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Lignin oxidation and depolymerisation in ionic liquids

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The depolymerisation of lignin directly in the black liquor was studied, comparing two ionic liquids as extracting solvents (butylimidazolium hydrogen sulphate and triethylammonium hydrogen sulphate), under oxidising conditions. H₂O₂ was chosen as the oxidant agent. It was observed that lignins derived from butylimidazolium hydrogen sulphate were more susceptible to degradation. The main degradation products found in the extracted oils were aromatic acids, such as vanillic acid, benzoic acid and 1,2-benzenedicarboxylic acid.

Introduction

According to the World Energy Council, about 82% of the world's energy needs are currently supplied from fossil resources such as petroleum, natural gas and coal.¹ The ecological disadvantages of this have come into prominence as the use of fossil energy sources suffers a number of ill consequences for the environment, including greenhouse gas emissions that are causing the climate change, air pollution, acid rain, etc..² These resources are not only used as energy sources, but also for the production more than 2500 different oil-based products. Crude oil is the major source for plastics, fibres and dyes. Approximately 10% of world-wide natural gas consumption, 21% of the liquefied natural gas, and 4% of crude oil are used for chemicals production.³ In order to reduce dependence on fossil fuels renewable sources and technologies have been widely investigated. One of these technologies is the conversion of biomass to fuels and chemicals in the so-called "Integrated Biorefinery".⁴

Lignocellulosic biomass is constituted principally of cellulose, lignin and hemicelluloses, in varying proportions depending on the individual biomass source, e.g., species, growing season, and geographic location. Lignocelluloses are a renewable source of materials and chemicals. Lignin due to its structure is the most abundant renewable source of aromatic compounds on earth⁵.

In the past and until now, the most common lignin application in the pulp and paper industry has been energy generation through its combustion. However, lignin's structure is unique

in nature and it has the potential to be an exceptional renewable source of aromatic compounds, if an economic means of extraction and depolymerisation can be developed. Lignin valorisation to high added value platform chemicals could provide a qualitative leap to the exploitation of this side stream of the pulp and paper industries and in future second generation bioethanol plants;⁶ biorefinery plant efficiency and profitability strongly rely on the maximum valorisation of the lignin.⁷ In addition, selective and controlled oxidation of lignin, would be extremely valuable as it is believed to be the only economically viable stream of renewable aromatic compounds for large scale production.⁸

Lignin conversion into simple aromatic products is a difficult task due to lignin's recalcitrant nature, its complex structure, variability of sources and extraction processes. There are some depolymerisation processes that are already under research namely pyrolysis of the isolated lignins, catalytic hydrogenolysis, alkaline hydrolysis, supercritical water and solvent depolymerisation.^{9,10,11} The C–C linkages of lignin are resistant towards cleavage and majority of these survive regardless of the depolymerisation process. Thus, depolymerisation of the isolated lignins results in a complex mixture of aromatic compounds in which the individual mass fraction of each compound barely exceeds few percent. In addition, the depolymerisation of lignin depends on the source of lignin, during the pulping processes a chemical modification of lignin occurs, with the formation of different structures depending on the pulping conditions, for example it is very hard to depolymerise kraft lignin due to the percentage of refractory C–C linkages between the propylphenol monomers being significantly higher than in the proto lignin initially present in the wood.^{12,13}

Recently, ionic liquids have been studied for biomass delignification and further treatments. In addition, solubilisation of lignin is under study; several ionic liquids have

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been used with this aim with good results compared to conventional solvents⁷, such as 1-butyl-3-methylimidazolium chloride [C₄C₁im][Cl], 1-allyl-3-methylimidazolium chloride [C₂C₁im][Cl],¹⁴ 1,3-dimethylimidazolium methylsulfate [C₁C₁im][MeSO₄],⁶ and 1-butyl-3-methylimidazolium methylsulfate [C₄C₁im][MeSO₄].⁵ Recently, it has been demonstrated that anions mostly affect the lignin reactivity in the order alkylsulphonates > lactates > acetates > chlorides > phosphates). This is explained by the nucleophilicity of the electronegative part of the anion.¹⁵ The cation has not yet been shown to have any great effect on the reactivity of the ionic liquid.

Due to its complex structure, there are few works that use lignin as a starting material to study its depolymerisation. However, there are many authors that have studied lignin model compounds in order to elucidate the reaction mechanism and the proper conditions to extend to the reaction to the whole lignin. The depolymerisation of lignin model compounds and lignin in ILs has been studied under reductive and oxidative conditions. The reductive conditions were achieved by adding Lewis and Brønsted acids as catalysts; however, these reactions were only briefly studied because of the low reactivity showed by the lignin despite the good yields obtained on lignin model compounds.¹⁶ Oxidation has been more extensively studied, in most cases coupling a metal catalyst such as Fe, Mn, Co, V and on oxidant such as O₂ or H₂O₂, in many different ILs under different conditions. The role of the ILs was as both reaction solvent and/or catalyst.^{8,15,17}

Jiang et al.,¹⁸ and Zhu et al.¹⁹ worked on the reactivity of lignin model compounds under different conditions and then they applied the optimum conditions to lignin itself.

Jiang et al.²⁰ studied the selective oxidation of primary alcohols into aldehydes or acids. First, methoxybenzylalcohol was used to check the optimum conditions.¹⁸ The influence of cocatalyst and IL structure was studied. It was observed that the aldehyde was obtained in 90% yield with 99% selectivity without adding the cocatalyst and using [C₄C₁im][PF₆] as the IL. To obtain the acid selectively Cu(II) 2-ethylhexanoate was added as cocatalyst and 1-hexyl-3-methylimidazolium triflate [C₆C₁im][OTf] was used as the solvent, but only 77% yield was obtained with 87% selectivity. With pyridinium ILs a complex mixture of products was obtained.¹⁸ Then lignin model compounds such as veratryl alcohol and vanillyl alcohol were oxidized under the same conditions to establish if the behavior of the catalyst could be extended to other phenolic structures. For vanillyl the primary alcohol was selectively oxidized and not the phenolic alcohol. For both veratryl and vanillyl alcohols, the oxidations stop at the aldehyde with 96% and 94% selectivity and 94% and 82% yields, respectively.²⁰

The use of nanoparticles as the catalyst was studied on lignin model compounds and lignin oxidation by Zhu et al. by

dispersing metal nanoparticles in the IL.²⁰ Palladium nanoparticles as catalyst, pyridinium salt of iron bis(dicarbollide) as cocatalyst, O₂ as oxidant and [C₄C₁im][MeSO₄] or [C₄C₁im][PF₆] as ILs were used for the oxidation of benzyl alcohol with different substituents (benzylalcohol, (4-methoxyphenyl)methanol, (2-methoxyphenyl)methanol, (3,4-dimethoxyphenyl)methanol and (3-phenoxyphenyl)methanol) and lignin. Substituted benzyl alcohols were selectively oxidized to their corresponding aldehydes; benzaldehyde, 4-methoxybenzaldehyde, 2-methoxybenzaldehyde, 3,4-dimethoxybenzaldehyde and 3-phenoxybenzaldehyde were obtained in 93%, 86%, 77%, 84% and 80% isolated yields respectively, under the optimum conditions. Lignin was treated under the same conditions (time and temperature), achieving 72% lignin conversion; the main products were identified as syringaldehyde, vanillin, *p*-hydroxybenzaldehyde mixed with a small amount of 2,6-dimethoxy-1,4-benzoquinone.¹⁹ The toxicity of the imidazolium derived ILs has been recently investigated.²¹ It was demonstrated that the toxicity varies more with the cation than with the anion, allowing for the potential to optimise both the biomass processing performance while minimising the toxicity of the ionic liquid..

In the work reported here, two ILs, butylimidazolium hydrogensulphate [HC₄im][HSO₄] and triethylammonium hydrogensulphate [Et₃NH][HSO₄] were used for the delignification of *Miscanthus Giganteus* and subsequent lignin depolymerization by oxidation with H₂O₂ directly applied to the black liquors. Due to imidazolium derived ILs toxicity we compare the obtained results with the ammonium derived IL in order to get a greener processes. H₂O₂ efficiency for lignin oxidation was previously demonstrated by Winermans et al.²²

Results and discussion

Characterization of *Miscanthus Giganteus* fibres was done according to TAPPI standard methods.²³ Moisture content (8.80 ± 0.03 wt.%) was determined after drying the samples at 105 °C for 24 h (TAPPI T264 cm-97). Chemical composition, given on an oven dry weight basis, was the following: 4.2 ± 0.5 % ash (TAPPI T211 om-93), 12.4 ± 0.2% hot water soluble matter (TAPPI T207 om-93), 36.8 ± 0.7% aqueous NaOH soluble matter (TAPPI T212 om-98), 7.9 ± 0.4% ethanol-benzene extractives (TAPPI T204 cm-97), 18.4 ± 0.4% lignin (TAPPI T222 om-98), 30.8 ± 2% hemicelluloses²⁴ and 36.2 ± 0.2% α-cellulose.²⁵

Reaction yields

The reaction yields and S/G ratios (S = syringyl-like lignin structures; G = guaiacyl-like lignin structures) of the obtained lignins are detailed in Table 1. $[\text{HC}_4\text{im}][\text{HSO}_4]$ is more reactive than $[\text{Et}_3\text{NH}][\text{HSO}_4]$, as the lignin yield after pretreatment was higher. In addition, BSL (lignin obtained by $[\text{HC}_4\text{im}][\text{HSO}_4]$ pretreatment) was more reactive under H_2O_2 conditions than ESL (lignin obtained by $[\text{Et}_3\text{NH}][\text{HSO}_4]$ pretreatment), as the lignin yield showed that degradation was higher, though H_2O_2 treatment degraded both lignins, and the degradation depended on H_2O_2 concentration. In general, it was observed that the lignin yield decreased with H_2O_2 concentration, oil yield was higher for 10% H_2O_2 concentration and IL recovery was not affected by the treatment, being around 85%. Although, lignin degradation was higher for $[\text{HC}_4\text{im}][\text{HSO}_4]$ than for $[\text{Et}_3\text{NH}][\text{HSO}_4]$, the oil yields were similar for both ILs. The S/G ratio was affected by H_2O_2 treatment, according to the results syringol is more easily oxidised than guaiacyl, as the S/G ratio decreased after oxidation.

Table 1 H_2O_2 depolymerisation treatment yields

Sample	Treatment	Lignin %	Oil %	S/G
BSL	Not treated	14.64 ± 0.03		0.94
BSL_10	$[\text{HC}_4\text{im}][\text{HSO}_4]$ H_2O_2 10% 1 h 120 °C	1.48	16.05	0.69
BSL_5	$[\text{HC}_4\text{im}][\text{HSO}_4]$ H_2O_2 5% 1 h 120 °C	3.16	10.08	0.58
BSL_2	$[\text{HC}_4\text{im}][\text{HSO}_4]$ H_2O_2 2% 1 h 120 °C	11.29	11.44	0.51
BSL_1	$[\text{HC}_4\text{im}][\text{HSO}_4]$ H_2O_2 1% 1 h 120 °C	17.39	12.15	0.90
ESL	Not treated	11.7 ± 0.4		1.11
ESL_10	$[\text{Et}_3\text{NH}][\text{HSO}_4]$ H_2O_2 10% 1 h 120 °C	4.39	18.50	0.78
ESL_5	$[\text{Et}_3\text{NH}][\text{HSO}_4]$ H_2O_2 5% 1 h 120 °C	7.56	9.40	0.88
ESL_2	$[\text{Et}_3\text{NH}][\text{HSO}_4]$ H_2O_2 2% 1 h 120 °C	7.52	9.19	0.82
ESL_1	$[\text{Et}_3\text{NH}][\text{HSO}_4]$ H_2O_2 1% 1 h 120 °C	10.46	4.24	0.85

Lignin characterization

Spectroscopic characterization

Treatment with $[\text{HC}_4\text{im}][\text{HSO}_4]$

Table 2 ATR-IR spectra band assignment for BSL

Band (cm ⁻¹)	Functional group assignment
3143	CH stretching on CH_3 and CH_2
2936	
1704	Carbonyl stretching in un-conjugated ketones and

	conjugated carboxyl
1596	Aromatic skeletal vibrations
1512	
1455	CH asymmetric deformation
1425	Aromatic skeletal vibrations
1209	Guaiacyl ring breathing with CO stretching
1115	-CH in plane deformation in syringyl ring
1029	-CH in plane deformation in guaiacyl and CO deformation in primary alcohols
834	Aromatic out of plane deformation

Residual lignins were characterized by ATR-IR (Fig 1). All the spectra up to 5% H_2O_2 concentration showed the same bands assigned as is shown in Table 2. However, the relative intensity of the bands changed in the different samples. It was observed that with increasing H_2O_2 concentration the intensity of the band at $1,704\text{ cm}^{-1}$ related to CO group increased, which means that lignin could be oxidising, and the intensity of the band at 1512 cm^{-1} decreased. This behaviour is relatively proportional up to 5% H_2O_2 , while at 10% H_2O_2 lignin lost its structure and its spectrum showed the formation of 3 new bands; the band at

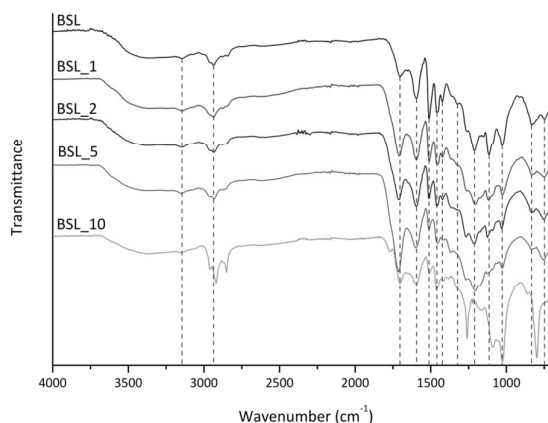


Fig 1 ATR-IR spectra of residual lignins after H_2O_2 treatments for $[\text{HC}_4\text{im}][\text{HSO}_4]$

the band at 1266 cm^{-1} was assigned to the guaiacyl ring and CO stretching, the band at 2854 cm^{-1} was assigned to CH stretching on CH_2 and CH_3 groups and the band at 804 cm^{-1} was assigned to CH harmonics on CH_2 and CH_3 groups, an intensity increase of the band at 2936 cm^{-1} assigned to CH stretching on CH_2 and CH_3 groups was also observed; the formation of these bands can be influenced by IL contamination.^{26,27}

Treatment with $[\text{Et}_3\text{NH}][\text{HSO}_4]$

After H_2O_2 treatment the same bands as for the initial lignin were observed (Fig. 2), they were assigned as shown in Table

3.^{28,29} Apart from the common bands, slight changes were observed for residual lignin after 10% H₂O₂ treatment; a band appeared at 1152 cm⁻¹ assigned to -OSO₃ due to IL contamination and the band at 1696 cm⁻¹ was slightly displaced due to oxidation of the lignin.³⁰

Table 3 ATR-IR spectra band assignment for ESL

Band (cm ⁻¹)	Functional group assignment
2936	CH stretching on CH ₃ and CH ₂
2840	
1696	Carbonyl stretching in un-conjugated ketones and conjugated carboxyl
1596	Aromatic skeletal vibrations
1512	
1455	CH asymmetric deformation
1424	Aromatic skeletal vibrations
1325	Syringyl ring breathing with CO stretching
1209	Guaicyl ring breathing with CO stretching
1114	-CH in plane deformation in syringyl ring
1027	-CH in plane deformation in guaiacyl and CO deformation in primary alcohols
834	Aromatic out of plane deformation

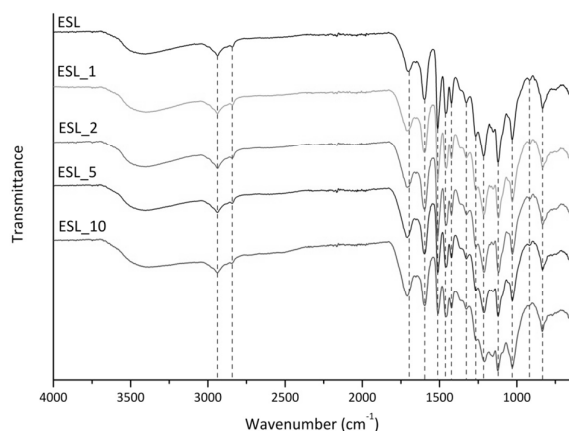


Fig. 2 ATR-IR spectra of residual lignins after H₂O₂ treatment for [Et₃NH][HSO₄]

In general it was observed that IL contamination was more evident in the samples with [HC₄im][HSO₄] as solvent, and only above 10% H₂O₂ concentration.

Chromatographic characterization

Residual lignins obtained after H₂O₂ treatment were characterized by HPSEC, the obtained results of M_w (average molecular weight), M_n (average molecular number) and polydispersity are shown in the Table 4. For both ILs it was observed that lignin was degraded by the action of H₂O₂ because its M_w decreased with increasing concentration of H₂O₂ up to 5%, above which it increased; this could

be due to re-polymerisation reactions which are common for lignin. The decrease of M_w was higher for [HC₄im][HSO₄] derived lignins, which suggests that H₂O₂ effectiveness for lignin degradation is higher for [HC₄im][HSO₄] than for [Et₃NH][HSO₄]. In Fig. 3 the molecular weight distribution (MWD) of residual lignins obtained from [HC₄im][HSO₄] is shown. The chromatograms were displaced to longer retention time which means lower M_w . It was observed that the MWD profile of residual lignins was similar to the initial lignin for low concentrations of H₂O₂, but it changed for 5 and 10% H₂O₂, where the peaks were wider, which agrees with previous polydispersity results.^{31,32}

Fig. 4 shows the MWD of residual lignin samples for [Et₃NH][HSO₄], in this case the MWD profile was the same for residual lignins and initial lignin, the chromatograms were displaced to longer retention time, for 5% H₂O₂ the highest displacement was achieved, this agreed with the fact that 5% H₂O₂ lignin had the lowest M_w .

Table 4 HPSEC results for lignins and residual lignins after H₂O₂ treatment

Samples	M_w	M_n	Polydispersity
BSL	6859	1273	5.39
BSL_1	5005	882	5.67
BSL_2	4642	738	6.29
BSL_5	1573	507	3.10
BSL_10	3464	667	5.19
ESL	10142	1643	6.17
ESL_1	9613	1303	7.37
ESL_2	8771	1325	6.62
ESL_5	7546	1151	6.55
ESL_10	8156	1242	6.56

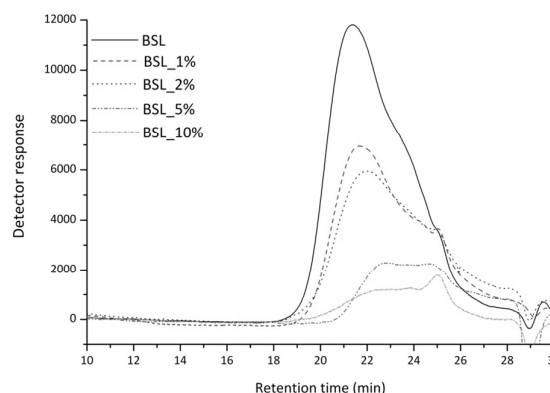


Fig. 3 MWD profiles for H₂O₂ treatment lignins

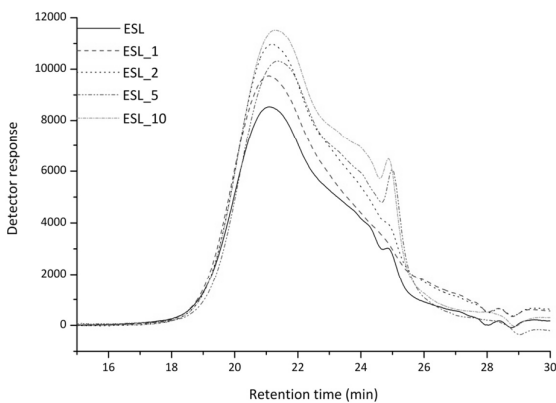


Fig. 4 MWD of 22 h lignin treated with H_2O_2

Residual lignins were characterized by pyrolysis GC-MS to analyze changes in the structure caused by H_2O_2 treatment. The peaks from 7 min to 23 min were assigned to different phenolic monomers which are part of the lignin, from 23 min the peaks were assigned to different acids and long chain molecules. Analyzing the chromatograms (Fig.5) of the $[HC_4im][HSO_4]$ treated samples shows that the residual lignin structure after 1% and 2% H_2O_2 treatments was not highly affected, but with increasing H_2O_2 concentration a decrease of the peak at 11.224 min assigned to butylimidazole was observed. The proportion of phenolic monomers decreased and the relative intensity of the peaks assigned to acid compounds that are part of residual lignin structure after H_2O_2 treatment increased.

For the residual lignins obtained from $[Et_3NH][HSO_4]$, there are several changes observed in the proportion of groups that form the lignin. It was observed that lignin after 5% H_2O_2 treatment showed a higher proportion of acid derived compounds, in addition, the proportions of the aromatic and sugar derived compounds showed lower values. The observed changes indicated that the residual lignin was oxidising by the action of H_2O_2 and losing phenol derived monomers from its structure.

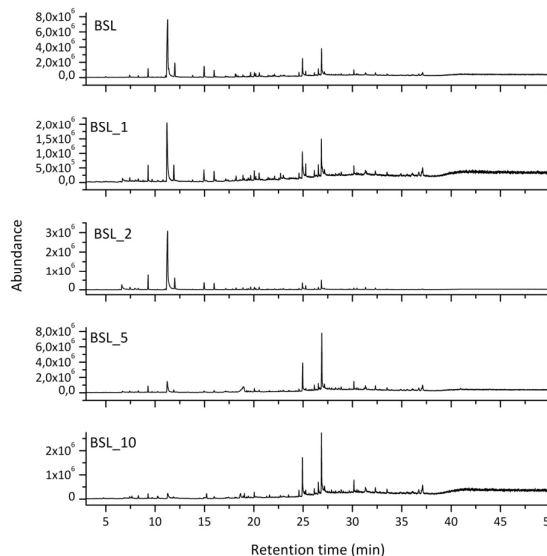


Fig. 5 Pyrolysis GC-MS chromatograms of lignins after H_2O_2 treatment

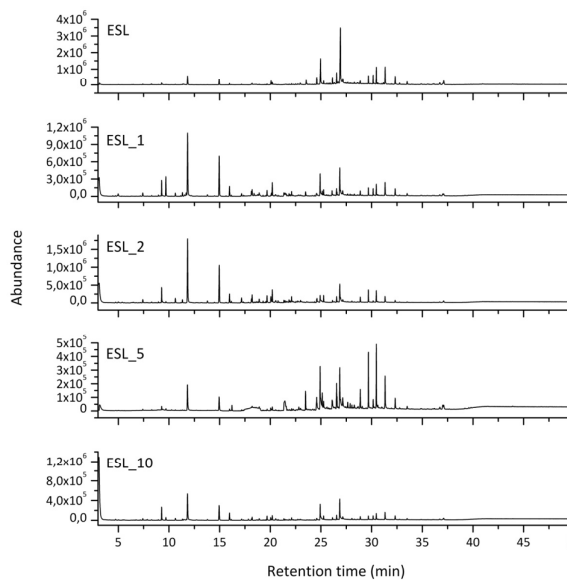


Fig. 6 Pyrolysis GC-MS chromatogram of 22 h pretreatment lignins after H_2O_2 treatment

Oil characterization

The obtained oils were characterized by GC-MS (Fig. 7 and Fig. 8). For $[HC_4im][HSO_4]$ pretreatment derived oils; it was observed that H_2O_2 concentration affects the compounds composing its extracted oils, at low H_2O_2 concentration the oil is mainly composed of typical lignin phenolic compounds, such as guaiacol and syringol, but when the H_2O_2 concentration is increased, oxidised compounds are more

abundant, such as vanillic acid (Table 5). At low H₂O₂ concentration, the main peak at 17.350 min of the chromatograms was assigned to butylated hydroxytoluene that is a stabiliser for MeTHF, but it was negligible for the 5 and 10% treatments with H₂O₂. Since the same quantity of solvent was used for all the extractions, this suggests that the proportion of lignin derived compounds in the oil increased considerably with the increase of H₂O₂ concentration. Apart from calibrated compounds, the oil was composed of other lignin derived products, such as benzoic acid and 3-phenyl-2-propenoic acid, hemicellulose derived compounds, such as 2(5H)-furanone and IL derived compounds such as 1-butyl-2,4,5-trioximidazolidine. In general oils after 5 and 10% H₂O₂ treatments were composed of a complex mixture of different compounds, which came from lignin, sugars and IL.^{33,34,35}

For the oils derived from [Et₃NH][HSO₄] pretreatment, it was observed that a peak which corresponded to butylated hydroxytoluene (Fig. 8) appeared again in all the chromatograms; this compound was used as a qualitative indicator of the composition of the oil. It was observed that for 1% H₂O₂ and 2% H₂O₂ treatment, the main peak corresponded to butylated hydroxytoluene, but with increasing H₂O₂ concentration the relative abundance of this peak decreased, so the oil was enhanced with lignin derived compounds (Fig. 8). Table 6 shows the concentration of different phenolic compounds that were previously calibrated. The highest phenolics concentration was obtained for 5% of H₂O₂. In all cases, phenolic acids, such as vanillic acid, 4-hydroxy-3-methoxyethyl ester, benzoic acid and 1,2-benzenedicarboxylic acid, mono(2-ethylhexyl) ester were the main products. It was observed that not only phenolic products derived from lignin but also hemicellulose derived compounds, such as maleic anhydride and furanone and other degraded structures of lignin as hexadecanoic acid or octadecanoic acid were present. In general, the obtained compounds were highly oxidised (Table 6).^{33,34,35}

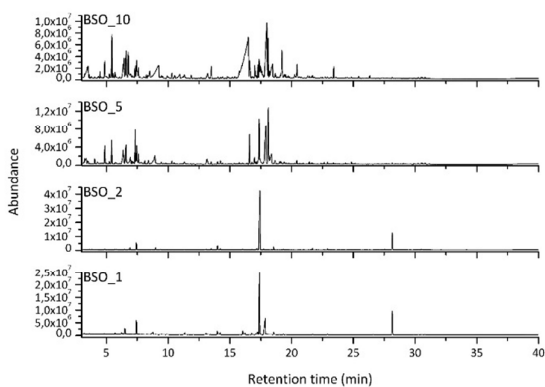


Fig. 7 GC-MS Chromatograms of H₂O₂ treatment derived oils for [HC₄im][HSO₄]

Table 5 H₂O₂ treatment oils calibrated compounds

R.t	Compounds	BSO_10	BSO_5	BSO_2	BSO_1
5.709	Phenol	0.260	0.080	0.105	0.161
6.587	o-cresol	0.012	-----	-----	-----
7.430	Guaiacol	0.335	0.363	1.294	0.962
9.412	Catechol	0.184	0.028	-----	-----
11.338	3-methoxycatechol	0.026	0.026	-----	0.023
13.995	Syringol	0.011	0.037	0.709	0.222
15.170	Vanillin	0.019	-----	0.018	-----
17.025	Acetovanillone	-----	0.006	0.049	0,007
17.677	4-hydroxy-3-methoxyphenyl acetone	-----	0.003	0.015	0.003
18.452	Vanillic acid	8.341	3.514	-----	-----
19.410	Syringaldehyde	0.007	-----	0.011	-----
20.523	3,5-dimethoxy-4-hydroxy acetophenone	-----	-----	0.022	0.004

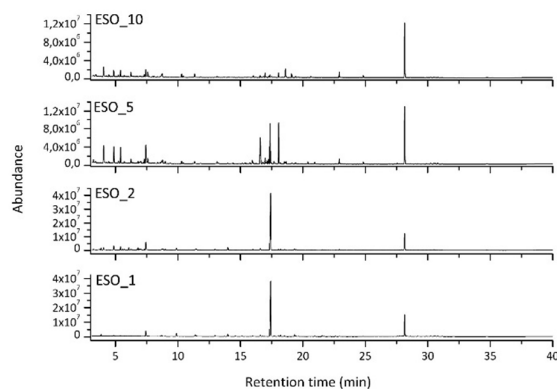


Fig. 8 GC-MS chromatogram of 22 h pretreatment and H₂O₂ treatment oils for [Et₃NH][HSO₄]

Table 6 GC-MS calibrated characterization of oils

R.T	Compounds	ESO_1	ESO_2	ESO_5	ESO_10
5.709	phenol	0.0932	0.1271	0.1492	0.1141
7.430	Guaiacol	0.2961	0.8387	1.2367	1.0246
9.412	Catechol	0.0412	0.0285	0.0171	-----
11.338	3-methoxycatechol	-----	0.0368	0.0683	0.0320
14.225	4-hydroxybenzaldehyde	-----	-----	0.0677	-----
3.995	Syringol	0.0049	0.0211	0.4434	0.3752
15.170	Vanillin	-----	-----	0.0193	0.0323
17.025	Acetovanillone	0.0108	0.0187	0.0071	0.0290

17.275	veratrol	0.0321	-----	-----	-----
17.677	4-hydroxy-3-methoxyphenyl acetone	-----	0.0071	0.0537	0.0816
18.452	Vanillic acid	0.0637	0.3847	0.4151	0.1209
19.410	Syringaldehyde	-----	-----	-----	0.0203
20.523	3,5-dimethoxy-4-hydroxy acetophenone	-----	-----	0.0074	0.0168

Experimental

Materials and methods

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. Spectral data were recorded as 30 scans in a range of 4000-700 cm^{-1} and resolution of 4 cm^{-1} .

Lignins were subjected to High Performance Size Exclusion Chromatography (HPSEC) to evaluate lignin molecular weight (MW) and MW distribution (MWD) using a JASCO instrument equipped with an interface (LC-NetII/ADC) and a reflex index detector (RI-2031Plus). PolarGel-M column (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 °C. Calibration was made using polystyrene standards (Sigma-Aldrich) ranging from to 266 to 70,000 g mol^{-1} .

GC-MS analysis was performed to identify and to quantify the monomers present in the oil. Thus, the oil was dissolved in ethyl acetate (HPLC grade). The solution was injected in an Agilent GC (7890A)-MS (5975C inert MSD with Triple-Axis Detector) 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 was raised to 120 °C at 10 °C min^{-1} , held for 5 min, raised to 280 °C at 10 °C min^{-1} , held for 8 min, raised to 300 °C at 10 °C min^{-1} and held 2 min. Helium was used as carrier gas. Calibration curves were done using pure compounds (Sigma-Aldrich) –phenol, *o*-cresol, *m*-cresol, *p*-cresol, guaiacol, catechol, 4-methylcatechol, syringol, acetovanillone, syringaldehyde, acetosyringone and 4-hydroxy-3-methoxyphenylacetone.

In order to determine the influence of the process on the nature of the ionic liquid and elucidate how the chemical structure of the $[\text{HC}_4\text{im}][\text{MeSO}_4]$ is affected ATR-IR spectra and NMR spectra were recorded at 30°C on a Bruker Avance 600 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.

Synthesis of ionic liquid

$[\text{HC}_4\text{im}][\text{HSO}_4]$ was synthesized by drop-wise addition of H_2SO_4 to butylimidazole using a ratio of 1:1, while the flask was cooled in an ice bath. The mixture was magnetically stirred for 24 h and dried under vacuum.

$[\text{Et}_3\text{NH}][\text{HSO}_4]$ was synthesized by drop-wise addition of 5 M H_2SO_4 on triethylamine using a ratio of 1:1, while the flask was cooled in an ice bath. The mixture was magnetically stirred for 24 h and dried under vacuum.

Pretreatment

Miscanthus, water and IL were homogeneously mixed in a mass ratio 1:2:8. $[\text{HC}_4\text{im}][\text{HSO}_4]$ mixtures were treated during 8 h at 120 °C and $[\text{Et}_3\text{NH}][\text{HSO}_4]$ mixtures were treated for 22 h at 120 °C. Then the resultant solutions were filtered with Whatman 542 filter paper and washed with 3 volumes of ethanol (30 ml). The ethanol of the black liquor was removed by evaporation.

Depolymerisation

The black liquors were treated with 30 % H_2O_2 at 1, 2, 5 and 10% related to IL+lignin weight for 1 h at 120 °C to depolymerise the lignin.

Residual lignin was precipitated by adding 2 volumes of distilled water (20 ml) and then centrifuged at 4000 rpm for 15 min. The residual lignin was washed with distilled water and dried at 70 °C for 16 hours.

The liquid phase was subjected to a liquid/liquid extraction process with MeTHF, in order to extract the small phenolic compounds. The ionic liquid was recovered after the centrifugation and dried by evaporation.

Conclusions

The lignin in the black liquor was successfully depolymerised by oxidation using two different ionic liquids. For $[\text{HC}_4\text{im}][\text{HSO}_4]$ treated black liquors, it was observed that 5% H_2O_2 produced smaller M_w lignin, but the oil yield was lower than for 10 % H_2O_2 . The oil obtained with 10% H_2O_2 had a higher proportion of phenolic derived compounds, vanillic acid being the main component of the oil. The drawback of these treatments was, that $[\text{HC}_4\text{im}][\text{HSO}_4]$ was also affected and oxidized, as a result 1-Butyl-2,4,5-trioxoimidazolidine was obtained as contaminant in the final oil.

The $[\text{Et}_3\text{NH}][\text{HSO}_4]$ was less reactive and lower lignin yields were obtained in the pretreatment. However, the lignin did not show evidence of IL contamination. In addition, the obtained oils were only composed of lignin and hemicellulose derived compounds. Despite the lower efficiency of $[\text{Et}_3\text{NH}][\text{HSO}_4]$, this IL produces non-contaminated phenolics. The recovery/regeneration of the IL was also important; it was observed that $[\text{Et}_3\text{NH}][\text{HSO}_4]$ was not affected by H_2O_2 which increases the possibility of its reutilization. The best phenolic yield results were obtained for 5% H_2O_2 and guaiacol was the main component of the oil.

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References

- Council, World Energy. 2013. World energy resources. London: World Energy Council.
- W. Soetaert and E. J. Vandamme, *Biofuels*, Wiley, Chichester, 2009.
- H. Danner and R. Braun, *Chem. Soc. Rev.*, 1999, **28**, 395–405.
- A. Brandt, J. Gräsvik, J. P. Hallet and T. Welton, *Green Chem.*, 2013, **15**, 550–583.
- P. Yungiao, J. Nan and A. J. Ragauskas, *J. Wood Chem. Technol.*, 2007, **27**, 23–33.
- S. S. Y. Tan, D. R. MacFarlane, J. Upfal, L. A. Edye, W. O. S. Doherty, A. F. Patti, J. M. Pringle and J. L. Scott., *Green Chem.*, 2009, **11**, 339–345.
- K. Stärk, N. Taccardi, A. Bösmann, P. Wasserscheid, *ChemSusChem.*, 2010, **3**, 719–723.
- S. R. Collinson, W. Thielemans, *Coord. Chem. Rev.*, 2010, **254**, 1854–1870
- K. Okuda, X. Man, M. Umetsu, S. Takami and T. Adschiri, *J. Phys.: Condens. Matter.*, 2004, **16**, 1325–1330.
- A. Toledano, L. Serrano and J. Labidi, *J. Chem. Technol. Biotechnol.* 2012, **87**, 1593–1599.
- K. Barta, T. D. Matson, M. L. Fettig, S. L. Scott, A. V. Iretskii and P. C. Ford, *Green Chem.*, 2010, **12**, 1640–1647.
- F. S. Chakar and A. J. Ragauskas, *Ind. Crops Prod.*, 2004, **20**, 131–141.
- J. Zakzeski, A. L. Jongerius and B. M. Weckhuysen, *Green Chem.*, 2010, **12**, 1225–1236.
- I. Kilpeläinen, H. Xie, Q. King, M. granstrom, S. Heikkinen and D. S. Argylopoulos, *J. Agric. Food Chem.*, 2007, **55**, 9142–9148.
- C. Xu, R.A.D. Aracon, J. Labidi, R. Luque, *Chem. Soc. Rev.*, 2014, **43**, 7485–7500.
- R. Prado, X. Erdocia and J. Labidi. Ed. A. Brooks, *Ionic liquids synthesis, characterization and applications*, Nova Publishers, New York, 2014, ch. 2, p.p. 43–63
- G. Chatel and R. D. Rogers, *ACS Sustainable Chem. Eng.*, 2014, **2**, 322–339.
- N. Jiang, and A. J. Ragauskas, *J. Org. Chem.*, 2007, **72**, 7030–7033.
- Y. Zhu, L. Chuanzhao, M. Sudarmadji, N. H. Min, A. O. Biying and J. A. Maguire and N. S. Hosmane, *Chem. Open*, 2012, **1**, 67–70.
- N. Jiang and A. J. Ragauskas, *Tetrahedron Lett.* 2007, **48**, 273–276.
- K.M. Docherty, C. F. Kulpa, *Green Chem.*, 2005, **7**, 185–189
- L. Wiermans, H. Schumacher, C.M. Klaaßen, P. Dominguez de María, *RSC Adv.* 2015, **5**, 4009–4018
- TAPPI Standards*, TAPPI Test Methods, 2007, Atlanta.
- L.E. Wise, M. Murphy and A.A. D'Adieco. *Paper Trade J.* 1946 **122**, 2, 35–43.
- R. Rowell, The chemistry of solid wood: based on short course and symposium sponsored by the division of cellulose, paper, and textile chemistry. The 185th meeting of the American Chemical Society, 1983,70–72.
- F. Shi and Y. Deng, *Spectrochim. Acta A*, 2005, **62**, 239–244.
- García, A. Toledano, L. Serrano, I. Egúés, M. González, F. Martín and J. Labidi, *Sep. Purif. Technol.*, 2010, **68**, 193–198.
- A.Toledano, A. García, I. Mondragon and J. Labidi, *Sep. Purif. Technol.*, 2010, **71**, 38–43.
- S. Lau and R. Ibrahim, *Pertanika*, 1992, **14**, 1, 78–81.
- E. Pretsch, P. Bühlmann, C. Affolter, A. Herrera and A. Martínez, *Structure determination of organic compounds*. New York: Springer-Verlag, 2000.
- A.U. Buranov, K.A. Ross and G. Mazza, *Bioresour. Technol.*, 2010, **101**, 7446–7455.
- R. El Hage, N. Brosse, L. Chrusciel, C. Sanchez, P. Sannigrahi and A. Ragauskas, *Polym. Degrad. Stab.* 2009, **94**, 1632–1638.
- O. Lanzalunga, M. Bietti, *J. Photochem. Photobiol. B*, 2000, **56**, 85–108.
- A. Toledano, L. Serrano, A. Pineda, A. A. Romero, R. Luque and Jalel Labidi, *Appl. Catal. B*, 2014, **145**, 43–55.
- M. P. Pandey and C. S. Kim, *Chem. Eng. Technol.*, 2011, **34**, 29–41.