Esterification of hexanoic acid to hexyl hexanoate with heterogeneous acid catalysts: preliminary evaluations with Amberlyst and niobium- zirconium-phosphates

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Significance and Relevance

Hexyl hexanoate (HexHex) is an ester of potentially relevant industrial interest, actually exploited as fragrance and lubricant, but also as an oxygenated additive for diesel fuels. It can be synthesised by esterification between hexanoic acid and 1-hexanol, a reaction occurring in the presence of an appropriate Brønsted acid catalyst. In this work, commercial heterogeneous Amberlyst resins and niobium- and zirconium-phosphates, have been tested for the synthesis of HexHex, optimized with the aim of reducing both the catalyst loading and the excess of the alcohol. After univariate screening of the reaction parameters, Amberlyst- A 35 was identified as the most interesting catalyst, identifying the best reaction conditions (catalyst loading: 0.5 wt%, temperature: 120°C, time: 8h, alcohol/acid molar ratio = 2), leading to a maximum hexanoic acid conversion of about 93 mol%, with a complete selectivity to the target ester. This promising achievement encourages further deepening of the kinetic aspects, to further improve its sustainable and clean production for energy uses.

(Preferred topic) Green chemistry and biomass transformation, renewable resources conversion; (2nd choice) Sustainable and clean energy production and transport
Preferred presentation: Only poster

Introduction and Motivations

Esters have great industrial interest, thanks to their various applications (solvents, flavours, lubricants, plasticisers, and biofuels). [1] The esterification reaction is an equilibrium reaction, needing of an appropriate Brønsted acid catalyst to overcome the kinetic issues. Moreover, an excess of the alcohol is generally employed (typically, alcohol/carboxylic acid molar ratio higher than 4), and the removal of the produced water is carried out to maximize its production. [2] In this wide scenario, HexHex is industrially attractive as fragrance and lubricant, but also potentially exploitable as oxygenated additive for diesel fuels. [1] As for other esters, sulfuric acid has been traditionally used to catalyse HexHex synthesis, but mineral acids lead to environmental corrosion and work-up issues. [3] For these reasons, in this work, as a part of PRIN 2022 REFIL, commercial acid resins (Amberlyst), and niobium or zirconium phosphates (NbPO and ZrPO, respectively), were tested for the HexHex production, aimed at improving the economy and the sustainability of this reaction. Further univariate optimization adopting the most performing Amberlyst- A 35 was carried out, reducing the catalyst loading at the best, keeping a low alcohol/carboxylic acid molar ratio (equal to 2). The obtained promising results encourage further deepening of the kinetic aspects of the HexHex synthesis, to further improve its sustainable and clean production for energy uses.

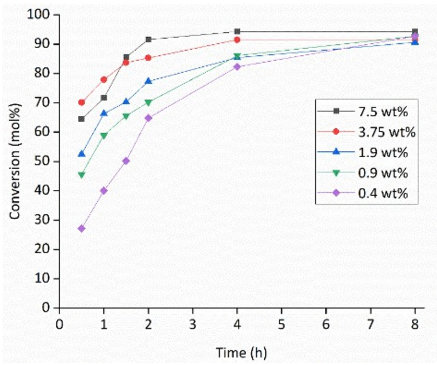
Materials and Methods

Esterification tests were carried out in a 160 mL pressure tube, which was loaded with the reagents and the catalyst (2 g of hexanoic acid, 3.5 g of 1-hexanol and the selected amount of catalyst). Afterwards, the pressure tube was sealed, placed in a thermostated oil-bath, and the reaction slurry was kept under magnetic constant stirring during the entire reaction. The analytical determinations were performed according to our previous work. [1]

Results and Discussion

Preliminary screening evaluations were carried out on the catalysts of interest, univariately changing the temperature (110-130 °C) and catalyst loading (12.0-0.4 wt%). The alcohol/acid molar ratio was kept constant at 2, which represents a good improvement over the available state of the art. [2] First of all, Amberlyst-A 15 (8 wt%) was adopted as the starting acid resin, operating at a temperature of 110°C, achieving the hexanoic acid conversion of about 83 mol% after 2 h and about 89 mol% after 8 h, an achievement which represents a good starting point for further optimization. In an attempt of further improving the substrate conversion and considering the low thermal stability of the Amberlyst-A 15 (maximum operating temperature = 120 °C), the use of more thermally stable Amberlyst-A 35 was considered, working at a higher reaction temperature (120 °C), with the same acidity of the previous Amberlyst-A 15 catalyst (Amberlyst-A 15= 4.7 meq H^+/g_{resin}, Amberlyst-A 35= 5 meq H^+/g_{resin}). Further increase of the temperature from 110 to 120 °C only slightly increased the hexanoic acid conversion from 89 to 94 mol%, and further temperature increase up to 130 °C did not allow any further improvement of the conversion parameter. The effect of the Amberlyst acidity was evaluated, trying to significantly lower the catalyst loading (within the range 7.5-0.4 wt%, corresponding to 2.24-0.20 meq H^+ in the reaction mixture), keeping constant the reaction temperature at 120 °C (Figure 1). The reaction rate slowed down by progressively decreasing the catalyst loading, whereas the plateau of conversion (and yield) was always achieved after 8 h. After having minimized the catalyst loading at the best (0.2 wt%), working at 120 °C, niobium and zirconium phosphates (NbPO and ZrPO, respectively) were tested for the same purpose, exploiting their well-known acidic properties. [4] In this context, the acidity of NbPO and ZrPO was kept constant (0.2 meq H^+ in the reaction mixture), achieving similar conversion data (58 and 60 mol% respectively). Based on these preliminary results, Amberlyst-A 35 was identified as the best catalyst for HexHex production, which encourages further deepening of the kinetic aspects. Further insight about the cheapest and simplest way for entrapping/removing the water of reaction is in progress, before moving towards the conversion of real hexanoic acid-rich feedstocks obtainable from the chain-elongation fermentation of a wide variety of waste biomasses.

Figure 1 Kinetics data for the HexHex synthesis at 120 °C, employing progressively lower catalyst loadings of Amberlyst-A 35.



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