

PAPER

Novel pre-treatment and fractionation method for lignocellulosic biomass using ionic liquids

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Sara P. Magalhães da Silva,^{a,b} André M. da Costa Lopes,^a Luisa B. Roseiro^a and Rafał Bogel-Lukasik^{*a}

An efficient lignocellulosic biomass pre-treatment is a crucial step for the valorization of these kind of raw materials. Lignocellulosic biomass is a potentially valuable resource for transformation into biofuels and bio-based products. The use of ionic liquids as media for the biomass pre-treatment is an alternative method that follows the green chemistry concept. This work proposes a new methodology for wheat straw pre-treatment with the ionic liquid (IL) 1-ethyl-3-methylimidazolium acetate ([emim][OAc]), which allowed the production of cellulose, hemicellulose and lignin-rich fractions in a rapid and simple three-step fractionation process. Various temperatures (80–140 °C) and processing times (2–18 h) of the pre-treatment were studied. The quantitative and qualitative analysis of each lignocellulosic biomass fraction was determined by FTIR measurements. The glucan content in recovered cellulose-rich fractions was investigated by enzymatic hydrolysis. The cellulose recovery dependence on the pre-treatment conditions was ascertained through regression analysis. The optimal result for the recovery of the cellulose-rich fraction was obtained at 140 °C during 6 h achieving 37.1% (w/w) of the initial biomass loading. For the same conditions, optimal results were also produced regarding the amount of glucan present (81.1% w/w_{biomass}) in cellulose-rich fractions, the carbohydrate enrichment in the hemicellulose fraction (96% wt) and the purity of lignin (97% wt). The recovery of IL was performed after each pre-treatment and the obtained yields were up to 86% (w/w). The recovered ILs were analyzed by ¹³C and ¹H NMR. The presence of value-added phenolic compounds in the recovered ILs was analyzed by capillary electrophoresis. Vanillin and its derivatives, as well as other lignin-based products, were identified.

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1. Introduction

Lignocellulosic biomass from agricultural residues, forestry wastes, waste paper, and energy crops has come under intense research as an alternative to fossil resources, due to their potential as starting materials for the production of biofuels and other value-added products.¹ Moreover, lignocellulosic biomass is a renewable, relatively carbon-neutral source of energy and is readily available.^{2,3}

The lignocellulosic material is composed mainly of cellulose (35–50%), hemicellulose (20–35%) and lignin (5–30%),⁴ wherein the composition variation depends mostly on the species, age and origin of biomass. Cellulose is a water-insoluble homopolysaccharide. Cellulose chains are completely linear and have a strong tendency to form intra- and intermolecular hydrogen bonds, which make cellulose a highly crystalline polymer. In contrast, hemicellulose is a non-crystalline, highly branched, water-insoluble heteropolysaccharide. On the other hand, lignin is an amorphous three-

dimensional polymer of phenylpropane units which are covalently linked to hemicellulose. Cellulose forms a skeleton which is surrounded by other substances forming a matrix (hemicelluloses) and encrusting (lignin) materials.⁵

Due to the complex structure of lignocellulosic materials, several pre-treatment technologies are currently employed to overcome this recalcitrance against chemical and microbial attack. Hence, the pre-treatment step is a key process in the biorefinery to convert lignocellulosic biomass into low-value high-volume fuels and high-value low-volume chemicals.⁶ The pre-treatment methods can be divided according to various criteria.^{7,8} Among these criteria, pre-treatments can be conventional^{9,10} or alternative, such as the pre-treatment with ionic liquids.¹¹

Ionic liquids (ILs) are salts usually composed of a large organic cation and an organic or an inorganic anion. The low lattice energy between cation and anion leads to a low melting point, usually below 100 °C.¹² These novel solvents possess interesting properties over molecular organic solvents, such as a negligible vapor pressure, high conductivity and thermal stability,¹³ high solvating capacity for either polar or nonpolar compounds.^{14–17} Due to a large number of possible cationic

^aLaboratório Nacional de Energia e Geologia, Unidade de Bioenergia, Lisboa, 1649-038, Portugal. E-mail: rafal.lukasik@lneg.pt; Fax: +351217163636; Tel: +351210924600 ext. 4224

^bUniversidade de Aveiro, Departamento de Química, Aveiro, 3810-193, Portugal