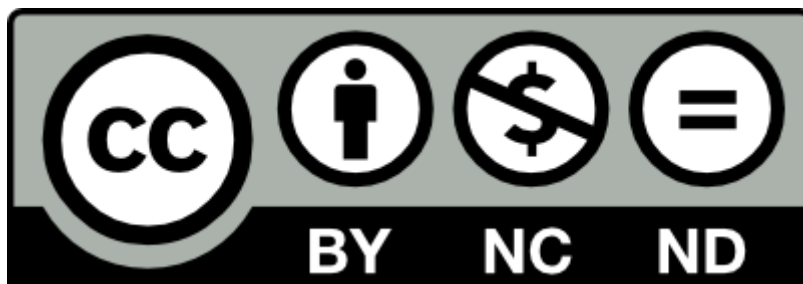


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Abstract: The development of green techniques for biomass processing and fractionation is crucial from the point of view of sustainability and environmental protection. Lignin is the second most abundant bio-renewable material on Earth and ionic liquids 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 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 it appeared ionic liquid contamination on the lignin and the performance decreased dramatically.

Keywords: Ionic liquid, Reutilization, Lignin, Extraction



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 bio-renewable 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 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 it appeared ionic liquid contamination on the lignin and the performance decreased dramatically.

Keywords: Ionic liquid, Reutilization, Lignin, Extraction

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).

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). 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 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 their behaviour; Formentín et al. (2004) used butyl methyl imidazolium hexafluoro phosphate [Bmim][PF₆] as solvent for Knoevenagel reaction with good yields until cycle 3, [Bmim][PF₆] 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-hydroxyethylammonium) acetate, 2-HE2AA could be used as biomass pretreatment for ethanol production.

It has been shown that some IL (such as 1-butyl-3-methyl- 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][MeSO₄]) 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][MeSO₄] 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[MeSO₄] ionic liquid was provided by Sigma Aldrich, and H₂SO₄ 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][MeSO₄] 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 ($8.80 \pm 0.03\%$ 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: $3.2 \pm 0.2\%$ ash (TAPPI T211 om-93), $16.7 \pm 0.2\%$ hot water soluble matter (TAPPI T207 om-93), $32.0 \pm 0.5\%$ aqueous NaOH soluble matter (TAPPI T212 om-98), $10.7 \pm 0.5\%$ ethanol-

benzene extractives (TAPPI T204 om-97), $26.15 \pm 0.09\%$ lignin (TAPPI T222 om-98), $57 \pm 1\%$ holocellulose (Wise et al., 1946) and $27.3 \pm 0.2\%$ 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][MeSO₄], 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 H₂SO₄ 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.

To recover the ionic liquid, the liquid phase was vacuum distilled in order to eliminate the water and dried at 105 °C in the oven for 16 h in order to achieve a 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 4000-700 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 analyzer with a dynamic scan from 25 to 800 °C at 10 °Cmin⁻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-hydrolyzed for 1 hour with 72% v/v sulphuric acid in a thermostatic bath at 30 °C. Then deionised water was added in order to dilute samples up to 4% sulphuric acid. Samples were then hydrolyzed for 3 hours at 100 °C, 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 °C. 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 H₂SO₄ prepared with 100% deionised and degassed water was used (0.35 mL min⁻¹ flow, 40 °C 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 mLmin⁻¹ and the analyses were carried out at 40

°C. Calibration was made using polystyrene standards (Sigma-Aldrich) ranging from 266 to 70,000 g mol^{-1} .

The chemical structure of lignin was studied by pyrolysis. The pyrolysis was carried out using a CDS analytical Pyroprobe 5150. The pyrolysis temperature was set at 400 °C for 15 sec with a heating rate of 2 °C msec^{-1} . Then the products were analyzed by GC (7890A)-MS (5975C inert MSD with Triple-Axis Detector) Agilent equipped with a capillary column HP-5MS ((5%-Phenyl)-methylpolysiloxane, 60 m x 0.32 mm). The temperature program started at 50 °C then, the temperature is raised to 120 °C at 10 °C min^{-1} , held 5 min, raised to 280 °C at 10 °C min^{-1} , held 8 min, raised to 300 °C at 10 °C min^{-1} and held 2 min. Helium was used as carrier gas.

2.4 Ionic liquid characterization

TGA analysis was run in order to determine the thermal stability of the IL and elucidate if it is suitable for reutilization under the process conditions.

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[MeSO₄] is affected ATR-IR spectra and NMR spectra were recorded at 30°C on a Bruker Avance 500 MHz equipped with a z-gradient BBI probe. Typically, 40 mg of sample were dissolved in DMSO-d₆. The spectral widths were 5000 and 25000 Hz for the ¹H and ¹³C dimensions, respectively.

3-Results and discussion

In Table 1 there are 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 also observed that the recovery of IL was about 90% in all cycles. Due to the viscosity of the ionic liquid, it remained stucked to

the biomass and to the walls of the reactor and it was very difficult to recover the 100% of it. The LIGY increased until cycle 3 and then decreased considerably. The dissolution of lignin with ionic liquid is based on a link between the IL and lignin, which is broken with the addition of water that acts as antisolvent, because the affinity of the [Bmim][MeSO₄] with water is higher than with lignin. However, this process is not quantitative, part of the lignin remained linked to the [Bmim][MeSO₄], so the [Bmim][MeSO₄] used in the second cycle was not totally lignin free, this fact led 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 is needed. For the cycle 4 it was not possible to measure the lignin purity because of the characteristics of the sample.

ATR-IR spectra of the lignins isolated in the fourth cycles were recorded (Fig.2). In these spectra following typical lignin structures could be identified: aromatic skeletal vibrations (1597, 1513 and 1456 cm⁻¹), syringyl ring breathing with C-O stretching (1327 cm⁻¹), C-H in plane deformation in guaiacyl ring and syringyl ring (1113 cm⁻¹), C-H in plane deformation in guaiacyl ring and C-O deformation in primary alcohol (1033 cm⁻¹) and aromatic C-H out of plane deformation (823 cm⁻¹). Other structures were also determined: OH- stretching (3450 cm⁻¹), C-H stretching in methyl and methylene groups (2927 and 2852 cm⁻¹), carbonyl stretching in un-conjugated ketones and conjugated carboxylic groups (1704 cm⁻¹), -OH deformation (1201 cm⁻¹), C-O-C asymmetric vibration (1165 cm⁻¹) and =C-H out of plane deformation (1002 cm⁻¹) (Toledano et al., 2010; Serrano et al., 2010). 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 of cycle 4; even the bands at 1002 and 1033 cm^{-1} were coupled to a single band at 1025 cm^{-1} .

ATR-IR spectra of the [Bmim][MeSO₄] the IL utilized in the fourth cycles was compared with the pure [Bmim][MeSO₄] (Fig. 3). In these spectra following typical [Bmim]⁺ structures can be identified: stretch vibrational mode of CH(5) and CH(4) (3147 cm^{-1}), stretch vibrational mode of CH(2) (3103 cm^{-1}), stretching of the CH₃ of the butyl chain attached to the imidazolium ring (2960 cm^{-1}), stretching of the CH₂ of the butyl chain attached to the imidazolium ring (2875 cm^{-1}), in plane C–C and C–N stretching vibrations of the imidazolium ring (1574 cm^{-1}), symmetrical CH vibration of imidazolium ring (1221 cm^{-1}), in plane –C–H deformation vibration of imidazolium ring (1169 cm^{-1}), in plane wagging vibrations of alkyl chain (1059 cm^{-1}) and C–H in plane vibration of imidazolium ring (856 cm^{-1}) (Jeon et al., 2008, Shi and Deng, 2005). Other structures were also determined: [SO₃–OMe] stretching (1338 and 1385 cm^{-1}) (Pretsch et al., 2000) and C=C out of plane deformation (1009 cm^{-1}). The intensity of the bands at 856 and 1221 cm^{-1} increased and they were displaced to lower wavenumber. This could be because a contamination caused by lignin since it presented a characteristic bands at 823 and 1201 cm^{-1} as it was observed in the Fig. 2. The intensity of the band at 1059 cm^{-1} increased and finally in the cycle 4 it was coupled with the band at 1009 cm^{-1} .

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][MeSO₄] pulping. The results of MW average (*MW*), Mn average (*Mn*) and polydispersity are shown in Table 2. The MWD profile was the same to the three first cycles, and a typical behaviour of other lignins (El Hage et al., 2009, Buranov et al., 2010), while in the

cycle 4 the MWD profile changes and it was produced a deviation towards higher detection time (Fig. 4). This behaviour indicates that the MW is lower as it is shown in Table 2. It was observed that in the first three cycles the MW was very similar 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. It indicated that the three first lignin were similar.

The thermogravimetric analysis was used in order to determine the thermal stability of IL during the whole process. As it was observed in Fig. 5 the [Bmim][MeSO₄] was stable until 300 °C, and taking into a count the isometric analysis (Fig. 5), the weight loss is 6% after 6 h and only 2% after 1 h which can be due to the moisture of the sample (Fig. 6). As each experiment took only 3 min, the [Bmim][MeSO₄] should not be affected by the experimental conditions.

The thermogravimetric analysis is widely used to study how the organic polymers decompose. It is observed in Table 3 that all samples showed a weight loss behind 100 °C, which was corresponded to moisture of the samples. The weight loss around 150–260 °C corresponded to hemicelluloses fraction degradation, and the weight loss between 260 and 400 °C 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 Table 3 that the lignins of the cycles 1, 2 and 3 showed a narrow peak and a shoulder between 300 and 400 °C, whereas the cycle 4 lignin only showed a peak, it indicated that LIGcycle 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 was 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).

The lignin structure was also studied by pyrolysis-GCMS in order to establish the proportion of nitrogenised groups from ionic liquids that are present in the lignin structure. At first appeared the lowest MW fractions, normally the monomeric phenolic compounds have retention times lower than 20 min (though it varies depending on the column and used method), and at higher retention times appeared condensed structures and complex phenolic compounds (Brebú et al., 2011, Klap et al., 1998). In Table 4 list of the main peak present in the chromatogram is shown. The proportion between butyl imidazole (Bim) and syringol (S) was measured over the cycles in order to determinate the rate of the ionic liquid contamination. The Bim:S ratio increased along the cycles; for LIGcycle 1 was 2.15, for LIGcycle 2 4.95, for LIGcycle 3 6.15 and for LIGcycle 4 was 6.32. As it was observed in Fig. 7 in the cycle 4 the proportion of condensed groups decreased, it corresponded with the results of MWD which showed a lower MW for LIGcycle 4 compared to other lignins, it could be due to the loss of efficiency of the ionic liquid extracting lignin feedstock and it was only capable of dissolving part of it.

^{13}C -NMR and ^1H -NMR characterization was carried out to evaluate the possible changes in the chemical structure of the Bmim[MeSO₄]. These bands are assigned to the structure according with other author's data (Jeon et al., 2008; Shi and Deng, 2005).

^{13}C -NMR spectra of Bmim[MeSO₄] of different cycles are shown in the Fig.8. The bands were assigned as follow; 13.42 ppm is assigned to -CH₃ (10), 18.80 ppm to -CH₂- (9), 31.54 ppm to -CH₂- (8), 35.75 to -CH₃ (6), 39.54 ppm to DMSO, 48.49 ppm to -CH₃ (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.

¹H-NMR spectra of Bmim[MeSO₄] of different cycles are shown in the Fig. 8. The following bands appeared in all the spectra, and were assigned as follow: 0.89 ppm (t) was assigned to -CH₃ (10), 1.26 ppm (q) to -CH₂- (9), 1.77 ppm (m) to -CH₂- (8), 2.51 ppm (s) to DMSO, 3.40 ppm (s) to -CH₃ (11), 3.86 (s) to -CH₃ (6), 4.17 ppm (t) to CH₂ (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; Shi and Deng, 2005). The differences started to occur in the cycle 3 where bands appeared at 5.61 ppm(s). This displacement could be caused by a ¹H from phenolic OH, a main structure present in the lignin. In the cycle 4 this band was more intense, which indicated more contamination of the ionic liquid by the lignin.

4- Conclusion

The extraction of lignin from biomass by ionic liquids was studied reutilizing the solvent several times without further purification. The Bmim[MeSO₄] can be reutilized without being purified during three cycles, in order to extract lignin from the biomass. The extraction yield and the lignin structure were not severely affected by the reutilization of Bmim[MeSO₄] until the cycle 4. The Bmim[MeSO₄] also underwent significant changes in its structure in the cycle 4 and contamination with hydroxyl groups was observed.

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Figures

Figure 1: Scheme of the process

Figure 2: ATR-IR spectra of lignins

Figure 3: ATR-IR of Bmim[MeSO₄]

Figure 4: MWD of different lignins

Figure 5: Thermogravimetric analysis of Bmim[MeSO₄]

Figure 6: Isothermal analysis at 180 °C of Bmim[MeSO₄]

Figure 7: Pyrolysis-GSMS of lignins

Figure 8: NMR analysis of Bmim[MeSO₄] samples, a) ¹³C-NMR spectra and b) ¹H spectra

Figure 1

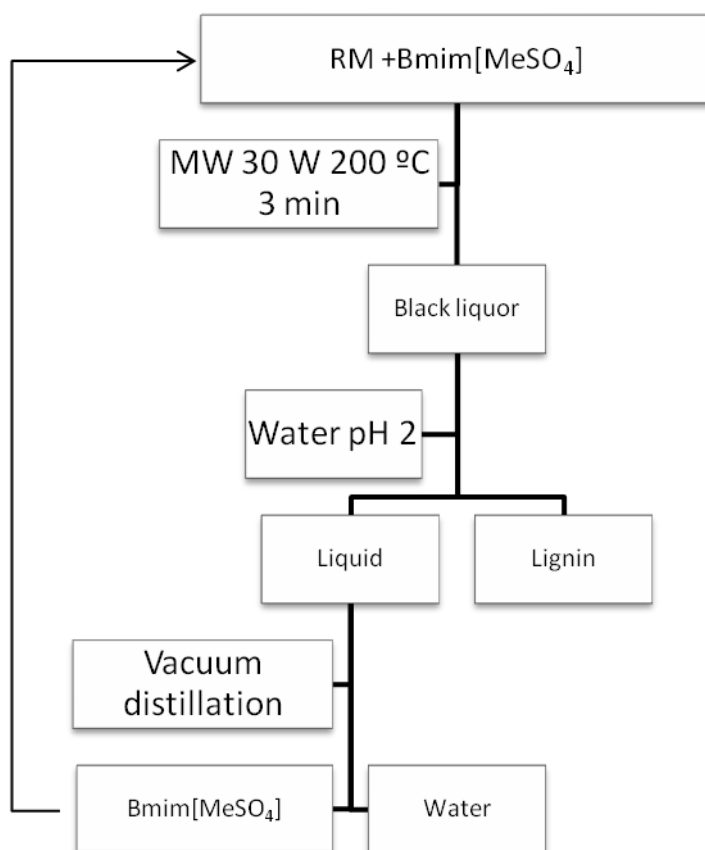


Figure 2

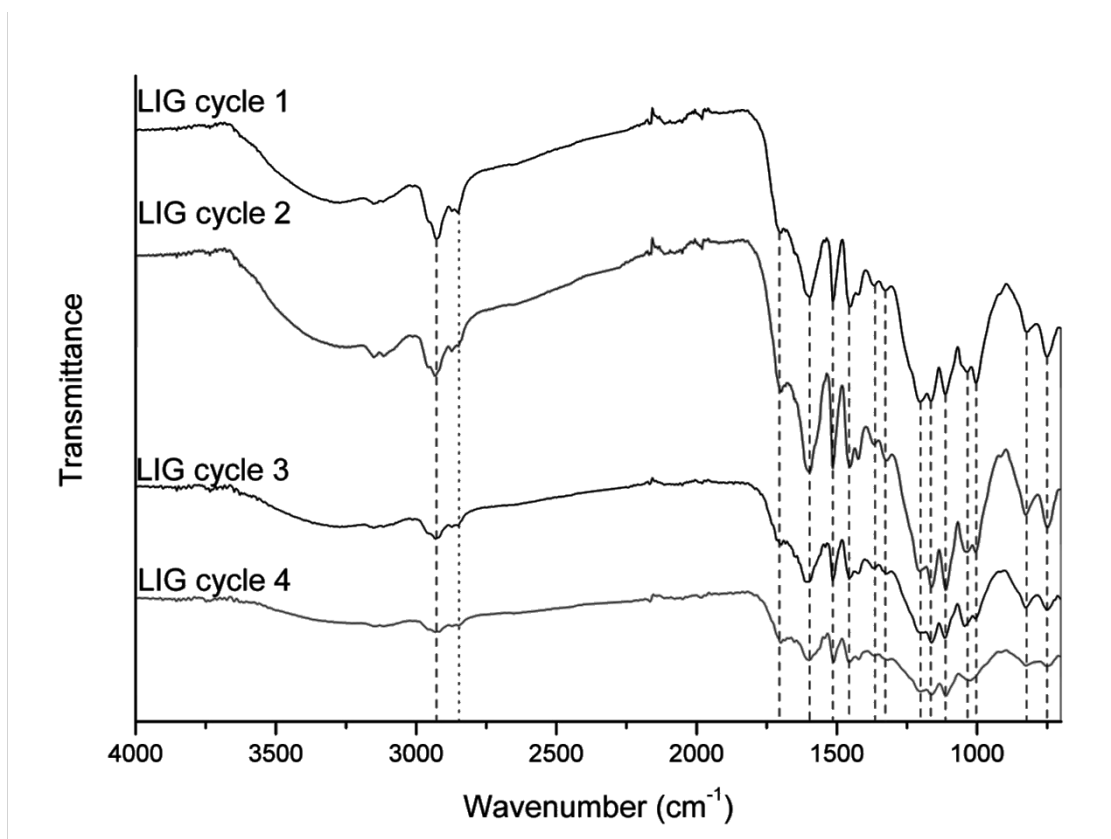


Figure 3

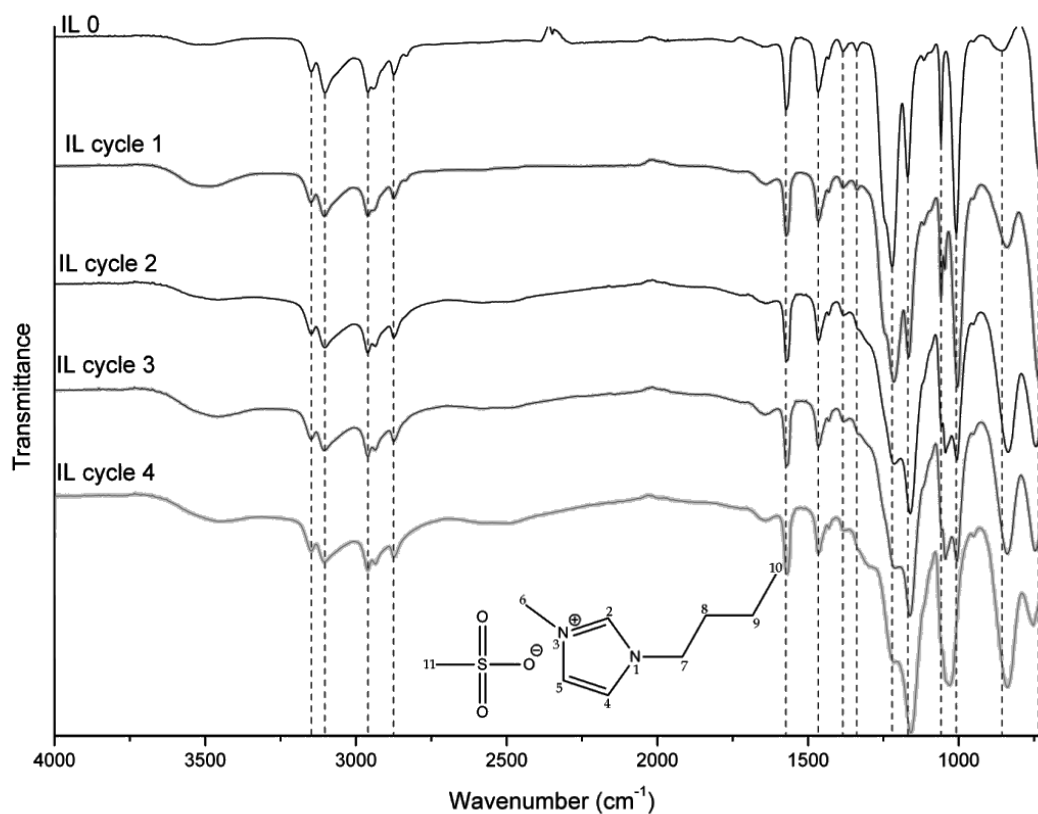


Figure 4

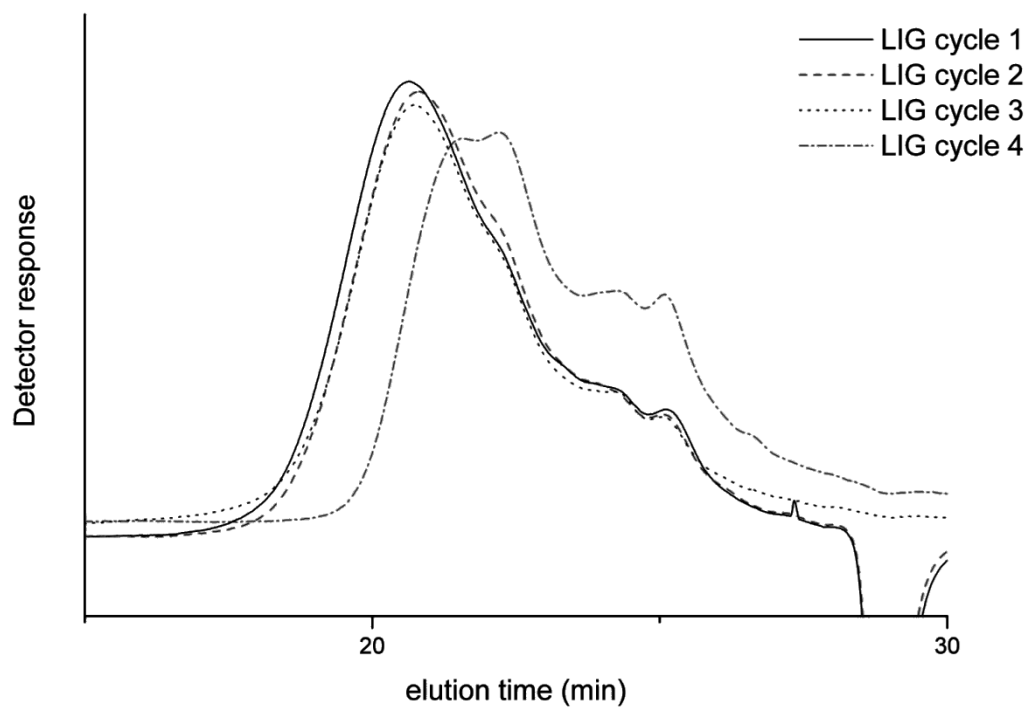


Figure 5

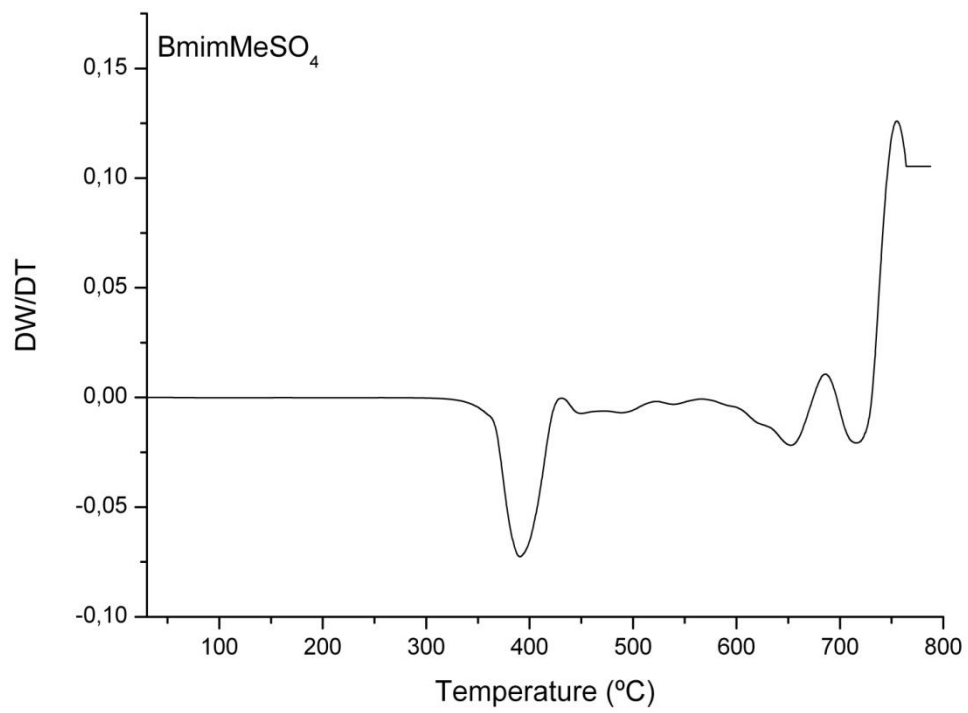


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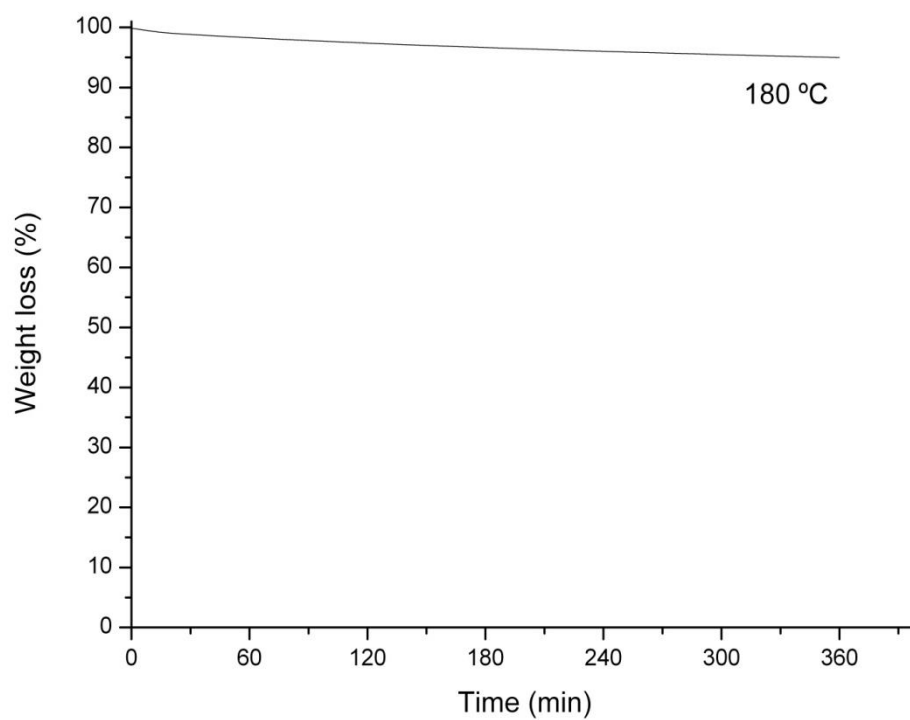


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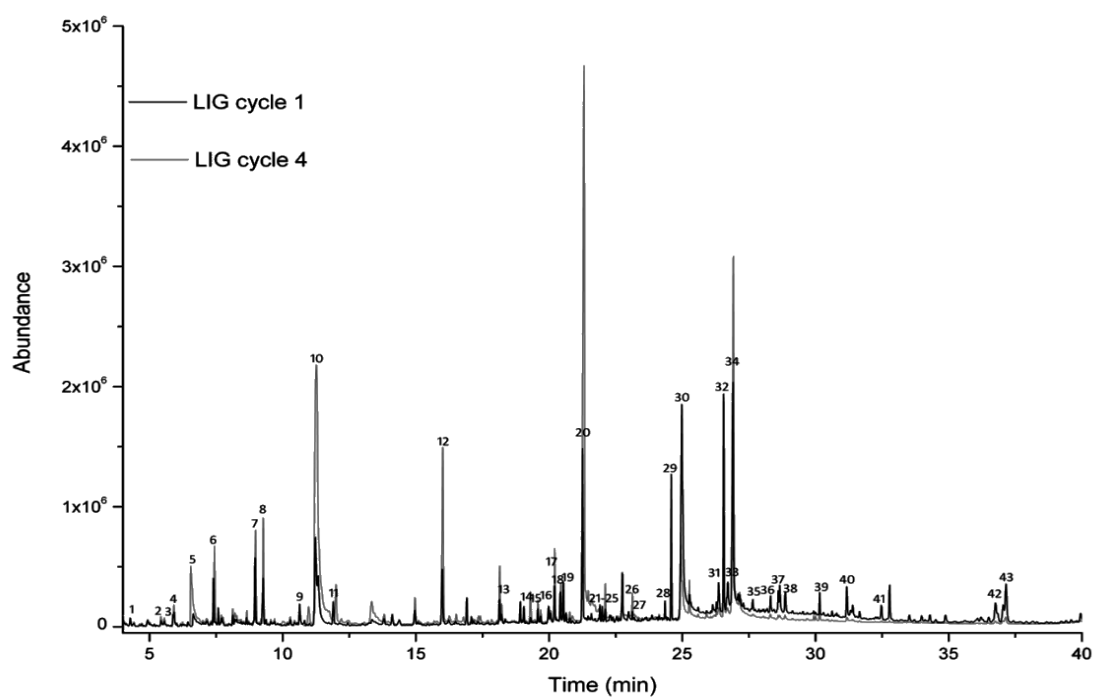
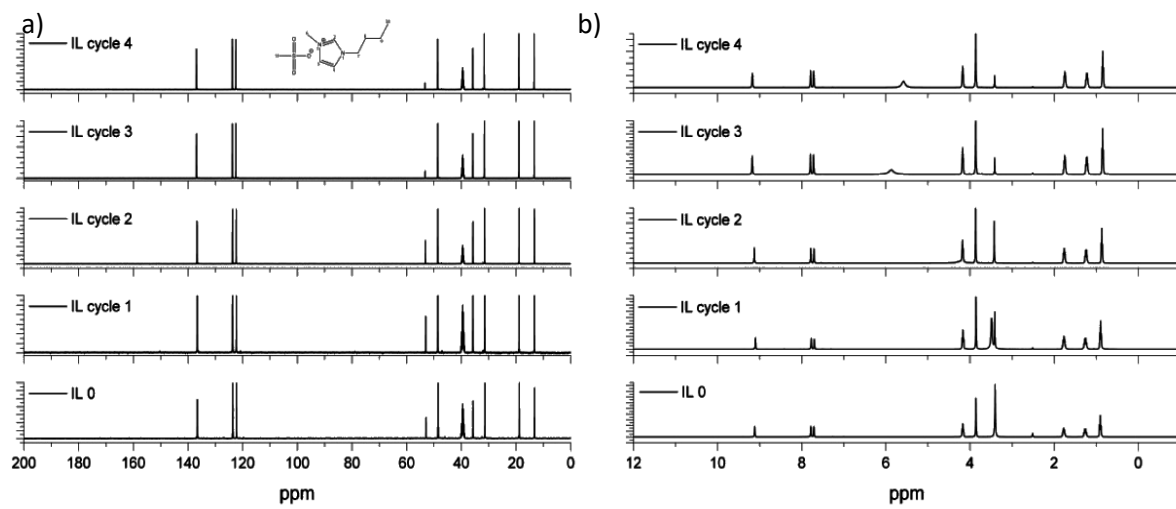


Figure 8



Tables

Table 1: Reaction yields and lignin purity

Table 2: Molecular weight results

Table 3: Temperature degradation results

Table 4: Obtained compounds of lignin degradation by Pyrolysis-GSMS analysis

Table 1

%	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	---	---

DL: Detection limit

Table 2

Sample	MW	Mn	Polydispersity
LIG cycle 1	15503	1756	8.83
LIG cycle 2	13186	1384	9.53
LIG cycle 3	15549	1631	9.54
LIG cycle 4	4382	879	4.99

Table 3

	Temperature °C	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	

Table 4

N°	Retention time	Compound
1	3.97	Toluene
2	5.91	Styrene
3	5.96	p-Xylene
4	6.62	Methyl imidazole
5	7.41	Phenol
6	7.58	Decene
7	8.94	p-Cresol
8	9.27	Guaiacol
9	10.64	p-ethylphenol
10	11.23	N-butylimidazole
11	11.89	Coumaran
12	16.00	Syringol
13	18.16	4-methoxy-3methoxy methylphenol
14	18.21	Trans-m-propenil-guaiacol
15	19.30	2,4-Di-tert-butyl-phenol
16	19.58	tertbutylpyrogallol
17	20.19	4-ethyl-2,5-dimethoxyphenyl-2-propanamine
18	20.42	Methyl-p-hydroxyhydrocinnamate
19	20.63	2,6,10-trimethyltetradecane
20	21.25	4-isopropylthiouracyl
21	21.90	Eicosene
22	22.00	2,6,10-trimethyltetradecane
23	22.105	Methoxyeugenol
24	22.28	Salsoline
25	22.74	Myristic acid
26	22.98	bypheniltetradecane
27	23.13	Hexadecanol
28	24.35	Heptadecanone
29	24.58	Palmitic acid methyl ester
30	24.98	Hexadecanoic acid
31	26.37	Dasycarpidan-1-methanol, acetate
32	26.53	Stearic acid methyl ester
33	26.70	Oleic acid
34	26.89	Stearic acid
35	27.65	Androst-5,7-dien-3-ol-17-one
36	28.606	Androst-5,7-dien-3-ol-17-one
37	28.66	Androgen 63
38	28.86	5,7,9(II)-Androtatriene-3-hydroxy-17-oxo
39	30.14	3',8,8''-trimethoxy-3-piperidyl-2,2''binapthalene-1,1'',4,4''tetrone
40	31.17	10,11, Dihydro-10-hydroxy-2,3-dimethoxybenz(b,f)oxepin
41	32.78	Squalene
42	36.77	7-Dihydrodiosgenin
43	37.15	Stigmastan-3,5-diene