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Study of the influence of reutilization ionic liquid on lignin extraction

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The development of green techniques for biomass processing and fractionation is crucial from the point of view of sustainability and environmental protection. Lignin is the second most abundant biorenewable material on Earth and ionic liquids are developed as green solvents because of their reutilization possibility and low vapour pressure. In this work, the recyclability of methylsulphate 1-butyl-3-methylimidazolium ionic liquid on the extraction of lignin from biomass was studied. The experimental results showed that the obtained lignins were similar until the third cycle and the extraction process showed good performances, whereas in the fourth cycle it appeared ionic liquid contamination on the lignin and the performance decreased dramatically.

1. Introduction

The efficient utilization of biomass is becoming increasingly important due to diminishing resources of fossil fuels as well as global warnings caused by greenhouse gas emissions (Kilpeläinen et al., 2007). Lignocellulose is the most abundant renewable material produced from biomass photosynthesis, it has a yearly supply of approximately 200 billion metric tons worldwide (Zhang et al., 2007). Lignocellulosic materials are renewable resource with an enormous potential for developing a bio-based economy centred in the production on chemical, materials and commodities complying with the principles of green chemistry and sustainable development, to replace the obtained products from the fossil oils (Peleteiro et al., 2014). Lignocellulose consists mainly of plant cell wall materials; it is a complex natural composite with three main biopolymers: cellulose (50%), hemicelluloses (25%) and lignin (25%) (Z. Fang and C. Fang, 2008). Lignocellulose structure and compositions vary greatly, depending on plant species, plant parts, growth conditions, etc (Zhang et al., 2007).

Lignin is a phenolic polymer built up by oxidative coupling of three major C6-C3 (phenylpropanoid) units, namely, syringyl alcohol, guaiacyl alcohol and *p*-coumaryl alcohol, which form a randomized structure in a three dimensional network inside the cell wall (García et al., 2009). In chemical pulping processes, around 100 million tons per year lignin arises as a by-product, most of which is burned to generate energy and to recover inorganic chemicals. Only a very small fraction of the lignin (ca. 1.2%) is utilized as material in industrial processes. It is necessary to purify lignin obtained by traditional methods, in order to obtain revalorized products. Due to its aromatic structure, lignin offers several applications. Therefore, there is an increasing demand for new processes that could provide new ways to use this resource in a more efficient manner, not only as fuel but also as starting material for chemical industry with the aim of producing commodity and fine chemicals (Kilpeläinen et al., 2007). The diversity of functional groups presented in lignin allows its use as dispersant in cement and gypsum blends (Yang et al., 2007), as emulsifier or chelating agent for removing heavy metals from industrial effluents (Sena-Martins et al., 2008).

Room-temperature ionic liquids (IL) are receiving much interest owing to their characteristics as environmentally friendly solvents for a range of chemical processes both for catalysed and uncatalysed reactions, or as possible constituents in electrochemical applications. Thus, molecular designs, synthesis and characterization of ILs have been the focus of many recent scientific investigations. Their unique properties like a large liquid state range, a very low vapour pressure and high thermal, chemical and electrochemical stability promise a wide applicability. Their properties can be adjusted by choosing specific combinations of cations and anions (Nockemann et al., 2005). Moreover, ionic liquids are recyclable and environmentally compatible and can alleviate environmental pollution (Wang et al., 2014).

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One of the main advantages of the ionic liquids is that are easily recovered and reutilized, so it is reduced the amount of wastes generates on a process. The combination of the reutilization with their low volatility is the reason why ionic liquids are considered as green solvents (Anastas et al., 2010). Their designation as green solvents is related principally to their negligible vapour pressure and not on the knowledge that they interact benignly to humans or the environment (Dharaskar et al., 2015).

The application of ionic liquid in polymer material is based on their good solubility on water and some organic solvents, as ethanol, acetone, so ionic liquid is used as solvent and water as coagulation agent (Liu et al., 2008). After coagulation of the polymer, the ionic liquid can be use as solvent again, for several cycles until saturation, and then further purification techniques are needed, as nanofiltration or ion exchange (Anastas et al., 2010).

There are in the literature several examples about ionic liquids reutilization and their behaviour; Formentín et al. (2004) used butyl methyl imidazolium hexafluoro phosphate [Bmim][PF_6] as solvent for Knoevenagel reaction with good yields until cycle 3, [Bmim][PF_6] was also used as solvent in Claisen Schmidt condensation with good yields until cycle 3 (Formentín et al., 2004), in addition, Wong et al. (2006) used ionic liquids in the Suzuki reaction with different results depending on the used co-solvent until cycle 14.

Several studies have reported the use of IL for dissolving partially or totally the lignocellulosic biomass. Rocha et al. (2014) have reported that protic ionic liquid bis(2-hidroxyethylammonium) acetate, 2-HE2AA could be used as biomass pretreatment for ethanol production.

It has been shown that some IL (such as 1-butyl-3methyl- and 1-allyl-3-methylimidazolium chloride, [Bmim][Cl] and [Amim][Cl], respectively) can effectively dissolve biopolymers (Sun et al., 2009). [Bmim][Cl] and [Amim][Cl] can also dissolve different types of lignin samples (Kilpeläinen et al., 2007; Pu et al., 2007). Lignin is also dissolved by 1,3-dimethylimidazolium methylsulfate, 1-butyl-3-methylimidazolium methylsulfate ([Bmim][$MeSO_4$]) and 1-hexyl-3-methylimidazolium trifluoromethane sulfonate (Tan and Macfarlane, 2009), the solubility of the lignin on the ionic liquid is based in the sulphate anion more than in the cation, as it was reported by Brandt et al. (Brandt et al., 2013).

Microwave techniques in synthetic chemistry often elicit a dramatic increase of the reaction rate and yields, and the decrease of reaction times. It is considered a greener technique, because, microwaves deliver an efficient use of energy. The ionic liquids transform microwave radiation into heat very fast due to their high ionic conductivity (Kappe et al., 2009) in addition the microwaves affect directly the solvent which enhanced the effectiveness of the energy transference.

In this work, the lignin was obtained by [Bmim][$MeSO_4$] directly from *Malus domestica*. The influence of the reutilization of ionic liquid on the obtained lignin structure was evaluated. In addition, the number of cycles of reutilization of ionic liquid without further purification was studied. The obtained lignins and ILs were characterized and compared.

2. Materials and methods

Apple tree pruning (*Malus domestica*), provided by a local farmer in the area of Guipuzkoa (Spain) was used as raw material, [Bmim][$MeSO_4$] ionic liquid was provided by Sigma Aldrich, and H_2SO_4 was provided by Scharlab.

The raw material was grinded and sieved to a homogeneous shape. Then, it was subjected to ionosolv process in order to extract the lignin selectively. Lignin was isolated from raw material by ionosolv process with [Bmim][$MeSO_4$] enhanced by microwave radiation.

The main objective of the study was to recover and reuse the IL several times, in order to evaluate the efficiency of the reutilization of the ionic liquid on the process yield. The scheme of the process is described in Fig. 1.

In order to determine the behaviour of the IL on the different cycles, it is very important to analyse and characterize the different products obtained in all the cycles, to be sure that the process is reproducible. For this reason the raw material was characterized by the TAPPI standards, lignin was characterized by ATR-Ir, TGA, HPSEC, py-GC-MS and the IL was characterized by TGA, ATR-Ir and NMR spectroscopy.

2.1. Analysis of the raw material

Characterization of apple tree pruning (*Malus domestica*) fibres was done according to standard methods (TAPPI, 2007). Moisture content (8.80 ± 0.03%wt) was determined after drying the samples at 105 °C for 24 h (TAPPI T264 om-97). Chemical composition, given on an oven dry weight basis, was the following: 3.2 ± 0.2% ash (TAPPI T211 om-93), 16.7 ± 0.2% hot water soluble matter (TAPPI T207 om-93), 32.0 ± 0.5% aqueous NaOH soluble matter (TAPPI T212 om-98), 10.7 ± 0.5% ethanol-benzene extractives (TAPPI T204 om-97), 26.15 ± 0.09% lignin (TAPPI T222 om-98), 57 ± 1% holocellulose (Wise et al., 1946) and 27.3 ± 0.2% α-cellulose (Rowell, 1983).

2.2. Ionosolv process

Ionosolv process was carried out following the conditions studied before (Prado et al., 2013). Raw material was mixed with [Bmim][$MeSO_4$], in a solid:liquid mass ratio 1:10, under microwave radiation, maximum power of 30 W, for 3 min at 180 °C on a CEM microwave Discover system model. The lignin was precipitated from the black liquor by adding acidified water at pH 2 achieved by adding H_2SO_4 solution. Then the liquor was centrifuged at 5000 rpm for 15 min. Precipitated lignin was separated, washed with acidified water and dried at 50 °C in an oven.

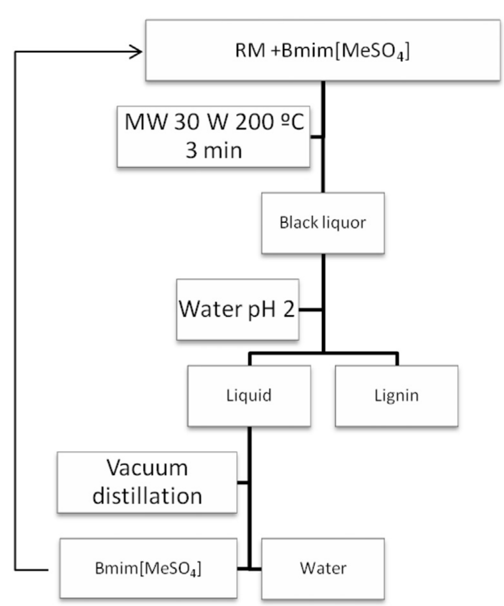

Fig. 1. Scheme of the process.