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Keywords: Lignin, Ionic liquids, Photocatalysis, Depolymerization

Effect of the photocatalytic activity of TiO_2 on lignin depolymerization

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Abstract

Lignin is a good candidate for photocatalytic cracking due to the presence of hydroxyl groups. The photocatalytic cracking reaction involves TiO_2 as heterogeneous catalyst.

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1 Introduction

Black liquor is one of the main byproducts in the pulp and paper industry. The black liquor contains lignin from 10 to 50 wt% (Ksibi et al., 2003). Chemical pulping processes have low yield (about 40-50%) and require significant waste treatment and chemical recycling operations. In the chemical pulping lignin contained in wood is dissolved at high pressure and temperatures, under aqueous alkaline, neutral or acidic conditions. Principal pulping methods are kraft, sulfite, soda and organosolv processes. Nowadays, other pulping methods are under study, in order to avoid emission of volatile

organic compounds, being the ionic liquids the most investigated solvents. Some of ionic liquids are used to dissolve, modify and re-precipitate cellulose as butyl methylimidazolium chloride (Lee et al., 2009). Otherwise, solubilization of lignin is also under study; several ionic liquids has been used with this aim, such as butyl methylimidazolium chloride, 1-allyl-3-methylimidazolium chloride (Kilpeläinen et al., 2007), 1,3-dimethylimidazolium methylsulfate (Tan and MacFarlane, 2009), and Bmim[$MeSO_4$] (1-butyl-3-methylimidazolium methylsulfate) (Yungiao et al., 2007).

During the pulping processes a chemical modification of lignin occurs, with the formation of different structures depending on the pulping properties. Lignin is potentially a renewable source of aromatic compounds if an economic means of extracting and depolymerising can be developed (Tan and MacFarlane, 2009; Zakzeski et al., 2010).

Lignin is a tridimensional phenolic polymer formed by a dehydrogenative polymerization of three phenylpropanoid precursors (*p*-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol), biosynthesized from l-phenylalanine via cinnamic acids, in a process promoted by the peroxidase-H_2O_2 system. This system effects the removal of the phenolic hydrogen atom from the precursors leading to phenoxyl radicals, which by non-enzymatic (random) radical-radical coupling produce a three dimensional amorphous polymer, without regular ordered repeating units (Lanzalunga and Bietti, 2000). Nevertheless, there are some typical bonding patterns that are repeated in the structure: β-Aryl ether (β-O-4), α-Aryl ether (α-O-4), Diphenyl ether (4-O-5), Biphenyl (5-5´), Diaryl propane (β-1) and phenylcoumaran (β-5) (Xu et al., 2008; Pandey and Kim, 2011).

Heterogeneous photocatalysis is a popular technique that has the great potential to degrade organic compounds by oxidation. The process is also known as "Advanced Oxidation Process" and it is suitable for the oxidation of dyes and phenolic compounds. Heterogeneous photocatalytic oxidation has attracted considerable attention particularly when it is used under solar light. Numerous studies have been carried out by researchers on the application of heterogeneous photocatalytic oxidation process using semiconductors as catalyst (Bubacz et al., 2010). These processes are highly influenced by the pH (Fernández et al., 2004; Ma et al., 2008). The photocatalytic activity of various forms of TiO_2, have been evaluated through degradation of dyes and or phenolic compounds under light irradiation.

It turned out that TiO_2 is excellent for photocatalytically breaking down organic compounds. Due to the phenolic character of the lignin it is thought that it can be degraded under photocatalytic conditions, there are other authors studies about the degradation of the lignin on the residual waters on paper industry (Ksibi et al., 2003). With the combination of TiO_2/ZnO lignin is degraded at pH 11 (Kansal et al., 2008).

In this work lignin is depolymerized with photocatalytic treatment, based on TiO_2 as catalyst under UV light for different periods of time, with the aim to determine the optimum conditions for obtaining added value products from lignin. For this purpose, two types of initial black liquors (organosolv and Bmim[$MeSO_4$]) were treated in order to determine which is the most suitable for the depolymerization and the obtaining of phenolic compounds.

2 Experimental

All chemicals were used as received without further purification. Titanium *n*-tertbutoxide, ethanol, HCl and H_2SO_4 were provided by Scharlab and 1-butyl-3-

methylimidazolium methylsulfate was provided by Sigma Aldrich. Apple tree pruning (Malus domestica) was provided by a local farmer in the area of Guipuzkoa (Spain).

2.1 Synthesis of the catalyst

TiO_2 powder was synthesized by sol-gel method, the procedure of synthesis consist on mixing titanium *n*-tertbutoxide (*n*-BuTi) and ethanol absolute (EtOH), when the mixture is homogeneous a solution of HCl in distilled water is added drop-wise until have a sol formed, with *n*-BuTi:EtOH:Water:HCl molar ratio of 1:10:4:0.01. First, the sol was heated at 40 ºC for 2 h with continuous stirring, and then heated at 80 ºC until becoming a gel by evaporation of ethanol. The gel is dried at 105 ºC for 16 h and subsequently treated at 600 ºC for 4 h.

2.2 Organosolv process

The organosolv pulping was carried out under the following conditions: 60% (v/v) ethanol solution, solid:liquid ratio of 1:4 at 180 ºC for 90 min. 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 ºC in an oven.

2.3 [Bmim][$MeSO_4$] Pulping

IL pulping was also carried out using [Bmim][$MeSO_4$], in a solid:liquid ratio 1:10, under microwave radiation, maximum power 30 W, 3 min at 200 ºC on a CEM microwave Discover system model. The lignin was obtained as described above for organosolv process.

2.4 Photocatalysis treatment

0.1 g of TiO_2 was added to several aliquots of 50 mL of organosolv black liquor and to another aliquots of 25 mL of Bmim[$MeSO_4$] black liquor also. These aliquots were treated under UV at 300 W during different periods of time from 0 to 7 h. The photoreactor is a black box with 4 lamps of 75 W ultraviolet radiations each arranged on the top in each corner. After the UV treatment, samples were filtered to recover the catalyst; the list of treated samples is shown in Table 1. The lignin was precipitated by the addition of 3 volumes of acidified water at pH 2 achieved with the addition of H_2SO_4 solution. Then was centrifuged at 5000 rpm for 15 min and the solid part was separated, washed with acidified water at pH 2 achieved by adding H_2SO_4 solution and dried at 50 ºC in an oven.

The liquid fraction was recovered, for the extraction of oil comprising phenolic compounds. The liquid/liquid extraction was carried out using ethyl acetate as oil extractor from aqueous solution of different black liquor aliquots. The ethyl acetate was evaporated by vacuum distillation and the resultant oils were characterized.

2.5 Characterization

The organosolv black liquor was characterized by TAPPI standards. Chemical composition, given on an oven dry weight basis, 0.11 ± 0.04% inorganic matter, 3.74 ± 0.17% organic matter, 1.85 ± 0.09 g in 50 mL lignin, 2,91 ± 0.02 g in 50 mL hemicellulose. These standards are not applicable to Bmim[$MeSO_4$] black liquor.

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}.

The char concentration is determined by dissolving 0.3 g of residual lignin on 25 mL of tetrahydrofurane under magnetic stirring for 3 h. Then is filtered and dried at 50 ºC in an oven for 16 h, the content of char is determined gravimetrically. To determine lignin concentration, the filtrate was rotary evaporated in a flask and dried at 50 ºC in the oven for 16 h. The solid residue which remains in the flask would be lignin, measured by difference.

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). 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 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 a 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 ºC then, the temperature is raised to 120 ºC at 10 ºC min^{-1}, held 5 min, raised to 280 ºC at 10 ºC min^{-1}, held 8 min, raised to 300 ºC at 10 ºC 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.

Oil was also analyzed by Matrix assisted Laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF) in order to evaluate the molecular weight distribution of the products present in the oil. MALDI-TOF analyses were carried out in a Voyager-DE STR Biospectrometry Workstation of Applied Biosystems. A 15 g L^{-1} solution of 3,4-diaminobenzophenone in a methanol-water mixture (8:2) was used as matrix. The analyses were developed in negative mode.

3 Result and discussion

The obtained lignins and extracted oils were analyzed to determine the degree of depolymerization of lignin caused by the photocatalytic effect of TiO_2 under UV light. In order to determine what type of pulping is more suitable for obtaining subsequent value-added products behind photocatalytic treatment. Because of the importance of the pH on the photocatalytic process (Fernández et al., 2004), the pH of the pulping processes was measured. Organosolv pulping had a pH of 4.79, while [Bmim][$MeSO_4$] had a pH of 7.03.

Table 1 shows the concentration of extracted oil related to the corresponding residual lignin. Oil concentration was independent of the time of treatment, it was about 20 wt% in organosolv pulping process and about 11 wt% in [Bmim][MSO_4] pulping process.

3.1 Char determination

During the degradation process of lignin, undesirable side product, like char, were also formed. In order to calculate properly the yield of the process and to estimate the viability, the concentration of char in the lignin samples was measured. The results are shown in Table 1.

In the organosolv pulping, the concentration of residual lignin decreased with the time of photocatalytic treatment, whereas the char concentration slightly decreased

with 1 h of treatment and return to similar concentration of the beginning with the increase of the reaction time.

In Bmim[$MeSO_4$] pulping, lignin and char concentrations do not vary much with the time of photocatalytic treatment.

In both cases char concentrations has not important variation with the time of photocatalityc treatment. Contrary, the lignin concentration is affected by photocatalytic activity, especially in organosolv pulping process lignin; it can be due to the pH of the black liquors (Ma et al., 2008).

3.2 Spectroscopic characterization

The lignins obtained from organosolv and Bmim[$MeSO_4$] black liquors treated are characterized by ATR-IR spectroscopy, in order to establish whether the main functional groups are present in the samples and to determine if there are changes in the chemical structure with the photocatalytic treatment. The main bands and their functional groups correspondences are shown in Table 2 (Derkacheva and Shukov, 2008; Toledano et al., 2010).

3.2.1 Organosolv lignin

As it is observed in Fig. 1 all the residual lignin samples have similar spectra, with the same characteristic bands, except the relative intensity of the bands is different, although these changes on relative intensity do not show any tendency with the time of treatment.

3.2.2 Bmim[$MeSO_4$] lignin

In the same way the spectra of the lignins obtained from Bmim[$MeSO_4$] black liquor aliquots are shown in Fig. 1. The spectrum of the Bmim[$MeSO_4$] is also included, with the aim of establish if there is any contamination of ionic liquid on the obtained

lignin. The spectra of the samples show characteristic bands belonging to aromatic groups present on lignin also. However, with the time of treatment at 2 and 3 h specifically, it appears two different bands at 3018 and 1009 cm^{-1} due to the degradation of lignin and the inclusion of the nitrogen from the Bmim[$MeSO_4$] in the lignin structure. Around 3000 cm^{-1} it appears a Fermi resonance of -CH in amines (Pretsch et al., 2000). The inclusion of the nitrogen can be explained by the extraction mechanism of lignin with ionic liquids proposed by other authors (Kim et al., 2011). In addition, the intensity of the band at 1731 cm^{-1} increased notoriously, it can be due to the oxidation of -OH groups from the lignin that is carried out during the photocatalytic process.

3.3 Weight distribution

3.3.1 HPSEC analysis

The HPSEC analyses were done in the attempt to estimate the effect of photocatalytic activity in the degradation of lignin. In turn, the effect it can have the type of pulping in such degradation. Number-average MW (M_n), MW average (M_w) and polydispersity (M_w/M_n) of the different fractions obtained are shown in Table 3. In both cases the M_w of the lignin without photocatalytic treatment corresponds with the normal lignin M_w (El Hage et al., 2009; Buranov et al., 2010).

When the lignin samples obtained from organosolv pulping process are analyzed, it was observed that the M_w of the lignin samples decreased until 1 h of photocatalytic treatment when it arrives at a minimum. On the other hand, analyzing the proportion of low MW fractions (molecular weight less than 500 g mol^{-1}) it is noted that this proportion increases until a maximum, which is achieved at 1 h of photocatalytic treatment (Table 3) (Fig. 2).

However, in Bmim[$MeSO_4$] pulping process, the M_w of the obtained lignins fluctuates; having a minimum on 0.5 h of treatment and then a maximum on 1 h of treatment. In 1 h it is likely to have stages of repolymerization. On the other hand, the proportion of low MW fractions has a maximum on 0.5 h of treatment. The sum of these effects is noted on the polydispersity, which is higher to lignins with higher M_w (Table 3, Fig. 2).

Taking into account the results reported in Table 3, the degradation of lignin by photocatalysis works better on lignins from organosolv pulping process than on Bmim[$MeSO_4$] pulping process, this fact can be explained by the pH effect.

3.3.2 MALDI-TOF

During the photocatalytic treatment due to radical reactions, different phenolic fragments (Britt et al., 1995; Lanzalunga and Bietti, 2000), with different MW are extracted from the lignin. In order to determine the MWD of the extracted fractions, the extracted oils were analyzed by MALDI-TOF mass spectroscopy. The use of this technique allowed us to estimate the lignin depolymerization degree reached in each experiment. Considering a prototype lignin subunit for instance, phenylpropane syringol has a MW of 197 g mol^{-1} and a phenylpropane guaiacol is about 166 g mol^{-1}, it can be observed in Fig. 3 that most of the obtained products were mainly monomers and also dimers. Although there are signals of some trimers (between 500-700 g mol^{-1}). It is observed in Fig. 3, that the MWD pattern changes depending on the exposure time to photocatalytic treatment. It is observed that after 1 h of treatment signals around 100 g mol^{-1} appear, which indicates that small monomers are forming, and it is also remarkable that the signals in the region between 500 and 700 g mol^{-1} disappear almost completely at 5 h of photocatalytic treatment, and at 7 h the amount of signals decreases all over the sprectrum.

When the oil extracted from Bmim[$MeSO_4$] pulping process is analyzed (Fig. 3), there are also signals that belong to monomers and dimers mainly, plus some low intensity sings belonging to trimers. When the time of treatment increased the signals belonging to trimers decreased and at 3 h of photocatalytic treatment the signals have disappeared almost completely.

Comparing the both pulping processes, the main difference is the number of signals present in the spectra, superior in the case of organosolv pulping process oil samples. In Bmim[$MeSO_4$] pulping process the presence of trimers is lower and their signals disappeared faster than for oil obtained from organosolv pulping process.

3.4 Oil characterization

During the photocatalytic treatment of the black liquors, several phenolic compounds are formed from lignin degradation (Lanzalunga and Bietti, 2000; Pandey and Kim, 2011). At the same time, the degradation of the hemicelluloses extracted with the lignin is done. These compounds formed the extracted oil. In order to identify these phenolic compounds; the extracted oil is also analyzed by GC-MS.

It is observed that not only lignin degradation products are formed, but also sugar degradation products as furfural are formed. Qualitatively several products were identified by the equipment library with good correlation indexes, the products yields have been calculated referred to the obtained oil. The most abundant signal detected were from furfural, hydroquinone, raspberryketone, isoeugenol and desaspinidol (1-(2,6-Dihydroxy-4-methoxyphenyl)-1-butanone). Whereas only few products were quantitatively determined, pirocathecol, syringol, vanillin, syringaldehyde and sinapylaldehyde (Table 4) (Okuda et al., 2004). It can be observe in Table 4 that the principal obtained compound is syringaldehyde and the treatment at 0.5 h shows the

best yields in both pulping processes, although it is noted that when organosolv liquor is treated has considerably better performance. In Bmim[$MeSO_4$] pulping process, nitrogen derived compounds are formed because of the degradation of ionic liquid at the same time with the lignin, by the action of photocatalytic treatment, due to the radical reactions, mixed compounds are obtained as isopropylethylamine, 4-Phenyl-3,4-dihydroisoquinoline and 1-Butyl-3-methyl-2,4,5-trioxoimidazoline. As can be observed in Table 4 the initial concentration of phenolic compounds in the black liquor decreased with the Bmim[$MeSO_4$] pulping photocatalytic treatment. This behaviour could be explained by the interactions of phenolic monomers with ionic liquid to form nitrogenated compounds mentioned before.

4 Conclusions

To sum up, the photocatalytic activity works properly in the degradation of lignin, especially when organosolv black liquor is treated. The characterization of the obtained lignins and oils showed the same conclusion. The photocatalysis works better when is applied on organosolv pulping black liquors than on Bmim[$MeSO_4$] pulping black liquors, this fact can be due to the pH of the liquors, and also because during the photocatalytic treatment, the Bmim[$MeSO_4$] can be degraded. As a result, the extracted phenol compounds from the depolymerization of the lignin are contaminated with nitrogen from Bmim[$MeSO_4$]. Other reason to the bad behavior of the Bmim[$MeSO_4$] as solvent on photocatalysis could be the lack of hydroxyl groups.

On the other hand the char formation is independent of the photocatalytic time treatment, whereas, the concentration of lignin and the M_w are affected. The optimum treatment time was determined at 1 h, after this time the M_w increased, the increase of

the M_w is possible due to the repolymerization reactions that can occur when radical intermediates are involved.

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5 References

Britt, P.F., Buchanan, A.C., Thomas, K.B., Lee, S.K., 1995. Pyrolysis mechanisms of lignin: surface-immobilized model compound investigation of acid-catalyzed and free-radical reaction pathways. J. Anal. Appl. Pyrolysis. 33, 1-19.

Bubacz, K., Choina, J., Dolat, D., Morawski, A.W., 2010. Methylene Blue and Phenol Photocatalytic degradation on nanoparticles of anatase TiO_2. Polish J. Environ. Stud. 19, 685-691.

Buranov, A.U., Ross, K.A., Mazza, G., 2010. Isolation and characterization of lignins extracted from flax shives using. Bioresour. Technol. 101, 7446–7455.

Derkacheva, O., Sukhov, D., 2008. Investigation of lignins by FTIR spectroscopy. Macromol. Symp. 265, 61–68.

El Hage, R., Brosse, N., Chrusciel, L., Sanchez, C., Sannigrahi, P., Ragauskas, A., 2009. Characterization of milled wood lignin and ethanol organosolv lignin from miscanthus. Polym. Degrad. Stab. 94, 1632–1638.

Fernández, J., Kiwi, J., Baeza, J., Freer, J., Lizama, C., Mansilla, H.D., 2004. Orange II photocatalysis on immobilised TiO_2. Appl. Catal. B 48, 205–211.

Kansal, S.K., Singh, M., Sud, D., 2008. Studies on TiO_2/ZnO photocatalysed degradation of lignin. J. Hazard. Mater. 153, 412-417.

Kilpeläinen, I., Xie, H., King, A., Granstrom, M., Heikkinen, S., Argyropoulos, D.S., 2007. Dissolution of wood in ionic liquids. J. Agric. Food Chem. 55, 9142-9148.

Kim, J.Y., Shin, E.J., Eoma, I.Y., Wonb, K., Kim,Y.H., Choi, D., 2011. Structural features of lignin macromolecules extracted with ionic liquid. Bioresour. Technol. 102, 9020–9025.

Ksibi, M., Amor, S.B., Cherif, S., Elaloui, E., Houas, A., Elaoui M., 2003. Photodegradation of lignin from black liquor using a UV/TiO_2 system. J. Photochem. Photobiol. A 154, 211-218.

Lanzalunga, O., Bietti, M., 2000. Photo- and radiation chemical induced degradation of lignin model compounds. J. Photochem. Photobiol. B 56, 85-108.

Lee, S.H., Doherty, T.V., Linhardt, R.J., Dordick, J.S., 2009. Ionic liquid-mediated selective extraction of lignin from wood leading to enhanced enzymatic cellulose hydrolysis, Biotechnol. Bioeng. 102, 1368-1376.

Ma, Y.S., Chang, C.N., Chiang, Y.P., Sung, H.F., Chao, A.C., 2008. Photocatalytic degradation of lignin using Pt/TiO_2 as the catalyst. Chemosphere 71, 998–1004.

Okuda, K., Umetsu, M., Takami, S., Adschiri, T., 2004. Disassembly of lignin and chemical recovery—rapid depolymerization of lignin without char formation in water–phenol mixtures. Fuel Process. Technol. 85, 803-813.

Pandey, M.P., Kim, C.S., 2011. Lignin Depolymerization and conversion: a review of thermochemical methods. Chem. Eng. Technol. 34, 29–41.

Pretsch, E., Bühlmann, P., Affolter, C., Herrera, A., Martínez, A., 2000. Structure determination of organic compounds. Springer-Verlag. New York.

Tan, S.S.Y., MacFarlane, D.R., 2009. Ionic liquids in biomass processing. Top Curr. Chem. 290, 311-339.

Toledano, A., García, A., Mondragon, I., Labidi, J., 2010. Lignin separation and fractionation by ultrafiltration. Sep. Purif. Technol. 71, 38–43.

Xu, F., Sun, R.C., Zhai, M.Z., Sun, J.X., Jiang, J.X., Zhao, G.J., 2008. Comparative study of three lignin fractions isolated from mild ball-milled tamarix austromogoliac and Caragana sepium. J. Appl. Polym. Sci. 108, 1158–1168.

Yungiao, P., Nan, J., Ragauskas, A.J., 2007. Ionic liquids as a green solvent for lignin. J. Wood Chem. Technol. 27, 23-33.

Zakzeski, J., Bruijnincx, P.C.A., Jongerius, A.L., Weckhuysen, B.M., 2010. The catalytic valorization of lignin for the production of renewable chemicals. Chem. Rev. 110, 3552–3599.

Table 1: Identification of treated samples and composition

Table 2: Principal IR bands of organosolv and Bmim[$MeSO_4$] treated lignins

Table 3: Molecular weight results

Table 4: Compounds of lignin degradation

Table 1: Identification of treated samples and composition

Sample	Pulping method	Time of UV treatment (h)	Oil (%)	Lignin (%)	Char (%)
0 OR	Organosolv	0			
0.5 h OR	Organosolv	0.5	20±0*	95±0*	10±0*
1 h OR	Organosolv	1	17±1	95±0*	4±1
2 h OR	Organosolv	2	24±0*	90±1	7±1
3 h OR	Organosolv	3	21±1	82±2	8±2
5 h OR	Organosolv	5	18±1	77±1	7±0*
7 h OR	Organosolv	7	19±0*	73±1	10±1
0 h IL	Bmim[$MeSO_4$]	0			
0.5 h IL	Bmim[$MeSO_4$]	0.5	11±0*	54±1	28±1
1 h IL	Bmim[$MeSO_4$]	1	12±0*	60±1	15±2
2 h IL	Bmim[$MeSO_4$]	2	11±0*	50±1	19±1
3 h IL	Bmim[$MeSO_4$]	3	13±0*	75±0*	14±0*

*** error less than 0.5%**

Table 2: Principal IR bands of organosolv and Bmim[$MeSO_4$] treated lignin

IR band (cm^{-1})	Correspondence
***h OR**	
3337	-OH group stretch
2921	CH stretch in CH_3 and CH_2
2841	
1697	C=O stretch on conjugated *p*-substituted aryl ketones
1595	Aromatic skeletal vibration plus C=O stretch
1512	Aromatic skeletal vibration
1456	CH deformation in CH_3 and CH_2
1418	Aromatic skeletal vibration combined with CH in plane
1320	Syringyl ring plus guaiacyl ring condensed vibration
1213	C-C plus C-O plus C=O stretch
826	C-H out of plane in positions 2, 5 and 6 of guaiacyl units
***h IL**	
3359	-OH stretch
2928	-CH stretch in CH_3 and CH_2
2836	
1731	C=O stretch in unconjugated ketone, carbonyl and ester group
1592	Aromatic skeletal vibration plus C=O stretch
1512	Aromatic skeletal vibration
1456	-CH deformation in CH_3 and CH_2
1421	Aromatic skeletal vibration combined with CH in plane
1369	Aliphatic in CH stretch in CH_3 and OH phenol
1320	Syringyl ring plus guaiacyl ring condensed vibration
1213	C-C plus C-O plus C=O stretch
911	-CH out of plane in aromatics
826	-CH out of plane in positions 2, 5 and 6 of guaiacyl units

Table 3: Molecular weight results

Sample	M_w (g mol^{-1})	M_n	Polydispersity (M_w/M_n)	% of small fraction
0 h OR	5810	941	6.2	33
0.5 h OR	5110	830	6.1	37
1 h OR	2882	725	4.0	43
2 h OR	3665	822	4.5	31
3 h OR	3439	765	4.5	34
5 h OR	3569	757	4.7	34
7 h OR	7079	763	9.3	35
0 h IL	8555	1407	6.1	26
0.5 h IL	2790	690	4.0	46
1 h IL	7594	744	10.2	44
2 h IL	3106	751	4.1	25
3 h IL	5810	941	6.2	33

Table 4: Compounds of lignin degradation

Sample	Pirocathecol (%)	Syringol (%)	Vanillin (%)	Syringaldehyde (%)	Sinapylaldehyde (%)
0 h	0	1.3	0.5	5.1	0.2
0.5 h OR	2.2±0.1	4.1±0.2	0.9±0.0*	14.2±0.6	0.3±0.0*
1 h OR	1.5±0.0*	3.0±0.1	0.6±0.0*	7.4±0.1	0.3±0.0*
2 h OR	2.0±0.1	3.5±0.2	0.8±0.1	10.5±0.8	0.3±0.0*
3 h OR	1.9±0.0*	3.0±0.1	0.7±0.1	10.3±0.6	0.3±0.0*
5 h OR	1.9±0.0*	2.8±0.1	0.7±0.0*	10.8±0.5	0.2±0.0*
7 h OR	2.2±0.1	3.0±0.2	0.7±0.0*	11.4±0.3	0.3±0.0*
0.5 h IL	0.0	0.4±0.1	0.1±0.0*	1.2±0.1*	0.07±0.03*
1 h IL	0.0	0.4±0.0*	0.1±0.0*	0.5±0.0*	0.04±0.0*
2 h IL	0.0	0.4±0.0*	0.1±0.0*	0.6±0.0*	0.05±0.0*
3 h IL	0.0	0.4±0.0*	0.1±0.0*	0.6±0.0*	0.05±0.0*

* Error less than 0.05%

Figure 1: ATR-IR spectra of *h OR lignin samples and *h IL lignin samples

Figure 2: Molecular weight distribution of *h OR lignin samples and *h IL lignin samples

Figure 3: MALDI-TOF results of *h OR oil samples and *h IL oil samples

Figure 1: ATR-IR spectra of *h OR lignin samples and *h IL lignin samples

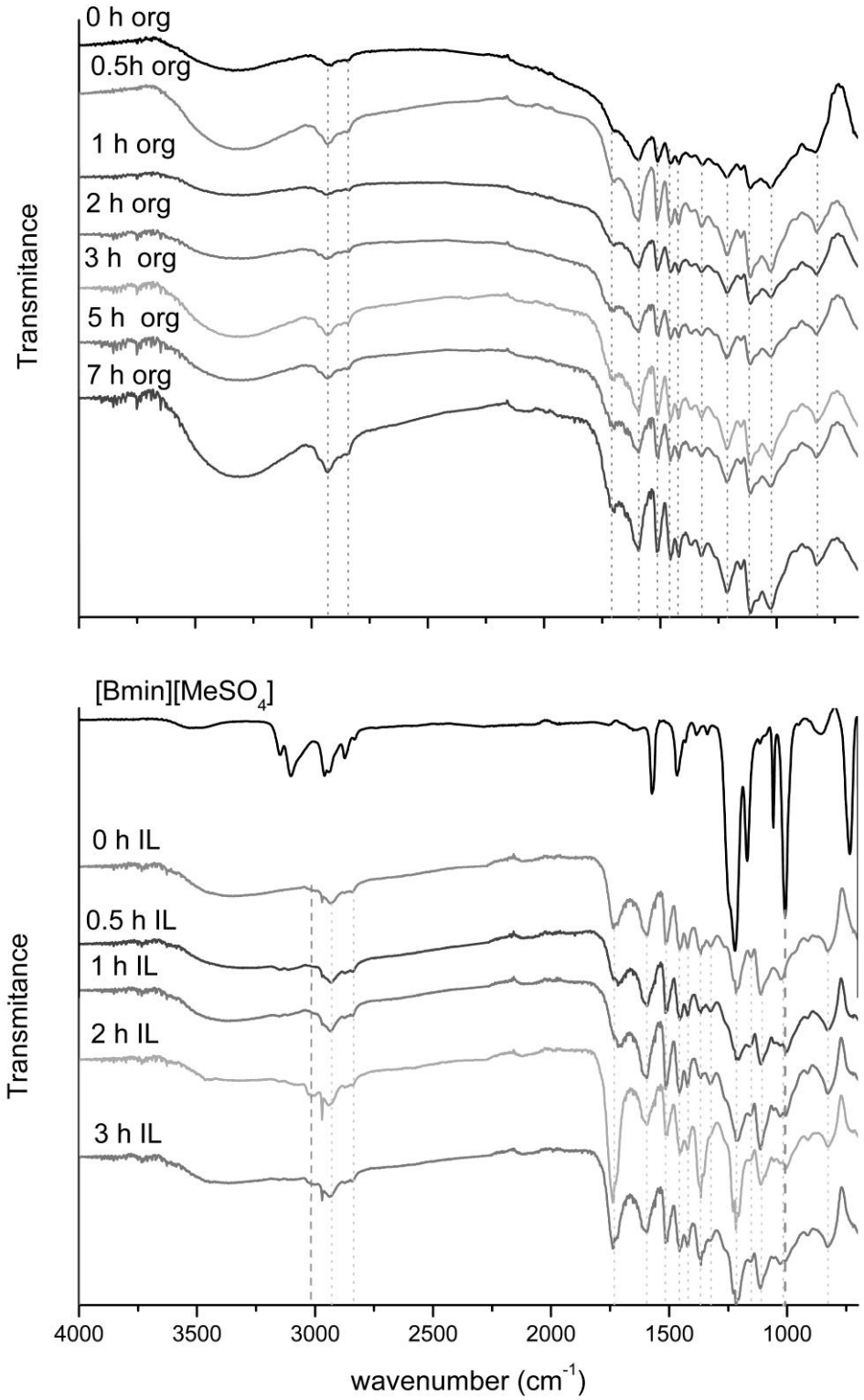

Figure 2: Molecular weight distribution of *h OR lignin samples and *h IL lignin samples

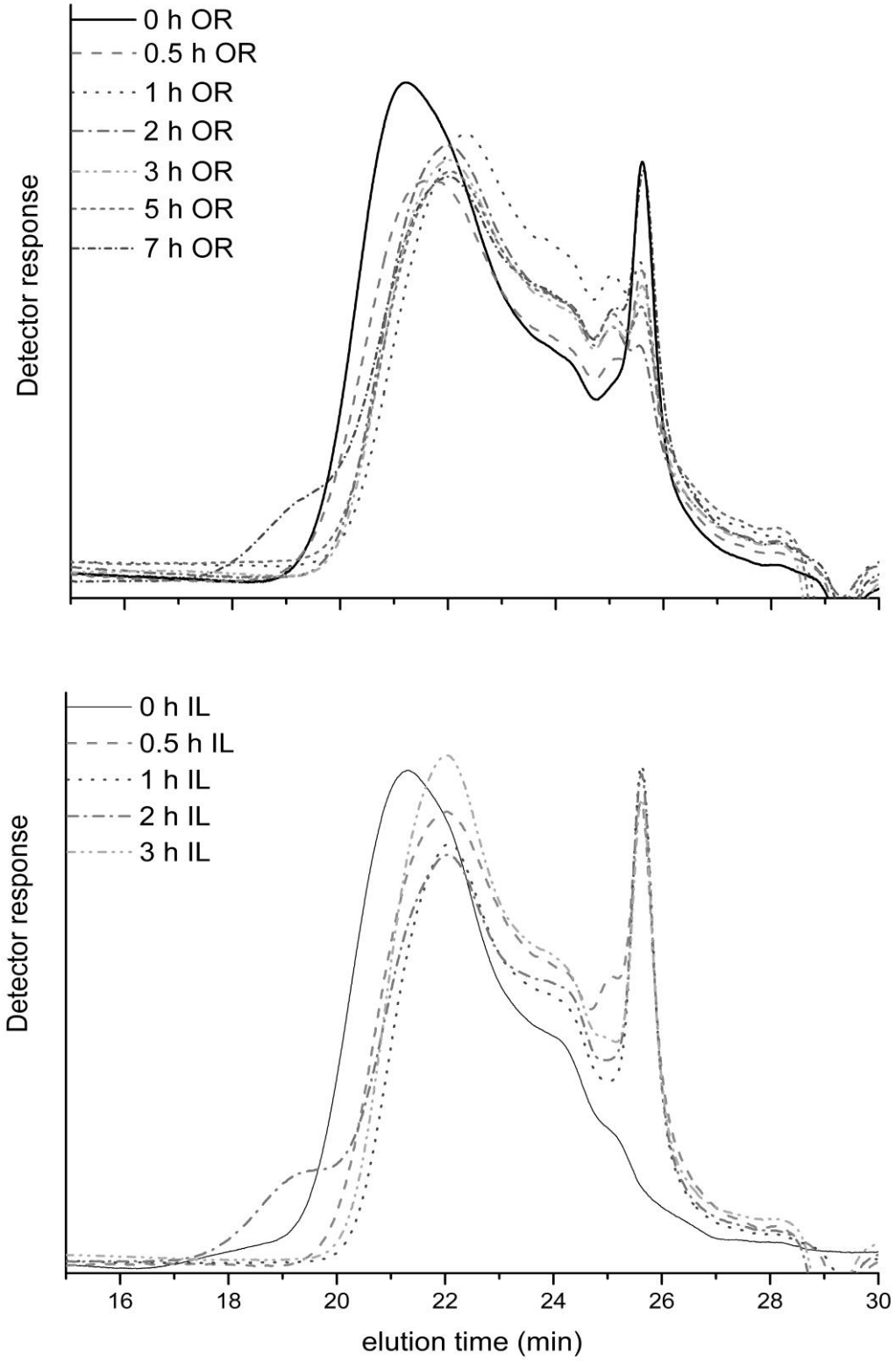
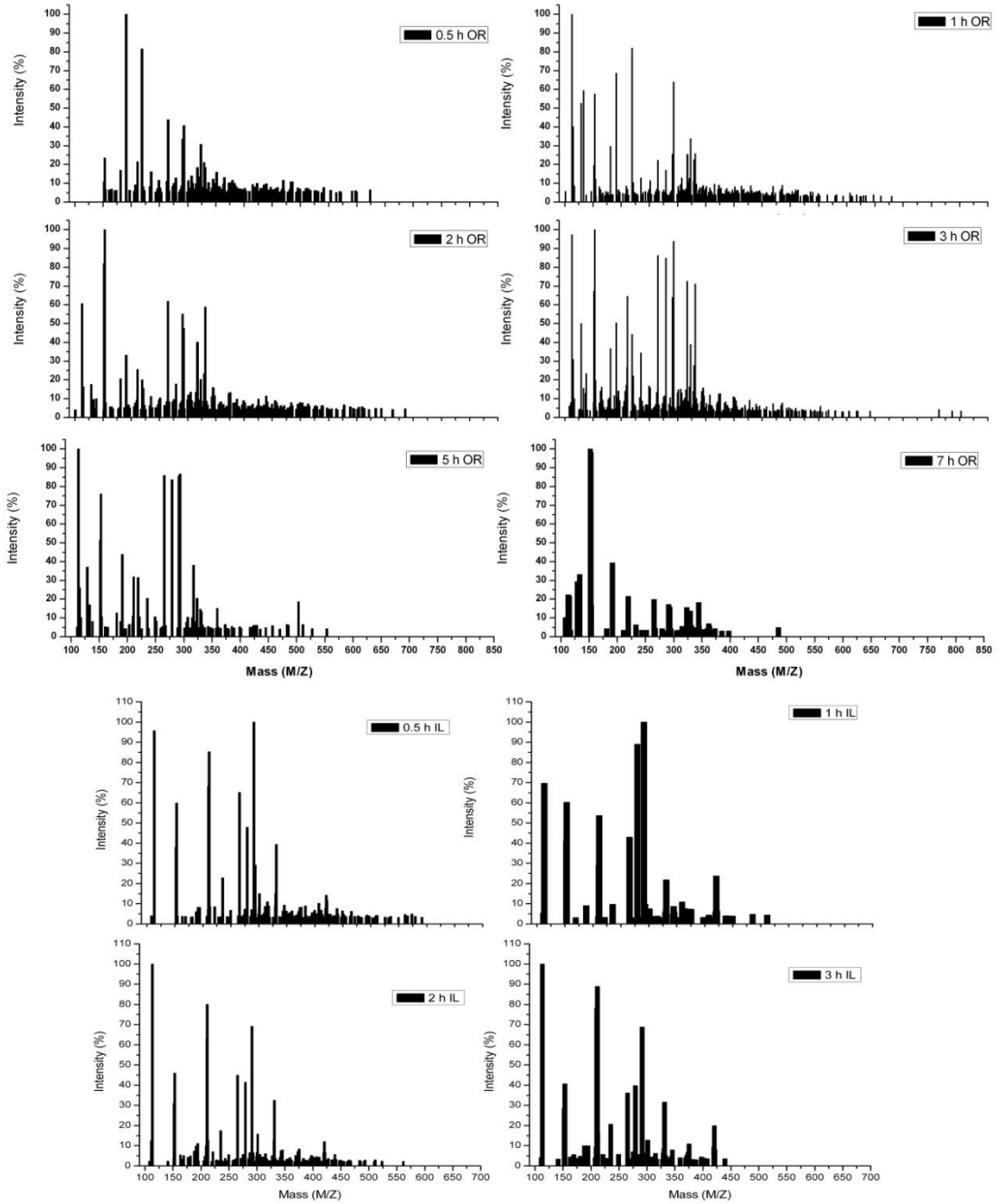
Figure 3: **MALDI-TOF results of *h OR oil samples and *h IL oil samples**