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Abstract

Differences and Similarities of Acid-Extracted Lignin versus DES-Extracted Lignin †

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In recent decades, the circular bioeconomy has been of major global interest. The minimization of biowaste, its recovery and long-term preservation, the closed loops of products, and their socio-economic benefits are the main objectives for a sustainable economy that is friendly to the environment [1]. Brewer's spent grain (BSG) is a valuable source of cellulose, lignin, carbohydrates, and polyphenols, with a high potential for recovery and valorization. In the current study, lignin was extracted from BSG via the classical method (with diluted sulfuric acid solution) and applying deep eutectic solvents (DESs). DESs are of current interest due to their advantages of being biodegradable, easy to remove from the system, eco-friendly, with potential applicability in several fields. The two types of lignin, acid-extracted lignin (AEL) and DES-extracted lignin (DESEL) were quantified and characterized using UV-Vis, gravimetric, and ATR-FT-IR analyses. For the characterization of BSG, the content of the extractable, holocellulose, hemicellulose, cellulose, and lignin were determined. The content of the extractables was determined by the extractables-acetone method [2]; to determine the holocellulose content, the protocol described by Wise was applied, hemicellulose was determined using the protocol applied by Mussatto and team [3], and cellulose was calculated as the difference between holocellulose and hemicellulose. To obtain acid-extracted lignin, the 72% sulfuric acid-based protocol described by Qin and his team [4] was applied. For DES-extracted lignin, a protocol described by Song and team [5] was applied. Two DESs were tested as follows: the first DES (DES1) was prepared from choline chloride (ChCl) as a hydrogen bond acceptor and lactic acid (LA) as a hydrogen bond donor in a molar ratio of 1:2; the second DES (DES2) was formed as a ternary mixture of ChCl and LA (1:2) with water (in a molar ratio of 6.5). Attenuated total reflectance (ATR)–Fourier transform infrared spectroscopy (ATR-FTIR) was used to confirm the formation of DES. Following gravimetric analyses, a lignin content of 9.2% was determined in the BSG substrate and confirmed via spectrophotometric analyses. The extraction capacity of DES1 was 65%, and for DES2, it was 78%. The ATR-FTIR analysis showed changes in some bands belonging to the precursors of DESs, which suggested the formation of hydrogen bonds between the components of DES. The two lignins (AEL and DESEL) presented similar spectra that attested the presence of aromatic structures, single and double bonds (C-O, C=O), sp^3 hybridized C-H bonds, as well as side-attached propenyl groups. By adding a polar solvent (water), the extraction yield of lignin in DES increased from 65% to 78%. DESs can compete with classical solvents in terms of their yield and purity. Between these two lignins, the results showed mostly similarities but also some differences due to the extraction method and the different modes of structural

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rearrangement. By adding a polar solvent (water), the extraction yield of lignin in DES increased from 65% to 78%. DESs can compete with classical solvents in terms of their yield and purity. Between the two lignins, the results showed mostly similarities but also some differences due to the extraction method and the different modes of structural rearrangement.

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