



Pre-treatment of lignocellulosic biomass using ionic liquids: Wheat straw fractionation



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HIGHLIGHTS

- An innovative method of biomass pre-treatment using [emim][CH₃COO] was developed.
- The valorization of biomass by the high purity biomass fraction samples.
- Enzymatic hydrolysis showed high purity cellulose fractions.
- Recovery and reuse of IL in a new pre-treatment process.

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ABSTRACT

This work is devoted to study pre-treatment methodologies of wheat straw with 1-ethyl-3-methylimidazolium acetate ([emim][CH₃COO]) and subsequent fractionation to cellulose, hemicellulose and lignin. The method developed and described here allows the separation into high purity carbohydrate and lignin fractions and permits an efficient IL recovery. A versatility of the established method was confirmed by the IL reuse.

The fractionation of completely dissolved biomass led to cellulose-rich and hemicellulose-rich fractions. A high purity lignin was also achieved.

To verify the potential further applicability of the obtained carbohydrate-rich fractions, and to evaluate the pre-treatment efficiency, the cellulose fraction resulting from the treatment with [emim][CH₃COO] was subjected to enzymatic hydrolysis. Results showed a very high digestibility of the cellulose samples and confirmed a high glucose yield for the optimized pre-treatment methodology.

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1. Introduction

The biorefinery concept integrates conversion processes and equipment to produce fuels, power and chemicals from biomass, such as lignocellulosic biomass. The implementation of the biorefinery concept is challenging due to technological limitations and thus an economic feasibility of such industries is still questionable. Besides a large generation of energy and biofuels, production of value added products from lignocellulose processing is a key aspect towards an economic sustainability of biorefineries.

Lignocellulose is essentially represented as hardwood, softwood, grasses, agricultural and forest residues, domestic and municipal solid wastes, and food industry residues. These

materials are mainly composed of cellulose, hemicellulose and lignin that form a complex and intricate structure. Cellulose, a semi-crystalline fibrous, linear and unbranched homopolymer of β-D-glucopyranose with cellobiose as the repeating unit and hemicellulose, an amorphous, branched heteropolysaccharide, build up the carbohydrate fraction. Lignin is a very complex and amorphous phenylpropanoid polymer. In the valorisation processes of lignocellulosic biomass, cellulose and hemicellulose are mostly hydrolysed to sugar monomers and subsequently converted into alcohols (ethanol, butanol), hydrogen or methane by fermentation processes, on biochemical platforms. Apart from biofuel and energy production, cellulose can be used to produce valuable products, such as hydroxymethylfurfural (HMF) (Zakrzewska et al., 2011). Hemicellulose can also serve as raw material for products with value added, such as xylitol or advanced fuels (Girio et al., 2010). The isolated lignin is required not only for the production of heat or

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fuel but also for manufacturing of several commodities, such as binders, dispersants, emulsifiers and sequestrants, polyurethane and polyesters (Bonini et al., 2005).

An efficient deconstruction of biomass is a path towards a full exploitation and valorisation of lignocellulosic biomass. However, recalcitrance of lignocellulose is a large obstacle to be overcome and none of the currently known pre-treatment processes is highly selective and efficient for a satisfactory and versatile use. Therefore, among alternative pre-treatment technologies studied broadly, one is focused on the ionic liquid application.

Ionic liquids (ILs) are characterized as molten salts with low melting point (below 100 °C). ILs are constituted solely by a large asymmetric organic cation and a polyatomic organic or inorganic counterion. ILs demonstrate a great variety of physico-chemical properties among which the most characteristic are high polarity, great thermal stability (even above 300 °C), high conductivity and large electrochemical window, great solvent power, negligible volatility and non-flammability (Zhang et al., 2006). The toxicity and biodegradability of ionic liquids are also studied extensively and large set of data are already available in literature (Coleman and Gathergood, 2010). Due to immeasurable combinations of cations and anions that can form ILs, ILs are often called designer solvents.

In the last decade, innumerable studies, focused on the dissolution of biogenic polymers in ILs, demonstrated a great potential of ILs as solvents (Swatloski et al., 2002). Cellulose was one of the most studied biopolymers exhibiting a high solubility in a variety of ILs (Zakrzewska et al., 2010). Afterwards, the use of ILs to dissolve lignocellulosic biomass gained an increasing interest in the scientific community. Several trials were performed demonstrating good dissolution power of certain ILs for lignocellulose (Fort et al., 2007; Singh et al., 2009). In fact, the ability of ILs to dissolve carbohydrates and lignin is considered as an effective disruption of the intricate network of non-covalent interactions between these polymers (Swatloski et al., 2002).

Nowadays, extraction and processing of carbohydrates and other compounds from lignocellulosic biomass using ILs have been explored intensively (Abe et al., 2010; Lee et al., 2009; Sun et al., 2009; Yang et al., 2013). Generally, pre-treatment with ILs assumes processing of the biphasic mixture (lignocellulosic material and IL at the determined solid/liquid ratio) at a certain temperature and period of time. Such dissolution can be partial or complete, although complete biomass dissolution improves an efficiency of the treatment. After the dissolution, regeneration of biomass with an addition of an antisolvent, such as water, acetone, dichloromethane, and acetonitrile is performed (Fort et al., 2007). The regenerated biomass fraction demonstrates to be composed essentially by carbohydrates, while lignin appears to be partially extracted in the IL/antisolvent mixture (Lee et al., 2009; Sun et al., 2009). The pre-treatment efficiency is dependent on IL, lignocellulosic biomass (type, moisture, size and load), temperature, time of pre-treatment and antisolvent used (da Costa Lopes et al., 2013). Until now, [emim][CH₃COO] seems to be the most suitable IL for the pre-treatment of lignocellulosic biomass, once it presents good solubility properties for these materials. Pre-treatment with ILs demonstrated to offer advantages over conventional methods allowing to: (i) alter physicochemical properties of the biomass macromolecular components, such as a reduction of lignin content (Lee et al., 2009) (the lignin content affects the biomass properties) and cellulose crystallinity (Doherty et al., 2010); (ii) extract a specific macromolecular component, such as isolation of lignin (Tan et al., 2009) and cellulose (Abe et al., 2010); (iii) perform different fractionation approaches after biomass dissolution in ILs (Dibble et al., 2011; Lan et al., 2011; Yang et al., 2013).

The use of ILs as a tool for biomass fractionation exhibits a great potential to maximize the recovery of biomass and simultaneously

to add value to the fractionated components within the biorefinery concept. In a recent fractionation approach cellulose, hemicellulose and lignin were obtained separately as solid fractions (Lan et al., 2011). The sugarcane bagasse pre-treatment was performed with 2% (w/w) of sugarcane bagasse at 110 °C for 4 h. The complete dissolution of biomass in [bmim][Cl] was achieved and followed by an addition of acetone/water (9:1, v/v) as antisolvent. Acetone soluble lignin was extracted to the liquid stream whereas cellulose, hemicellulose and alkaline lignin were fractionated from the regenerated solid fraction using a 3% (w/w) NaOH solution and ethanol as selective solvents.⁴⁰ Results demonstrated to be promising as fractions of high purity were obtained. Therefore, not only the pre-treatment step of biomass but also the performance of a subsequent and successful fractionation is of utmost importance for the biorefinery concept.

The aim of this work was to develop a new fractionation methodology using [emim][CH₃COO] as a pre-treatment agent (Fig. 1 in ESI). The fractionation approach was optimized based on three previously published works (Lan et al., 2011; Sun et al., 2009; Tan et al., 2009) and focused on a maximal exploitation of wheat straw biomass. The developed method is beneficial due to the separation of high purity cellulose, hemicellulose and lignin fractions obtained accompanied by a high IL recovery. The effect of the pre-treatment on cellulose crystallinity was evaluated by FTIR measurements. Additionally, in order to verify the potential for the further applicability of the obtained carbohydrate-rich fractions as well as to evaluate the pre-treatment efficiency, the cellulose-rich fractions were subjected to enzymatic hydrolysis.

2. Experimental

2.1. Materials

Wheat straw was supplied by Estação Nacional de Melhoria de Plantas (Elvas, Portugal). The feedstock material was grounded with a knife mill IKA® WERKE, MF 10 basic (Germany) to particles smaller than 0.5 mm, homogenized in a defined lot, and stored in plastic containers at room temperature. The dry matter content was 92 % (w/w) (Carvalho et al., 2009).

[Emim][CH₃COO] with stated purity >95% was purchased from Io-li-tec GmbH – Heilbronn, Germany. IL was prior to use in the pre-treatment dried under vacuum (0.1 Pa) at room temperature for at least 24 h. The water content in IL was 2800 ppm and was determined by a volumetric Karl-Fischer titration.

In pre-treatment experiments the following reagents were used: 0.1 M and 3% (w/w) NaOH aqueous solutions prepared from NaOH pellets (99% purity) supplied by Eka Chemicals/Akzonobel – Bohus, Sweden, 1 M and 4 M HCl aqueous solutions prepared from fuming HCl 37% (w/w) with a purity grade for analysis (Merck – Darmstadt, Germany). Ethanol 96% (v/v) and acetonitrile of HPLC-gradient purity for analysis (Carlo Erba Group – Arese, Italy) and acetone (98% purity) was supplied by Valente & Ribeiro, Ltda – Belas, Portugal. For the preparation of NaOH and HCl solutions distilled water (17 M Ω cm⁻¹) and ultrapure water (18.2 M Ω cm⁻¹) both produced by the PURELAB Classic of Elga system were used. For filtration, paper and glass microfiber filters (Whatman GE Healthcare Bio-Sciences Corp. – Piscataway, NJ, USA) and nylon filters, 0.45 μm HNPW (Merck Millipore – Billerica, MA, USA) were used.

Acid hydrolysed wheat straw (130 °C, 150 min and 1.5% H₂SO₄), with known composition (62.6% glucan, 29.9% lignin, 7.5% ash and others content) (Carvalho et al., 2009) was used for the construction of FTIR calibration curves. All FTIR samples were prepared with KBr (>99% trace metals basis) purchased from Sigma-Aldrich Co. (St. Louis, MO, USA). The cellulose used

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