Analysis of different methods of olive tree pruning delignification using deep eutectic solvents

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1. Introduction

Olive tree pruning (OTP) is one of the main agricultural residues of the olive oil industry, especially relevant in Mediterranean countries, obtained during the removal of unproductive branches of the tree with the aim of regenerating its leaf mass and improve its production (Díaz et al., 2023). This lignocellulosic biomass has a high lignin content, around 18-20 %, whose valorization in the biorefinery framework is of interest from an environmental, social and economic point of view (Mabrouk et al., 2018).

Lignin is a complex amorphous aromatic polymer formed by three phenylpropanoid units (H-unit, G-unit and S-unit) connected by ether and carbon-carbon bonds (Tocco et al., 2021). It is a low-cost, renewable polymer with high carbon content, high thermal stability, biodegradability and antioxidant activity (Garlapati et al., 2020). These characteristics have allowed the use of lignin in various industrial sectors for the production of biofuels, biomaterials and food products (Gutiérrez-Villanueva et al., 2020).

A biorefinery process is considered cost-effective if the pretreatment carried out allows maximum lignin extraction while preserving or minimizing carbohydrate loss (Jamaldheen et al., 2022). Deep eutectic solvents (DES), due to their excellent physicochemical properties such as high polarity, low toxicity and biodegradability, are considered solvents with high potential for efficient delignification of different lignocellulosic biomasses (Mankar et al., 2021) and, in addition, allow higher or similar extraction yields to conventional pretreatments (Contreras et al., 2023). DES are mixtures of hydrogen bond donor and acceptor species with low melting points.

The objective of this research was to evaluate several OTP delignification processes using DES in the context of a biorefinery.

2. Materials and methods

First, the delignification of OTP using DES composed of cholinium chloride, *p*-toluenesulfonic acid and ethylene glycol (ChCl:*p*TSA:EG) at a ratio of 1:1:9 at 80 °C for 4 hours was studied. Secondly, an aqueous extraction (120 °C, 60 min, 10 % S/L) followed by delignification with DES was applied. Finally, before delignification with DES, OTP was subjected to sequential extraction (aqueous extraction followed by acid pretreatment). Figure 1 shows the scheme followed in the delignification of OTP.

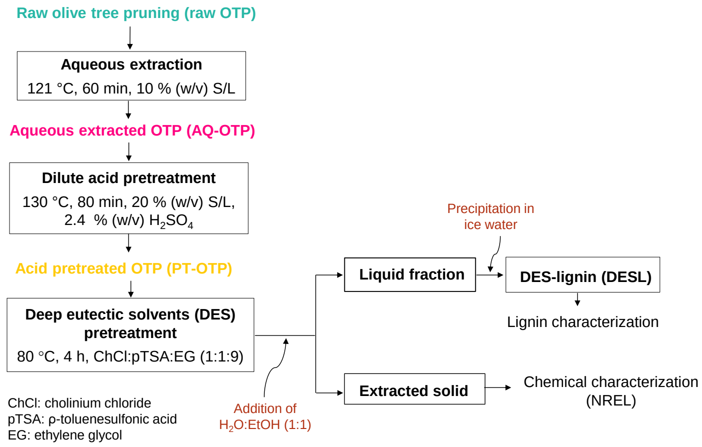

Figure 1. Schematic of the OTP delignification process using deep eutectic solvents

3. Results and discussion

The three processes produced a cellulose-enriched solid and a lignin-rich liquid fraction. The delignification percentages were found to be around 38 %, 39 % and 59 % for the three processes, respectively. The lignins obtained in each process were extensively characterized using several techniques (purity analysis, FTIR, 2D NMR, ^{31}P NMR, elemental analysis, TGA, DSC and GPC). It was observed that the three lignins showed a similar chemical structure with a high content of aliphatic OH groups. However, the lignin obtained only by DES extraction exhibited higher purity (86 %), TPC (760 mg GAE/g lignin) and thermal stability (T_g= 151 ºC) than that of the others.

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