Fully Renewable Diphenolic Acid Production in Batch and Continuous Reactors in the presence of new biomass-derived acid catalysts and LCA assessment of the entire process

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Significance and Relevance

The synthesis of a fully renewable diphenolic acid (DPA) represents a significant step forward as a "*green*" alternative to bisphenol A (BPA) for the production of epoxy resins and polycarbonates. This innovative process integrates levulinic acid (LA), phenol (PhOH) and catalysts derived from lignocellulosic biomass, making the entire production pathway renewable and environmentally friendly. In particular, in the presence of *ad-hoc* char-derived acid catalysts obtained from glucose and xylose, *p,p'*-DPA yields of about 20 mol% were achieved, paving the way for its fully sustainable production.

Preferred and 2nd choice for the topic: 1. Green chemistry and biomass transformation, renewable resources conversion; 2. Circular economy.
Preferred presentation: (Oral only / Oral preferred or Short Oral / Poster): Oral only

Introduction and Motivations

Nowadays, DPA is receiving significant relevance as an environmentally friendly alternative of BPA, due to its structural similarity and reduced environmental and toxicological impact.[1] The *p,p'*-DPA isomer, known for its promising properties, is traditionally synthesized through the condensation reaction between PhOH and LA in the presence of Brønsted acids catalysts, in particular mineral ones.[2] However, this approach leads to significant corrosion and difficult catalyst recycling. On this basis, the use of heterogeneous systems, especially those derived from renewable resources, is becoming crucial and in this context, the PRIN 2020 LEVANTE project aims to synthesize a fully renewable *p,p'*-DPA, in agreement with the principles of green chemistry. In this perspective, lignocellulosic waste biomasses represent promising renewable resources to be transformed into LA (cellulose and hemicellulose fractions) and into PhOH and substituted phenolic derivatives, such as catechol (lignin fraction). Additionally, the use of biomass-derived catalysts offers the opportunity to make the entire DPA synthesis fully renewable.[3] To achieve this goal, new *ad-hoc* acid catalysts were synthesized by sulfonating xylose- and glucose-derived hydrochars and tested for the selective production of *p,p'*-DPA and its derivative *p,p'*-DPAC (the corresponding DPA obtained from catechol) in batch and continuous reactors. The effects of main reaction parameters on the *p,p'*-DPA yield were investigated and optimized for both reactor configurations. Under the best reaction conditions, *p,p'*-DPA yields of about 23 mol% were reached in batch reactor and 12 mol% in continuous one, with ongoing efforts to improve the feasibility of *p,p'*-DPAC production. Simultaneously, a Life Cycle Assessment (LCA) was performed to compare the environmental impacts of this renewable DPA synthesis method with conventional mineral acid-based processes, aimed at the evaluation of the overall sustainability and environmental benefits of this investigated novel approach.

Materials and Methods

Ad-hoc char-derived acid catalysts (HTC-G-S and HTC-X-S from glucose and xylose respectively) were synthesized from glucose and xylose respectively, through a two-step procedure. This required a first hydrothermal carbonization step (HTC), carried out at 220 °C for 5 h with the starting biomass loading of 20 wt%, followed by a sulfonation functionalization carried out employing 15 mL of 96 wt%

H_2SO_4/g char. The synthesized catalysts were characterized by ultimate analysis, FT-IR, SEM, TGA, BET and Brønsted acidity.[3] In batch reactor, the reaction was performed in a pressure tube at 60-100 °C for 24-90 h under solvent-free conditions, whereas the continuous configuration consisted in a packed bed reactor made of stainless steel pipe (outer diameter ¼", length 30 cm) packed with the synthesized catalyst (0.5 g), feeding the LA/PhOH 1:2 solution in ethanol 1:5 via syringe pump. The reaction mixtures were analyzed by High-Performance Liquid Chromatography system, whereas the DPAC product was detected through quantitative Nuclear Magnetic Resonance. LCA analysis was performed adopting a comparative approach within the cradle-to-gate boundaries referring to the production of 1kg of *p,p'*-DPA (functional unit). The SimaPro software was used as the main tool and the ReCiPe method was selected to assess environmental impacts at both midpoint and endpoint level.

Results and Discussion

The synthesized HTC-G-S and HTC-X-S catalysts were preliminarily characterized, revealing an increase of sulfur content, due to the sulfonation treatment (1.23 – 1.13 wt% compared to < 0.1 wt% in the pristine samples), confirming the success of the derivatization procedure. At the same time, a notable increase of acidity (about 30-35 %) was observed, further highlighting their promising use in acid catalysis. Thus, the synthesized HTC-G-S and HTC-X-S catalysts were employed for the DPA synthesis in batch and continuous reactors, monitoring the kinetics (24-72h) at different temperatures and acidities (100 and 120 °C with molar ratio LA/H^+ of 3.4 and 6.8), adopting the LA/PhOH molar ratio of 1:4. These catalysts enabled us to obtain appreciable *p,p'*-DPA yields in batch processes, about 17-23 mol%, with high *p,p'*-DPA/*o,p'*-DPA molar ratios (≥ 16), even at reduced acidity (Figure 1A). These systems also allowed us to achieve *p,p'*-DPA yields between 8 and 12 mol% in continuous reactors. For comparison, the reaction conditions already optimized for PhOH were applied to catechol, thus confirming the effectiveness of the synthesized catalysts for the proposed application and their potential for synthesizing new DPA-derivatives. Finally, the LCA analysis demonstrated that this new process is competitive with traditional methods with strong mineral acids, showing that the use of these heterogeneous catalysts can reduce environmental impacts by enabling catalyst recycling and reuse across consecutive reaction cycles, thus simplifying the purification procedure.

In conclusion, in this research, the synthesis of a fully renewable DPA from biomass has been performed (Figure 1B), adopting a totally eco-sustainable perspective.

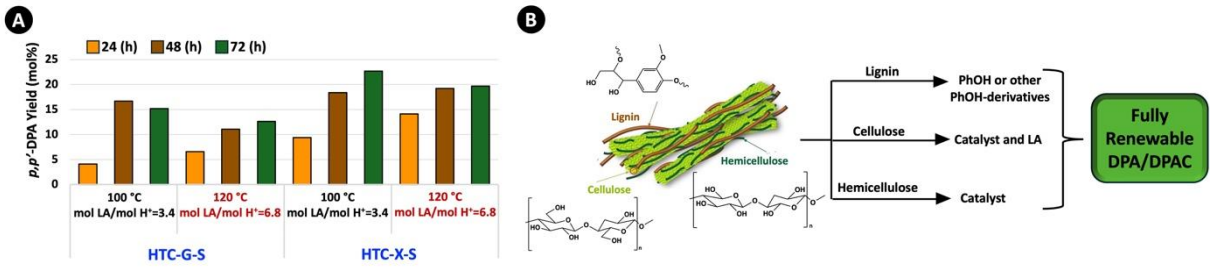

Figure 1 Catalytic results of the DPA synthesis in the presence of HTC-G-S and HTC-X-S catalysts (A) and fully renewable DPA synthesis from biomass (B)

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