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Study of the Influence of Reutilization of Ionic Liquid for 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 bio-renewable material on Earth. Ionic liquids are considered as green solvents due to their low vapour pressure and their reuse possibility. In this work, the recyclability of Methyl sulphate Butylmethylimidazolium ionic liquid on the obtaining 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, obtained lignin was contaminated by ionic liquid and the performance of ionic liquid 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). Lignocelluloses is the most abundant renewable material produced from biomass photosynthesis, has a yearly supply of approximately 200 billion metric tons worldwide (Zhang et al., 2007). 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 %) (Erdocia et al., 2012)

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 are produced as byproduct, most of which is burned to generate the energy required by the process. Only a very small fraction of the lignin (ca. 1.2 %) is used as material in industrial processes. The revalorisation of lignin obtained by traditional methods requires several treatments prior to its use for materials application or for building blocks obtaining. 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).

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 range, 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).

One of the main advantages of the ionic liquids is that they are easily recovered and reutilized, so it is reduced the amount of wastes generated 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).

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The application of ionic liquid in polymer material is based on their good solubility on water, 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 used 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 the 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 (Fomentín 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.

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 (Kilpeläinen et al., 2007); and [amim]Cl are also able to dissolve different types of lignin samples (Pu et al., 2007). In addition, lignin is dissolved by 1,3-dimethylimidazolium methylsulphate, 1-butyl-3-methylimidazolium methylsulphate (Bmim[$MeSO_4$]) and 1-hexyl-3-methylimidazolium trifluoromethanesulphonate (Tan and Macfarlane, 2009), the solubility of the lignin on the ionic liquid is based in the sulphate anion more than in the cation.

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.

2. Material and methods

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

Lignin was isolated from raw material by ionosolv process with Bmim[$MeSO_4$] enhanced by microwave radiation. The IL was reused several times, in order to evaluate the efficiency of the reutilization of the ionic liquid on the process yield.

2.1 Analysis of the raw material

Characterization of apple tree pruning (Malus domestica) fibres was done according to standard methods (TAPPI, 2008). Moisture content (8.80 ± 0.03 % wt) was determined after drying the samples at 105 ºC 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 ºC 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 5,000 rpm for 15 min. Precipitated lignin was separated, washed with acidified water and dried at 50 ºC in an oven.

To recover the ionic liquid, the liquid phase was vacuum distilled in order to eliminate the water and dried at 105 ºC in the oven for 16 h in order to achieve moisture < 2.5 %.

The whole process was repeated reutilizing ionic liquid until saturation.

2.3 Lignin characterization

All lignin samples were characterized by attenuated-total reflectance infrared spectroscopy (ATR-IR) by direct transmittance in a single-reflection ATR System (ATR top plate fixed to an optical beam condensing unit with ZnSe lens) with an MKII Golden Gate SPECAC instrument. Spectrums data was 30 scans in a range of 4,000-700 cm^{-1} and resolution of 4 cm^{-1}.

Thermogravimetric analysis (TGA) of lignin was carried out under nitrogen atmosphere using a Mettler Toledo TGA/SDTA RSI analyser with a dynamic scan from 25 to 800 ºC at 10 ºC min^{-1}.

The purity of lignin samples was determined based on modified TAPPI standards (T222 om-83 and T249 cm-85). Each dry lignin sample was pre-hydrolysed for 1 h with 72 % v/v sulphuric acid in a thermostatic bath at 30 ºC. Then deionised water was added in order to dilute samples up to 4 % sulphuric acid. Samples were then hydrolysed for 3 hours at 100 ºC, and afterwards ice cooled. The acid insoluble fraction of lignin samples (Klason lignin) was separated by filtration (glass microfiber filters MFV3, Filter-

Lab Inc.), washed with deionised water until neutral pH and oven-dried at 105 ± 3 ºC. The Klason lignin content of each sample corresponded to the acid insoluble fraction gravimetrically determined. From each experiment, the resulting hydrolysates were reserved for the subsequent monosaccharide content and acid soluble lignin (ASL) determination. In order to determine the content of sugars in lignin samples, the filtered solutions were characterized by High Performance Liquid Chromatography (HPLC) Jasco LC-Net II /ADC equipped with a photodiode array detector, refractive index detector and Rezex ROA_Organic Acid H^+ (8 %) column. As mobile phase, dissolution of 0.005 N H_2SO_4 prepared with 100 % deionised and degassed water was used (0.35 mL min^{-1} flow, 40 ºC and injection volume 20 µL). High purity xylose, glucose, galactose, mannose and arabinose purchased from Sigma–Aldrich were used for calibration. A linear calibration ($R^2 > 0.999$) was obtained for all sugars.

Lignins were subjected to High Performance Size Exclusion Chromatography (HPSEC) to evaluate lignin molecular weight (MW) and molecular weight distribution (MWD) using a JASCO instrument equipped with an interface (LC-NetII/ADC) and a reflex index detector (RI-2031Plus). Two PolarGel-M columns (300 x 7.5 mm) and PolarGel-M guard (50 x 7.5 mm) were employed. Dimethylformamide + 0.1 % lithium bromide was the eluent. The flow rate was 0.7 mL min^{-1} and the analyses were carried out at 40 ºC. Calibration was made using polystyrene standards (Sigma-Aldrich) ranging from 266 to 70,000 g mol^{-1}.

2.4 Ionic liquid characterization

In order to determine the influence of the process on the nature of the ionic liquid and elucidate how the chemical structure of the Bmim[$MeSO_4$] was affected ATR-IR spectra and NMR spectra were recorded at 30 ºC on a Bruker Avance 500 MHz equipped with a z-gradient BBI probe. Typically, 40 mg of sample were dissolved in DMSO-d_6. The spectral widths were 5,000 and 25,000 Hz for the ^1H and ^{13}C dimensions, respectively.

3. Results and discussion

In Table 1 is shown raw material dissolution yield (RMY) and extracted lignin yield (LIGY). It was observed that the raw material was not totally dissolved, and the RMY was a bit lower in the cycle 4. It was observed that the recovery of IL was about 90 % in all cycles, due to the viscosity of the ionic liquid was very hard to recover the 100 % of it because it remains stitched to the biomass and the walls of the reactor. The LIGY increased until cycle 3 and then decreased considerably. The mechanism of dissolution of lignin with ionic liquid was done with a link which was broken with the addition of water that acted as antisolvent because the affinity of the Bmim[$MeSO_4$] with water is higher than with lignin. However, this process was not quantitative, part of the lignin remained linked to the Bmim[$MeSO_4$], so the Bmim[$MeSO_4$] used in the second cycle was not totally lignin free, this fact leaded to an increment in the recovery of lignin in the following cycles, until cycle 4 where the behaviour changed completely.

It was observed that the lignin purity was very similar in the 3 first cycles and total sugar content was negligible (Table 1). This fact could mean that the obtained lignin in the 3 first cycles was similar, in any case, to confirm this fact more extensive characterization was needed. For the cycle 4, it was not possible to measure the lignin purity because of the characteristics of the sample.

Table 1: Reaction yields and lignin purity

%	RMY	LIGY	Lignin purity	Sugar content
Cycle 1	53±6	18.84±0.02	92±2	<DL
Cycle 2	48±5	25.1±0.1	93±2	<DL
Cycle 3	53±8	32.8±0.3	93±1	0.7±0.1
Cycle 4	38±4	15.24±0.01	---	---

ATR-IR spectra of the lignins isolated in the fourth cycles were recorded (Figure 1). In these spectra following typical lignin structures could be identified: aromatic skeletal vibrations (1,597, 1,513 and 1,456 cm^{-1}), syringyl ring breathing with C-O stretching (1,327 cm^{-1}), C-H in plane deformation in guaiacyl ring and syringyl ring (1,113 cm^{-1}), C-H in plane deformation in guaiacyl ring and C-O deformation in primary alcohol (1,033 cm^{-1}) and aromatic C-H out of plane deformation (823 cm^{-1}). Other structures were also determined: OH- stretching (3,450 cm^{-1}), C-H stretching in methyl and methylene groups (2,927 and 2,852 cm^{-1}), carbonyl stretching in un-conjugated ketones and conjugated carboxylic groups (1,704 cm^{-1}), -OH deformation (1,201 cm^{-1}), C-O-C asymmetric vibration (1,165 cm^{-1}) and =C-H out of plane deformation (1,002 cm^{-1}) (Garcia et al., 2011) it was observed that for the cycles 1 to 3, the lignins showed the same characteristic bands, while the intensity and definition of the bands decreased considerably for the lignin in cycle 4; even the bands at 1,002 and 1,033 cm^{-1} were coupled to a single band at 1,025 cm^{-1}.

ATR-IR spectra of the Bmim[$MeSO_4$] ionic liquid utilized in the fourth cycles was compared with pure ionic liquid (Figure 1). In these spectra following typical $Bmim^+$ structures were identified: stretch vibrational mode of CH in the imidazolium ring (3,147 cm^{-1}), stretch vibrational mode of CH in the imidazolium ring (3,103 cm^{-1}), stretching of the CH_3 of the butyl chain attached to the imidazolium ring (2,960 cm^{-1}), stretching of the CH_2 of the butyl chain attached to the imidazolium ring (2,875 cm^{-1}), in plane C-C and C-N stretching vibrations of the imidazolium ring (1,574 cm^{-1}), symmetrical CH vibration of imidazolium ring (1,221 cm^{-1}), in plane –C-H deformation vibration of imidazolium ring (1,169 cm^{-1}), in plane wagging vibrations of alkyl chain (1,059 cm^{-1}) and C-H in plane vibration of imidazolium ring (856 cm^{-1}) (Jeon et al., 2008). Other structures were also determined: SO_3-OMe stretching (1,338 and 1,385 cm^{-1}) (Pretsch et al., 2000) and C=C out of plane deformation (1,009 cm^{-1}). The intensity of the bands at 856 and 1,221 cm^{-1} increased and it were displaced to lower wave-number. This could be due to lignin contamination since it presented characteristic bands at 823 and 1,201 cm^{-1} as it was observed in the Figure 1. The intensity of the band at 1,059 cm^{-1} increased and finally in the cycle 4 it was coupled with the band at 1,009 cm^{-1}.

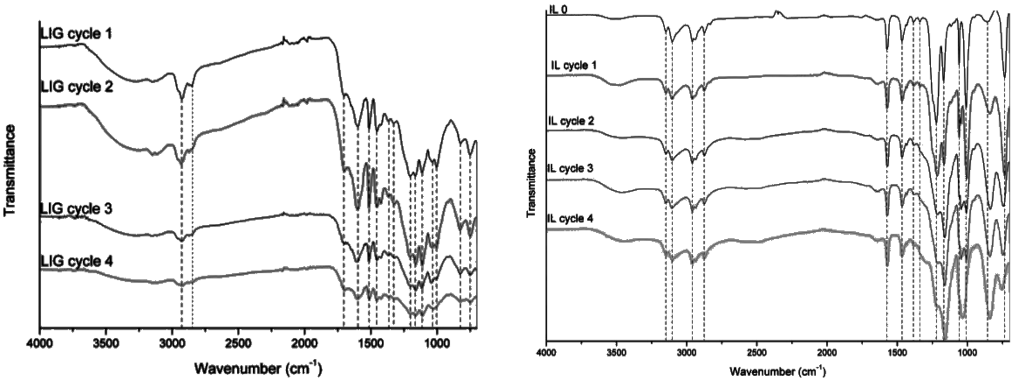

Figure 1: ATR-IR spectra of a) lignins and b) Bmim[$MeSO_4$]

The obtained lignins of consecutive processes RM* were subjected to HPSEC analysis in order to obtain the MW and MWD of different lignins obtained by Bmim[$MeSO_4$] pulping. The results of MW average (*MW*), Mn average (*Mn*) and polydispersity are shown in Table 2. This behaviour indicated that the *MW* were similar for the 3 first cycles as it is shown in the Table 2, whereas in the cycle, 4 decreased considerably. Otherwise, in Table 2 it was also observed that the *Mn* and polydispersity were similar into the three first cycles. However, in the fourth cycle decreased considerably (Hage et al., 2009). It indicated that lignins obtained in first three cycles were similar, but the 4 cycle lignin was completely different.

Table 2: Molecular weight results

Sample	*MW*	*Mn*	Polydispersity
LIG cycle 1	15,503	1,756	8.83
LIG cycle 2	13,186	1,384	9.53
LIG cycle 3	15,549	1,631	9.54
LIG cycle 4	4,382	879	4.99

The thermogravimetric analysis is widely used to study how the organic polymers decompose. It was observed in the Table 3 that all samples showed a weight loss behind 100 ºC, which was corresponded to moisture of the samples. The weight loss around 150-260 ºC corresponded to hemicelluloses fraction degradation, and the weight loss between 260 and 400 ºC corresponded to lignin fraction degradation (Sun et al., 2000). The lignin degradation occurs in two steps due to its complex structure, it was observed in the Table 3 that the lignins of the cycles 1, 2 and 3 showed a narrow peak and a shoulder between 300 and 400 ºC, whereas the cycle 4 lignin only showed a peak, it indicated that LIG cycle 4 had simpler structure than other lignins. These results were in agreement with HPSEC results because more complex structures with higher MW tend to degrade at higher temperatures. In the cycles 1 and 2 there were not hemicelluloses degradation peak which confirmed the results obtained by HPLC. The final inorganic residue was similar in all samples, and it was around 45 %, which was in agreement with the results obtained by other authors (Toledano et al., 2010).

Table 3: Temperature degradation results

Sample	Temperature ºC	Weight loss (%)	Residue (%)
LIG Cycle 1	85.0	2.0	44.6
	310.9	29.5	
	387.3	23.9	
LIG Cycle 2	84.3	1.4	42.3
	316.0	30.6	
	394.5	25.1	
LIG Cycle 3	78.2	1.8	46.3
	189.8	1.1	
	313.2	27.5	
	389.5	23.3	
LIG Cycle 4	97.0	0.9	46.9
	146.8	0.7	
	308.0	51.5	

^{13}C-NMR spectra of Bmim[MeSO$_4$] of different cycles are shown in the Figure 2. The bands were assigned as follow; 13.42 ppm to -CH$_3$ (10), 18.80 ppm to -CH$_2$- (9), 31.54 ppm to -CH$_2$- (8), 35.75 to -CH$_3$ (6), 39.54 ppm to DMSO, 48.49 ppm to –CH$_3$ (11), 52.92 ppm to CH2 (7), 122.12 to =CH (4), 123.71 ppm to =CH (5) and 136.62 to =CH (2) (Pretsch et al., 2000). The same bands appeared in all the spectra, so it seemed that C linkage structure had no change over the cycles.

^{1}H-NMR spectra of Bmim[MeSO$_4$] of different cycles are shown in the Figure 2. The following bands appeared in all the spectra, and were assigned as follow: 0.89 ppm (t) was assigned to -CH$_3$ (10), 1.26 ppm (q) to -CH$_2$- (9), 1.77 ppm (m) to -CH$_2$- (8), 2.51 ppm (s) to DMSO, 3.40 ppm (s) to –CH$_3$ (11), 3.86 (s) to -CH$_3$ (6), 4.17 ppm (t) to CH$_2$ (7), 7.71 ppm (s) to =CH- (4), 7.78 ppm (s) to =CH- (5) and 9.13 ppm (s) to =CH- (2) (Jeon et al., 2008;). The differences started to occur in the cycle 3 where a new band appeared at 5.61 ppm(s) (Shi and Deng, 2005). This displacement could be caused by a ^{1}H from phenolic OH, the main structure present in the lignin. In the cycle 4 this band was more intense, which indicated more contamination on the ionic liquid by the lignin.

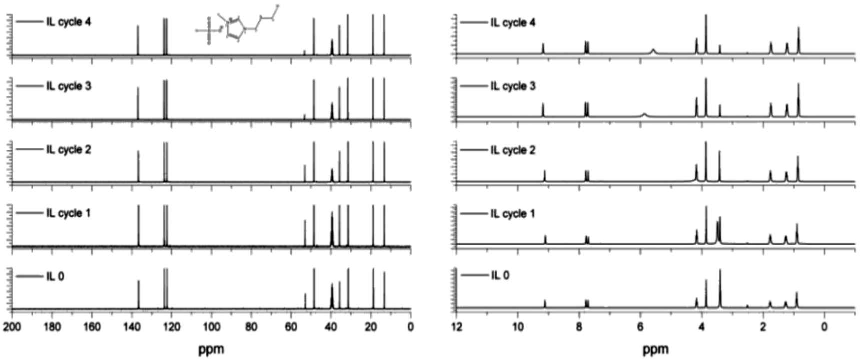

Figure 1: NMR analysis of Bmim[MeSO$_4$] samples, a) ^{13}C-NMR spectra and b) ^{1}H spectra

4. Conclusion

The extraction of lignin from biomass by ionic liquids was studied reutilizing the solvent several times without further purification. The Bmim[MeSO$_4$] can be reutilized without being purified during three cycles to extract lignin from the biomass. The extraction yield and the lignin structure were not severely affected by the reutilization of Bmim[MeSO$_4$] until the cycle 4. The Bmim[MeSO$_4$] also underwent significant changes in its structure in the cycle 4 and contamination with hydroxyl groups was observed.

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