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

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### Abstract

1. In this study, an acidic deep eutectic solvent (DES) was used as benign solvent to valorise
2. technical lignins by breaking down their structure into value-added aromatic compounds.
3. The action of an acidic DES composed of cholinium chloride ([Ch]Cl) and oxalic acid
4. (Oxa), at molar ratio 1:1, towards depolymerisation of Kraft and Organosolv lignins (KL
5. and OL) was studied at mild conditions (80 °C, for 1 to 6 h). Furthermore, the addition of
6. hydrogen peroxide (H2O2) or sulfuric acid (H2SO4) as co-catalysts was also performed.
7. The obtained data showed maximum yields between 26.1 wt% and 27.8 wt% of lignin
8. depolymerisation products after KL and OL breakdown. Moreover, the profile of
9. depolymerisation products was distinct between examined lignins as well as between
10. acidic ([Ch]Cl:Oxa and [Ch]Cl:Oxa/H2SO4) and acidic oxidative treatments
11. ([Ch]Cl:Oxa/H2O2). The acidic treatments of KL favoured the formation of syringol and
12. acetosyringone, while vanillic and syringic acids were the main products in the acidic
13. treatments of OL. On the other hand, the presence of H2O2 in DES revealed the ability to
14. promote electrophilic substitutions of chloride from [Ch]Cl in the aromatic ring of lignin
15. monomers. After depolymerisation, the regenerated lignin samples presented a different
16. molecular weight, while FT-IR data showed structural changes, including esterification
17. with oxalic acid and formation of phenolic groups as consequence of aryl ether bond
18. breakdown. The insights gained in this study provide a better understanding on lignin
19. depolymerisation mechanisms with DES (in presence and absence of co-catalysts) and
20. envisage process integration through the production of lignin monomers (and oligomers)
21. combined with functionalisation of regenerated lignin.

23

1. **Keywords**. Lignin, deep eutectic solvents, depolymerisation, acidolysis, oxidation,
2. value-added aromatic compounds.
3. **Introduction**
4. Lignin is one of the three major macromolecular components of plant biomass, besides
5. cellulose and hemicelulloses, and is the second most abundant resource in nature after
6. cellulose.1 It exhibits structural and protective functions in plants against external biotic
7. attacks and its content can reach 15 to 40 % of plant dry weight. Lignin is a randomly
8. branched macromolecule constituted by three phenylpropanoid units, namely guaiacyl
9. (G), syringyl (S) and p-hydroxyphenyl (H), linked by different types of C-O (*e.g.* β-O-4
10. and α-O-4) and C-C (*e.g.* β-β, β-1 and β-5) covalent bonds.2,3 Therefore, this
11. macromolecule represents a valuable source of aromatics and stands as one of the most
12. important candidates to replace fossil-based feedstocks in the production of commodities,
13. such as fuels, chemicals and materials within the scope of the biorefinery concept.4,5
14. Currently, most of the available lignin is produced as by-product of cellulose pulp and
15. 2G bioethanol industrial activities, while its current fate is to serve as fuel in boilers to
16. produce energy into the grid.6 Bearing in mind all the potentialities of this aromatic carbon
17. source, this is a low value chain strategy that must be upgraded. However, the
18. heterogeneous and complex structure of lignin as well as its low reactivity restrict the
19. development of applications towards novel materials and value-added chemicals.7,8 A
20. possible solution relies on the effective depolymerisation of this macromolecule into its
21. monomeric constituents providing an opportunity to generate new products and also to
22. overcome scientific and technological barriers upon lignin valorisation.
23. Nevertheless, the development of efficient lignin depolymerisation processes has been
24. a massive challenge. The intricate structure of lignin, allied with highly stable C-C
25. chemical bonds, hinders the depolymerisation that requires high energy input to promote
26. effective linkage disruption. Amongst those chemical bonds, β-O-4 aryl ether are the most
27. representative linkages in lignin structure (about 60%),6 thus their cleavage has been
28. intensively approached.9 However, simultaneous breakdown of C-C bonds is of utmost
29. importance specially when targeting the production of low molecular weight aromatic
30. compounds, such as lignin monomers and oligomers, which may disclose a high market
31. value in the future.4
32. In literature, heterogeneous10,11 and homogeneous4,12 catalysis have been reported as
33. technologies capable of disrupting lignin chemical bonds (C-C and C-O) towards the
34. production of aromatic chemicals. 4,10,13 The heterogeneous catalysis of lignin typically
35. involves the application of metal catalysts, but they exhibit some disadvantages. Catalysts
36. containing noble metals (palladium, platinum, ruthenium14) have disclosed high
37. efficiency, but their high cost is a drawback, while cheap metal-based catalysts possessing
38. zinc or copper are less efficient and their surface is quite often saturated with lignin
39. fragments, preventing their appropriate reuse.15 On the other hand, the homogeneous
40. catalysis of lignin stands as an alternative by overcoming some of the disadvantages of
41. heterogeneous conversion. However, it often relies on the application of strong mineral
42. acids or alkaline solutions, posing undesired technical issues, especially in downstream
43. processing.16 A more sustainable solution may lie in the use of green tools, such as green
44. solvents or green catalysts, to overcome these environmental and health limitations.
45. In this regard, ionic liquids (ILs) stand as an attractive class of green solvents.17,18
46. Since the initial report on their ability to dissolve cellulose,19 several studies have been
47. describing the application of acidic ILs towards biomass fractionation, while some of
48. them have shown their capacity for lignin depolymerisation.20–22 For instance, Cox et al.23
49. demonstrated the depolymerisation of lignin using 1-H-3-methylimidazolium chloride
50. under the temperature range of 110-150°C. In another study, Jia et al.24 reported the
51. hydrolysis of β-O-4 bonds in two lignin model compounds using the same IL with a yield
52. greater than 70% at 150°C. Furthermore, SO3H-based ILs applied in water:methanol
53. mixtures up to 1:1 molar ratio demonstrated a high conversion yield of dealkaline lignin
54. into aromatic monomers (95-97%) at temperature range of 110-170°C.22 Although some
55. of these technologies demonstrated ILs as suitable solvents/catalysts for lignin
56. depolymerisation, the availability and high cost of ILs have been limiting their application
57. in depolymerisation reactions of large amounts of lignin.25 Therefore, other green
58. alternatives have been investigated.
59. Recently, deep eutectic solvents (DES) have been studied and applied as green
60. solvents in several applications.26 Introduced by Abbott et al.,27 DES is a mixture of at
61. least one hydrogen bond donor (HBD) and one hydrogen bond acceptor (HBA) capable
62. of establishing strong hydrogen bonds and form an eutectic solution with inherent
63. negative deviation to the melting temperature of the ideal mixture.27,28 This depression in
64. the melting temperature allows a large number of DES to be liquid at room temperature
65. enabling their use as solvents. In addition, DES possess other favourable characteristics,
66. including low vapor pressure, easy preparation and tailored physicochemical properties
67. (acidity, basicity, polarity, among others).29
68. These features drew the attention to apply DES in lignin dissolution30 and biomass
69. delignification.31,32 Several studies have been reporting acidic DESs, such as those
70. formed by the combination of cholinium chloride ([Ch]Cl) as HBA and carboxylic acids,
71. including oxalic acid (Oxa), formic acid (For) and lactic acid (Lac) as HBD, as efficient
72. solvents for the extraction and dissolution of lignin from biomass.33–35 A small group of
73. works have stressed out small changes to lignin structure after its delignification with
74. DES,36 while others have proven the ability of DES to disrupt lignin chemical bonds,35
75. specially β-O-4 ether bonds.37 These apparent contradictory observations result mostly
76. from the acidity of the HBD as well as the mild *vs* severe conditions applied in biomass
77. delignification. Notwithstanding these differences, a close inspection on the
78. delignification mechanisms and performance of acidic DES was investigated.38,39
79. Alvarez-Vasco et al. reported that the cleavage of β-O-4 bond in a lignin model compound
80. (guaiacylglycerol-β-guaiacyl) by [Ch]Cl:Lac is similar to lignin acidolysis catalysed by
81. hydrochloric acid.38 In another work, da Costa Lopes et al.40 demonstrated that [Ch]Cl:p-
82. toluenesulfonic acid (pTSA) and its bromide equivalent ([Ch]Br:pTSA) are able to cleave
83. efficiently β-O-4 bonds of another lignin model compound (1-phenyl-2-phenoxyethanol).
84. Through DFT calculations, the authors revealed a nucleophilic role of the halide anion
85. (chloride or bromide) that substitutes the hydroxyl group neighbouring the β-O-4 ether
86. linkage, forming a halide intermediate that energetically favours the cleavage.40 On the
87. other hand, Hong et al.39 evaluated the structural changes of alkali lignin after its
88. treatment with [Ch]Cl:Oxa and [Ch]Cl:Lac. In both cases, the cleavage of ether bonds
89. was preceded by the following steps: i) removal of the Cα alcohol and the formation of
90. highly reactive benzylic carbocations in the lignin side chains; ii) oxidation of the Cα
91. position and acylation of the Cγ position.39
92. Bearing all this in mind, the application of DES as both solvent and catalyst may
93. provide a new and sustainable process for lignin depolymerisation, besides biomass
94. delignification. However, there are still few studies that explore the performance of DES
95. to depolymerise lignin in its monomeric and oligomeric fragments.39,41 The present study
96. aims at giving an initial contribution to understand the mechanisms behind this process.
97. [Ch]Cl:Oxa (1:1 molar ratio), which previously showed an improved performance on
98. lignin cleavage in contrast to other acidic DES,37 was chosen as representative medium
99. to dissolve and depolymerise two technical lignins, namely Kraft and Organosolv, under
100. moderate conditions (80 °C, 1-6 h). In addition, sulfuric acid (H2SO4) and hydrogen
101. peroxide (H2O2) were used as co-catalysts to address different mechanistic possibilities
102. in the disruption of lignin chemical linkages. Moreover, a brief demonstration on the
103. physicochemical modifications of remaining lignin solid fraction induced by these
104. systems were also addressed by GPC, FT-IR and elemental analysis.

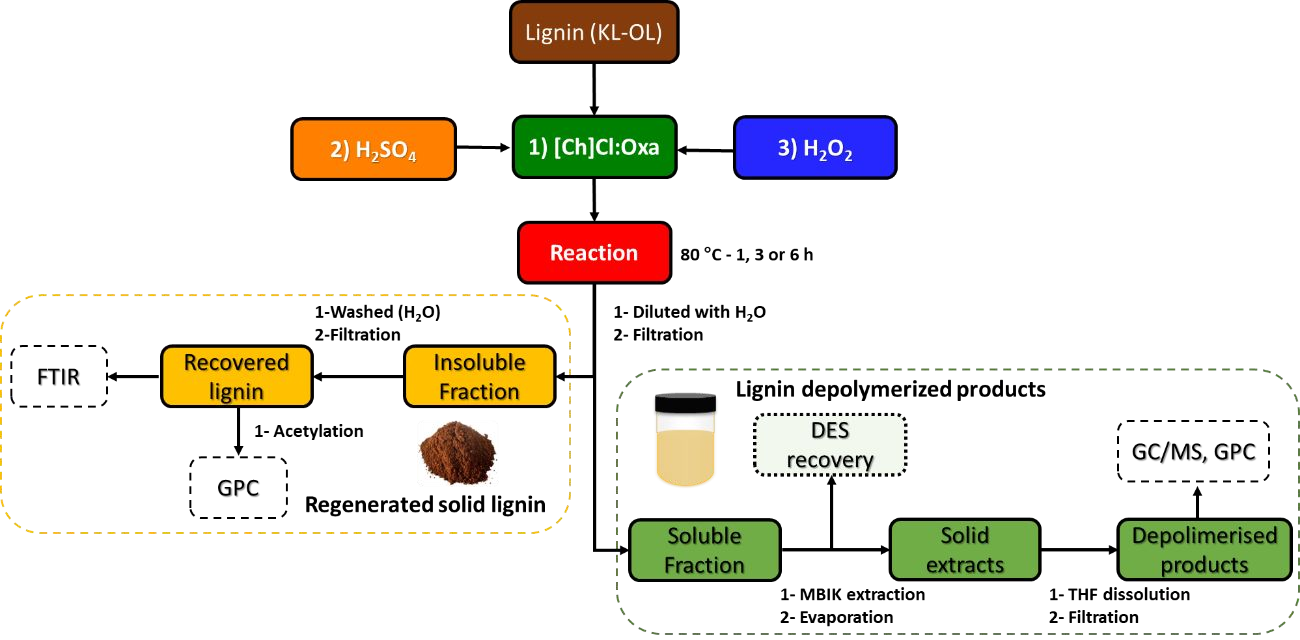
## Materials and Methods

1. Chemicals. Kraft Lignin (KL) isolated from Eucalyptus urograndis was directly
2. supplied by Suzano Papel & Celulose (Brazil). KL was precipitated from the industrial
3. black liquor by employing carbon dioxide. On the other hand, Organosolv Lignin (OL)
4. was directly supplied by Fraunhofer (Germany). OL was extracted from beech wood with
5. 50 % (v/v) ethanol solution and sulphuric acid as a catalyst. The HSQC NMR spectra of
6. both lignins and corresponding 13C-1H assignments are shown in Figure S1 and Table S1,
7. respectively. Cholinium chloride ([Ch]Cl, 98.0 wt% purity) was purchased from Acros
8. Organics (New Jersey, US). Oxalic acid (Oxa, 99.5% purity), tetrahydrofuran (THF, 99
9. wt% purity and methyl benzoate (99 wt% purity) were purchased from Merck (Darmstadt,
10. Germany). Both hydrogen peroxide (H2O2, 30 % v/v) and methyl isobutyl ketone (MIBK,
11. 98.5 wt% purity) were purchased from Riedel-de Haën - Honeywell (Charlotte, US),
12. while sulfuric acid (H2SO4, 96 wt% purity) was supplied by Fisher Chemical (New Jersey,
13. US).

### DES Preparation

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

### Lignin depolymerisation assays

1. The methodology of lignin depolymerisation and post-processing steps are briefly
2. described in Figure 1. KL or OL (300 mg) was added to [Ch]Cl:Oxa (1:1) (6.0 g) in 250
3. mL glass flasks from 6 Plus Reaction Station™ carousel (Radleys, United Kingdom),
4. which allows parallel reactions at the same temperature and agitation. The mixture was
5. heated up to 80 °C and reaction was left for 1, 3 and 6 h under constant agitation (200
6. rpm) provided by the magnetic bar stirrer. Both technical lignins were treated with three
7. distinct systems: i) DES; ii) DES with catalytic amount of H2SO4 (1 wt%); and iii) DES
8. with catalytic amount of H2O2 (2 wt%).
9. 
10. **Figure 1.** The flowchart of lignin treatment and post-processing analysis performed in
11. this work.
12. After reaction, the glass flasks were placed in ice bath (5 °C) and 20 mL of water was
13. added to the mixture enabling lignin precipitation. The precipitated lignin was separated
14. by vacuum filtration, washed with water (3 x 10 mL), and finally freeze dried before its
15. gravimetric quantification. The lignin recovery yields were determined by the equation
16. 1. The liquid phase containing lignin depolymerised products was collected and stored in
17. a fridge before analysis. The obtained yields of lignin depolymerisation product were
18. calculated by closing the mass balance of the initial lignin as disclosed by the equation 2.

𝑚𝐿𝑖𝑔𝑟𝑒𝑐 ∙ (1 ― 𝐴𝑠ℎ𝐿𝑖𝑔𝑟𝑒𝑐)

𝑚𝐿𝑖𝑔

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𝑙𝑖𝑔𝑛𝑖𝑛 𝑟𝑒𝑐𝑜𝑣𝑒𝑟𝑦 𝑦𝑖𝑒𝑙𝑑 (𝑤𝑡%) =

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* (1 ― 𝐴𝑠ℎ
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𝐿𝑖𝑔𝑖𝑛𝑖𝑡

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𝑃𝑟𝑜𝑑𝑢𝑐𝑡 𝑦𝑖𝑒𝑙𝑑 (𝑤𝑡%) =

𝑚𝐿𝑖𝑔𝑖𝑛𝑖𝑡

.(1 ― 𝐴𝑠ℎ

* + 100 (2)

𝐿𝑖𝑔𝑖𝑛𝑖𝑡

1. where 𝑚𝐿𝑖𝑔𝑟𝑒𝑐 is the total amount of recovered lignin (g), 𝑚𝐿𝑖𝑔𝑖𝑛𝑖𝑡 is the initial amount
2. of lignin (g), 𝐴𝑠ℎ𝐿𝑖𝑔𝑟𝑒𝑐 is the ash content in recovered lignin, and 𝐴𝑠ℎ𝐿𝑖𝑔𝑖𝑛𝑖𝑡 is the ash content
3. in initial lignin.

### Extraction of lignin depolymerisation products from DES.

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

### Lignin acetylation.

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

### Characterisation of lignin depolymerisation products and remaining lignin solid

1. **fractions**
2. *Gas chromatography/mass spectrometry (GC/MS) analysis*
3. The identification and semi-quantification of lignin depolymerisation products was
4. carried out using a gas chromatograph/mass spectrometer Shimadzu QP2010 Ultra,
5. equipped with an AOC‐20i autosampler and high‐performance quadrupole mass filter.
6. The separation of reaction products was carried out in a DB‐5 ms column (30 m length,
7. 0.25 mm i.d. and 0.25 μm film thickness) using helium as the carrier gas (40 cm s−1). The
8. chromatographic conditions were as follows: isothermal at 80 °C for 5 min, ramped from
9. 80 to 250 °C (8 °C min−1), ramped from 250 to 300 °C (4 °C min−1) and then isothermal
10. at 300 °C for 5 min; injector temperature of 320 °C; and split ratio equal to 1:10. The MS
11. was operated in the electron impact mode with an electron impact energy of 70 eV and
12. data was collected at a rate of 1 scan s−1 over a range of m/z 50–1000. The ion source was
13. kept at 200 °C and the interface temperature at 300 °C.
14. Identification of compounds was performed by comparing chromatographic peaks
15. retention times and their mass spectra with the equipment mass spectral library (NIST14s
16. MS Library Database or WILEY229 MS Library Database). The m/z value of the
17. molecular ion together with the fragmentation was used to figure out the structure of the
18. compound. A semi-quantitative analysis was carried out by considering the ratio between
19. the peak area of compound and the peak area of the internal standard as shown by the
20. equation 3:

% 𝑅𝑒𝑙𝑎𝑡𝑖𝑣𝑒 𝑃𝑒𝑎𝑘 𝐴𝑟𝑒𝑎𝑖 =

𝐴𝑖

∑𝑛𝐴 ·100 (3)

𝑖 𝑖

1. where 𝐴𝑖 is the peak area of compound “*i”, and “n”* is the number of compounds*.*
2. *Gel Permeation Chromatography (GPC) analysis*
3. GPC analyses of acetylated lignin samples and depolymerisation products were
4. performed on a gel permeation chromatographic system (HP — AGILENT system)
5. equipped with a UV detector (set at 280 nm). Analyses were carried out at ambient
6. temperature using THF as eluent at a flow rate of 1 mL·min-1. Aliquots (100 µL) of
7. acetylated lignin dissolved in THF (1.5 mg·mL-1) were injected into PLgel 3 µm MIXED
8. E 7.5 x 300 mm. The column specifications allow for the separation of molecular masses
9. up to 3.0 x 104 g·mol-1. The GPC system was calibrated with polystyrene standards (Mw

231 = 162, 672, 890, 2280, 4840, 5180, 9630, 25500, 61400, 127000 g·mol-1). Moreover,

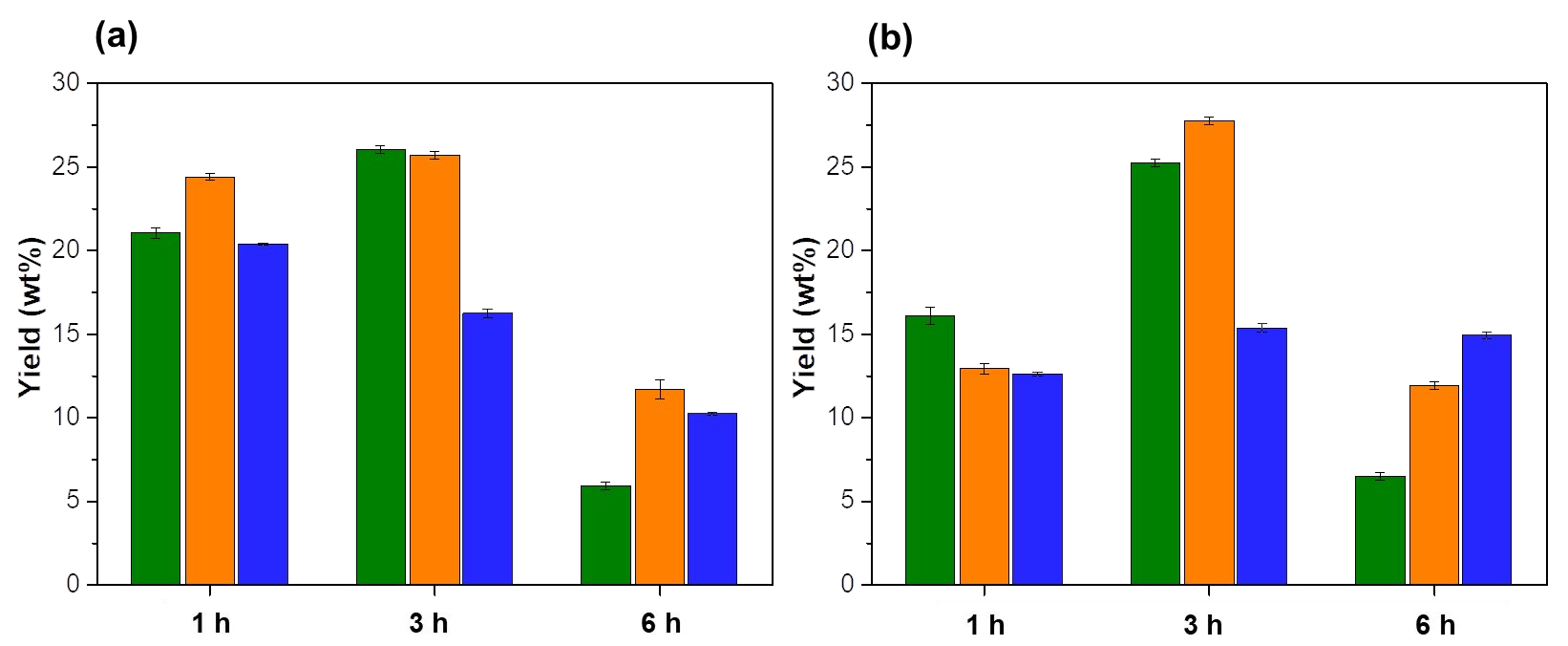
1. guaiacylglycerol-β-guaiacyl ether (>99 % purity, TCI Chemicals, Belgium), known as β-
2. O-4 linkage-lignin model compound (Mw 320 g·mol-1) was used to construct the
3. calibration curve aiming to increase the accuracy of the measured values in the low
4. molecular weight region. The chromatographic data were processed with the PSS
5. (Polymer Standards Service) WinGPC Unity software.
6. *Fourier Transform InfraRed (FT-IR) analysis*
7. The FT-IR spectra of lignin samples (not acetylated) were recorded on a PerkinElmer
8. Spectrum BX spectrometer equipped with a horizontal Golden Gate ATR cell and a
9. diamond crystal. A total of 32 scans were made for each sample with a resolution of 4
10. cm-1 in a wave range between 4000 cm-1 and 400 cm-1.
11. ***Elemental Analysis***
12. The elemental analysis of lignin samples was conducted with a TruSpec series 630-
13. 200-200 elemental analyser (Michigan, US). The combustion furnace temperature and
14. the afterburner temperature were maintained at 1075 °C and 850 °C, respectively. The
15. oxygen content was determined by the difference.

### Experimental and analytical error analyses

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

## Results

### Characterisation of lignin depolymerisation products

1. Kraft and Organosolv lignins (KL and OL) were treated with three distinct solvent
2. systems: i) [Ch]Cl:Oxa; ii) [Ch]Cl:Oxa/H2SO4; and iii) [Ch]Cl:Oxa/H2O2. Their ability
3. for lignin depolymerisation at 80 ºC was evaluated over time (1, 3 and 6 h) and the
4. obtained depolymerisation product yields are depicted in Figure 2.
5. At first sight, depolymerisation product yields were all higher than 6.0 wt%,
6. suggesting that the studied systems were able to convert at least a small portion of the
7. initial lignin. Furthermore, reactions of OL and KL with both [Ch]Cl:Oxa and
8. [Ch]Cl:Oxa/H2SO4 revealed an increase of the depolymerisation product yield from 1 to
9. 3 h, but a sharply decrease at 6 h was verified. Maximum yields between 26.1 wt% and
10. 27.8 wt% of lignin depolymerisation products were obtained in the reaction of both KL
11. and OL with these DES systems at 3 h. However, an exception to this trend was observed
12. for DES comprising a catalytic amount of H2O2, which exhibited a different behaviour in
13. the depolymerisation of both KL and OL in contrast to other DES systems. For KL
14. treatment with [Ch]Cl:Oxa/H2O2, a maximum depolymerisation product yield (20.4 wt%)
15. was detected at 1 h, while it decreased continuously over time up to one half after 6 h. On
16. the other hand, no relevant changes in yields (between 12.6 and 15.3 wt%) during OL
17. treatment with [Ch]Cl:Oxa/H2O2 were observed.
18. 
19. **Figure 2.** Yields of lignin depolymerisation products in the liquid phase after a) KL and
20. (b) OL treatment with [Ch]Cl:Oxa (■), [Ch]Cl:Oxa/H2SO4 (■) and [Ch]Cl:Oxa/H2O2 (■)

277 at 80 °C.

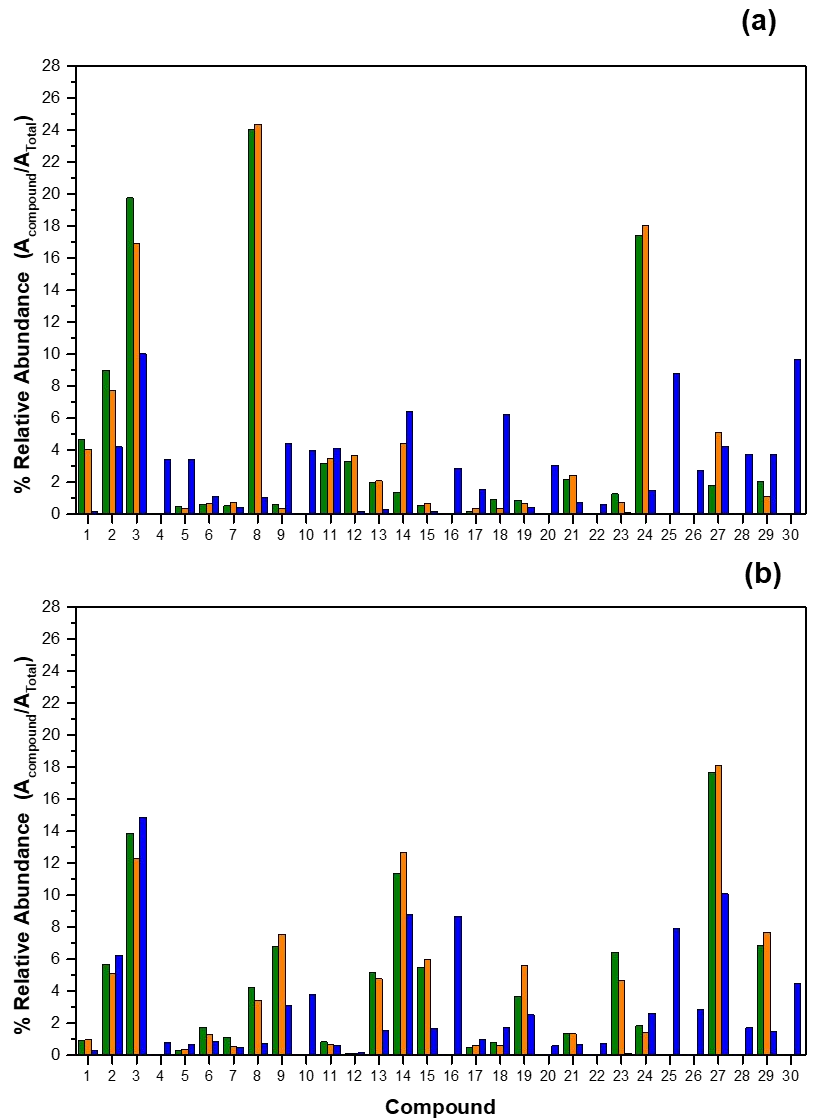
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1. Afterwards, lignin depolymerisation products were tentatively identified by GC/MS.
2. Initially, 60 compounds were labelled, but among these, the 30 most representative
3. compounds were selected (Table 1) to compare the catalytic behaviour of the examined
4. DES systems. The obtained products were identified as aromatic monomers derived from
5. syringyl (S) and guaiacyl (G) units containing alcohols, ketones, aldehydes and
6. carboxylic acids as functional groups attached to the aromatic ring or to the carbon chain
7. at α, β and γ positions of those units. Due to the nature of KL (*E. grandis* wood) and OL
8. (beech wood), which are mostly comprised by S and G units,43,44 compounds derived
9. from hydroxyphenyl (H) units were not identified in this work. Furthermore, the
10. chromatograms of depolymerisation extracts from KL and OL showed the same peaks,
11. although with different relative abundances (Figure S2 in SI).
12. **Table 1.** Main compounds identified by GC-MS (chemical structures are represented in
13. 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 |

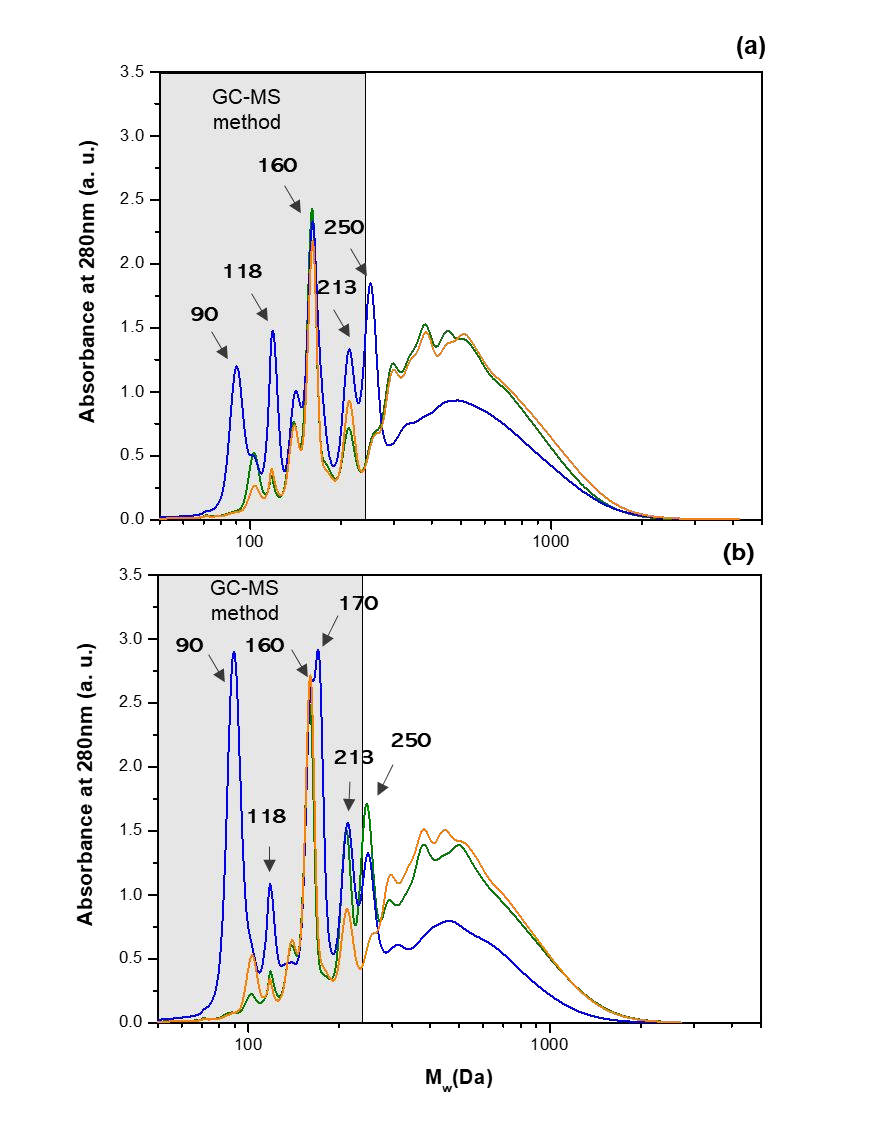
* 1. 3,5-dichloro-2,6-dimethoxyphenol 221.99 18.370
  2. 3-(4-hydroxy-3-methoxyphenyl)-2-oxopropanoic acid 210.05 18.640
  3. 3,4,5-trichloro-2-methoxyphenol 225.94 18.655
  4. 2-(4-hydroxy-3,5-dimethoxyphenyl)acetaldehyde 196.20 19.050
  5. acetosyringone 196.19 19.137
  6. 2,6-dichloro-3,5-dimethoxybenzenediol 239.50 19.685
  7. 5-chlorovanillic acid 202.17 19.792

27 syringic acid 198.17 20.150

1. 1-(6-chloro-4-hydroxy-3,5-dimethoxyphenyl)ethanone 230.30 20.323
2. 1-(4-hydroxy-3,5-dimethoxyphenyl)propanedione 224.25 20.373
3. 2-chloro-4-hydroxy-3,5-dimethoxybenzoic acid 232.01 22.275
4. \*Internal Standard
5. The composition of lignin depolymerisation extracts was performed by semi-
6. quantitative analysis. Figure 3 depicts the relative abundances of the identified 30
7. compounds after treatment of both KL (3a) and OL (3b) with the three examined DES
8. systems at 80 ºC for 3 h. The obtained data showed once more a distinct behaviour
9. between both [Ch]Cl:Oxa and [Ch]Cl:Oxa/H2SO4 when compared with
10. [Ch]Cl:Oxa/H2O2 in the formation of lignin depolymerisation products. For the first two
11. systems, lignin monomers, including 2-(3,4-dihydroxy-5-methoxyphenyl)acetaldehyde
12. **(3)**, syringol **(8)** and acetosyringone **(24),** were detected in higher amount than other
13. compounds in KL depolymerisation. In fact, syringol reached approximately 25 % of all
14. identified compounds in KL depolymerisation with neat DES and in presence of H2SO4.
15. However, when looking to the depolymerisation products achieved with
16. [Ch]Cl:Oxa/H2O2, compound **(3)** stood as the most abundant monomer resultant from the
17. KL treatment (≃ 10%). On the other hand, by changing the lignin sample to OL, besides
18. compound **(3)** the formation of vanillic **(14)** and syringic **(27)** acids were favoured in the
19. three DES systems. Furthermore, it should be also highlighted that the presence of H2O2
20. promotes the formation of distinct chlorinated species, including **(10)**, **(16)**, **(25)**, **(28)** and
21. **(30)**, which were not produced in its absence. The corresponding data obtained for the
22. lignin treatments with all DES systems at 1 and 6 h are presented in SI (Figures S3 and
23. S4, respectively).
24. 
25. **Figure 3.** Relative abundance (%) of lignin depolymerisation products from (a) KL and
26. (b) OL depolymerisation at 80 °C for 3 hours with [Ch]Cl:Oxa (■), [Ch]Cl:Oxa/H2SO4

317 (■) and [Ch]Cl:Oxa/H2O2 (■).

318

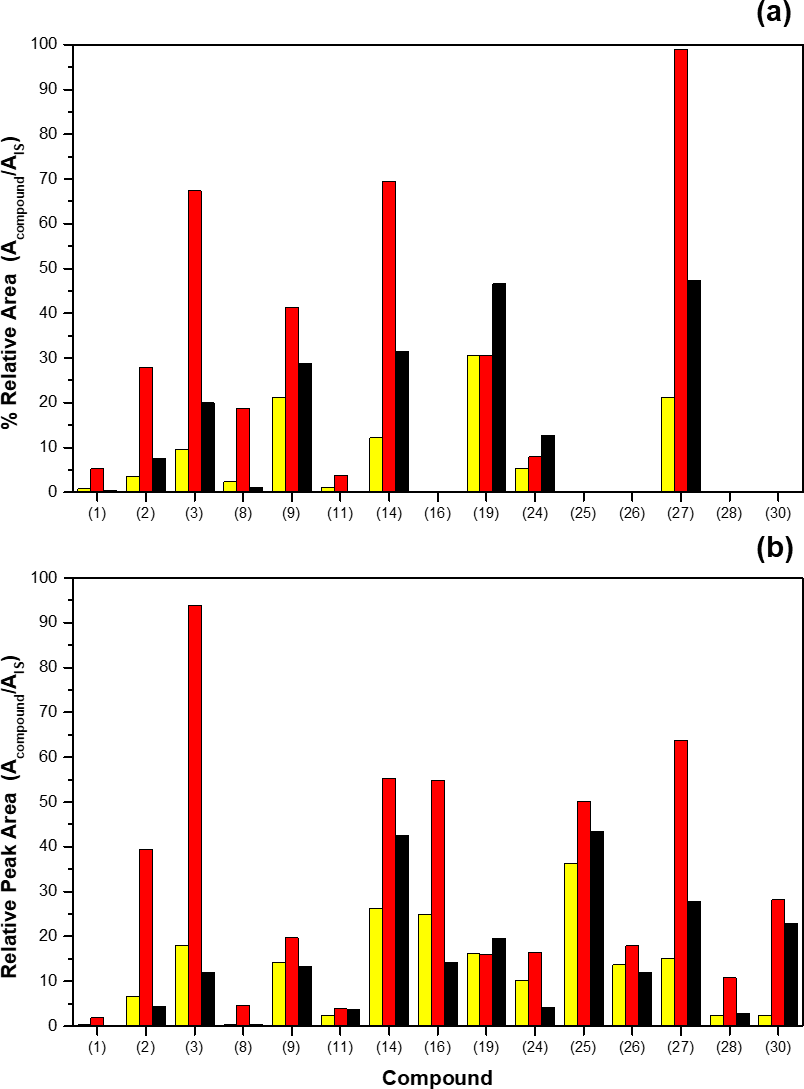
1. As aforementioned, the GC/MS data allowed the identification of several monomeric
2. compounds with maximum molecular weight (MW) between 124 of 232 Da (Table 1).
3. However, the existence of oligomeric products is highly probable after depolymerisation
4. with examined DES systems. Therefore, to evaluate the MW distribution of
5. depolymerised lignin extracts during time, acetylated samples were analysed by GPC. As
6. an example, chromatograms of KL depolymerisation products obtained with the three
7. DES systems at 1 h and 6 h are presented in Figure 4 (results for OL are shown in Figure
8. S5 in SI).
9. On the left of Figure 4, the MW fraction below 240 Da is highlighted in grey,
10. corresponding to lignin monomers that were detectable by the GC/MS method. It is
11. possible to identify 4 main peaks with maximum at 90, 118, 160 and 170 Da, the last two
12. being the most intense. Amongst the 30 compounds identified by GC-MS, around 21 have
13. a molecular mass between 140 and 190 Da, which may comprise the GPC peaks at 160
14. and 170 Da. Surprisingly, the peaks at 90 and 118 Da are very pronounced in the KL
15. depolymerisation fraction obtained with DES/H2O2. They may comprise low molecular
16. weight aromatic compounds that were not identified by the GC/MS method used in this
17. work (*e.g.* toluene and benzene, which are eluted simultaneously with the solvent). On
18. the other hand, oligomers with wide distributed MWs can be observed on the right of
19. Figure 4, representing a substantial fraction in each depolymerisation extract. These
20. oligomeric fragments were also not identified by the GC/MS. The GPC data revealed that
21. a higher quantity of oligomers seems to be produced by neat DES and DES/H2SO4. On
22. the contrary, the oxidative environment promoted by H2O2 favoured the formation of low
23. molecular weight compounds to the detriment of lignin oligomers.
24. 
25. **Figure 4.** GPC analysis of lignin depolymerisation products from KL treatment at 80 °C
26. during (a) 1 h and (b) 6 h with [Ch]Cl:Oxa (■), [Ch]Cl:Oxa/H2SO4 (■) and

345 [Ch]Cl:Oxa/H2O2 (■).

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### Lignin depolymerisation over time

1. The formation and consumption of depolymerisation products was tracked over time
2. to understand the mechanisms behind lignin depolymerisation assisted by the three
3. examined DES systems. The kinetics of 15 relevant aromatic compounds, previously
4. identified by GC/MS, were represented as relative peak area of each compound to the
5. internal standard (methyl benzoate). The data obtained from KL depolymerisation with
6. the three DES systems between 1 and 6 h is presented as a model in Figure 5.
7. At first sight, treatments at 3 h disclosed the highest formation of aromatic monomers,
8. which correlates well with the depolymerisation yields presented in Figure 1. Once more,
9. this is an indication that the reaction time directly affects lignin depolymerisation.
10. Furthermore, the kinetic profile of the 15 compounds are similar between treatments with
11. [Ch]Cl:Oxa (Figure S6 in SI) and [Ch]Cl:Oxa/H2SO4 (Figure 5a), but noticeably different
12. in lignin depolymerisation mediated by [Ch]Cl:Oxa/H2O2 (Figure 5b).
13. The KL depolymerisation under acidic conditions ([Ch]Cl:Oxa/H2SO4) revealed that
14. a major fraction of monomeric compounds, including guaiacol **(1)**, syringol **(8)**,
15. acetovanillone **(11)**, vanillic acid **(14)**, a demethylated ketone **(2)** and a demethylated
16. aldehyde **(3)** presented a remarkable formation from 1 to 3 h, but was followed by their
17. drastic consumption up to 6 h. Although a similar trend was observed for acetosyringone
18. **(24)**, its consumption rate was moderate. On the other hand, syringic acid **(27)** presented
19. a maximum yield at 1 h and was followed by a decreasing trend over time. On the
20. opposite, vanillin **(9)** and syringaldehyde **(19)** relative peak areas increased during time,
21. although their representation in depolymerisation extract is very low.
22. 
23. **Figure 5.** Relative peak area of identified compounds after KL depolymerisation at 80 °C
24. for 1 h (■),3 h (■) and 6 h (■) with (a) [Ch]Cl:Oxa/H2SO4 and (b) [Ch]Cl:Oxa/H2O2.
25. Considering that all these compounds are expected to participate in
26. repolymerisation/condensation reactions in prolonged times leading to their
27. consumption,45 it seems that produced monomeric alcohols (1 and 8), demethylated
28. compounds (2 and 3) and vanillic acid are more prone to those type of reactions. On the
29. other hand, syringic acid, vanillin and syringaldehyde are less reactive and more stable
30. during lignin treatment in presence of [Ch]Cl:Oxa/H2SO4 (or [Ch]Cl:Oxa, Figure S6 in
31. SI).
32. The kinetics of OL depolymerisation with the three DES systems were also studied
33. and obtained results are depicted in Figure 6. Similar to KL depolymerisation, treatments
34. of OL at 3 h revealed the highest formation of aromatic monomers. However, the kinetic
35. profiles of OL depolymerisation revealed differences from those achieved with KL.



1. **Figure 6.** Relative peak area of identified compounds after OL depolymerisation at 80 °C
2. for 1 h (■),3 h (■) and 6 h (■) with (a) [Ch]Cl:Oxa/H2SO4 and (b) [Ch]Cl:Oxa/H2O2.
3. Depolymerisation of OL under acidic conditions ([Ch]Cl:Oxa/H2SO4) revealed that
4. most monomeric compounds, including 3-(3,4,5-trihydroxyphenyl)propanal **(3)**, vanillin
5. **(9)**, vanillic acid **(14)**, syringic acid **(27)** showed an extensive production up to 3 h, but a
6. drastic decrease was observed for longer times. Unlike KL depolymerisation, the
7. formation of syringic acid **(27)** and vanillic acid **(14)** were favoured to the detriment of
8. syringol **(8)** and guaiacol **(1)** in both [Ch]Cl:Oxa and [Ch]Cl:Oxa/H2SO4. This is an
9. evidence that lignin nature, which is dependent on its biomass origin and delignification
10. process, exhibits a significant impact on the final composition of depolymerisation
11. products. Furthermore, the corresponding precursors, syringaldehyde **(9)** and vanillin
12. **(19)**, were found in higher amount in OL depolymerised fraction than in the case of KL
13. depolymerisation.
14. Regarding the OL depolymerisation with [Ch]Cl:Oxa/H2O2, vanillic acid **(14)** was
15. again a major product after 6 h of reaction, while consumption of compound **(25)** was not
16. as fast as that observed for KL. The strong oxidative medium provided by H2O2 allowed
17. the substitution at different positions of the aromatic chloride ring, resulting in the same
18. chlorinated compounds (**(16)**, **(25)**, **(26)**, **(28)** and **(30)**) as highlighted above.

### Structural characterisation of the recovered lignin.

1. The impact of the depolymerisation reactions mediated by the studied systems on the
2. remaining solid lignin was also evaluated. The lignin molecular weight distribution was
3. first evaluated by GPC and the obtained results, including average molecular weight
4. (Mw), number average molecular weight (Mn) and polydispersity index (PDI), are
5. presented in Figure 7 and Table S3.
6. The Mw values of both KL and OL were 2500 and 3300 g·mol-1, while the
7. polydispersity indexes (PDI) were determined to 2.1 and 2.2, respectively (Table 2). After
8. depolymerisation with studied DES systems, recovered lignin samples at 1 h and 6 h of
9. treatment disclosed reduced Mw and Mn values in contrast to initial KL and OL,
10. confirming depolymerisation mediated by all systems. Although the highest yields of
11. lignin depolymerisation was observed at 3 h treatment (Figures 2, 5 and 6), the
12. corresponding recovered lignins presented the highest Mw and Mn values (Figure 7). This
13. means that albeit lignin monomers are extensively produced at 3 h, simultaneous side
14. reactions between remaining lignin fragments are favoured at cleavage sites enabling the
15. formation of higher molecular weight lignin macromolecules.46 In turn, this high
16. molecular weight fraction influences the average Mw and Mn values (Figure 7). The
17. increase of lignin Mw and Mn values at 3 h is more pronounced in the presence of H2O2.
18. The oxidative nature of this catalyst induces the formation of reactive OH radical and
19. radical lignin sites, increasing the rate of side reactions.47 After 6 h of treatment, Mw and
20. Mn values decreased, which is associated not only to the gradual degradation of the
21. formed fragments through cleavage of the remaining ether bonds, but also to the
22. repolymerisation of lignin monomers into insoluble low molecular weight fragments.
23. This explains the decreasing yield of lignin depolymerisation products after 6 h of
24. treatment as stated above (Figure 2). Moreover, at this stage, the side reactions between
25. lignin fragments might be suppressed, due to the peroxide radical neutralisation over time,
26. favouring the reduction of both Mw and Mn values.

4500

4000

3500

**Molecular Weight (g.mol-1)**

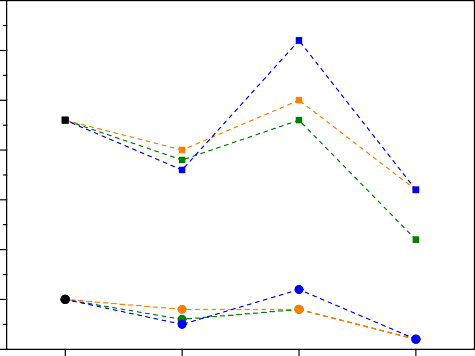
3000

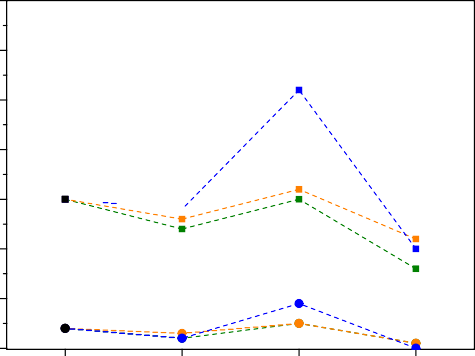
2500

2000

1500

**(a) (b)**

4500



4000

3500

**Molecular Weight (g.mol-1)**

3000

2500

2000

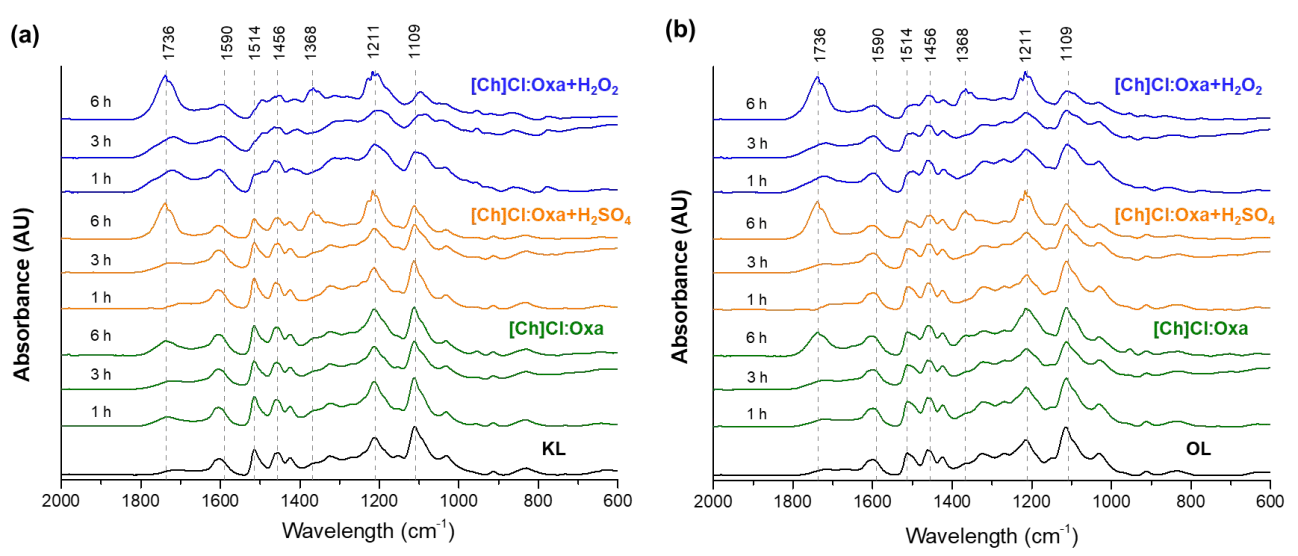
1500

1000

KL 1 h 3 h 6 h

1000

OL 1 h 3 h 6 h

1. **Figure 7.** Molecular weight average (Mw - ■) and molecular number average (Mn - ●)
2. of technical lignins and corresponding recovered lignin samples after treatment with
3. [Ch]Cl:Oxa (Mw - ■; Mn - ●), [Ch]Cl:Oxa/H2SO4 (Mw - ■; Mn - ●) and
4. [Ch]Cl:Oxa/H2O2 (Mw - ■; Mn - ●) at 80 °C during time. a) KL; b) OL
5. In addition, FT-IR analyses of recovered lignin samples were performed to address
6. possible chemical modifications induced by DES systems during depolymerisation
7. process. All infrared spectra showed lignin fingerprint with typical vibrational bands as
8. reported in literature.48–52 The list of all lignin vibrational bands and corresponding
9. assignments are presented in SI (Table S4). Figure 8 shows magnified FT-IR spectra of
10. KL, OL and corresponding recovered lignins (2000-600 cm-1). The most relevant were
11. observed in the region 1800-750 cm-1 with remarkable high intensities at 1109, 1211,
12. 1368, 1456, 1514, 1590 and 1736 cm-1. However, significant changes in the absorbance
13. of specific bands were detected after depolymerisation with DES systems.
14. One of the most prominent differences was the substantial increase of the vibrational
15. band at 1736 cm-1 over time in all systems and both lignins. This vibration corresponds
16. to the elongation of C=O chemical linkage, specifically associated to ester groups, which
17. means that esterification was promoted between lignin hydroxyl groups and oxalic acid
18. from DES. This phenomenon was already mentioned in a previous work.37 Moreover, this
19. esterification was more evident in DES with catalysts than neat DES, suggesting that both
20. H2SO4 and H2O2 might boost this parallel reaction. These results also reveal that
21. depolymerisation product yields might be higher than those shown in Figure 1. The
22. esterification of oxalic acid in lignin structure directly increases the recovery yield of
23. regenerated lignin affecting the calculations of depolymerisation product yield (equation
24. 2, section 2.3).
25. 
26. **Figure 8.** Magnified FT-IR spectra of technical lignins and corresponding recovered
27. lignin samples after treatment with [Ch]Cl:Oxa (■), [Ch]Cl:Oxa/H2SO4 (■) and
28. [Ch]Cl:Oxa/H2O2 (■) at 80 °C during time.
29. On the other hand, the vibrational band at 1109 cm-1 decreased sharply during lignin
30. treatments, while an opposite behaviour was observed for the vibrational band at 1368
31. cm-1. The last represents the C-OH vibrations of phenolic hydroxyl groups,53,54 which
32. increased during time as consequence of the direct cleavage of aryl ether bonds (e.g. β-
33. O-4 and α-O-4), represented by the first one (C-O vibration in ether bonds).55,56 Once
34. more, these chemical changes were more pronounced when using [Ch]Cl:Oxa/H2SO4 and
35. [Ch]Cl:Oxa/H2O2.
36. Another important change to be highlighted from these data is the conservation or
37. deformation of the aromatic structure of lignin directly represented by the aromatic
38. skeletal vibrations, namely 1456, 1514, and 1590 cm-1, after treatments. As observed in
39. Figure 8, treatments of both lignins with [Ch]Cl:Oxa did not affect these bands, but those
40. with [Ch]Cl:Oxa/H2SO4 (6 h) and [Ch]Cl:Oxa/H2O2 (1, 3 and 6 h) altered significantly
41. their shape and absorbance. This is more pronounced for treatments with H2O2,
42. suggesting that aromatic skeletal structure of lignin is highly disrupted or substantially
43. changed under oxidative conditions. This behaviour is in agreement with the results
44. reported by Wan et al.57 The authors verified that after acidic oxidative treatment of lignin
45. (phosphonic acid and hydrogen peroxide) HO+ or HO radical was produced, being
46. responsible for an extensive ring-opening on the aromatic substructure. Furthermore,
47. aromatic ring substitution by chloride atoms may also be favoured in similar way as
48. chlorinated compounds were formed during depolymerisation in presence of H2O2.
49. The results obtained from the elemental analysis (Table S5) of depolymerised lignins
50. showed an impact of depolymerisation on carbon, hydrogen, nitrogen and sulfur contents
51. in recovered lignins. This impact is mostly pronounced in acidic oxidative medium
52. ([Ch]Cl:Oxa/H2O2), in which the carbon and sulfur content decreased almost 1.2- and
53. 3.2-fold, respectively. In this case, the substitution of chloride atoms in the aromatic ring
54. structure may lead to such drastic decrease of carbon content.
55. **Discussion**
56. Overall, the present work demonstrated that acidic DES such as [Ch]Cl:Oxa can act as
57. both solvent and catalyst to simultaneously allow partial lignin depolymerisation into
58. desired monomeric and oligomeric compounds and partial lignin modification into a
59. functionalised material. In the chemical point of view, no substantial difference between
60. the performances of neat DES or DES with catalytic amount of H2SO4 was observed,
61. while on the opposite using H2O2 as catalyst provided severe side reactions that changed
62. both depolymerisation product profile and the remaining lignin structure.
63. The inherent acidity of oxalic acid (pka ≃ 1.5) *per se* was sufficient to give [Ch]Cl:Oxa
64. the ability to promote lignin depolymerisation for all studied system.39,58 However,
65. additional catalytic amount of a strong acid like H2SO4 (pka ≃ -3.0) slightly favoured the
66. disruption of lignin chemical bonds, specially β-O-4 bond cleavage,59,60 increasing the
67. depolymerisation efficiency. The maximum yield of 27.8 wt% is at the same level of
68. lignin depolymerisation with DES reported in literature. Hong et al.39 observed that the
69. process of alkaline lignin treatment with [Ch]Cl:Lac or [Ch]Cl:Oxa at 80-120 °C for 6 h
70. resulted in depolymerisation yields ranging from 25 to 56 % of the initial lignin.39
71. Furthermore, for treatments with [Ch]Cl:Oxa and [Ch]Cl:Oxa/H2SO4, a decrease of
72. lignin depolymerisation product yield at 6 h can be explained by the existence of
73. condensation and repolymerisation reactions between formed products.6,39 This enables
74. the formation of insoluble products and subsequently increases the yield of regenerated
75. lignin. These undesired reactions, which are favoured at long treatments, are also one of
76. the major limitations in several lignin depolymerisation processes.61,62 The condensation
77. and repolymerisation reactions during time was more evident in KL treatment with
78. [Ch]Cl:Oxa/H2O2.
79. The identification of depolymerised products by GC/MS plainly shows that the
80. composition of lignin depolymerisation extract is highly dependent on lignin nature.
81. Although 2D HSQC NMR of both KL from *E. grandis* wood and OL from beech wood
82. did not reveal significant structural differences (Figure S1 in SI), distinct lignin
83. monomers were produced under similar treatment conditions (DES system, temperature,
84. and time). This might be associated to the sulfur content in KL (approximately 2 wt%),
85. that will influence the reactivity in contact with DES and subsequently its
86. depolymerisation.63,64 Furthermore, treating KL under acidic conditions ([Ch]Cl:Oxa and
87. [Ch]Cl:Oxa/H2SO4) enables a selective formation of syringol **(8)**, which means that
88. propyl side chains of S type units present in KL are favourably cleaved apart from the
89. aromatic ring. On the contrary, this cleavage seems to not be favoured when OL is the
90. feedstock, since syringic acid **(27)** is formed in higher content than syringol **(8)** under the
91. same acidic conditions. On the other hand, the acidic oxidative medium
92. ([Ch]Cl:Oxa/H2O2) favoured the formation of vanillic acid **(14)** from KL, probably as a
93. result of the strong oxidation of G type units, like acetovanillone **(11)** and vanillin **(9)**,
94. mediated by H2O2.65 Similar observation was found for OL treatment under same
95. oxidative conditions, in which syringic and vanillic acids were two of the most produced
96. monomers. Moreover, chlorinated aromatic compounds were detected in higher amount
97. in presence of H2O2, resulting from the electrophilic substitution of chloride anion in the
98. aromatic ring.
99. Lignin depolymerisation in acidic DES has been tackled over the last few years, where
100. several authors have used lignin model compounds to mimic and to understand the
101. mechanisms acting in real lignin samples.38,40,66,67 For instance, Alvarez-Vasco et al.38
102. used guaiacylglycerol-β-guaiacil ether (GG) as lignin model compound to evaluate the
103. ability of [Ch]Cl:Lac to cleave its β-O-4 ether bond. The authors found that GG was
104. completely converted into guaiacol and a Hibbert ketone in almost stoichiometric
105. proportion. The proposed mechanism was similar to the acidolysis mechanism of lignin
106. catalysed by hydrochloric acid.59 Bearing this in mind and looking to products of KL and
107. OL depolymerisation with both [Ch]Cl:Oxa and [Ch]Cl:Oxa/H2SO4, it is possible to
108. propose a plausible reaction pathway for this acidic lignin depolymerisation. The reaction
109. starts through an attack of acidic protons from Oxa and/or H2SO4 to the α-hydroxyl group
110. surrounding the β-O-4 linkage, generating a carbocation through the release of a
111. molecular unit of H2O.68–70 The elimination reaction between α positive charge and β-H
112. results in an enol ether intermediate and simultaneous regeneration of the proton. This
113. intermediate energetically favours the cleavage of the ether bond enabling the formation
114. of S or G type Hibbert ketones (compounds (21) and (29)) and simultaneous liberation of
115. an aromatic alcohol, guaiacol (1) or syringol (8).68–70 From those very unstable Hibbert
116. ketones, all other identified compounds are formed through distinct reactions (e.g.
117. dehydration, oxidation, acylation, demethoxylation, etc.) and their stability is dependent
118. on the chemical environment offered by DES media. Although this mechanism finds well
119. the KL depolymerisation, the low formation of guaiacol and syringol during OL
120. treatments with both [Ch]Cl:Oxa and [Ch]Cl:Oxa/H2SO4 suggests that other kind of
121. depolymerisation mechanism is favoured in OL.
122. As mentioned above, both KL and OL depolymerisation with [Ch]Cl:Oxa/H2O2
123. provided a distinct profile of monomeric aromatic compounds, with the formation of
124. chlorinated compounds. The oxidative action of H2O2 in presence of [Ch]Cl:Oxa led to a
125. wide extent of several types of chlorinated substitutions at the aromatic ring of lignin
126. monomers. Syringol **(8),** one of the most produced monomers in acidic depolymerisation,
127. and its precursor **(18)** were substituted in different positions of the aromatic ring by
128. chloride (compounds **(16)**, **(20)** and **(25)**). In fact, compounds **(16)** and **(25)**, single and
129. double substituted with chloride (at positions 2 and 6), respectively, represented the major
130. monomer compounds of the KL depolymerisation extract at 1 h. During treatment, the
131. amount of those compounds decreased. As consequence of these chlorinated
132. substitutions, guaiacol and syringol were barely formed in [Ch]Cl:Oxa/H2O2 medium.
133. Moreover, chlorination of other G and S type monomers, including vanillic acid **(14)**,
134. acetosyringone **(24)** and syringic acid **(27)** into compounds **(26)**, **(28)** and **(30),** was also
135. observed. Their formation had a maximum at 3 h, while further consumption up to 6 h
136. was observed, which means that lignin monomer substitution with chloride do not prevent
137. further condensation and repolymerisation reactions. Surprisingly, the chlorination of
138. acetovanillone **(11)** and vanillic acid **(14)** was not favoured. For instance, the amount of
139. chlorinated vanillic acid **(26)** was much lower than its chlorinated counterparts, while
140. vanillic acid stands as one of the major compounds in both lignin depolymerisation
141. extracts at 6 h.
142. Therefore, lignin depolymerisation given by [Ch]Cl:Oxa/H2O2, not only provides an
143. acid-based catalysis of lignin into different lignin monomers, but also enables their
144. chlorination. The oxidation power of H2O2 gives chloride an electrophilic behaviour to
145. substitute the aromatic ring in different positions.71,72 Since chlorinated aromatic
146. compounds are highly toxic, their production from lignin depolymerisation in presence
147. of [Ch]Cl:Oxa/H2O2 might be seen as a disadvantage. Although there was a wide market
148. for these kind of compounds in the past, to be used as pesticides, herbicides and
149. desinfectants,73,74 their poor biodegradation poses some environmental concerns.75
150. Therefore, their substitution by other more environmentally friendly compounds have
151. been pursued lately.76,77 Therefore, the use of [Ch]Cl-based DES (or other DES composed
152. of halide salts) in combination with H2O2 is not recommended for lignin depolymerisation
153. technologies.
154. Apart from the depolymerised product fraction, the remaining lignin suffered
155. physicochemical modifications that are relevant for further valorisation.
156. The data of lignin molecular weight distribution highlights the performance of
157. [Ch]Cl:Oxa without additional catalyst, since recovered lignin samples from treatments
158. at 6 h using this system presented the lowest values of Mw and PDI. The PDI value was
159. even lower than that of initial KL and OL, an indication that such recovered lignin
160. exhibits a narrow dispersity of molecular weights,34 probably as consequence of less
161. severe and more selective depolymerisation. On the other hand, the more acidic (H2SO4)
162. and oxidative (H2O2) DES systems provided severe and wider depolymerisation of lignin
163. fragments leading to higher PDI values (Table S3).
164. Furthermore, an increase of COOH (oxalic esterification) and phenolic OH sites 602 (cleavage of aryl ether bonds) in remaining lignin structures was unveiled, which 603 enhances the reactivity potential of these lignin samples for several applications, 604 including grafting reactions with high density polyethylene (HDPE)78 as well as the 605 preparation of functionalised lignin nanoparticles for new bio-based composites.79 It 606 should be emphasised that although the esterification reaction between DES and lignin 607 during depolymerisation leads to slight DES consumption, these results show that 608 recovered lignins can be considered as functionalised materials. Moreover, the sulfur 609 content in KL was substantially reduced with depolymerisation, which is also beneficial, 610 since sulfur content is one the major deterrents of Kraft lignin valorisation.

611 Therefore, an integration of depolymerisation and functionalisation of lignin with DES 612 is herein presented as an alternative process to increase cost efficiency in the production 613 of value-added compounds and new bio-based composites and materials from technical 614 lignins. Yet, future work regarding the fine-tune and optimization of this process should 615 be carried out.

616

617 **Conclusion**

618 This work demonstrated the potential of an acidic DES ([Ch]Cl:Oxa at molar ratio 1:1) 619 in presence or absence of co-catalysts (H2SO4 and H2O2) towards the depolymerisation 620 of Kraft and Organosolv lignins at mild conditions (80 ºC). At least a quarter of the initial 621 lignin can be converted into monomers and oligomers in 3 h, while longer times favoured 622 condensation and repolymerisation reactions decreasing the yield of depolymerisation 623 products. Furthermore, the final product content is dependent on lignin nature as well as 624 on the chemical environment provided by DES systems, namely acidic ([Ch]Cl:Oxa and 625 [Ch]Cl:Oxa/H2SO4) or acidic oxidative treatments ([Ch]Cl:Oxa/H2O2). For instance, the

626 acidic treatments of Kraft lignin favoured the formation of syringol and acetosyringone, 627 while vanillic and syringic acids were the main products in the acidic treatments of 628 Organosolv lignin. On the other hand, the presence of H2O2 in DES revealed an opposite 629 behaviour by inducing electrophilic substitutions of chloride from [Ch]Cl in the aromatic 630 ring of produced lignin monomers from both lignin types. Bearing in mind the toxicity of 631 these chlorinated compounds, it seems prudent to avoid the use of H2O2 as an additive in 632 lignin depolymerisation with [Ch]Cl-based DES or other DES composed of halide salts. 633 Moreover, the regenerated lignin samples after depolymerisation reveal different 634 characteristics in contrast to their precedent technical lignins. Different molecular weight 635 and significant chemical changes, including esterification with oxalic acid and increase 636 of phenolic group content as consequent of aryl ether bond cleavage, were observed. 637 Overall, the data herein presented is a first step to accomplish a sustainable lignin 638 valorisation using DES.

639

## 640 Conflicts of interest

641 There are no conflicts to declare.

642

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659

660 **Abbreviations**

661 DES, deep eutectic solvent; HBA, hydrogen bond acceptor; HBD, hydrogen bond donor; 662 [Ch]Cl, cholinium chloride; KL, Kraft Lignin; OL, Organosolv Lignin; Oxa, oxalic acid, 663 LA, lactic acid; pTsa, p-toluenesulfonic acid; DFT, Density functional theory.

664

665 **Author Contributions**

666 **Filipe H. B. Sosa:** Conceptualisation, Methodology, Investigation, Data Curation Writing 667 - Original Draft, Visualisation; **Ana Bjelić:** Investigation; **João A. P. Coutinho:** Writing 668 - Review & Editing, Supervision; **Mariana C. Costa:** Writing - Review & Editing, 669 Supervision, Funding acquisition; **Blaž Likozar:** Writing - Review & Editing; **Edita** 670 **Jasiukaitytė-Grojzdek:** Conceptualisation, Methodology, Data Curation, Writing - 671 Review & Editing; **Miha Grilc:** Conceptualisation, Writing - Review & Editing, 672 Supervision, Funding acquisition; **André M. da Costa Lopes**: Conceptualisation, 673 Methodology, Data Curation, Writing - Review & Editing, Supervision, Funding 674 acquisition.

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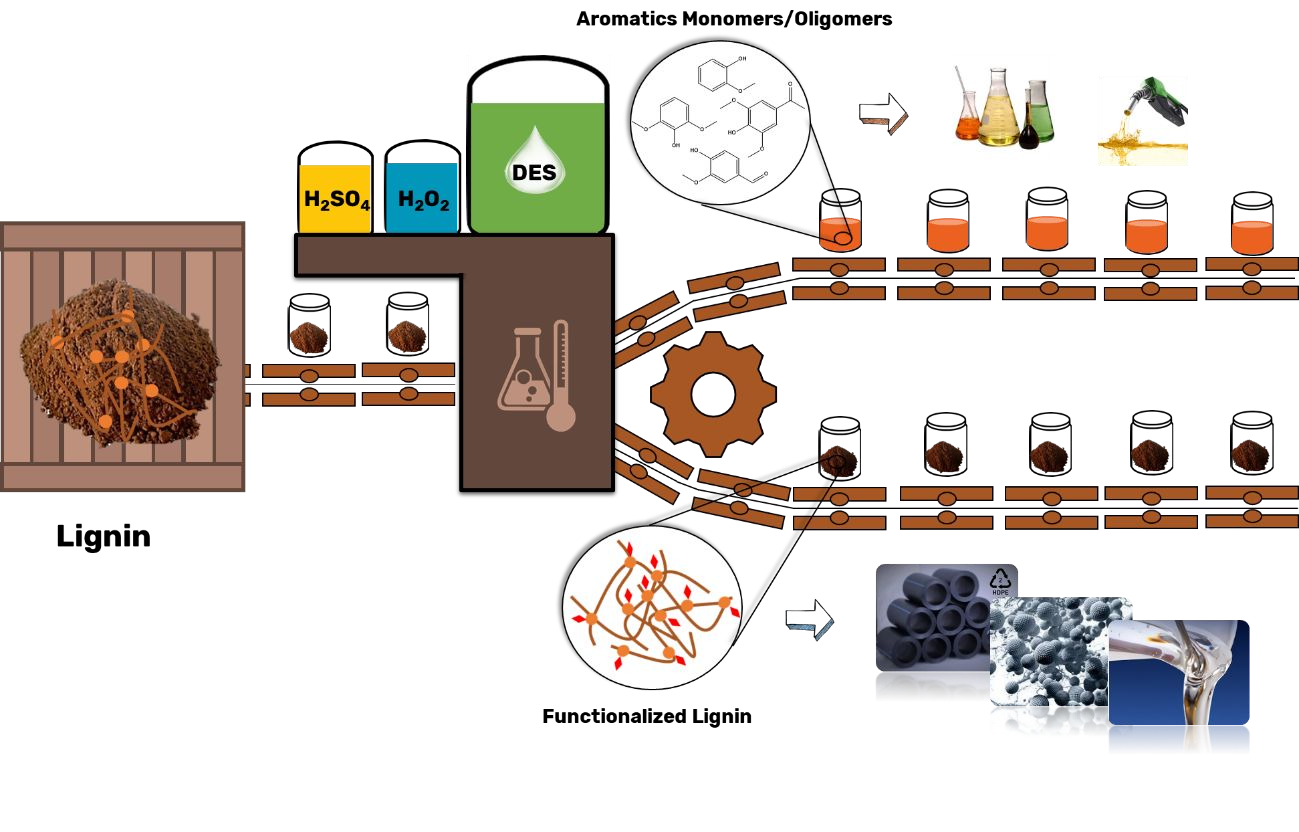
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### 826 TOC/Abstract Graphic

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828 **Synopsis.** The valorisation of technical lignins by conversion is herein demonstrated 829 using an acidic deep eutectic solvent in absence or presence of co-catalyst (H2SO4 or 830 H2O2).

**SUPPLEMENTARY INFORMATION**

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

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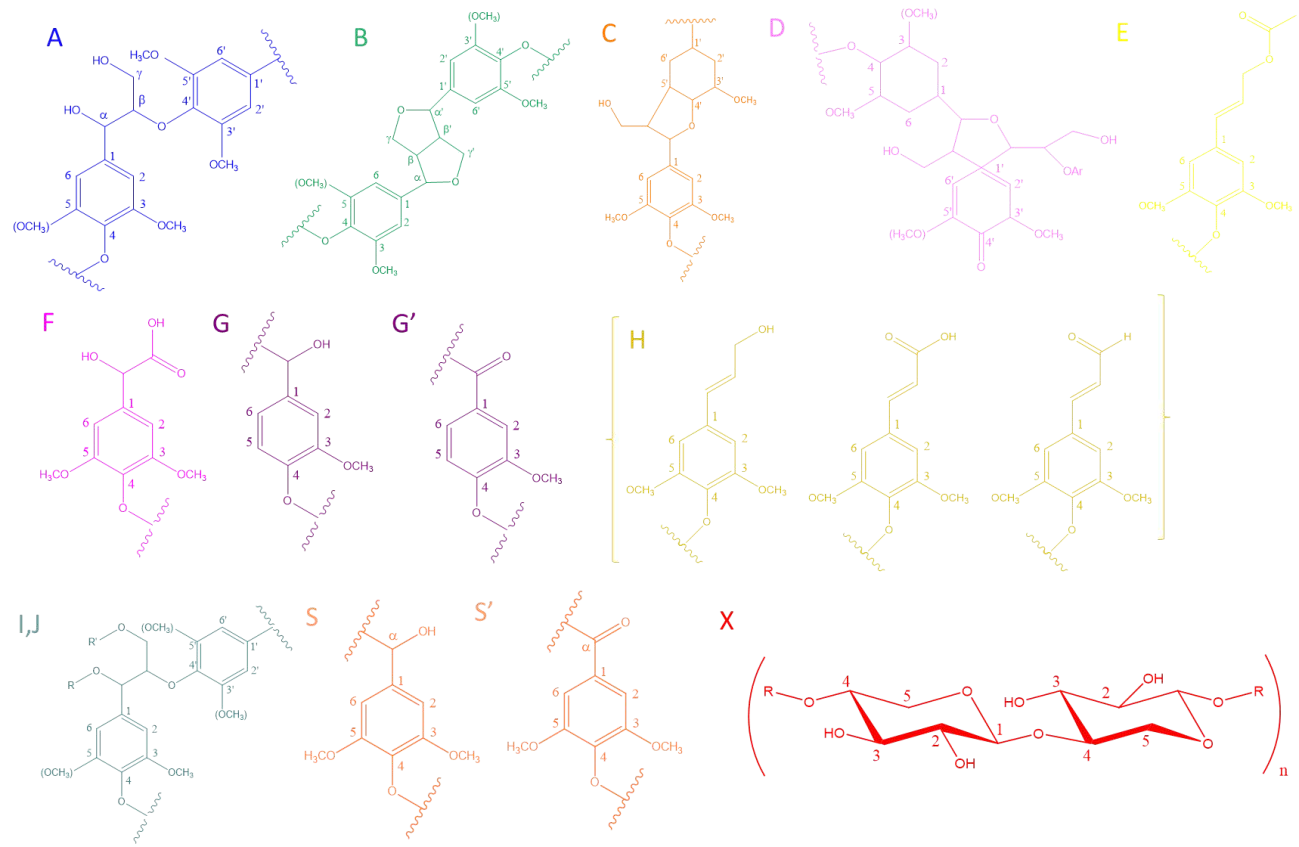
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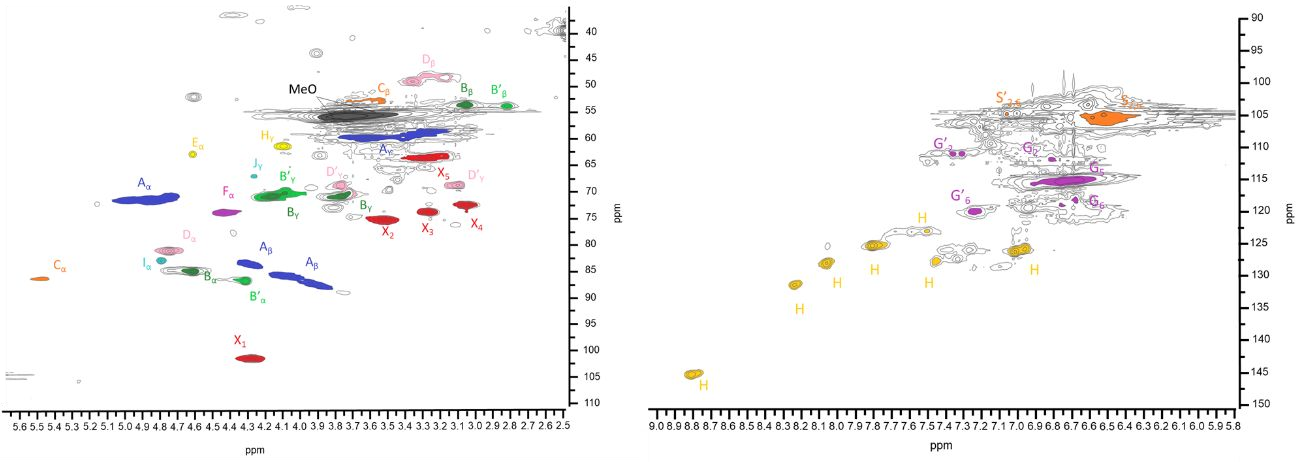
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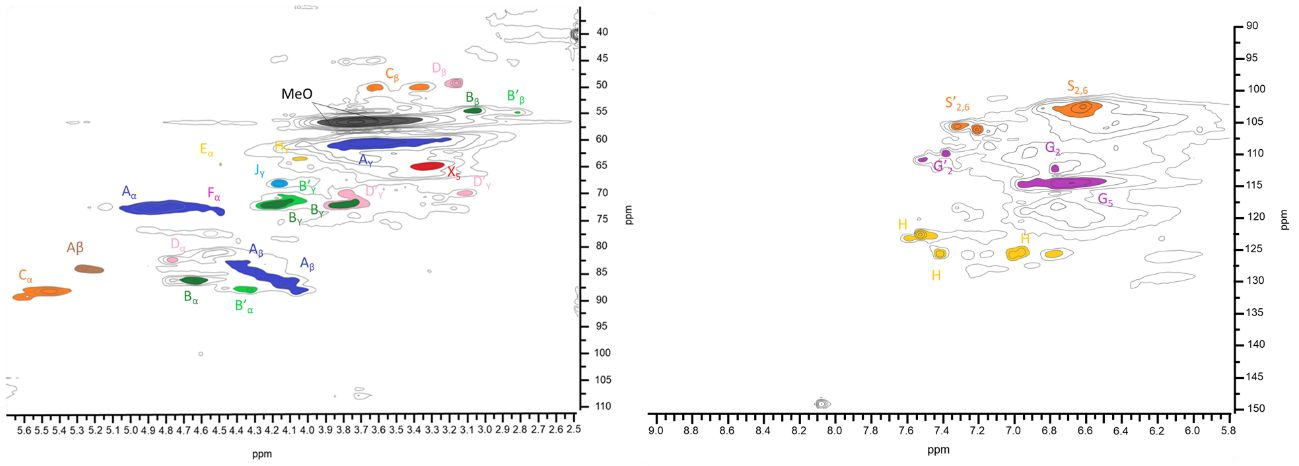
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### S1 – 2D HSQC NMR characterization of initial Kraft and Organosolv lignins





(A)



(B)

**Figure S1.** 2D HSQC NMR spectra of (A) Kraft lignin and (B) Organosolv Lignin with corresponding assignments of lignin substructures.

**Table S1.** Assignments of main lignin 1H-13C correlation signals found in the HSQC spectra.

|  |  |  |  |
| --- | --- | --- | --- |
| **Labels** | **δC** | **δH** | **Assignment** |
| Dβ | 49.61 | 3.39 | Cβ-Hβ in β-1’ spirodienone substructures (D) |
| Bβ | 53.50 | 3.07 | Cβ-Hβ in resinol substructures (B) |
| Cβ | 53.71 | 3.46 | Cβ-Hβ in β-5 phenylcoumaran |
| B’β | 54.20 | 2.82 | Cβ-Hβ in epiresinol substructures (B) |
| MeO | 56.06 | 3.75 | C-H in methoxyls |
| Aγ | 59.00 | 3.2 | Cγ-Hγ in β-O-4’ substructures (A) |
| Aγ | 59.87 | 3.71 | Cγ-Hγ in β-O-4’ substructures (A) |
| Hγ | 61.59 | 4.11 | Cγ-Hγ in p-hydroxycynnamyl alcohol |
| Eα | 63.16 | 4.64 | Cα-Hα in p-hydroxycinnamyl alcohol |
| Cγ | 63.26 | 3.89 | Cγ-Hγ in β-5 phenylcoumaran |
| X5 | 63.63 | 3.28 | C5-H5 in xylan |
| Jγ | 66.88 | 4.28 | Cγ-Hγ in β-O-4’ Cα- etherified with carbohydrate |
| Dγ’ | 68.89 | 3.79 | Cγ-Hγ in β-1’ spirodienone substructures (D) |
| Dγ’ | 68.92 | 3.13 | Cγ-Hγ in β-1’ spirodienone substructures (D) |
| B’β | 70.56 | 4.09 | Cβ-Hβ in epiresinol substructures (B) |
| Bγ | 71.07 | 3.79 | Cγ-Hγ in resinol substructures (B) |
| Bγ | 71.14 | 4.2 | Cγ-Hγ in resinol substructures (B) |
| Aα | 71.62 | 4.91 | Cα-Hα in β-O-4’ substructures (A) |
| X4 | 72.85 | 3.06 | C4-H4 in xylan |
| Fα | 74.18 | 4.43 | Cα-Hα in Ar-CHOH-COOH unit |
| X3 | 74.28 | 3.28 | C3-H3 in xylan |
| X2 | 75.84 | 3.53 | C2-H2 in xylan |
| B’α | 81.36 | 4.78 | Cα-Hα in epiresinol substructures (B) |
| Cα | 82.92 | 5.51 | Cα-Hα in β-5 phenylcoumaran |
| Iα | 83.41 | 4.83 | Cα-Hα in β-O-4’ Cα- etherified with carbohydrate |
| Aβ | 83.96 | 4.31 | (G) CβHβ in β-O-4’ linked to G units |
| Aβ | 83 | 5.2 | Cβ−Hβ in β-O-4′ substructures |
| Bα | 85.3 | 4.67 | Cα-Hα in resinol substructures (B) |
| Dβ’ | 86.89 | 4.44 | Cβ -Hβ in β-1’ spirodienone substructures (D) |
| B’α | 87.22 | 4.33 | Cα-Hα in epiresinol substructures (B) |
| Aβ | 87.23 | 3.69 | (S) Cβ-Hβ in β-O-4’ linked to S units |

|  |  |  |  |
| --- | --- | --- | --- |
| X1 | 101.8 | 4.29 | C1-H1 in xylan |
| S’2.6 | 104.88 | 7.07 | C2.6 - H2.6 in oxidized Syringyl units (S’) |
| S2.6 | 105.22 | 6.47 | C2.6 - H2.6 in Syringyl units (S) |
| G2 | 111.00 | 6.95 | C2-H2 in Guaiacyl units (G) |
| G2’ | 111.04 | 7.33 | C2-H2 in oxidized Guaiacyl units (G) |
| G5 | 115.00 | 6.75 | C5-H5 in Guaiacyl units (G) |
| G6 | 119.00 | 6.75 | C6-H6 in Guaiacyl units (G) |
| G6’ | 120.14 | 7.24 | C6-H6 in oxidized Guaiacyl units (G) |
| H | 122.98 | 7.56 | Cynnamyl alcohols. aldehydes or acids (aromatic and end groups) |
| H | 125.53 | 7.79 | Cynnamyl alcohols. aldehydes or acids (aromatic and end groups) |
| H | 126.16 | 4.00 | Cynnamyl alcohols. aldehydes or acids (aromatic and end groups) |
| H | 127.01 | 7.35 | Cynnamyl alcohols. aldehydes or acids (aromatic and end groups) |
| H | 128.42 | 8.09 | Cynnamyl alcohols. aldehydes or acids (aromatic and end groups) |
| H | 131.29 | 8.23 | Cynnamyl alcohols. aldehydes or acids (aromatic and end groups) |
| H | 145.73 | 8.8 | Cynnamyl alcohols. aldehydes or acids (aromatic and end groups) |

### S2 – Characterization of lignin depolymerized fraction

**Table S2.** Main compounds identified in the GC-MS.

### Entry Molecular structure Entry Molecular structure

O

OH OH

**1 2**

O OH

OH

OH

Cl OH

HO

**3 4**

O O

HO

OH HO

**5 6**

O O

OH

OH

**7 8**

O O

O OH

HO

**9 10**

O

O

OH

OH

Cl O

O

O

O

O

**11 12**

HO

HO OH

1. HO

O

O

O

1. OH

O HO

OH

O

Cl

HO

**15 16**

O O

O OH

OH

HO

O

**17 18**

O OH O O

OH

O

HO

**19 20**

O

O

Cl Cl

O O

OH

O

O

O

OH

**21 22**

HO

Cl OH

Cl O

Cl

O

O O

HO

**23 24**

HO

O O

O

OH O

Cl Cl O

OH

**25 26**

O O HO

OH Cl

O O

Cl

O O

OH

**27 28**

HO HO

O O

O

O

O

Cl

O

HO OH

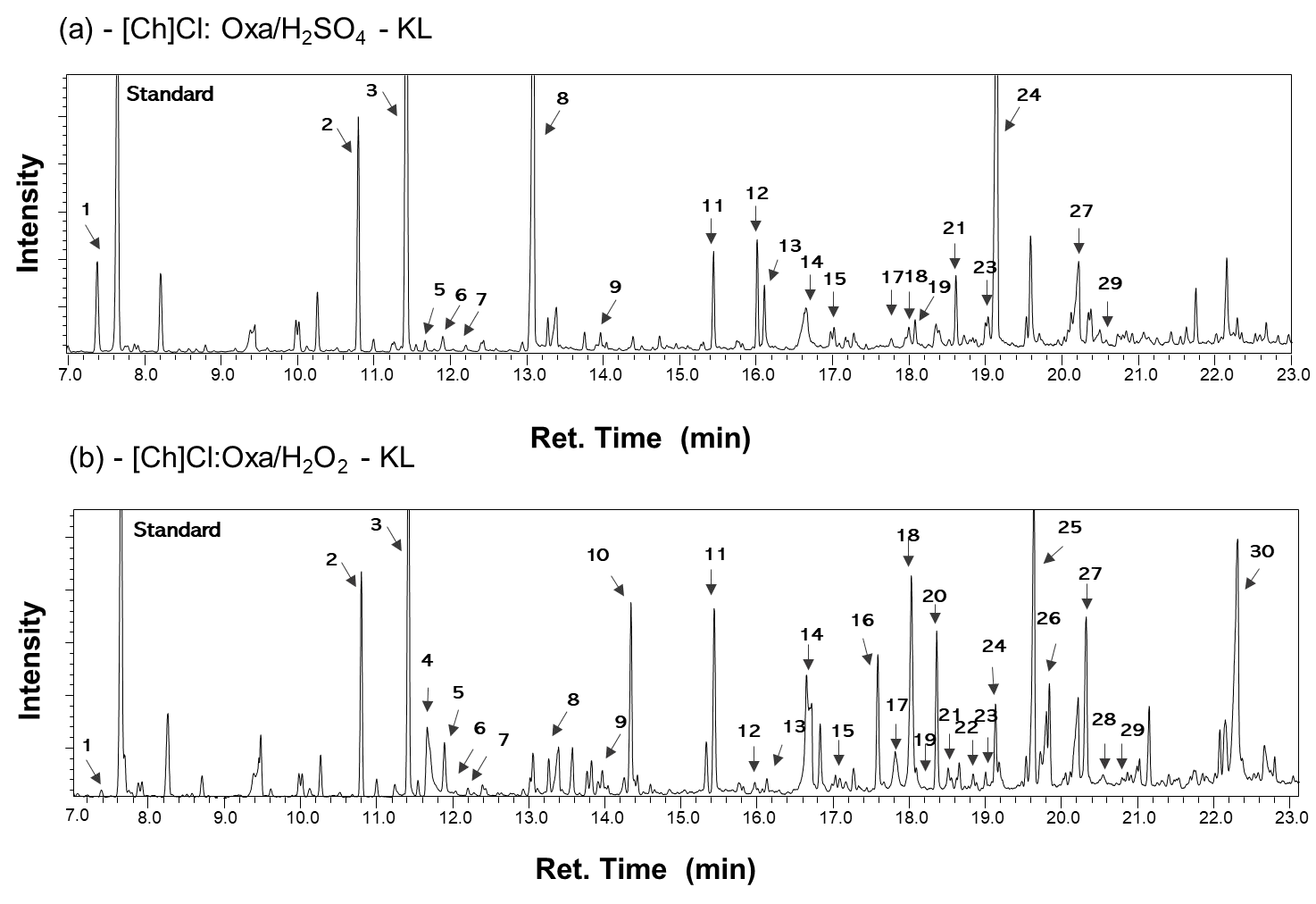
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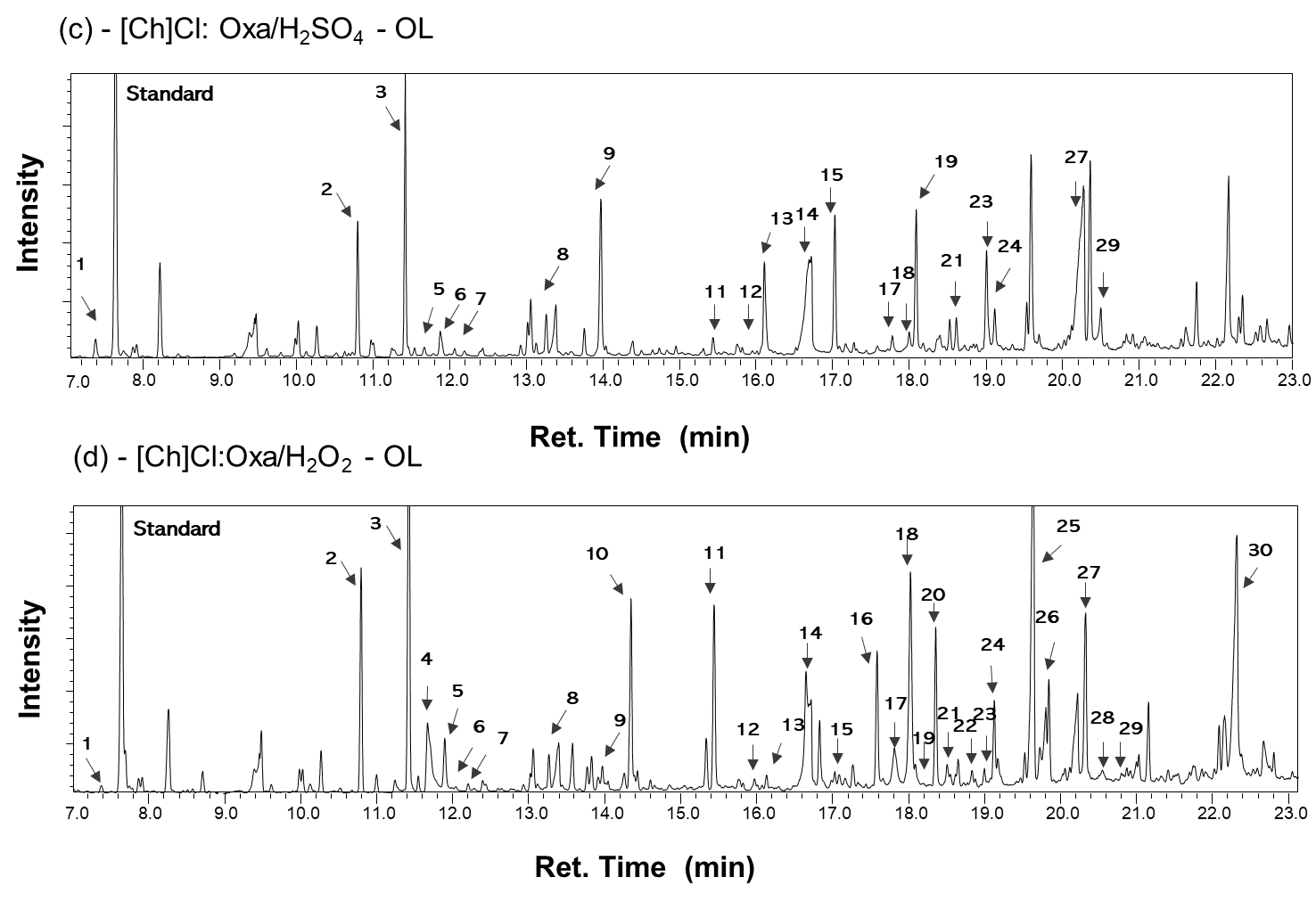
HO

O

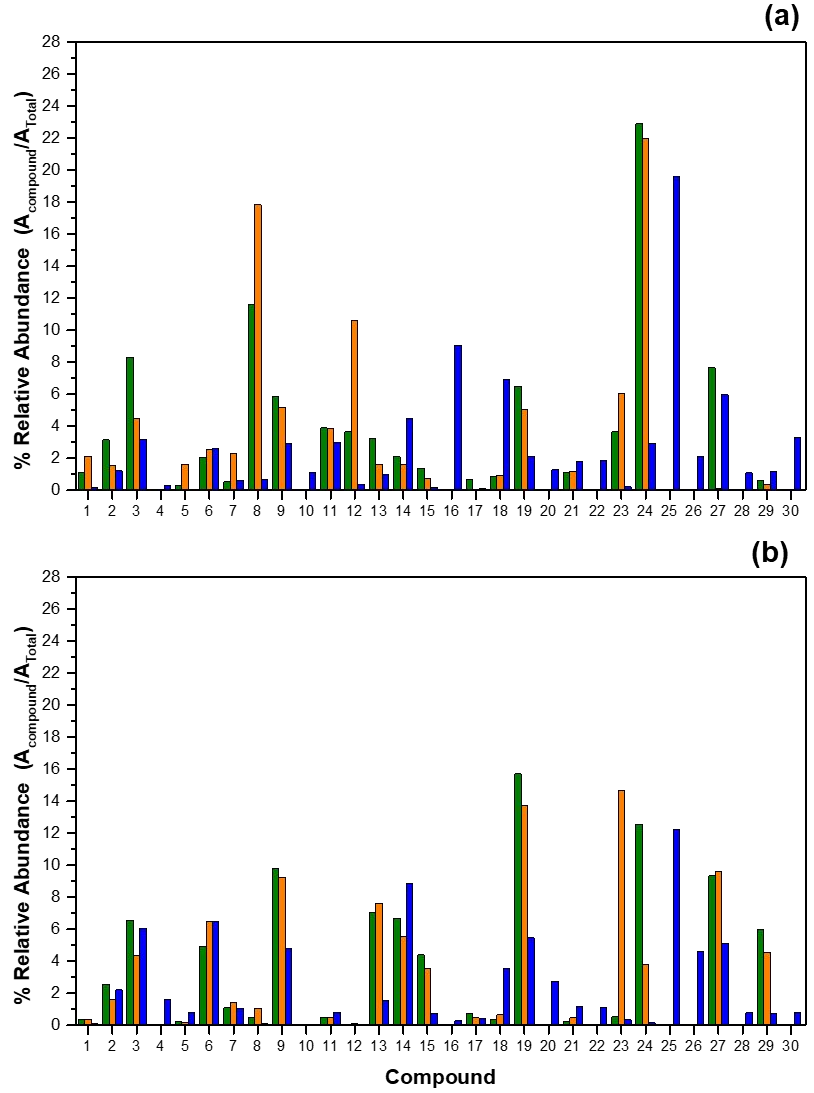
O

O

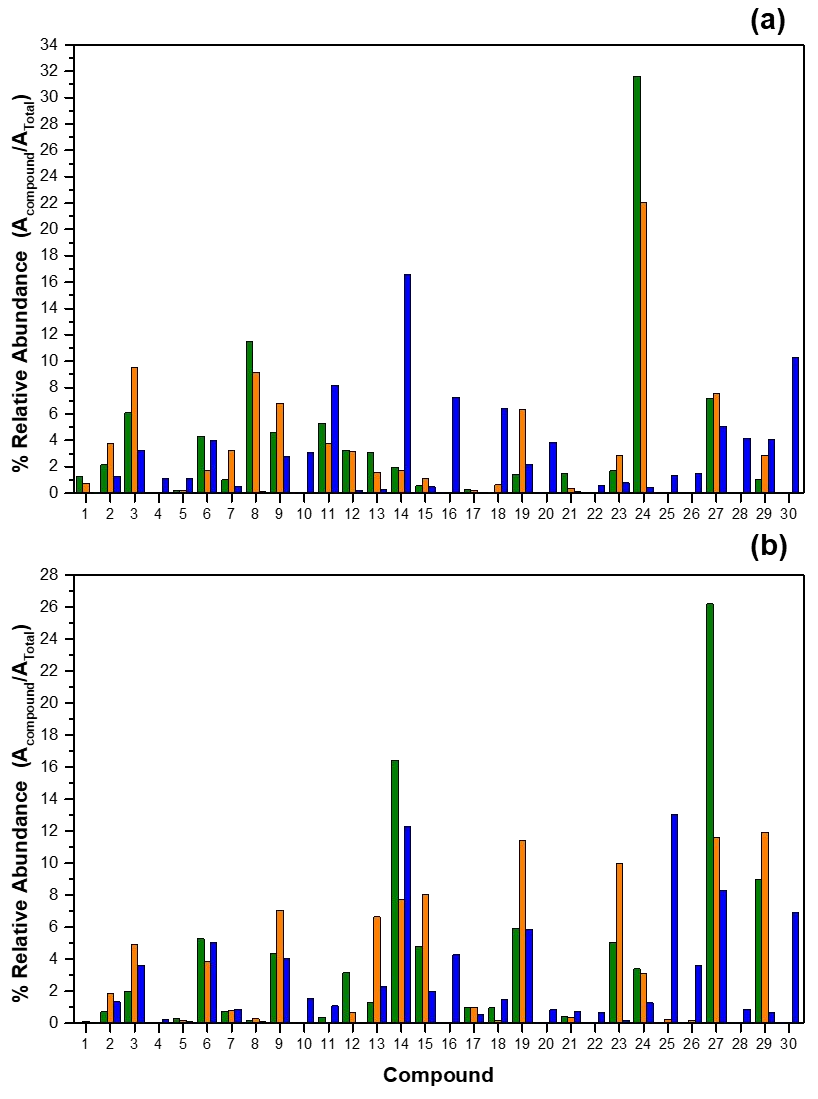




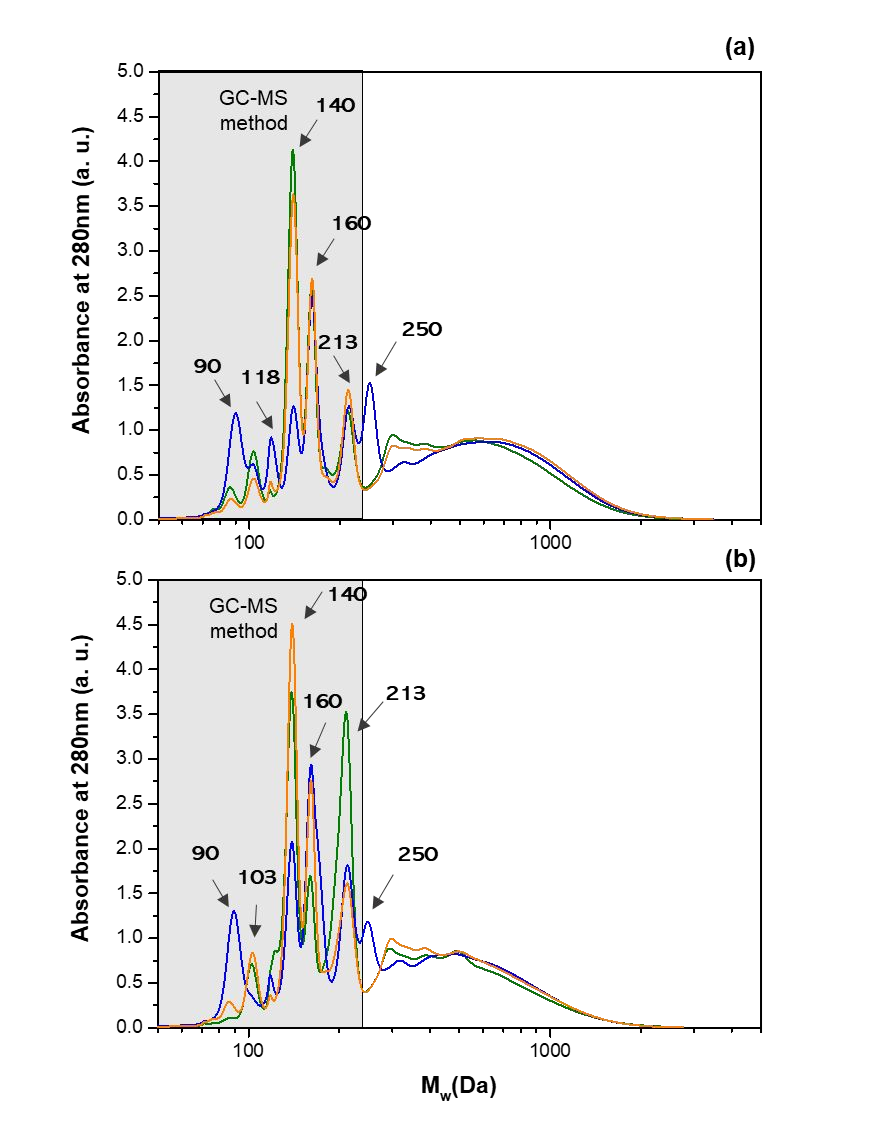
**Figure S2**. Gas chromatogram of lignin depolymerisation products obtained after treatment of Kraft lignin with (a) [Ch]Cl:Oxa/H2SO4 and (b) [Ch]Cl:Oxa/H2O2 and Organolsolv lignin with (c) [Ch]Cl:Oxa/H2SO4 and (d) [Ch]Cl:Oxa/H2O2. The reactions were performed at 80 ºC for 3 h. Methyl benzoate was used as a standard compound.



**Figure S3.** Relative abundance (%) of lignin depolymerisation products from (a) KL and (b) OL treatments at 80 °C for 1 hour with (■) [Ch]Cl:Oxa, (■) [Ch]Cl:Oxa/H2SO4 and (■) [Ch]Cl:Oxa/H2O2.



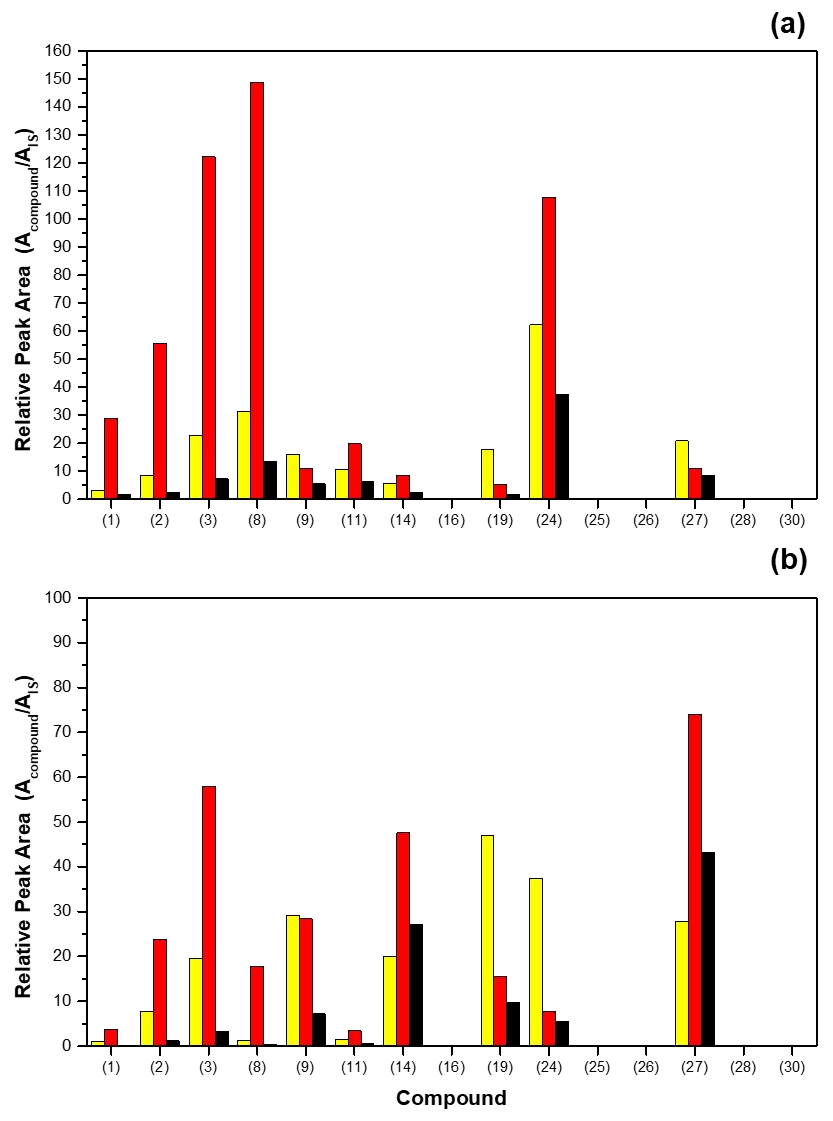
**Figure S4.** Relative abundance (%) of lignin depolymerisation products from (a) KL and (b) OL treatments at 80 °C for 6 hours with (■) [Ch]Cl:Oxa, (■) [Ch]Cl:Oxa/H2SO4 and (■) [Ch]Cl:Oxa/H2O2.



**Figure S5.** GPC analysis of lignin depolymerisation products from OL treatment at 80

°C during (a) 1 h and (b) 6 h with (■) [Ch]Cl:Oxa, (■) [Ch]Cl:Oxa/H2SO4 and (■) [Ch]Cl:Oxa/H2O2.

### S3 – Kinetics of lignin depolymerisation



**Figure S6.** Relative peak area of identified compounds after (a) KL and (b) OL depolymerisation at 80 °C for (■) 1 h, (■) 3 h and (■) 6 h with [Ch]Cl:Oxa.

### S4 - Structural characterization of regenerated lignin samples

**Table S3.** Molecular weight average (Mw), molecular number average (Mn) weights (g.mol−1) and polydispersity (Mw/Mn) of lignin*.*

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **Sample** | **Kraft Lignin** | | | **Organosolv Lignin** | | | |
| **Mw** | | **Mn** | **PDI** |  | **Mw** | **Mn** | **PDI** |
| **Untreated** 2500 | | 1200 | 2.1 |  | 3300 | 1500 | 2.2 |
|  | |  | **1 hour** |  |  |  |  |
| **[Ch]Cl:Oxaa** 2200 | | 1100 | 2.0 |  | 2900 | 1300 | 2.2 |
| **[Ch]Cl:Oxa +H2SO4** 2300  **a** | | 1150 | 2.0 |  | 3000 | 1400 | 2.1 |
| **[Ch]Cl:Oxa + H2O2** 2400  **a** | | 1100 | 2.2 |  | 2800 | 1250 | 2.2 |
|  | |  | **3 hours** |  |  |  |  |
| **[Ch]Cl:Oxa** 2500 | | 1250 | 2.0 |  | 3300 | 1400 | 2.4 |
| **[Ch]Cl:Oxa/H2SO4** 2600 | | 1250 | 2.1 |  | 3500 | 1400 | 2.5 |
| **[Ch]Cl:Oxa/H2O2** 3600 | | 1450 | 2.5 |  | 4100 | 1600 | 2.6 |
|  | |  | **6 hours** |  |  |  |  |
| **[Ch]Cl:Oxaa** 1800 | | 1050 | 1.7 |  | 2100 | 1100 | 1.9 |
| **[Ch]Cl:Oxa +H2SO4** 2100  **a** | | 1050 | 2.0 |  | 2600 | 1100 | 2.4 |
| **[Ch]Cl:Oxa + H2O2** 2000  **a** | | 1000 | 2.0 |  | 2600 | 1100 | 2.4 |

**Table S4.** FTIR vibrational bands/regions and corresponding assignments for lignin.

**Vibrational band (cm-1) Assignments**

3200-3500 O-H vibrations1

2844-2980 Aliphatic C–H and CH2 stretching vibrations1

1775-1750 C=O of esters, ketones, aldehydes and acids. ( C=O stretching, non

conjugated2

1731 C=O stretching in xylan, C=O stretching of acetyl or carboxylic acid3,4

1700 Unconjugated C=O (ketone, carboxyl or ester stretching)3,5

1600 - 1690 Aromatic skeletal vibration6–8

1514 Aromatic skeletal vibration6–8

1456 Aromatic skeletal vibration and C-H deformations6–8

1425 Aromatic skeletal vibrations combined with C-H in-plane deformation6–8

1370-1365 Phenolic hydroxyl group9,10

1327 - 1365 Syringyl unit breathing with C=O stretching and condensed Guaiacyl

rings6–8

1241 Guaiacyl ring breathing C–O stretch in lignin and for C–O linkage in guiacyl aromatic methoxyl groups11

1212 C-C plus C-O plus C=O stretch; Guaiacyl condensed > Guaiacyl etherified6–8

1152 C–O–C vibration (Cellulose and hemicellulose)11

1109 β-O-4 ether bond (Ether-O-)12,13

1040 Aromatic C H in-plane deformation (Guaiacyl > Syringyl) plus C-O deformation in primary alcohols plus C=O stretch (unconjugated) 6–8

979 C–O valance vibration; aromatic C–H in plane deformation14

925 Aromatic C-H out-of-plane6

838 Aromatic C-H out-of-plane deformation in Guaiacyl and Syringyl units15

**Table S5**. Elemental characterization and ash content of Kraft lignin (KL), Organosolv lignin (OL) and recovered lignins from depolymerization reactions with [Ch]Cl:Oxa, [Ch]Cl:Oxa/H2SO4, and [Ch]Cl:Oxa/H2O2 at 80 °C for 1, 3 and 6 hours.

**Elemental Analysis (wt%)**

**Samples Reaction time**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | **C** | **H** | **N** | **S** | **O** |  |
| KL | 58.65±0.13 | 5.29±0.16 | 0.19±0.01 | 2.08±0.54 | 32.31±0.26 | 1.47±0.10 |
| 1h | 58.69±0.35 | 5.83±0.01 | 0.56±0.01 | 1.89±0.28 | 32.82±0.03 | 0.22±0.02 |
| [Ch]Cl:Oxa 3h | 58.78±0.91 | 5.73±0.02 | 0.54±0.01 | 1.68±0.07 | 32.85v0.50 | 0.42±0.03 |
| 6h | 58.07±0.61 | 6.34±0.49 | 0.72±0.04 | 1.16±0.17 | 33.03±0.45 | 0.68±0.03 |
| 1h | 59.57±0.26 | 5.27±0.1 | 0.37±0.01 | 1.79±0.27 | 32.63±0.04 | 0.38±0.03 |
| [Ch]Cl:Oxa/H2SO4 3h | 59.33±0.03 | 5.43±0.01 | 0.47 ±0.02 | 1.75±0.07 | 32.16±0.04 | 0.86±0.04 |
| 6h | 58.76±0.41 | 5.43±0.17 | 0.59±0.05 | 0.97±0.02 | 33.57±0.32 | 0.68±0.03 |
| 1h | 50.05±0.73 | 4.27±0.16 | 0.51±0.02 | 1.02±0.25 | 43.98±0.33 | 0.19±0.03 |
| [Ch]Cl:Oxa/H2O2 3h | 48.53±0.84 | 4.32±0.27 | 0.76±0.06 | 0.76±0.02 | 44.90±0.59 | 0.73±0.05 |
| 6h | 50.55±0.38 | 4.87±0.1 | 0.74±0.03 | 0.62±0.03 | 42.63±0.27 | 0.59±0.04 |
| OL | 61.88±0.16 | 5.35±0.03 | 0.23±0.01 | 0.00±0.00 | 32.13±0.10 | 0.42±0.06 |
| 1h | 60.30±1.41 | 5.35±0.10 | 0.41±0.00 | 0.00±0.00 | 33.81±0.75 | 0.14±0.02 |
| [Ch]Cl:Oxa 3h | 61.31±0.41 | 5.44±0.04 | 0.46±0.02 | 0.00±0.00 | 32.44±0.23 | 0.36±0.04 |
| 6h | 59.79±0.23 | 5.34±0.07 | 0.51±0.02 | 0.00±0.00 | 34.28±0.16 | 0.08±0.01 |
| 1h | 60.58±0.07 | 5.59±0.05 | 0.32±0.01 | 0.00±0.00 | 33.27±0.01 | 0.24±0.03 |
| [Ch]Cl:Oxa/H2SO4 3h | 60.36±0.02 | 5.47±0.41 | 0.41±0.01 | 0.00±0.00 | 33.28±0.05 | 0.48±0.03 |
| 6h | 60.15±0.12 | 5.26±0.06 | 0.46±0.01 | 0.00±0.00 | 34.00±0.04 | 0.12±0.02 |
| 1h | 53.52±0.32 | 4.30±0.02 | 0.38±0.02 | 0.00±0.00 | 41.60±0.16 | 0.20±0.02 |
| [Ch]Cl:Oxa/H2O2 3h | 56.20±0.04 | 4.49±0.02 | 0.47±0.01 | 0.00±0.00 | 38.49±0.01 | 0.35±0.01 |
| 6h | 53.53±0.49 | 4.55±0.04 | 0.65±0.01 | 0.00±0.00 | 40.89±0.22 | 0.39±0.03 |

**Ash (%)**

(KL)

(KL)

(KL)

(OL)

(OL)

(OL)

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