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Conversion of Organosolv and Kraft lignins into value-added compounds assisted by an acidic deep eutectic solvent

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Abstract

In this study, an acidic deep eutectic solvent (DES) was used as benign solvent to valorise technical lignins by breaking down their structure into value-added aromatic compounds. The action of an acidic DES composed of cholinium chloride ([Ch]Cl) and oxalic acid (Oxa), at molar ratio 1:1, towards depolymerisation of Kraft and Organosolv lignins (KL and OL) was studied at mild conditions (80 °C, for 1 to 6 h). Furthermore, the addition of hydrogen peroxide (H_2O_2) or sulfuric acid (H_2SO_4) as co-catalysts was also performed. The obtained data showed maximum yields between 26.1 wt% and 27.8 wt% of lignin depolymerisation products after KL and OL breakdown. Moreover, the profile of depolymerisation products was distinct between examined lignins as well as between acidic ([Ch]Cl:Oxa and [Ch]Cl:Oxa/H_2SO_4) and acidic oxidative treatments ([Ch]Cl:Oxa/H_2O_2). The acidic treatments of KL favoured the formation of syringol and acetosyringone, while vanillic and syringic acids were the main products in the acidic treatments of OL. On the other hand, the presence of H_2O_2 in DES revealed the ability to promote electrophilic substitutions of chloride from [Ch]Cl in the aromatic ring of lignin monomers. After depolymerisation, the regenerated lignin samples presented a different molecular weight, while FT-IR data showed structural changes, including esterification with oxalic acid and formation of phenolic groups as consequence of aryl ether bond breakdown. The insights gained in this study provide a better understanding on lignin depolymerisation with DES (in presence and absence of co-catalysts) and envisage process integration through the production of lignin monomers (and oligomers) combined with functionalisation of regenerated lignin.

Keywords. Lignin, deep eutectic solvents, depolymerisation, acidolysis, oxidation, value-added aromatic compounds.

Introduction

Lignin is one of the three major macromolecular components of plant biomass, besides cellulose and hemicelulloses, and is the second most abundant resource in nature after cellulose.[1] It exhibits structural and protective functions in plants against external biotic attacks and its content can reach 15 to 40 % of plant dry weight. Lignin is a randomly branched macromolecule constituted by three phenylpropanoid units, namely guaiacyl (G), syringyl (S) and p-hydroxyphenyl (H), linked by different types of C-O (*e.g.* β-O-4 and α-O-4) and C-C (*e.g.* β-β, β-1 and β-5) covalent bonds.[2,3] Therefore, this macromolecule represents a valuable source of aromatics and stands as one of the most important candidates to replace fossil-based feedstocks in the production of commodities, such as fuels, chemicals and materials within the scope of the biorefinery concept.[4,5]

Currently, most of the available lignin is produced as by-product of cellulose pulp and 2G bioethanol industrial activities, while its current fate is to serve as fuel in boilers to produce energy into the grid.[6] Bearing in mind all the potentialities of this aromatic carbon source, this is a low value chain strategy that must be upgraded. However, the heterogeneous and complex structure of lignin as well as its low reactivity restrict the development of applications towards novel materials and value-added chemicals.[7,8] A possible solution relies on the effective depolymerisation of this macromolecule into its monomeric constituents providing an opportunity to generate new products and also to overcome scientific and technological barriers upon lignin valorisation.

Nevertheless, the development of efficient lignin depolymerisation processes has been a massive challenge. The intricate structure of lignin, allied with highly stable C-C chemical bonds, hinders the depolymerisation that requires high energy input to promote effective linkage disruption. Amongst those chemical bonds, β-O-4 aryl ether are the most representative linkages in lignin structure (about 60%),[6] thus their cleavage has been intensively approached.[9] However, simultaneous breakdown of C-C bonds is of utmost importance specially when targeting the production of low molecular weight aromatic compounds, such as lignin monomers and oligomers, which may disclose a high market value in the future.[4]

In literature, heterogeneous[10,11] and homogeneous[4,12] catalysis have been reported as technologies capable of disrupting lignin chemical bonds (C-C and C-O) towards the production of aromatic chemicals. [4,10,13] The heterogeneous catalysis of lignin typically involves the application of metal catalysts, but they exhibit some disadvantages. Catalysts containing noble metals (palladium, platinum, ruthenium[14]) have disclosed high efficiency, but their high cost is a drawback, while cheap metal-based catalysts possessing zinc or copper are less efficient and their surface is quite often saturated with lignin fragments, preventing their appropriate reuse.[15] On the other hand, the homogeneous catalysis of lignin stands as an alternative by overcoming some of the disadvantages of heterogeneous conversion. However, it often relies on the application of strong mineral acids or alkaline solutions, posing undesired technical issues, especially in downstream processing.[16] A more sustainable solution may lie in the use of green tools, such as green solvents or green catalysts, to overcome these environmental and health limitations.

In this regard, ionic liquids (ILs) stand as an attractive class of green solvents.[17,18] Since the initial report on their ability to dissolve cellulose,[19] several studies have been describing the application of acidic ILs towards biomass fractionation, while some of them have shown their capacity for lignin depolymerisation.[20–22] For instance, Cox et al.[23] demonstrated the depolymerisation of lignin using 1-H-3-methylimidazolium chloride under the temperature range of 110-150°C. In another study, Jia et al.[24] reported the hydrolysis of β-O-4 bonds in two lignin model compounds using the same IL with a yield greater than 70% at 150°C. Furthermore, SO_3H-based ILs applied in water:methanol mixtures up to 1:1 molar ratio demonstrated a high conversion yield of dealkaline lignin into aromatic monomers (95-97%) at temperature range of 110-170°C.[22] Although some of these technologies demonstrated ILs as suitable solvents/catalysts for lignin depolymerisation, the availability and high cost of ILs have been limiting their application in depolymerisation reactions of large amounts of lignin.[25] Therefore, other green alternatives have been investigated.

Recently, deep eutectic solvents (DES) have been studied and applied as green solvents in several applications.[26] Introduced by Abbott et al.,[27] DES is a mixture of at least one hydrogen bond donor (HBD) and one hydrogen bond acceptor (HBA) capable of establishing strong hydrogen bonds and form an eutectic solution with inherent negative deviation to the melting temperature of the ideal mixture.[27,28] This depression in the melting temperature allows a large number of DES to be liquid at room temperature enabling their use as solvents. In addition, DES possess other favourable characteristics, including low vapor pressure, easy preparation and tailored physicochemical properties (acidity, basicity, polarity, among others).[29]

These features drew the attention to apply DES in lignin dissolution[30] and biomass delignification.[31,32] Several studies have been reporting acidic DESs, such as those formed by the combination of cholinium chloride ([Ch]Cl) as HBA and carboxylic acids, including oxalic acid (Oxa), formic acid (For) and lactic acid (Lac) as HBD, as efficient solvents for the extraction and dissolution of lignin from biomass.[33–35] A small group of works have stressed out small changes to lignin structure after its delignification with DES,[36] while others have proven the ability of DES to disrupt lignin chemical bonds,[35] specially β-O-4 ether bonds.[37] These apparent contradictory observations result mostly from the acidity of the HBD as well as the mild *vs* severe conditions applied in biomass delignification. Notwithstanding these differences, a close inspection on the delignification mechanisms and performance of acidic DES was investigated.[38,39] Alvarez-Vasco et al. reported that the cleavage of β-O-4 bond in a lignin model compound (guaiacylglycerol-β-guaiacyl) by [Ch]Cl:Lac is similar to lignin acidolysis catalysed by hydrochloric acid.[38] In another work, da Costa Lopes et al.[40] demonstrated that [Ch]Cl:p-toluenesulfonic acid (pTSA) and its bromide equivalent ([Ch]Br:pTSA) are able to cleave efficiently β-O-4 bonds of another lignin model compound (1-phenyl-2-phenoxyethanol). Through DFT calculations, the authors revealed a nucleophilic role of the halide anion (chloride or bromide) that substitutes the hydroxyl group neighbouring the β-O-4 ether linkage, forming a halide intermediate that energetically favours the cleavage.[40] On the other hand, Hong et al.[39] evaluated the structural changes of alkali lignin after its treatment with [Ch]Cl:Oxa and [Ch]Cl:Lac. In both cases, the cleavage of ether bonds was preceded by the following steps: i) removal of the C_α alcohol and the formation of highly reactive benzylic carbocations in the lignin side chains; ii) oxidation of the C_α position and acylation of the C_γ position.[39]

Bearing all this in mind, the application of DES as both solvent and catalyst may provide a new and sustainable process for lignin depolymerisation, besides biomass delignification. However, there are still few studies that explore the performance of DES to depolymerise lignin in its monomeric and oligomeric fragments.[39,41] The present study aims at giving an initial contribution to understand lignin depolymerization in DES. [Ch]Cl:Oxa (1:1 molar ratio), which previously showed an improved performance on lignin cleavage in contrast to other acidic DES,[37] was chosen as representative medium to dissolve and depolymerise two technical lignins, namely Kraft and Organosolv, under moderate conditions (80 °C, 1-6 h). In addition, sulfuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2) were used as co-catalysts to address different mechanistic possibilities in the disruption of lignin chemical linkages. Moreover, a brief demonstration on the physicochemical modifications of remaining lignin solid fraction induced by these systems were also addressed by GPC, FT-IR and elemental analysis.

Materials and Methods

Chemicals. Kraft Lignin (KL) isolated from Eucalyptus urograndis was directly supplied by Suzano Papel & Celulose (Brazil). KL was precipitated from the industrial black liquor by employing carbon dioxide. On the other hand, Organosolv Lignin (OL) was directly supplied by Fraunhofer (Germany). OL was extracted from beech wood with 50 % (v/v) ethanol solution and sulphuric acid as a catalyst. The HSQC NMR spectra of both lignins and corresponding ^{13}C-^{1}H assignments are shown in Figure S1 and Table S1, respectively. Cholinium chloride ([Ch]Cl, 98.0 wt% purity) was purchased from Acros Organics (New Jersey, US). Oxalic acid (Oxa, 99.5% purity), tetrahydrofuran (THF, 99 wt% purity and methyl benzoate (99 wt% purity) were purchased from Merck (Darmstadt, Germany). Both hydrogen peroxide (H_2O_2, 30 % v/v) and methyl isobutyl ketone (MIBK, 98.5 wt% purity) were purchased from Riedel-de Haën - Honeywell (Charlotte, US), while sulfuric acid (H_2SO_4, 96 wt% purity) was supplied by Fisher Chemical (New Jersey, US).

DES Preparation

The binary mixture of [Ch]Cl and Oxa at molar ratio 1:1 was sealed in glass vials, heated in oil bath at 60 °C and kept at constant magnetic stirring until a transparent liquid (approximately 2 hours) was formed. The prepared DES was cooled down to room temperature and water content was measured by Metrohm 831 Karl-Fischer coulometer. Water content in DES was corrected to 5 wt% afterwards to uniform every batch.

Lignin depolymerisation assays

The methodology of lignin depolymerisation and post-processing steps are briefly described in Figure 1. KL or OL (300 mg) was added to [Ch]Cl:Oxa (1:1) (6.0 g) in 250 mL glass flasks from 6 Plus Reaction Station™ carousel (Radleys, United Kingdom), which allows parallel reactions at the same temperature and agitation. The mixture was heated up to 80 °C and reaction was left for 1, 3 and 6 h under constant agitation (200 rpm) provided by the magnetic bar stirrer. Both technical lignins were treated with three distinct systems: i) DES; ii) DES with catalytic amount of H_2SO_4 (1 wt%); and iii) DES with catalytic amount of H_2O_2 (2 wt%).

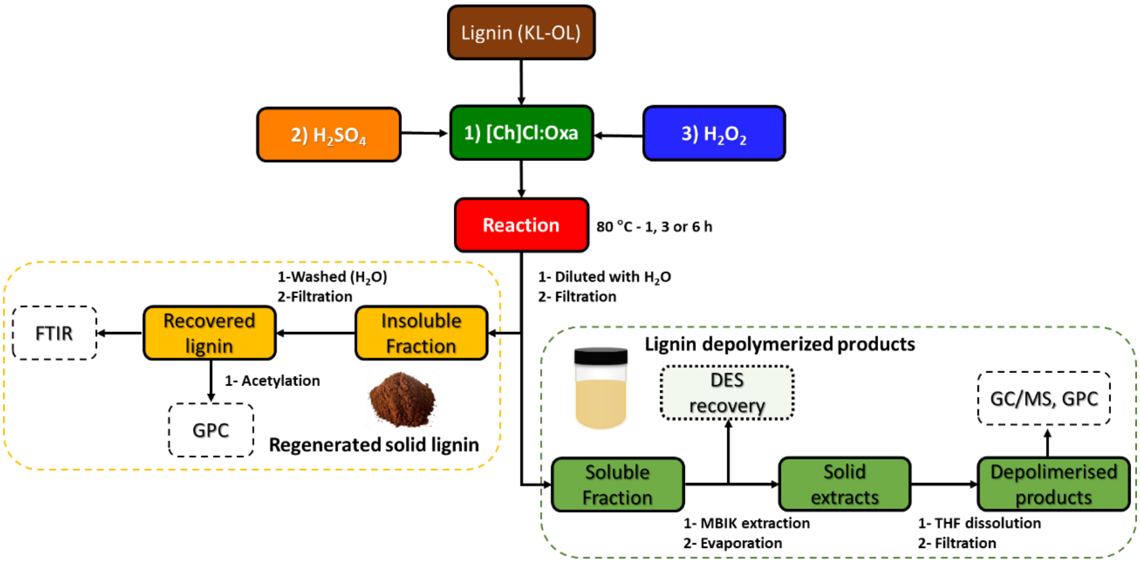

Figure 1. The flowchart of lignin treatment and post-processing analysis performed in this work.

After reaction, the glass flasks were placed in ice bath (5 °C) and 20 mL of water was added to the mixture enabling lignin precipitation. The precipitated lignin was separated by vacuum filtration, washed with water (3 x 10 mL), and finally freeze dried before its gravimetric quantification. The lignin recovery yields were determined by the equation

1. The liquid phase containing lignin depolymerised products was collected and stored in a fridge before analysis. The obtained yields of lignin depolymerisation product were calculated by closing the mass balance of the initial lignin as disclosed by the equation 2.

$$lignin\ recovery\ yield\ (wt\%) = \frac{m_{Lig_{rec}} \cdot \left(1 - Ash_{Lig_{rec}}\right)}{m_{Lig_{init}} \cdot \left(1 - Ash_{Lig_{init}}\right)} \cdot 100 \qquad (1)$$

$$Product\ yield\ (wt\%) = \frac{m_{Lig_{init}} \cdot \left(1 - Ash_{Lig_{init}}\right) - m_{Lig_{rec}} \cdot \left(1 - Ash_{Lig_{rec}}\right)}{m_{Lig_{init}} \cdot \left(1 - Ash_{Lig_{init}}\right)} \cdot 100 \qquad (2)$$

where $m_{Lig_{rec}}$ is the total amount of recovered lignin (g), $m_{Lig_{init}}$ is the initial amount of lignin (g), $Ash_{Lig_{rec}}$ is the ash content in recovered lignin, and $Ash_{Lig_{init}}$ is the ash content in initial lignin.

Extraction of lignin depolymerisation products from DES.

The collected liquid phase (≈20 mL) was subjected to a liquid/liquid extraction with MIBK (10 mL) to separate the lignin depolymerisation products from DES.[6,42] The MIBK phase enriched with those compounds was then separated from DES phase. This liquid/liquid extraction step was repeated twice and MIBK phases were collected in the same flask and further evaporated in a centrifugal vacuum concentrator (MiVac, US)**.** The samples were dissolved in 5 mL THF followed by filtration to remove any trace of [Ch]Cl (insoluble in THF). Subsequently, THF was evaporated in centrifugal vacuum concentrator. The resulting solid extracts were re-dissolved in THF to obtain a known concentration (20.0 mg·L^{-1}) for GC-MS analysis.

Lignin acetylation.

The regenerated lignin samples (section 2.3) were acetylated with pyridine and acetic anhydride (2:1) v/v mixture at 50 °C. After 8 hours of reaction, the pH of the solutions was adjusted to approximately 3.0 with a HCl (0.1 N) solution and left at room temperature for 12 h with continuous stirring (approximately 200 rpm) to avoid lignin agglomeration. The obtained suspensions were centrifuged for 10 min at 4500 rpm and the resulting acetylated lignin was exhaustively washed with distilled water (5 x 10 mL) and freeze-dried. The acetylated lignin samples were analysed by GPC.

Characterisation of lignin depolymerisation products and remaining lignin solid fractions

Gas chromatography/mass spectrometry (GC/MS) analysis

The identification and semi-quantification of lignin depolymerisation products was carried out using a gas chromatograph/mass spectrometer Shimadzu QP2010 Ultra, equipped with an AOC-20i autosampler and high-performance quadrupole mass filter. The separation of reaction products was carried out in a DB-5 ms column (30 m length, 0.25 mm i.d. and 0.25 μm film thickness) using helium as the carrier gas (40 cm s^{-1}). The chromatographic conditions were as follows: isothermal at 80 °C for 5 min, ramped from 80 to 250 °C (8 °C min^{-1}), ramped from 250 to 300 °C (4 °C min^{-1}) and then isothermal at 300 °C for 5 min; injector temperature of 320 °C; and split ratio equal to 1:10. The MS was operated in the electron impact mode with an electron impact energy of 70 eV and data was collected at a rate of 1 scan s^{-1} over a range of m/z 50–1000. The ion source was kept at 200 °C and the interface temperature at 300 °C.

Identification of compounds was performed by comparing chromatographic peaks retention times and their mass spectra with the equipment mass spectral library (NIST14s

MS Library Database or WILEY229 MS Library Database). The m/z value of the molecular ion together with the fragmentation was used to figure out the structure of the compound. A semi-quantitative analysis was carried out by considering the ratio between the peak area of each compound and the sum of peak area of all detected compounds as shown by the equation 3:

$$\%\, Relative\ Peak\ Area_i = \frac{A_i}{\sum_i^n A_i} \cdot 100 \tag{3}$$

where A_i is the peak area of compound "i", *and* "n" is the number of compounds.

Gel Permeation Chromatography (GPC) analysis

GPC analyses of acetylated lignin samples and depolymerisation products were performed on a gel permeation chromatographic system (HP — AGILENT system) equipped with a UV detector (set at 280 nm). Analyses were carried out at ambient temperature using THF as eluent at a flow rate of 1 mL·min^{-1}. Aliquots (100 µL) of acetylated lignin dissolved in THF (1.5 mg·mL^{-1}) were injected into PLgel 3 µm MIXED E 7.5 x 300 mm. The column specifications allow for the separation of molecular masses up to 3.0 x 104 g·mol-1. The GPC system was calibrated with polystyrene standards (Mw = 162, 672, 890, 2280, 4840, 5180, 9630, 25500, 61400, 127000 g·mol-1). Moreover, guaiacylglycerol-β-guaiacyl ether (>99 % purity, TCI Chemicals, Belgium), known as β-O-4 linkage-lignin model compound (Mw 320 g·mol-1) was used to construct the calibration curve aiming to increase the accuracy of the measured values in the low molecular weight region. The chromatographic data were processed with the PSS (Polymer Standards Service) WinGPC Unity software.

Fourier Transform InfraRed (FT-IR) analysis

The FT-IR spectra of lignin samples (not acetylated) were recorded on a PerkinElmer Spectrum BX spectrometer equipped with a horizontal Golden Gate ATR cell and a diamond crystal. A total of 32 scans were made for each sample with a resolution of 4 cm^{-1} in a wave range between 4000 cm^{-1} and 400 cm^{-1}.

Elemental Analysis

The elemental analysis of lignin samples was conducted with a TruSpec series 630-200-200 elemental analyser (Michigan, US). The combustion furnace temperature and the afterburner temperature were maintained at 1075 °C and 850 °C, respectively. The oxygen content was determined by the difference.

Experimental and analytical error analyses

All the experiments were performed in duplicate and the obtained results were expressed as means with associated standard deviation errors (u). The applied temperature in the reactions demonstrated a $u(T)=1$ °C. All the mass determinations were performed with a given $u(m)=0.1$ mg.

Results

Characterisation of lignin depolymerisation products

Kraft and Organosolv lignins (KL and OL) were treated with three distinct solvent systems: i) [Ch]Cl:Oxa; ii) [Ch]Cl:Oxa/H_2SO_4; and iii) [Ch]Cl:Oxa/H_2O_2. Their ability for lignin depolymerisation at 80 ºC was evaluated over time (1, 3 and 6 h) and the obtained depolymerisation product yields are depicted in Figure 2.

At first sight, depolymerisation product yields were all higher than 6.0 wt%, suggesting that the studied systems were able to convert at least a small portion of the initial lignin. Furthermore, reactions of OL and KL with both [Ch]Cl:Oxa and [Ch]Cl:Oxa/H_2SO_4 revealed an increase of the depolymerisation product yield from 1 to 3 h, but a sharply decrease at 6 h was verified. Maximum yields between 26.1 wt% and 27.8 wt% of lignin depolymerisation products were obtained in the reaction of both KL and OL with these DES systems at 3 h. However, an exception to this trend was observed for DES comprising a catalytic amount of H_2O_2, which exhibited a different behaviour in the depolymerisation of both KL and OL in contrast to other DES systems. For KL treatment with [Ch]Cl:Oxa/H_2O_2, a maximum depolymerisation product yield (20.4 wt%) was detected at 1 h, while it decreased continuously over time up to one half after 6 h. On the other hand, no relevant changes in yields (between 12.6 and 15.3 wt%) during OL treatment with [Ch]Cl:Oxa/H_2O_2 were observed.

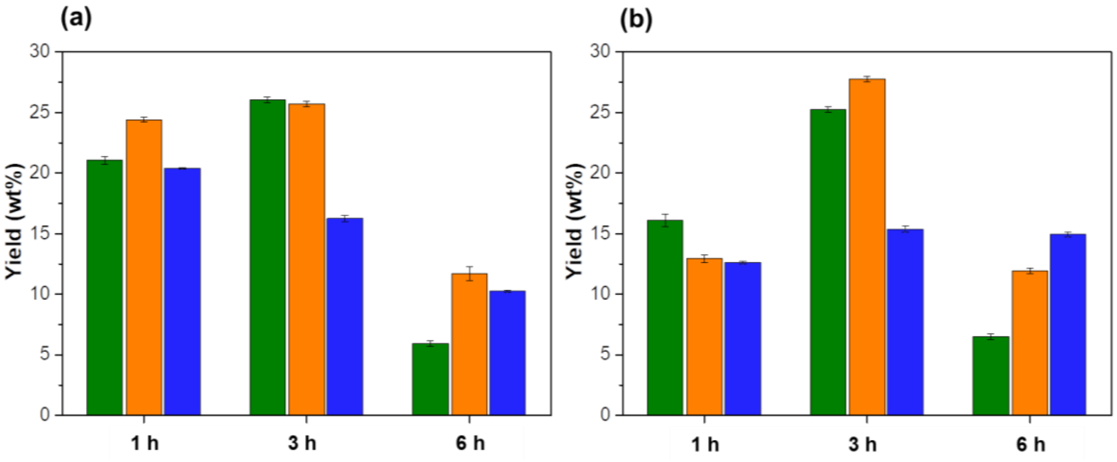

Figure 2. Yields of lignin depolymerisation products in the liquid phase after a) KL and (b) OL treatment with [Ch]Cl:Oxa (🟩), [Ch]Cl:Oxa/H_2SO_4 (🟧) and [Ch]Cl:Oxa/H_2O_2 (🟦) at 80 °C.

Afterwards, lignin depolymerisation products were tentatively identified by GC/MS. Initially, 60 compounds were labelled, but among these, the 30 most representative compounds were selected (Table 1) to compare the catalytic behaviour of the examined DES systems. The obtained products were identified as aromatic monomers derived from syringyl (S) and guaiacyl (G) units containing alcohols, ketones, aldehydes and carboxylic acids as functional groups attached to the aromatic ring or to the carbon chain at α, β and γ positions of those units. Due to the nature of KL (*E. grandis* wood) and OL (beech wood), which are mostly comprised by S and G units,[43,44] compounds derived from hydroxyphenyl (H) units were not identified in this work. Furthermore, the chromatograms of depolymerisation extracts from KL and OL showed the same peaks, although with different relative abundances (Figure S2 in SI).

Table 1. Main compounds identified by GC-MS (chemical structures are represented in Table S2 in SI).

Entry	Compounds	MW (Da)	Ret. Time (min)
1	guaiacol	124.14	7.380
IS*	methyl benzoate	136.15	7.645
2	1-(3,4,5-trihydroxyphenyl)propanone	182.17	10.818
3	3-(3,4,5-trihydroxyphenyl)propanal	182.17	11.430
4	5-chloroguaiacol	158.01	11.609
5	4-ethyl-guaiacol	152.19	11.663
6	2-methoxy-4-vinylphenol	150.22	11.903
7	3-methoxycatechol	140.05	11.285
8	syringol	154.16	13.062
9	vanillin	152.15	14.011
10	1-chloro-5-methoxybenzene-3,4-diol	174.01	14.358
11	acetovanillone	166.17	15.485
12	3,4-dihydroxy-5-methoxyacetophenone	182.17	16.027
13	guaiacylacetone	182.17	16.130
14	vanillic acid	168.14	16.690
15	4-allyl-2,6-dimethoxyphenol	194.23	17.037
16	2-chloro-3,5-dimethoxybenzene-1,4-diol	204.02	17.680
17	homovanillic acid	182.17	17.760
18	2,5-dimethoxy-1,4-benzenediol	170.16	18.002
19	syringaldehyde	182.17	18.072

20	3,5-dichloro-2,6-dimethoxyphenol	221.99	18.370
21	3-(4-hydroxy-3-methoxyphenyl)-2-oxopropanoic acid	210.05	18.640
22	3,4,5-trichloro-2-methoxyphenol	225.94	18.655
23	2-(4-hydroxy-3,5-dimethoxyphenyl)acetaldehyde	196.20	19.050
24	acetosyringone	196.19	19.137
25	2,6-dichloro-3,5-dimethoxybenzenediol	239.50	19.685
26	5-chlorovanillic acid	202.17	19.792
27	syringic acid	198.17	20.150
28	1-(6-chloro-4-hydroxy-3,5-dimethoxyphenyl)ethanone	230.30	20.323
29	1-(4-hydroxy-3,5-dimethoxyphenyl)propanedione	224.25	20.373
30	2-chloro-4-hydroxy-3,5-dimethoxybenzoic acid	232.01	22.275

*Internal Standard

The composition of lignin depolymerisation extracts was performed by semi-quantitative analysis. Figure 3 depicts the relative abundances of the identified 30 compounds after treatment of both KL (3a) and OL (3b) with the three examined DES systems at 80 ºC for 3 h. The obtained data showed once more a distinct behaviour between both [Ch]Cl:Oxa and [Ch]Cl:Oxa/H_2SO_4 when compared with [Ch]Cl:Oxa/H_2O_2 in the formation of lignin depolymerisation products. For the first two systems, lignin monomers, including 2-(3,4-dihydroxy-5-methoxyphenyl)acetaldehyde **(3)**, syringol **(8)** and acetosyringone **(24),** were detected in higher amount than other compounds in KL depolymerisation. In fact, syringol reached approximately 25 % of all identified compounds in KL depolymerisation with neat DES and in presence of H_2SO_4. However, when looking to the depolymerisation products achieved with [Ch]Cl:Oxa/H_2O_2, compound **(3)** stood as the most abundant monomer resultant from the KL treatment (≃ 10%). On the other hand, by changing the lignin sample to OL, besides compound **(3)** the formation of vanillic **(14)** and syringic **(27)** acids were favoured in the three DES systems. Furthermore, it should be also highlighted that the presence of H_2O_2 promotes the formation of distinct chlorinated species, including **(10)**, **(16)**, **(25)**, **(28)** and **(30)**, which were not produced in its absence. The corresponding data obtained for the lignin treatments with all DES systems at 1 and 6 h are presented in SI (Figures S3 and S4, respectively).

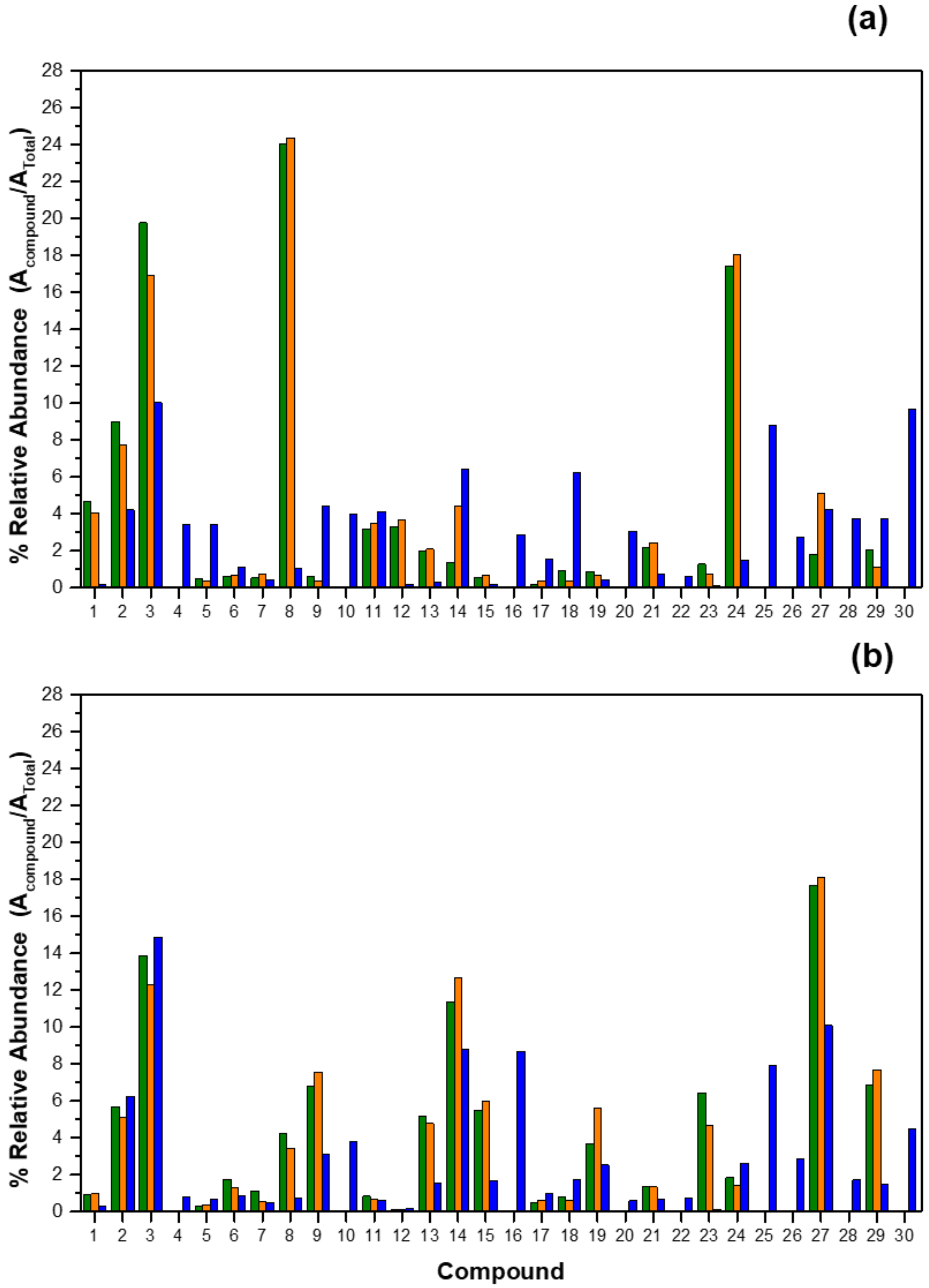

Figure 3. Relative abundance (%) of lignin depolymerisation products from (a) KL and (b) OL depolymerisation at 80 °C for 3 hours with [Ch]Cl:Oxa (🟩), [Ch]Cl:Oxa/H_2SO_4 (🟧) and [Ch]Cl:Oxa/H_2O_2 (🟦).

As aforementioned, the GC/MS data allowed the identification of several monomeric compounds with maximum molecular weight (MW) between 124 of 232 Da (Table 1). However, the existence of oligomeric products is highly probable after depolymerisation with examined DES systems. Therefore, to evaluate the MW distribution of depolymerised lignin extracts during time, acetylated samples were analysed by GPC. As an example, chromatograms of KL depolymerisation products obtained with the three DES systems at 1 h and 6 h are presented in Figure 4 (results for OL are shown in Figure S5 in SI).

On the left of Figure 4, the MW fraction below 240 Da is highlighted in grey, corresponding to lignin monomers that were detectable by the GC/MS method. It is possible to identify 4 main peaks with maximum at 90, 118, 160 and 170 Da, the last two being the most intense. Amongst the 30 compounds identified by GC-MS, around 21 have a molecular mass between 140 and 190 Da, which may comprise the GPC peaks at 160 and 170 Da. Surprisingly, the peaks at 90 and 118 Da are very pronounced in the KL depolymerisation fraction obtained with DES/H_2O_2. They may comprise low molecular weight aromatic compounds that were not identified by the GC/MS method used in this work (*e.g.* toluene and benzene, which are eluted simultaneously with the solvent). On the other hand, oligomers with wide distributed MWs can be observed on the right of Figure 4, representing a substantial fraction in each depolymerisation extract. These oligomeric fragments were also not identified by the GC/MS. The GPC data revealed that a higher quantity of oligomers seems to be produced by neat DES and DES/H_2SO_4. On the contrary, the oxidative environment promoted by H_2O_2 favoured the formation of low molecular weight compounds to the detriment of lignin oligomers.

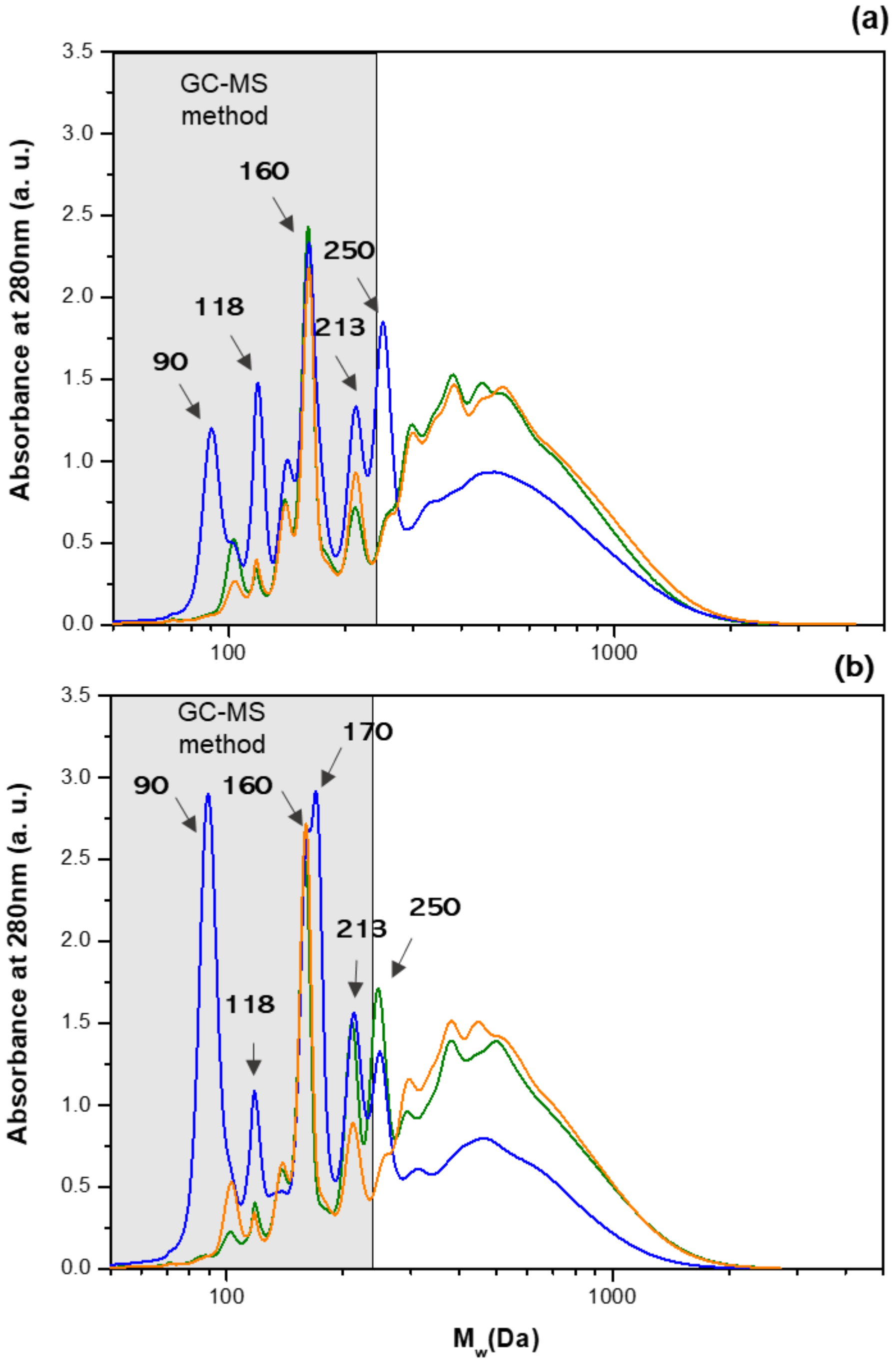

Figure 4. GPC analysis of lignin depolymerisation products from KL treatment at 80 °C during (a) 1 h and (b) 6 h with [Ch]Cl:Oxa (🟩), [Ch]Cl:Oxa/H_2SO_4 (🟧) and [Ch]Cl:Oxa/H_2O_2 (🟦).

Lignin depolymerisation over time

The formation and consumption of depolymerisation products was tracked over time to understand lignin depolymerisation assisted by the three examined DES systems. The behaviour over time of 15 relevant aromatic compounds, previously identified by GC/MS, was followed by the relative peak area of each compound. The data obtained from KL depolymerisation with the three DES systems between 1 and 6 h is presented as a model in Figure 5.

At first sight, treatments at 3 h disclosed the highest formation of aromatic monomers, which correlates well with the depolymerisation yields presented in Figure 1. Furthermore, the profile of the 15 compounds over time are similar between treatments with [Ch]Cl:Oxa (Figure S6 in SI) and [Ch]Cl:Oxa/H_2SO_4 (Figure 5a), but noticeably different in lignin depolymerisation mediated by [Ch]Cl:Oxa/H_2O_2 (Figure 5b).

The KL depolymerisation under acidic conditions ([Ch]Cl:Oxa/H_2SO_4) revealed that a major fraction of monomeric compounds, including guaiacol **(1)**, syringol **(8)**, acetovanillone **(11)**, vanillic acid **(14)**, a demethylated ketone **(2)** and a demethylated aldehyde **(3)** presented a remarkable formation from 1 to 3 h, but was followed by their drastic consumption up to 6 h. Although a similar trend was observed for acetosyringone **(24)**, its consumption rate was moderate. On the other hand, syringic acid **(27)** presented a maximum yield at 1 h and was followed by a decreasing trend over time. On the opposite, vanillin **(9)** and syringaldehyde **(19)** relative peak areas increased during time, although their representation in depolymerisation extract is very low.

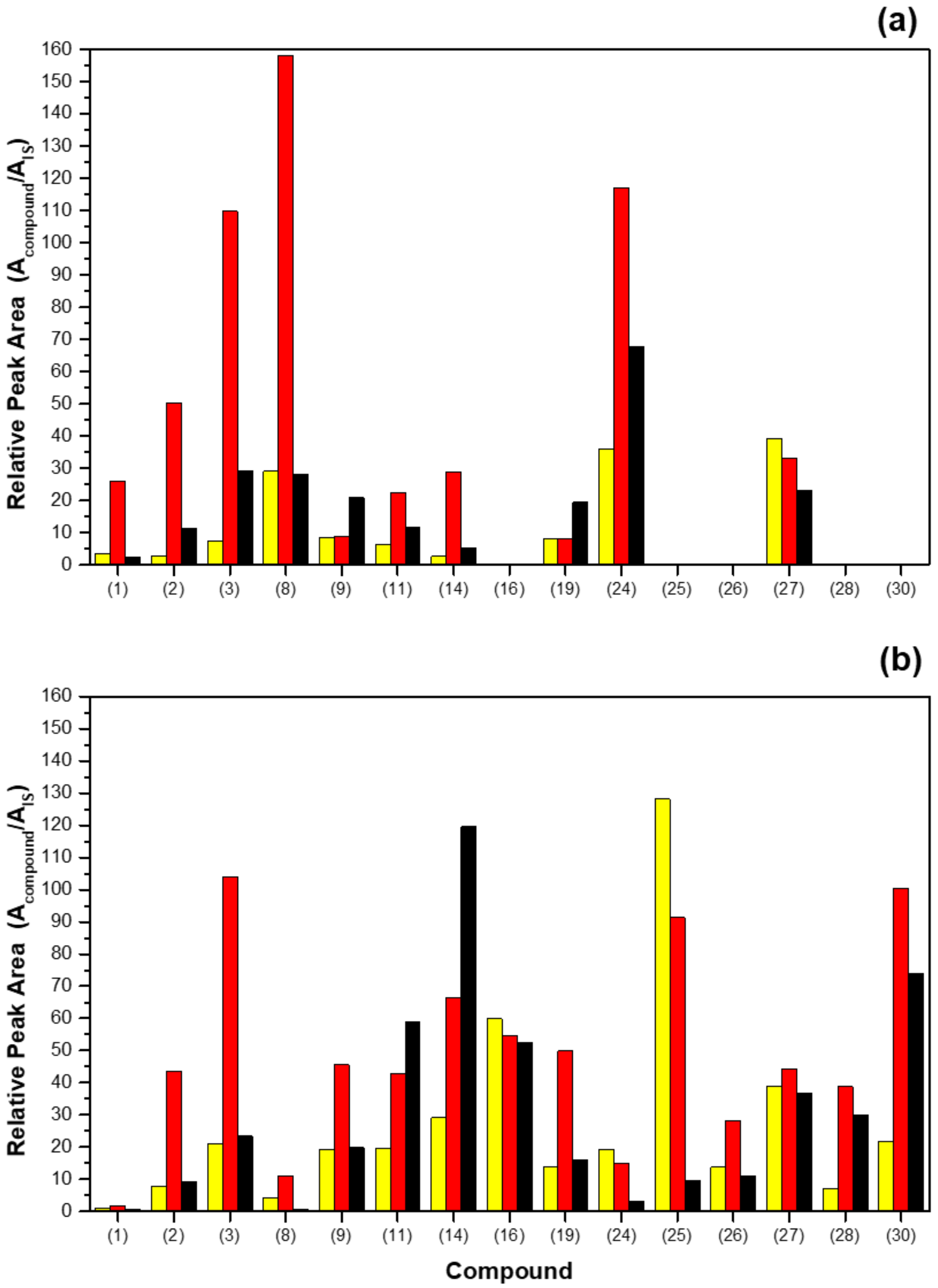

Figure 5. Relative peak area of identified compounds after KL depolymerisation at 80 °C for 1 h (🟨),3 h (🟥) and 6 h (■) with (a) [Ch]Cl:Oxa/H_2SO_4 and (b) [Ch]Cl:Oxa/H_2O_2.

Considering that all these compounds are expected to participate in repolymerisation/condensation reactions in prolonged times leading to their consumption,[45] it seems that produced monomeric alcohols (1 and 8), demethylated compounds (2 and 3) and vanillic acid are more prone to those type of reactions. On the other hand, syringic acid, vanillin and syringaldehyde are less reactive and more stable during lignin treatment in presence of [Ch]Cl:Oxa/H_2SO_4 (or [Ch]Cl:Oxa, Figure S6 in SI).

The OL depolymerisation over time with the three DES systems were also studied and obtained results are depicted in Figure 6. Similar to KL depolymerisation, treatments of OL at 3 h revealed the highest formation of aromatic monomers. However, the compound profiles of OL depolymerisation revealed differences from those achieved with KL.

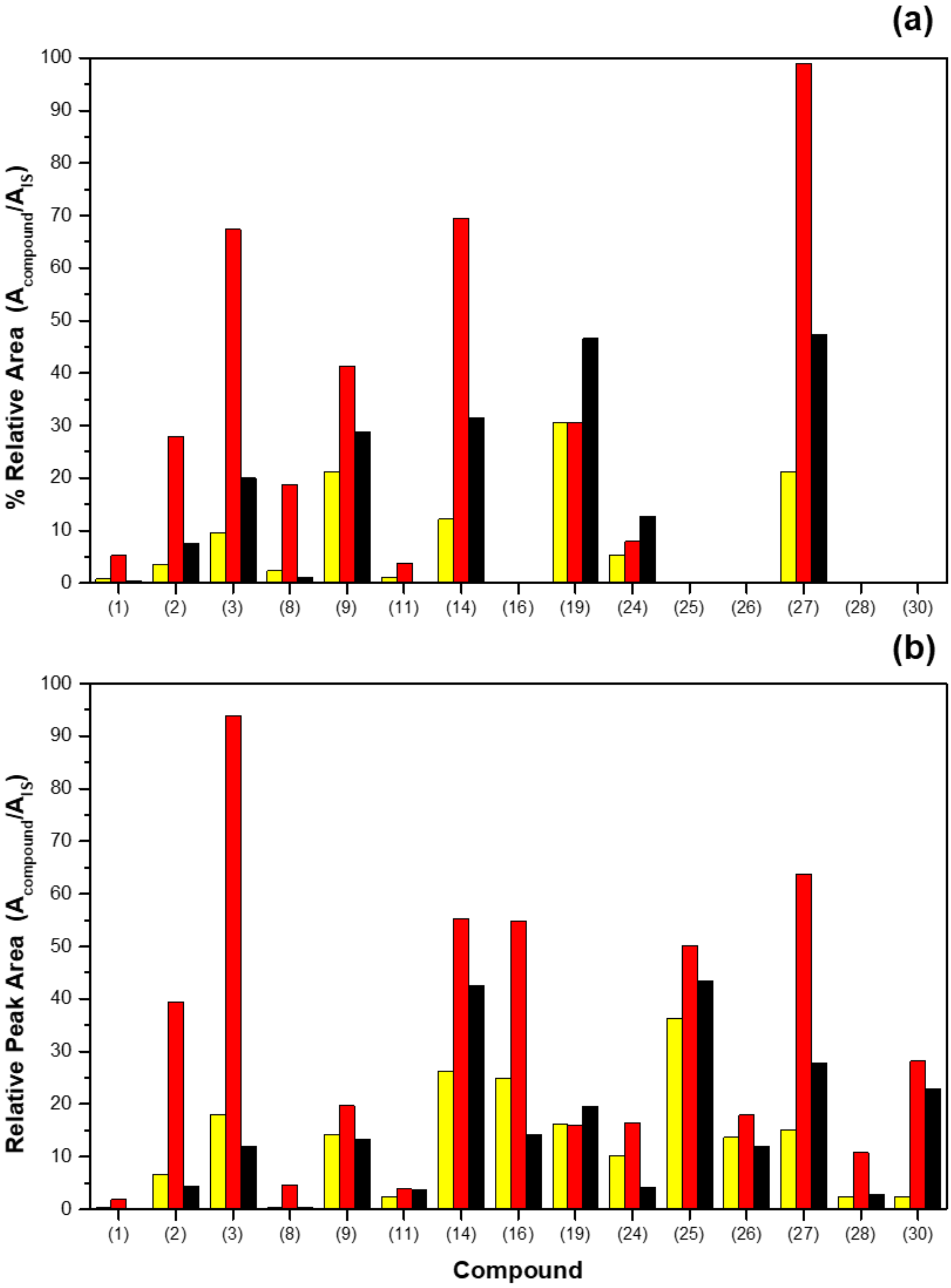

Figure 6. Relative peak area of identified compounds after OL depolymerisation at 80 °C for 1 h (🟨),3 h (🟥) and 6 h (■) with (a) [Ch]Cl:Oxa/H_2SO_4 and (b) [Ch]Cl:Oxa/H_2O_2.

Depolymerisation of OL under acidic conditions ([Ch]Cl:Oxa/H_2SO_4) revealed that most monomeric compounds, including 3-(3,4,5-trihydroxyphenyl)propanal **(3)**, vanillin

(9), vanillic acid **(14)**, syringic acid **(27)** showed an extensive production up to 3 h, but a drastic decrease was observed for longer times. Unlike KL depolymerisation, the formation of syringic acid **(27)** and vanillic acid **(14)** were favoured to the detriment of syringol **(8)** and guaiacol **(1)** in both [Ch]Cl:Oxa and [Ch]Cl:Oxa/H_2SO_4. This is evidence that lignin nature, which is dependent on its biomass origin and delignification process, exhibits a significant impact on the final composition of depolymerisation products. Furthermore, the corresponding precursors, syringaldehyde **(9)** and vanillin **(19)**, were found in higher amount in OL depolymerised fraction than in the case of KL depolymerisation.

Regarding the OL depolymerisation with [Ch]Cl:Oxa/H_2O_2, vanillic acid **(14)** was again a major product after 6 h of reaction, while consumption of compound **(25)** was not as fast as that observed for KL. The strong oxidative medium provided by H_2O_2 allowed the substitution at different positions of the aromatic chloride ring, resulting in the same chlorinated compounds (**(16)**, **(25)**, **(26)**, **(28)** and **(30)**) as highlighted above.

Structural characterisation of the recovered lignin.

The impact of the depolymerisation reactions mediated by the studied systems on the remaining solid lignin was also evaluated. The lignin molecular weight distribution was first evaluated by GPC and the obtained results, including average molecular weight (Mw), number average molecular weight (Mn) and polydispersity index (PDI), are presented in Figure 7 and Table S3.

The Mw values of both KL and OL were 2500 and 3300 $g \cdot mol^{-1}$, while the polydispersity indexes (PDI) were determined to 2.1 and 2.2, respectively (Table 2). After depolymerisation with studied DES systems, recovered lignin samples at 1 h and 6 h of treatment disclosed reduced Mw and Mn values in contrast to initial KL and OL, confirming depolymerisation mediated by all systems. Although the highest yields of lignin depolymerisation was observed at 3 h treatment (Figures 2, 5 and 6), the corresponding recovered lignins presented the highest Mw and Mn values (Figure 7). This means that albeit lignin monomers are extensively produced at 3 h, simultaneous side reactions between remaining lignin fragments are favoured at cleavage sites enabling the formation of higher molecular weight lignin macromolecules.[46] In turn, this high molecular weight fraction influences the average Mw and Mn values (Figure 7). The increase of lignin Mw and Mn values at 3 h is more pronounced in the presence of H_2O_2. The oxidative nature of this catalyst may induce the formation of reactive OH radical and radical lignin sites, increasing the rate of side reactions.[47] After 6 h of treatment, Mw and Mn values decreased, which is associated not only to the gradual degradation of the formed fragments through cleavage of the remaining ether bonds, but also to the repolymerisation of lignin monomers into insoluble low molecular weight fragments. This explains the decreasing yield of lignin depolymerisation products after 6 h of treatment as stated above (Figure 2). Moreover, at this stage, the side reactions between lignin fragments might be suppressed, due to the peroxide radical neutralisation over time, favouring the reduction of both Mw and Mn values.

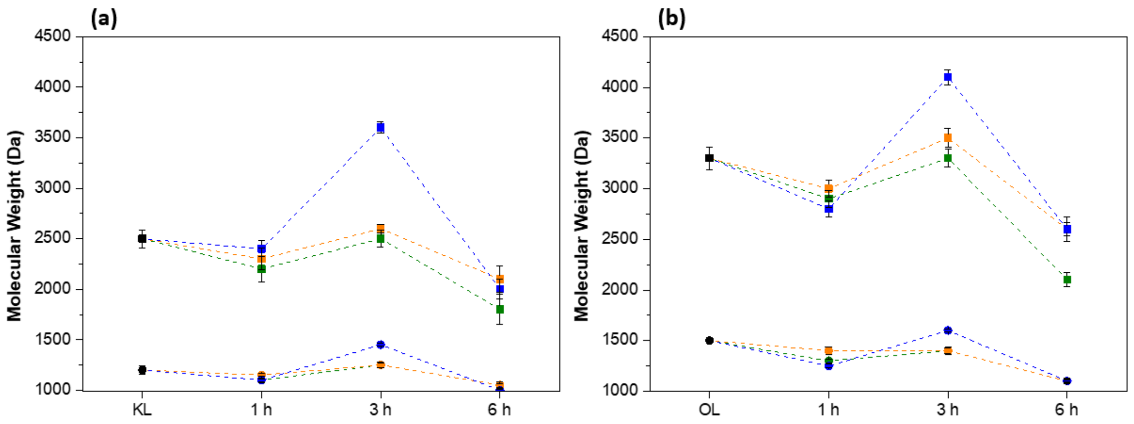

Figure 7. Molecular weight average (Mw - ■) and molecular number average (Mn - ●) of technical lignins and corresponding recovered lignin samples after treatment with [Ch]Cl:Oxa (Mw - 🟩; Mn - 🟢), [Ch]Cl:Oxa/H_2SO_4 (Mw - 🟧; Mn - 🟠) and [Ch]Cl:Oxa/H_2O_2 (Mw - 🟦; Mn - 🔵) at 80 °C during time. a) KL; b) OL

In addition, FT-IR analyses of recovered lignin samples were performed to address possible chemical modifications induced by DES systems during depolymerisation process. All infrared spectra showed lignin fingerprint with typical vibrational bands as reported in literature.[48–52] The list of all lignin vibrational bands and corresponding assignments are presented in SI (Table S4). Figure 8 shows magnified FT-IR spectra of KL, OL and corresponding recovered lignins (2000-600 cm^{-1}). The most relevant were observed in the region 1800-750 cm^{-1} with remarkable high intensities at 1109, 1211, 1368, 1456, 1514, 1590 and 1736 cm^{-1}. However, significant changes in the absorbance of specific bands were detected after depolymerisation with DES systems.

One of the most prominent differences was the substantial increase of the vibrational band at 1736 cm^{-1} over time in all systems and both lignins. This vibration corresponds to the elongation of C=O chemical linkage, specifically associated to ester groups, which means that esterification was promoted between lignin hydroxyl groups and oxalic acid from DES. This phenomenon was already mentioned in a previous work.[37] Moreover, this esterification was more evident in DES with catalysts than neat DES, suggesting that both H_2SO_4 and H_2O_2 might boost this parallel reaction. These results also reveal that depolymerisation product yields might be higher than those shown in Figure 1. The esterification of oxalic acid in lignin structure directly increases the recovery yield of regenerated lignin affecting the calculations of depolymerisation product yield (equation 2, section 2.3).

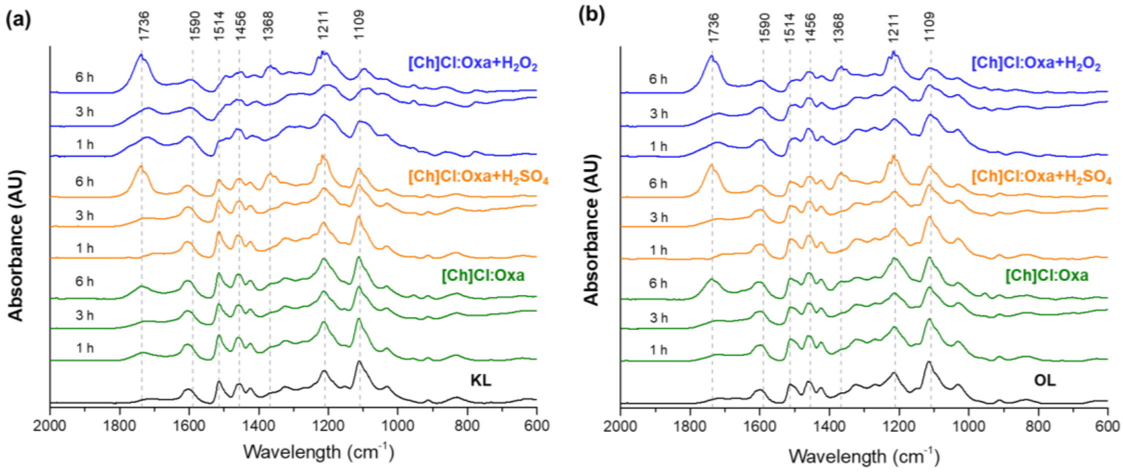

Figure 8. Magnified FT-IR spectra of technical lignins and corresponding recovered lignin samples after treatment with [Ch]Cl:Oxa (🟩), [Ch]Cl:Oxa/H_2SO_4 (🟧) and [Ch]Cl:Oxa/H_2O_2 (🟦) at 80 °C during time.

On the other hand, the vibrational band at 1109 cm^{-1} decreased sharply during lignin treatments, while an opposite behaviour was observed for the vibrational band at 1368 cm^{-1}. The last represents the C-OH vibrations of phenolic hydroxyl groups,[53,54] which increased during time as consequence of the direct cleavage of aryl ether bonds (e.g. β-O-4 and α-O-4), represented by the first one (C-O vibration in ether bonds).[55,56] Once more, these chemical changes were more pronounced when using [Ch]Cl:Oxa/H_2SO_4 and [Ch]Cl:Oxa/H_2O_2.

Another important change to be highlighted from these data is the conservation or deformation of the aromatic structure of lignin directly represented by the aromatic skeletal vibrations, namely 1456, 1514, and 1590 cm^{-1}, after treatments. As observed in Figure 8, treatments of both lignins with [Ch]Cl:Oxa did not affect these bands, but those with [Ch]Cl:Oxa/H_2SO_4 (6 h) and [Ch]Cl:Oxa/H_2O_2 (1, 3 and 6 h) altered significantly their shape and absorbance. This is more pronounced for treatments with H_2O_2, suggesting that aromatic skeletal structure of lignin is highly disrupted or substantially changed under oxidative conditions. This behaviour is in agreement with the results reported by Wan et al.[57] Based on previous analysis, these authors suggested that after acidic oxidative treatment of lignin (phosphonic acid and hydrogen peroxide) HO^+ or HO radical was produced, being responsible for an extensive ring-opening on the aromatic substructure. Furthermore, aromatic ring substitution by chloride atoms may also be favoured in similar way as chlorinated compounds were formed during depolymerisation in presence of H_2O_2.

The results obtained from the elemental analysis (Table S5) of depolymerised lignins showed an impact of depolymerisation on carbon, hydrogen, nitrogen and sulfur contents in recovered lignins. This impact is mostly pronounced in acidic oxidative medium ([Ch]Cl:Oxa/H_2O_2), in which the carbon and sulfur content decreased almost 1.2- and 3.2-fold, respectively. In this case, the substitution of chloride atoms in the aromatic ring structure may lead to a drastic decrease of carbon content, which in turn, increases the O/C atomic ratio as depicted by the Van Krevelen diagram in Figure 9.

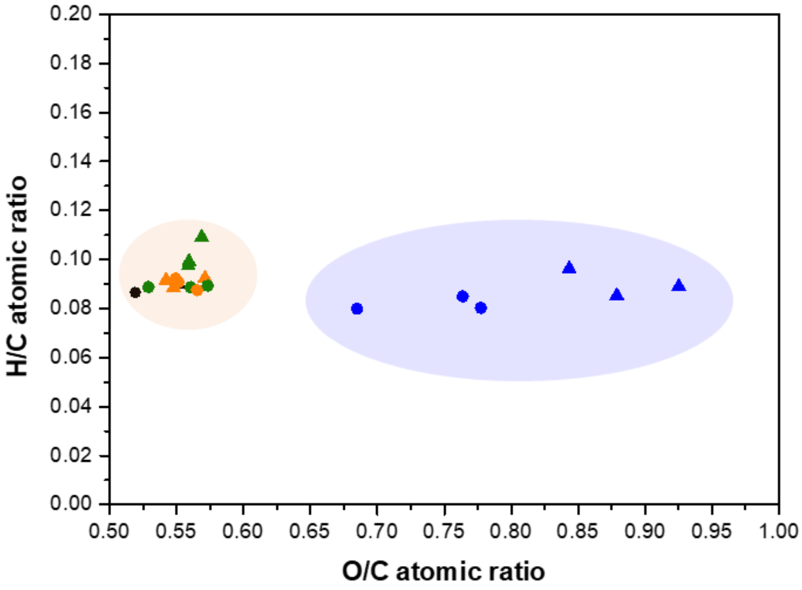

Figure 9. Van Krevelen diagram for Kraft lignin (KL -▲), Organosolv Lignin (OL - ●) and corresponding recovered lignin samples after all examined treatments with [Ch]Cl:Oxa (KL - ▲; OL - ●), [Ch]Cl:Oxa/ H_2SO_4 (KL - ▲; OL - ●) and [Ch]Cl:Oxa/ H_2O_2 (KL - ▲; OL - ●) at 80 °C.

Discussion

Succinctly, the present work demonstrated that acidic DES, such as [Ch]Cl:Oxa, can act as both solvent and catalyst to simultaneously allow partial lignin depolymerisation into desired monomeric and oligomeric compounds and partial lignin modification into a functionalised material. In the chemical point of view, no substantial difference between the performances of neat DES or DES with catalytic amount of H_2SO_4 was observed, while on the opposite using H_2O_2 as catalyst provided other side reactions that changed both depolymerisation product profile and the remaining lignin structure.

The inherent acidity of oxalic acid (pka ≃ 1.5) *per se* was sufficient to give [Ch]Cl:Oxa the ability to promote lignin depolymerisation for all studied system.[39,58] However, additional catalytic amount of a strong acid like H_2SO_4 (pka ≃ -3.0) slightly favoured the disruption of lignin chemical bonds, specially β-O-4 bond cleavage,[59,60] increasing the depolymerisation efficiency. The maximum yield of 27.8 wt% is at the same level of lignin depolymerisation with DES reported in literature. Hong et al.[39] observed that the process of alkaline lignin treatment with [Ch]Cl:Lac or [Ch]Cl:Oxa at 80-120 °C for 6 h resulted in depolymerisation yields ranging from 25 to 56 % of the initial lignin.[39]

Lignin depolymerisation in acidic DES has been tackled over the last few years, where several authors have used lignin model compounds to mimic and to understand the mechanisms acting in real lignin samples.[38,40,61,62] For instance, Alvarez-Vasco et al.[38] used guaiacylglycerol-β-guaiacyl ether (GG) as lignin model compound to evaluate the ability of [Ch]Cl:Lac in the cleavage of β-O-4 ether bond. The authors found out that GG was completely converted into guaiacol and a Hibbert ketone in almost stoichiometric proportion. The proposed mechanism was similar to the acidolysis mechanism of lignin catalysed by hydrochloric acid.[59] Bearing this in mind and looking to products of KL and OL depolymerisation with both [Ch]Cl:Oxa and [Ch]Cl:Oxa/H_2SO_4, a plausible reaction pathway for this acidic lignin depolymerisation can be proposed as demonstrated in Figure 10. The reaction starts through an attack of acidic protons from Oxa and/or H_2SO_4 to the α-hydroxyl group surrounding the β-O-4 linkage, generating a carbocation through the release of a molecular unit of H_2O.[63–65] The elimination reaction between α positive charge and β-H results in an enol ether intermediate and simultaneous regeneration of the proton. This intermediate energetically favours the cleavage of the ether bond enabling the formation of S or G type Hibbert ketones (compounds **(21)** and **(29)**) and simultaneous liberation of an aromatic alcohol, guaiacol **(1)** or syringol **(8)**.[63–65] From those very unstable Hibbert ketones, all other identified compounds are formed through distinct reactions (e.g. dehydration, oxidation, acylation, demethoxylation, etc.) and their stability is dependent on the chemical environment offered by DES media. Although this reaction pathway finds well the KL depolymerisation, the low formation of guaiacol and syringol during OL treatments with both [Ch]Cl:Oxa and [Ch]Cl:Oxa/H_2SO_4 suggests that other reactions are favoured.

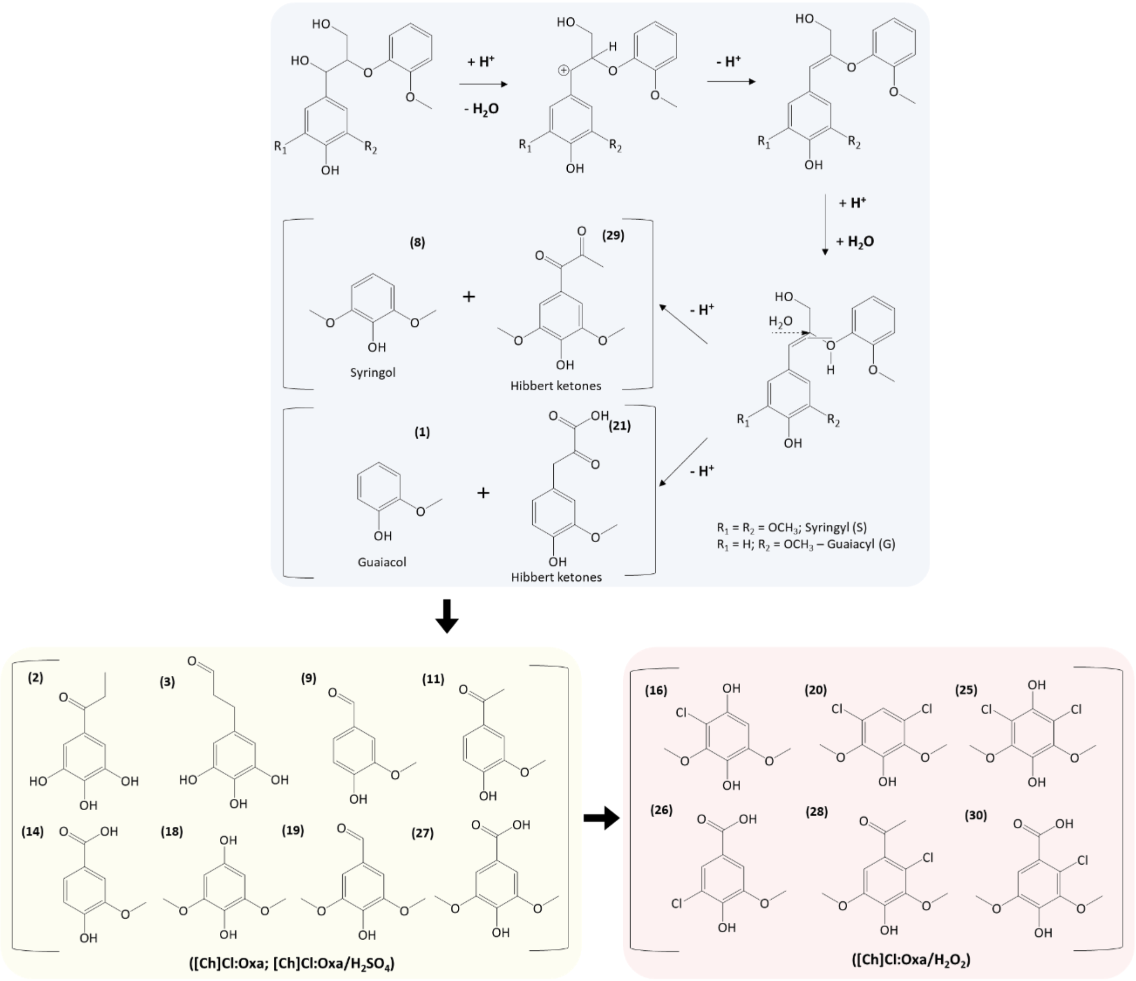

Figure 10. A proposed reaction pathway of β-O-4 bond cleavage in the presence of [Ch]Cl:Oxa (blue) and subsequent depolymerization profile (main products) obtained in absence and presence of H_2SO_4 (yellow) and in presence of H_2O_2 (orange). The names of compounds are described in Table 1.

On the other hand, the acidic oxidative medium ([Ch]Cl:Oxa/H_2O_2) favoured the formation of vanillic acid **(14)** from KL, probably as a result of the strong oxidation of G type units, like acetovanillone **(11)** and vanillin **(9)**, mediated by H_2O_2.[66] However, the oxidative action of H_2O_2 in presence of [Ch]Cl:Oxa led to a wide extent of chlorinated substitutions at the aromatic ring of lignin monomers. Syringol **(8),** one of the most produced monomers in acidic depolymerisation, and its precursor **(18)** were substituted in different positions of the aromatic ring by chloride (compounds **(16)**, **(20)** and **(25)**). In fact, compounds **(16)** and **(25)**, single and double substituted with chloride (at positions 2 and 6), respectively, represented the major monomer compounds of the KL depolymerisation extract at 1 h. As consequence of these chlorinated substitutions, guaiacol and syringol were barely formed in [Ch]Cl:Oxa/H_2O_2 medium. Moreover, chlorination of other G and S type monomers, including vanillic acid **(14)**, acetosyringone **(24)** and syringic acid **(27)** into compounds **(26)**, **(28)** and **(30),** was also observed (Figure 10). These chlorinated reactions are associated to the oxidation power of H_2O_2 that gives chloride an electrophilic behaviour to substitute the aromatic ring in different positions.[67,68]

Furthermore, this work also showed that the composition of lignin depolymerisation extract is highly dependent on lignin nature. Although 2D HSQC NMR of both KL from *E. grandis* wood and OL from beech wood did not reveal significant structural differences (Figure S1 in SI), distinct lignin monomers were produced under similar treatment conditions (DES system, temperature, and time). This might be associated to the sulfur content in KL (approximately 2 wt%), that will influence the reactivity in contact with DES and subsequently its depolymerisation.[69,70]

Apart from the depolymerised product fraction, the remaining lignin suffered physicochemical modifications that are relevant for further valorisation. The data of lignin molecular weight distribution highlights the performance of [Ch]Cl:Oxa without additional catalyst, since recovered lignin samples from treatments at 6 h using this system presented the lowest values of Mw and PDI. The PDI value was even lower than that of initial KL and OL, an indication that such recovered lignin exhibits a narrow dispersity of molecular weights,[34] probably as consequence of less severe and more selective depolymerisation. On the other hand, the more acidic (H_2SO_4) and oxidative (H_2O_2) DES systems provided severe and wider depolymerisation of lignin fragments leading to undesired higher PDI values (Table S3). Furthermore, an increase of COOH (oxalic esterification) and phenolic OH sites (cleavage of aryl ether bonds) in remaining lignin structures was unveiled, which enhances the reactivity potential of these lignin samples for several applications, including grafting reactions with high density polyethylene (HDPE)[71] as well as the preparation of functionalised lignin nanoparticles for new bio-based composites.[72] It should be emphasised that although the esterification reaction between DES and lignin during depolymerisation leads to slight DES consumption, these results show that recovered lignins can be considered as functionalised materials. Moreover, the sulfur content in KL was substantially reduced with depolymerisation (almost half of the original), which is also beneficial, since sulfur content is one the major deterrents of Kraft lignin valorisation.

Therefore, an integration of depolymerisation and functionalisation of lignin with DES is herein presented as an alternative process to increase cost efficiency in the production of value-added compounds and new bio-based composites and materials from technical lignins. Yet, future work regarding the fine-tune and optimization of this process should be carried out.

Conclusion

This work demonstrated the potential of an acidic DES ([Ch]Cl:Oxa at molar ratio 1:1) in presence or absence of co-catalysts (H_2SO_4 and H_2O_2) towards the depolymerisation of Kraft and Organosolv lignins at mild conditions (80 ºC). At least a quarter of the initial lignin can be converted into monomers and oligomers in 3 h, while longer times favoured condensation and repolymerisation reactions decreasing the yield of depolymerisation products. Furthermore, the final product content is dependent on lignin nature as well as on the chemical environment provided by DES systems, namely acidic ([Ch]Cl:Oxa and

[Ch]Cl:Oxa/H_2SO_4) or acidic oxidative treatments ([Ch]Cl:Oxa/H_2O_2). For instance, the acidic treatments of Kraft lignin favoured the formation of syringol and acetosyringone, while vanillic and syringic acids were the main products in the acidic treatments of Organosolv lignin. On the other hand, the presence of H_2O_2 in DES revealed an opposite behaviour by inducing electrophilic substitutions of chloride from [Ch]Cl in the aromatic ring of produced lignin monomers from both lignin types. Bearing in mind the toxicity of these chlorinated compounds, it seems prudent to avoid the use of H_2O_2 as an additive in lignin depolymerisation with [Ch]Cl-based DES or other DES composed of halide salts. Moreover, in contrast to their precedent technical lignins, the regenerated lignin samples after depolymerisation revealed functionalisation. Different molecular weight and significant chemical changes, including esterification with oxalic acid and increase of phenolic group content as consequent of aryl ether bond cleavage, were observed. Overall, the data herein presented is a first step to accomplish a sustainable lignin valorisation using DES.

Conflicts of interest

There are no conflicts to declare.

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Abbreviations

DES, deep eutectic solvent; HBA, hydrogen bond acceptor; HBD, hydrogen bond donor; [Ch]Cl, cholinium chloride; KL, Kraft Lignin; OL, Organosolv Lignin; Oxa, oxalic acid, LA, lactic acid; pTsa, p-toluenesulfonic acid; DFT, Density functional theory.

Author Contributions

Filipe H. B. Sosa: Conceptualisation, Methodology, Investigation, Data Curation Writing - Original Draft, Visualisation; **Ana Bjelić:** Investigation; **João A. P. Coutinho:** Writing - Review & Editing, Supervision; **Mariana C. Costa:** Writing - Review & Editing, Supervision, Funding acquisition; **Blaž Likozar:** Writing - Review & Editing; **Edita Jasiukaitytė-Grojzdek:** Conceptualisation, Methodology, Data Curation, Writing - Review & Editing; **Miha Grilc:** Conceptualisation, Writing - Review & Editing, Supervision, Funding acquisition; **André M. da Costa Lopes**: Conceptualisation, Methodology, Data Curation, Writing - Review & Editing, Supervision, Funding acquisition.

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