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Insights on the mechanisms of biomass delignification mediated by deep eutectic solvents using lignin model compounds

AUTHORS
André M. DA COSTA LOPES / UNIVERSITY OF AVEIRO/CICECO, COMPLEXO DE LABORATÓRIOS TECNOLÓGICOS, CAMPUS UNIVERSITÁRIO DE SANTIAGO, AVEIRO
Belinda SOARES / UNIVERSITY OF AVEIRO/CICECO, COMPLEXO DE LABORATÓRIOS TECNOLÓGICOS, CAMPUS UNIVERSITÁRIO DE SANTIAGO, AVEIRO
Carmen S. R. FREIRE / UNIVERSITY OF AVEIRO/CICECO, COMPLEXO DE LABORATÓRIOS TECNOLÓGICOS, CAMPUS UNIVERSITÁRIO DE SANTIAGO, AVEIRO
João A. P. COUTINHO / UNIVERSITY OF AVEIRO/CICECO, COMPLEXO DE LABORATÓRIOS TECNOLÓGICOS, CAMPUS UNIVERSITÁRIO DE SANTIAGO, AVEIRO
Armando J. D. SILVESTRE / UNIVERSITY OF AVEIRO/CICECO, COMPLEXO DE LABORATÓRIOS TECNOLÓGICOS, CAMPUS UNIVERSITÁRIO DE SANTIAGO, AVEIRO

PURPOSE OF THE ABSTRACT

Lignocellulosic biomass is a renewable feedstock with increasing potential to be a sustainable alternative to pollutant fossil-based resources [1]. Wood is a noble example of this type of biomass and is composed of three major components, namely cellulose, hemicellulose and lignin. In the current scenario of wood valorisation, cellulose is a target macromolecule to produce pulp, paper, cardboards and novel cellulose-based materials/composites, while hemicellulose and lignin are practically converted into heat and power. Nowadays, the existing energy intensive processes lead to hemicellulose and lignin degradation and their potential of valorisation is undermined [1]. Therefore, the development of more sustainable methods of fractionation and conversion of biomass into added value materials and chemicals is of utmost importance in the frame of the biorefinery concept [2]. A key strategy lies on the application of more selective and benign solvents, in which the use of deep eutectic solvents (DES) stands as a main example.

The application of DES in the processing of lignocellulosic biomass has been attracting attention as innovative and green technology with a high potential to fractionate biomass components at lower cost and with reduced environmental impact than fossil-based technologies. Their capacity to dissolve and extract lignin selectively and to increase lignin quality for a direct application are promising features to achieve higher sustainability [3, 4]. However, the mechanisms behind biomass delignification and lignin depolymerization mediated by DES and the influence of the main variables on such processes are still barely studied.

The present work was focused on understanding the chemistry behind lignin depolymerization using DES and their aqueous solutions. In this context, the ability of these systems to cleave beta-O-4 ether linkages present in a lignin model compound was examined. The structure and acidic nature of each DES influenced the cleavage of ether linkages and the occurrence of further reactions between cleavage products. The results showed that a good solvent for technical lignins, namely PA:U (propionic acid/urea), is not capable to cleave beta-O-4 linkages. This means that a good lignin solvent could be not necessarily effective for the delignification process. On the other hand, LA:ChCl (lactic acid/choline chloride) cleaved beta-O-4 linkages, but also demonstrated to react with hydroxyl groups of lignin model compound through esterification and is followed by side chain polymerization of lactic acid. Among tested solvents, PTSA:ChCl (p-toluene sulfonic acid/choline chloride) demonstrated the highest performance on the cleavage, although the high acidity of this system leaded to extended side reactions. This

limitation can be avoided by changing the acid character of the system and by adding water as well. The present work highlights DES and their aqueous solutions as promising solvents to achieve a selective delignification and, therefore, a sustainable biomass fractionation.

FIGURES

FIGURE 1

FIGURE 2

KEYWORDS

deep eutectic solvents | lignin model compounds | lignin depolymerization | sustainability

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