields into the corresponding *n*-hexyl esters, e.g. hexyl acetate (59 mol%), hexyl propionate (66 mol%) and hexyl butyrate (51 mol%), within a reasonable time of reaction (after 8 h). The conversion of these waste crudes is strategic, improving the production of short- and medium-chain esters through innovative and sustainable approaches, and will support their industrial development for high-value applications.

Keywords: *n*-hexyl esters, carboxylic acids, anaerobic fermentation, grape pomace, municipal solids

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