Base-catalysed depolymerization of lignins in supercritical water: Influence of lignin nature and valorisation of pulping and biorefinery by-products

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ABSTRACT

Different lignins from different sources (hardwoods, softwoods and crop residues) and obtained as by-products of different processes such pulping or biorefining were depolymerized in alkaline supercritical water (SCW: 386 °C and 260 bar) in an intensified continuous process to produce high value-added compounds with low-molecular-weight in only 300 ms of reaction time. The products obtained were analysed to determine the yield, selectivity to monomers, chemical structure and molecular weight distribution.

The char formation was low in most cases, but the proportion of heavy and light oils were variable upon the starting material used. The monoaromatics yield depends mostly on the type of lignin utilized being the non-wood biorefinery lignins less suitable for monomers production than the technical wood ones (13-8%). The monomer distribution depends on the biomass of origin and the pulping method. This technology is equally effective when directly treating a black liquor and better results are obtained if compared to the corresponding isolated lignin.

1. Introduction

Lignocellulose is the most abundant, cheapest and easiest grown form of biomass. It is composed mainly of cellulose (30–50%), hemicellulose (20–40%) and lignin (15–35%) [1]. These fractions represent potential feedstocks for bio-sourced commodity chemicals. However, due to their different chemical functionalities (lignin is an aromatic polymer, hemicelluloses are formed by C5 and C6 sugars and cellulose by C6 sugars) fractionation steps are necessary to isolate the individual components (e.g. sugars for cellulose/hemicellulose and aromatic units for lignin) and the strategy depends on the particular application.

Nowadays, the industry that produces the largest amount of lignin is the pulp and paper industry. In the most common pulping process, Kraft pulping, cellulose fibres are separated from hemicellulose and lignin by cooking wood in an alkaline solution of NaOH with addition of Na_2S. The resulting solution is called black liquor and consists of a complex mixture of lignin (and related substances), hemicelluloses degradation products, soaps (originated from lipophilic extractives) and inorganic salts. Approximately 7 tonnes of black liquor are produced in the manufacture of one tonne of pulp [2]. Black liquor is generally burned to recover the pulping chemicals and to produce energy however, a part of it can be used to isolate Kraft lignin [3,4]. Kraft lignins can be used for various applications, but the demand is much lower that the production capacity. Alternatively, depolymerization of lignin into low molecular weight aromatics is an attractive approach to produce high-value platform chemicals.

Another approach of biomass utilization focusses on the production of chemicals and fuels from renewable sources to reduce the dependence and consumption of oil. This target can be achieved by a so-called biorefinery, based on fractionating biomass into its individual building blocks for their subsequent valorisation [5]. Different processes are proposed to separate lignocellulosic biomass in a biorefinery. They include Kraft and Organosolv pulping [6,7]; but also sub- and supercritical water hydrolysis [8,9]. These pretreatments are usually followed by enzymatic hydrolysis to produce monomeric sugars. Lignins obtained from these processes are Sulphur-free (except Kraft lignin) and may contain certain proportion of carbohydrates. Lignocellulosic biorefineries are very successful in converting cellulose and hemicellulose into value-added chemicals. However, lignin valorisation is not

List of abbreviations

SCW	Supercritical water
H	p-hydroxyphenyl units
G	Guaiacyl units
S	Syringyl units
SKL	Sulphonated Kraft lignin
OS	Organosolv lignin
WS	Wheat straw lignin
BP	Beep pulp lignin
TOB	Tobacco vein lignin
BL-EC	Black liquor from ENCE
KL-EC	Kraft lignin from ENCE
BC-SCWD	Base catalysed supercritical water depolymerization
SEMR	Sudden expansion micro reactor

sufficiently addressed yet [10]. This is a crucial problem because lignin is the only large-scale renewable source of aromatic chemicals and can be a game-changer for the biorefinery [11].

Nowadays, much research has been focused on achieving and understanding an effective depolymerization of this biopolymer. Among the different approaches, hydrothermal depolymerization was preferred because it is significantly cleaner and safer due to the absence of organic solvents. Moreover, it offers the possibility of direct treatment of the spent liquor simplifying the process and lowering the costs. Unfortunately, this approach faces two important obstacles: a) the uncontrolled repolymerization reactions that result in low product yield and high amounts of char [12]. b) The complex structure of lignin and its variability among different lignins, which makes difficult to understand the mechanisms occurring.

In previous reports we demonstrated that sulphonated Kraft lignin can be depolymerized in supercritical water at very short reaction times to obtain up to 60% of an aromatic light oil containing 20% of monomeric compounds [13,14]. The amount of residual char was also very low, 2.6%. The optimum conditions were 386 °C, 260 bar, 300 ms reaction time and 0.2 mol L^{-1} NaOH as catalyst. The present report explores the possibility of extending this treatment to other lignins obtained from different pulp and biorefining process, focusing on the variability of the structure of the starting product and its effect on this Base-Catalysed Supercritical Water Depolymerization (BC-SCWD) process. There are solid evidences that the pulping method alters the properties of lignin [15] and this can affect its valorisation [16], Several reports exist in literature about hydrothermal depolymerization of lignins of diverse type, i.e. Kraft [13,17], lignosulfonates [12,18], organosolv [19,20], etc. However, there is lack of a comparative study about how the different structure of them affect the depolymerization products.
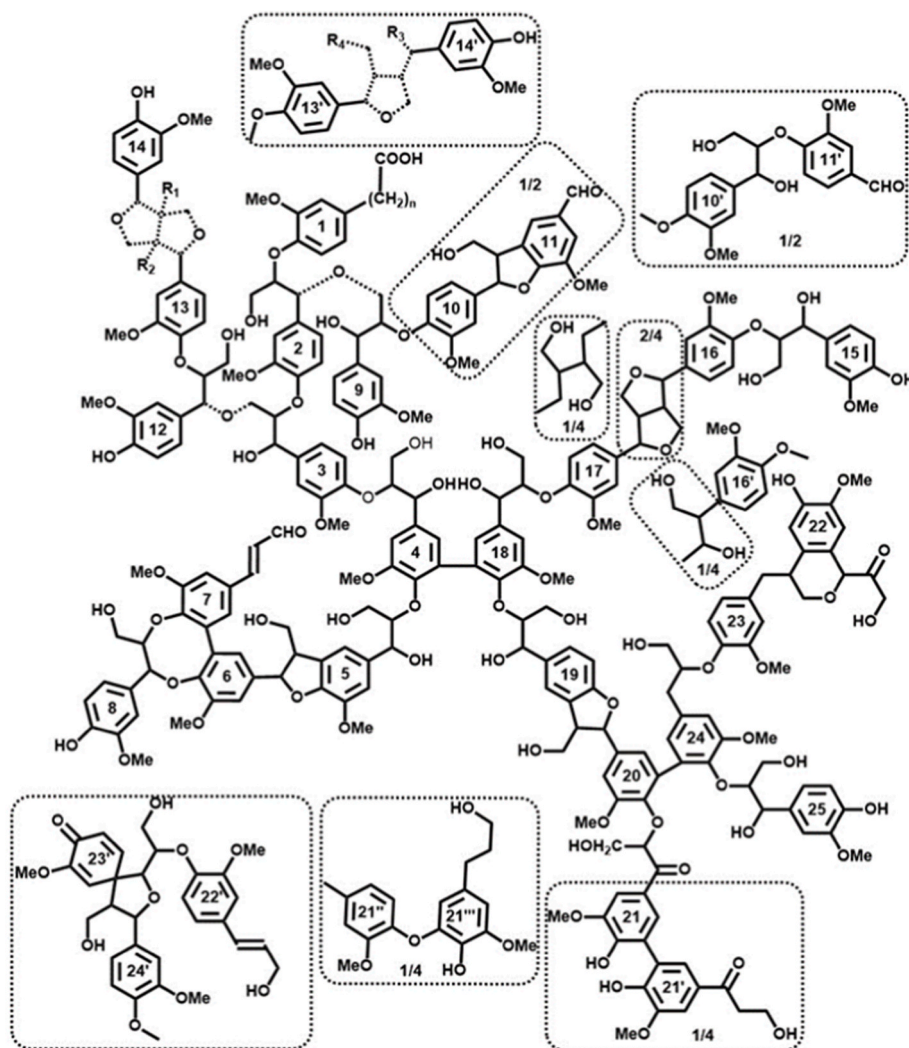

Fig. 1. A plausible structure of a spruce milled wood lignin (MWL), a lignin preparation close to the structure of native softwood lignin [24].

Lignin is a complex irregular polymer consisting of 3 types of monomeric units: p-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) respectively. The most common linkage in native lignins is β-O-4 ether bond but they can be linked in many other different ways forming multiple types of functional groups and structures [21–23]. A plausible model of native softwood lignin is shown in Fig. 1 [24]. Lignin structure varies from specie to specie. Hardwood lignins are primarily composed by syringyl and guaiacyl units, whereas softwood lignins are composed mainly of guaiacyl units (more than 90% of the total); both lignin types contain small amounts of p-hydroxyphenyl units [21]. Grass lignins are also of guaiacyl-syringyl type. However, unlike wood lignins, grass lignins additionally contain certain amounts of structural elements derived from p-coumaryl type units, particularly cinnamic acids attached to lignin polymer by ester linkages (at the α-position of the side chain) [25].

Hence, the physicochemical behaviour of lignins, which is dependent on their chemical structures, will be strongly affected by the biomass source. In addition, biomass processing strongly affects lignin structure. These methods use different operational conditions including high temperature, different solvents and digesting agents, and pH ranges that end up altering the chemical structure and linkages of the native lignin [16,21]. All these modifications to the native structure of lignin will necessarily change the outcome of the valorisation using SCW. In this report, different lignins from different vegetable sources obtained as by-products in pulp and paper industry and in biorefinery processes were depolymerized at the optimum conditions abovementioned and the effect of the lignin nature in the results was studied using different analytical techniques. The comparison between the direct depolymerization of a black liquor and that of the counterpart lignin is also done, thus assessing the possibility of a valorisation step that can be easily coupled to the process of pulp and paper industry.

2. Materials and methods

2.1. Characterization of lignins and chemicals utilized

Different technical lignins and biorefinery residues with high lignin content, as well as black liquors containing low amounts of lignin were studied in the present work. Sulphonated softwood Kraft lignin (sulphur content of 4%) was purchased from Sigma-Aldrich and named as SKL; organosolv lignin was obtained from Fraunhofer Center for Chemical-Biotechnological Processes CBP (Germany), and it was named as OS; lignin from wheat straw (WS) was supplied by the Institute of Thermal Separation Processes, Hamburg University of Technology and it was obtained by subcritical water extraction at 200 °C and 30 min followed by an enzymatic hydrolysis step. Lignins obtained after the fractionation of beet pulp (BP) and tobacco vein (TOB) were extracted in our laboratory (High Pressure Processes Group, University of Valladolid), BP was obtained in two steps: Subcritical Water Extraction (160 °C, 80 min) to remove hemicellulose and Ultrafast Supercritical Water Hydrolysis at 393 °C and 60 ms to separate cellulose [9,26]. TOB however was directly extracted by one step of Supercritical Water Hydrolysis (370–382 °C;

0.15–0.31s). Finally, both a hardwood (70% E. globulus, 30% E. Nítens) black liquor and the corresponding Kraft lignin isolated by acid precipitation were produced and supplied by ENCE Energía y Celulosa, S.A. They were labelled as BL-EC and KL-EC, respectively. A summary on the characteristics of the starting materials are presented in Table 1.

Distilled water was used as the reaction medium to run the experiments. Sodium hydroxide used as catalyst and sulphuric acid (96%) and ethyl acetate (>99%), used for carrying out the fractionation of the products, were purchased from Sigma-Aldrich.

The calibration standards used in the GC-MS analysis were all purchased from Sigma-Aldrich (USA): syringol (≥98%), acetosyringone (97%), guaiacol (≥99%), creosol (≥98%), acetovanillone (≥98%), vanillin (99%), syringaldehyde (≥97%), as well as the internal standard, 2-phenyl ethanol (≥99%).

All compounds used for ^{31}P NMR were also purchased from Sigma-Aldrich: 2–chloro–4,4,5,5–tetramethyl–1,3,2–dioxaphospholane, n-hydroxy-5-norbornene-2,3-dicarboximide (98%), chromium (III) acetylacetonate, deuterated pyridine, deuterated chloroform.

The total amount of lignin, sugars and ashes in the raw materials were determined according to the standard methods published by the National Renewable Energy Laboratory (NREL) [27]. To determine the carbohydrate and lignin composition, the samples were hydrolysed with sulphuric acid and the resulting monosaccharides were determined by HPLC using a column SUGAR SH-1011 (Shodex) with a 0.01 N of sulphuric acid solution as a mobile phase. To identify the soluble products, two detectors were used: Waters IR detector 2414 (210 nm) and Waters dual λ absorbance detector 2487 (254 nm). The insoluble lignin from the hydrolysis was determined gravimetrically. Acid soluble lignin in the hydrolysate was quantified by ultraviolet spectroscopy (Table S2).

2.2. Lignin depolymerization and fractionation

The depolymerization of the lignins and the black liquor was carried out by Base-catalysed supercritical water depolymerization (BC-SCWD) in continuous fashion using a Sudden Expansion Micro-Reactor (SEMR). Lignin + NaOH solution is rapidly heated up by mixing it with a hot water stream and passed by a tubular micro reactor. The products are cooled down by Sudden Expansion thanks to Joule-Thomson effect. Details of the procedure are given elsewhere [13]. In this study, the reactions were performed for every lignin at the optimal operating conditions determined in our previous work for SKL (i.e. 386 °C, 260 bar and 300 ms). A reactor of 1.6 ml of volume was used with a total flow of around 7 kg h^{-1}. The lignin concentration at the inlet of the reactor was in all cases 5000 ppm (0.5 wt%) in a basic solution of NaOH (0.2 M). In the case of the black liquor, it was diluted until reaching 5000 ppm of lignin at the inlet of the reactor as well for comparison purposes.

From each experiment of the 6 different lignins and one black liquor, four fractions were obtained, as described in previous reports by fractionation after acidification according to the solubility in water and ethyl acetate [12,13]. Briefly, **light oil** (water and ethyl acetate soluble) containing monomers and di-trimers, **heavy oil** (water non-soluble, ethyl acetate soluble) containing oligomers and small

Table 1
Composition of lignins and black liquors: Lignin content (Insoluble + Soluble), ash and carbohydrates. Elemental analysis. All data are expressed in wt% and calculated on dry basis.

	Extraction method	Biomass	Proximate Analysis			Elemental Analysis					
			Lignin %	Ash %	Carbohydrates %	%C	%H	%N	%S	H:C (mol/mol)
SKL	Kraft process	Softwood	96.0	0.0	0.0	49.1	4.6	0.1	4.1	1.12
KL-EC	Kraft process	Hardwood	86.4	0.3	3.3	57.0	5.1	0.0	2.2	1.07
OS	Organosolv process	Hardwood	96.5	0.0	0.4	63.3	5.7	0.0	0.0	1.08
WS	SWE + EH	Wheat straw	78.2	11.0	10.8	50.8	5.5	1.1	0.0	1.30
BP	SWE + SCWH	Beet pulp	50.8	4.4	44.8	40.8	5.3	0.6	0.0	1.56
TOB	SCWH	Tobacco	79.7	0.0	23.8	41.5	5.6	1.3	0.0	1.62

EH: enzymatic hydrolysis; SWE: Subcritical water extraction; SCWH: Supercritical water hydrolysis.

repolymerization fragments, **char** (water and ethyl acetate non-soluble) including large repolymerization products and the **aqueous residue** (water soluble and ethyl acetate non-soluble). The latter was formed mainly by inorganic salts produced during the fractionation process of the depolymerization products, and small non-reacted water-soluble lignin fragments. Due to the difficulty in analysing this fraction and its low organic content, it was not further considered. The yield of a fraction or a monomer is calculated as the mass obtained divided by the lignin loaded. The selectivity of a monomer in light oil calculated as the mass of the monomer divided by the mass of the light oil [13].

2.3. Characterization procedures

The starting lignins and the fractions after depolymerization were characterized by FTIR (Bruker Tensor 27, mode ATR), Micro-Elemental Analysis CHNS (LECO CHNS-932), Thermo Gravimetrical Analysis (TGA) with a TGA/SDTA RSI analyser of Mettler Toledo. The content of monomers in light and heavy oils were determined by a gas chromatograph (GC-MS) equipped with a quadrupole mass spectrometer detector (5977A-Agilent Technologies, USA). These analyses were carried out following standard procedures (details reported elsewhere [12]). The molecular weight profile was estimated by Gel Permeation Chromatography (GPC) with a Jordi Gel Sulphonated Plus 10000 Å 250 × 10 mm column, the samples were dissolved in eluent (water + methanol 90:10, pH = 12) and filtered before analysis.

The biorefinery lignins were extracted with 1% NaOH [28] to produce soluble lignin samples suitable for NMR analysis. KL-EC and OS (completely soluble in NMR solvents) were used as is. ^{13}C NMR [16] and HSQC [29,30] analysis of lignins were carried out per earlier reported protocols. ^{31}P NMR was performed to quantify hydroxyl groups [31] using a modified procedure [32]. Details of the procedure can be found in Supplementary Information.

3. Results and discussion

3.1. Characterization of the starting lignins

As can be seen in Table 1, the technical lignins SKL, KL-EC and OS have low ash and carbohydrates contents. While, WS, BP and TOB showed high amounts of sugars (up to 45 wt%) and ashes (up to 11 wt %). On the other hand, black liquor, BL-EC is a complex mixture formed by high amounts of salts (see Table S1) and a low amount of lignin.

Elemental composition of the raw materials can also be seen in Table 1. Only Kraft lignins (especially sulphonated Kraft lignin) contained sulphur, as expected as it is the only pulping process that uses sulphur-containing cooking compounds. BP, TOB and WS presented nitrogen, which can be attributed to protein impurities, either from the original biomass or/and from enzymatic hydrolysis. All lignins presented a similar hydrogen content (4.6–5.7 wt%), while they differed more in the carbon content (40.8–63.3 wt%), The ratio H:C is also included, as it can provide useful information about the saturation degree of the sample (proportion of multiple bonds and cycles). Samples with higher proportion of carbohydrates present generally a higher H:C ratio, which is expected as carbohydrates have higher saturation degree. Technical lignins (Kraft and organosolv), on the other hand, have higher C proportion and lower H:C ratio indicating that they do not contain carbohydrate impurities and present a higher degree of degradation due to condensation reactions. SKL have low proportion of carbon due to the presence of sulphonic groups.

^{31}P NMR spectroscopy of lignin enables the quantification of different types of hydroxyl groups, such as aliphatic or aromatic alcohols or carboxylic acids. These functional groups are among the major lignin functionalities and therefore their quantification is important in lignin structural analysis. Quantification of –OH functionality reveals significant differences between lignins (Fig. 2). The amount of 3,5-substituted –OH (syringyl and condensed guaiacyl units) is higher than guaiacyl
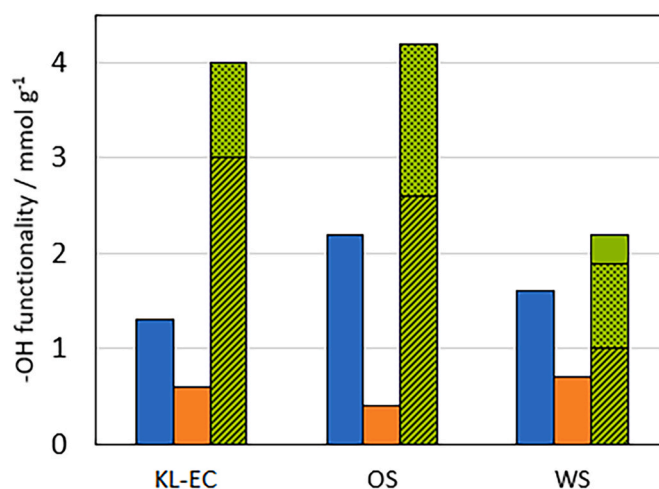

Fig. 2. OH functionality determined by ^{31}P NMR for three lignins studied in this work. (■): Aliphatic, (■): COOH, (▨): 3,5-substituted, (■): 3-substituted (guaiacyl non-condensed), (■): non-substituted (H units).

–OH for KL-EC and OS, which is expectable in hardwood lignins.

The isolation method also seems to have a great influence on the functionality, OS has a much higher proportion of aliphatic OH than KL-EC. It seems that, although both pulping methods alter greatly the native structure of lignin, organosolv process degrades less the aliphatic alcohols. Apart from G and S units, WS also contains a proportion of H units as expected. However, the total phenolic OH is ca. 40% lower than KL-EC and OS while the proportion of aliphatic and acidic hydroxyl remains comparable to the other two samples.

Only KL-EC and OS were soluble in NMR solvent (DMSO) and can be comprehensively analysed by a combination of quantitative ^{13}C and HSQC methods [16,29,33,34], in general, the ^{13}C and HSQC data are in good correlation (e.g., S:G ratio, β-O-4 content) and well complement each other; ^{13}C reports comprehensive information on the content of different lignin functionalities while the HSQC method is very useful to quantify some specific structural moieties. Both lignins were of high purity with low amounts of carbohydrate impurities. Fig. 3 shows the 2D HSQC NMR spectra of KL-EC and OS, both the aliphatic and the aromatic region and Table 2 gathers a quantification of the moieties. Additionally, the proportion of some functionalities can also be determined using ^{13}C NMR (Table 3). See reference 16 for details.

The most obvious difference was in the S:G content, which was significantly higher in KL-EC (Table 3). This was due to the differences in the biomass lignin used for pulping: Eucalyptus lignin used in Kraft pulping has significantly higher S:G ratio than beech lignin used in OS pulping [21]. The corresponding difference in methoxy-group content was a natural consequence of that. As a result, the degree of condensation of KL-EC was significantly lower than that of OS. As expected, both lignins were dramatically degraded from their native stage showed by degradation in the side chain (from 300 to ca 190), strong decrease in the Oxygenated Aliphatic region in general and β-O-4 units specifically (decreased from 60-65% to 2–4%), increase in Saturate Aliphatic region, CO and COOH moieties. However, the degradation of KL-EC was stronger as evidenced by the lower amount of Oxygenated Aliphatic moieties. The main difference in lignin structure associated with the process type was the presence of ethoxylated groups, both ether and ester types, in OS lignin. Also, a typical difference [16] was higher amounts of COOR groups in KL. Usually, OS have much higher amounts of CO groups [16] than alkaline lignins, which was not the case, however. Difference in the amounts of some degradation products detected were also due to the difference in the reaction mechanisms between acidic (OS) and alkaline (KL) delignification [35]. This was also illustrated by the HSQC "fingerprint" reported for KL and OS earlier [11] and
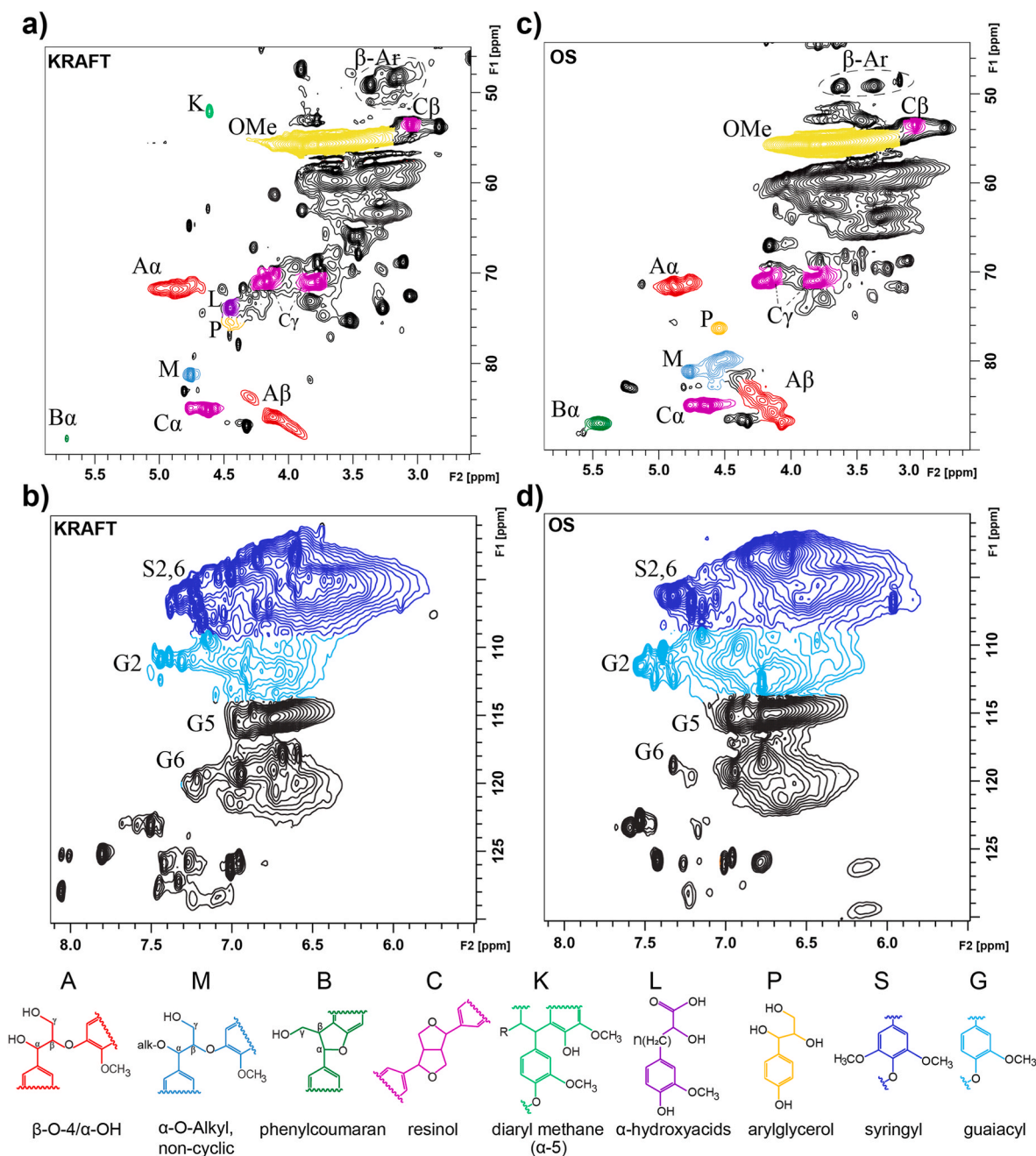
Fig. 3. 2D HSQC NMR spectra of KL-EC and OS. Top pictures correspond to the aliphatic region and bottom ones to the aromatic region, the coloured structures are used to show main structural linkages in lignin samples.

shown for these specific lignins in Fig. 3.

GPC traces provide a semi-quantitative description of the molecular weight distribution. It can be considered that the peak maxima are indicative of the average molecular weight of the distribution of the solubilized sample, the lower is the GPC retention time, the bigger is the fragment. It can be seen in Fig. 4 that in general, herbaceous lignins obtained in our laboratory using sub and supercritical water (BP, TOB) are the lightest while the technical lignins (SKL, KL-EC, OS) are heavier, which agrees to re-condensation reactions forming bigger fragments during the pulping step. WS also present a high molecular weight distribution probably due to the harsh conditions used (200 °C and 30 min). It is worth noticing that WS, TOB and BP also contain a certain proportion of high-molecular-weight fragments since they present shoulders at the lowest retention time (7–8 min), and also low-molecular-weight fragments (shoulders at 10–11 min), they could be attributed

to sugar polymers (cellulose or hemicellulose) and monomers (oligosaccharides) present in the sample as indicated in Table 1. An interesting observation is the significant difference between the molecular weight distribution of lignin KL-EC and BL-EC being the former significantly larger. This result confirms the previous observation that upon precipitation step, smaller fragments are lost [36].

Since all lignins presented different compositions, properties and structure, it is expected that their behaviour in the depolymerization process will be different in terms of optimal reaction time, fractionation yields and tendency with time.

3.2. Base-catalysed SCWD: effect of lignin nature on the reaction products

According to previous reports about SCWD of lignin and subsequent

Table 2
Quantification of some units of KL-EC and OS using 2D HSQC NMR. Values given in number per 100 aromatic units.

Moieties	KL-EC	OS
β-O-4:α-OH (A)	3.2	3.6
β-O-Alk, non-cyclic (M)	1.0	4.9
resinol (C)	3.2	3.7
phenylcoumaran (B)	0.1	1.8
β-Ar (not phenylcoumaran)	5.2	3.7
α-5 (K)	0.5	
arylglycerol (P)	0.5	0.8
α-hydroxyacids (L)	1.2	0.1
dehydroconiferyl alcohol	1.0	0.8
vinyl ethers	0.1	0.1
total carbohydrates	0.7	0.6
S:G ratio	2.84	1.16

Table 3
Quantification of some functionalities of KL-EC and OS using ^{13}C NMR. Values given in number per 100 aromatic units.

Moieties	KL-EC		OS	
	per 100Ar	mmol g^{-1}	per 100Ar	mmol g^{-1}
CO non-conjugated	7	0.37	7	0.38
CO conjugated	10	0.53	8	0.44
total CO	17	0.90	15	0.82
COOR nonconjugated	18	0.95	6	0.33
COOR conjugated	2	0.11	1	0.05
total COOR	20	1.06	7	0.38
OMe	130	6.88	111	6.07
S:G ratio	2.52		1.14	
ArH	191	10.11	184	10.05
Degree of Condensation, %	25		46	
Oxygenated Aliphatic	63	3.33	97	5.30
Saturated Aliphatic	86	4.55	78	4.26
side chain	186	9.84	197	10.77
β-O-4 total	2	0.11	4	0.22
carbohydrates	<1		<1	
EtO-ether	na		8	0.44
EtO-ester	na		3	0.16
EtO-total	na		11	0.60

Fig. 4. GPC traces for starting lignins.

fractionation, the different fractions contain lignin-derived fragments at different stages of the reaction. Their molecular weight followed the tendency light oil < heavy oil < char being the latter degradations materials at later stages of repolymerization. The products from the lignins studied in this report also behave in the same way (see Fig. 5). In every case, light oil was lighter than heavy oil and char, corroborating that the former was the lower-molecular-weight products. In the case of KL-EC, OS and WS, char molecules were heavier than lignin molecules showing clearly that the former are repolymerization products. Notice that retention time for all the chars was similar (except for WS which was slightly lower) regardless of the original size of lignin. This homogenizing role of SCW treatment in molecular weight distribution has been previously observed for other lignins at 390 °C and longer reaction times (5 s) [12]. Size of light and heavy oil molecules is more variable, particularly those from SKL, which are both very similar and larger than those from the rest of the lignins. It seems that, at the condition reactions studied, molecular size of the starting material influences the size of the oils obtained.

Table 4 shows the results from BC-SCWD of the different lignins and black liquor studied. The yield of the different fractions and of the concentration of the detected monomers in the light oil is reported. Notice that for all the experiments the yield of char remains very low, confirming that these conditions are suitable for avoiding lignin degradation upon base-catalysed SCWD. However, the results obtained were very different in terms of oil yields.

A comparison between the three woody lignins reveals that the highest light oil yield of 60.0% was obtained for the case of SKL
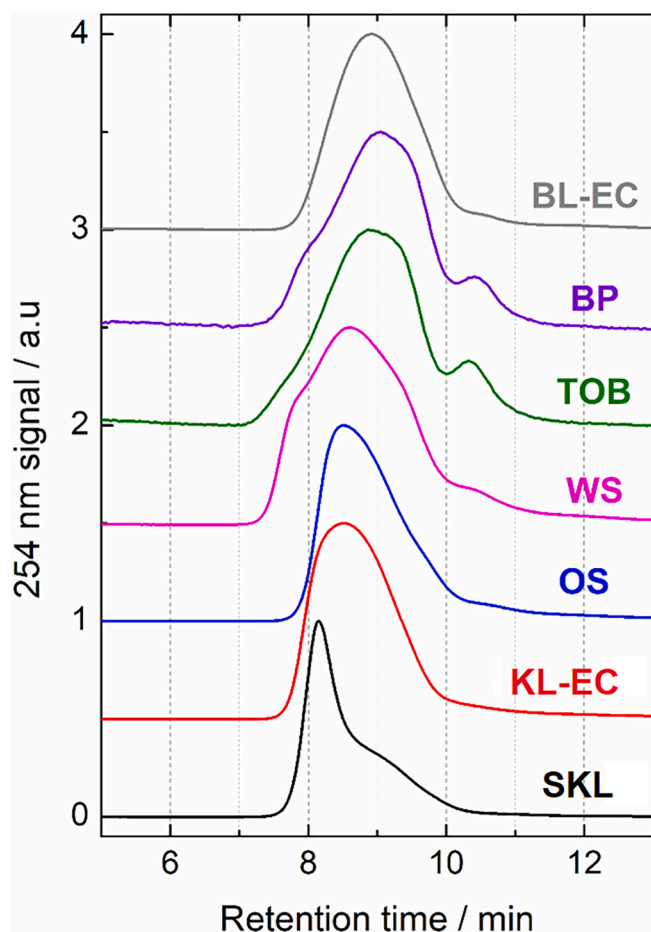
(softwood), which was the lignin chosen to optimize the parameters [13, 14] while the yield of heavy oil was only 12.6%, thus it cannot be discarded that the optimal reaction time differed for each lignin. For KL-EC and OS (hardwood) the yield of heavy oil is larger than for light oil, also the yields of char, are also slightly higher for the latter. This suggests a higher tendency to repolymerization for non-sulfonated lignins as compared to sulfonated SKL, where potential condensation centres are occupied by sulfonic groups. Another explanation can be that as KL-EC and OS have a lower molecular weight than SKL, the former are over-reacted at 300 ms and partial repolymerization has occurred. The yields of monomeric compounds are also similar for KL-EC and OS. These two lignins come from the same type of biomass and have some similar characteristics such molecular weight distribution and number of C=O and -OMe moieties, however, they also present some significant differences in their structure such as aliphatic –OH functionality, degree of condensation and S:G proportion.

Ultra-fast BC-SCWD is a promising technique to valorise lignin as the results are, in general, superior to those reported in literature for extracted technical lignins [37,38]. For example, the best experiment found was carried out with sulfonated Kraft lignin at 350 °C and 40 min giving yields of bio-oils lower than 45%, and a monomer yield lower than 6.5% [17]. In another study [19], an acetosolv lignin was depolymerized by alkaline hydrolysis in a batch reactor obtaining as the highest oil yield 18.5%. Slightly better results can be obtained using organic solvents [20,39], but that implies increased costs.

The monomeric selectivity in light oil and the total yield is also shown in Table 4. The starting lignins contain a certain amount of free co-precipitated monomers, as determined by the blank experiments (see also Table S5). In any case, BC-SCWD was able to increase the yield of
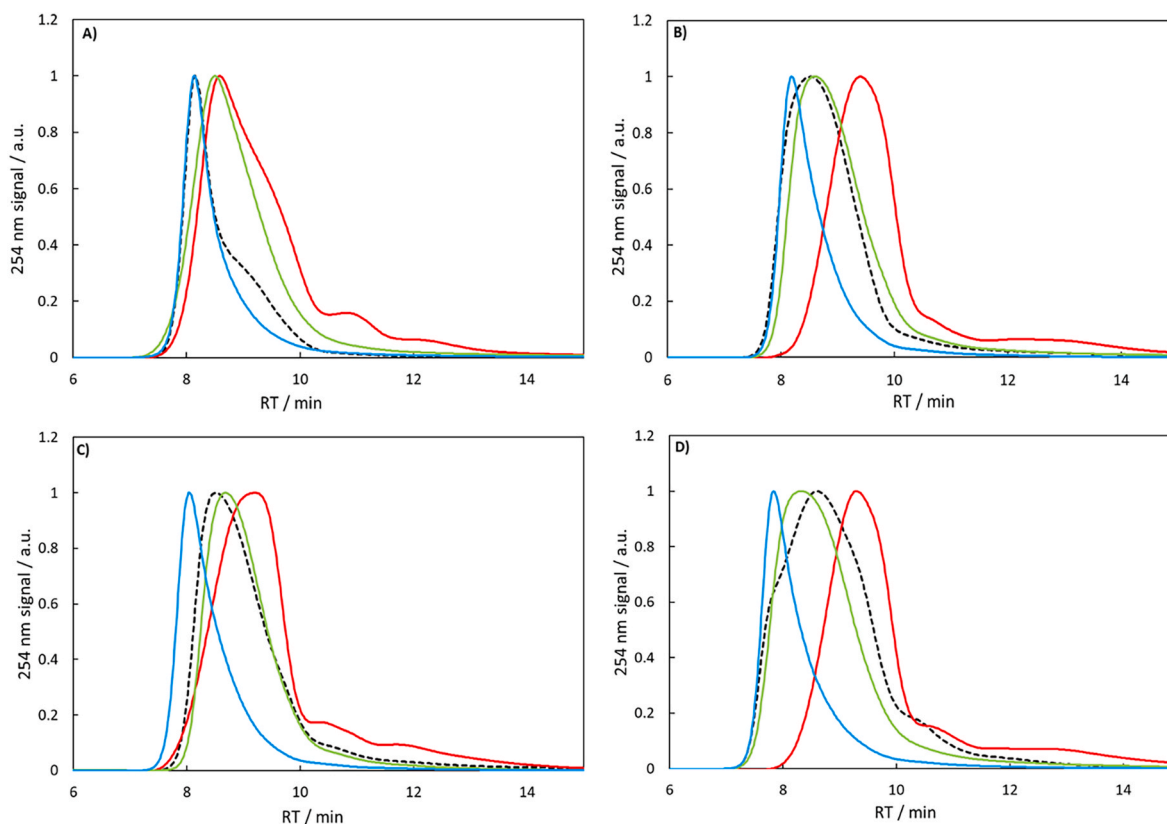
Fig. 5. GPC for A) SKL; B) KL-EC; C) OS; D) WS. Original lignin (black dotted line), char (blue line), light oil (red line) and heavy oil (green line). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 4
Fractionation yields (wt%) and selectivity for the major monomers contained in the light oil after BC-SCWD process of the different lignins and black liquor at 386 °C and 300 ms.

	SKL	KL-EC	OS	WS	BP	TOB	BL-EC
Yield of fractions							
Light oil	60.0	23.5	28.5	21.3	75.0	53.8	51.3
Heavy oil	12.6	68.0	62.8	7.0	13.4	36.3	45.0
Char	2.6	3.8	5.6	0.4	6.1	15.0	5.0
Selectivity of monomers							
Guaiacol	3.9	0.8	0.2	0.7	0.0	0.1	2.7
Creosol	2.0	0.0	0.0	0.0	0.0	0.0	0.8
Vanillin	4.1	0.3	0.8	0.4	0.0	0.2	0.6
Acetovanillone	3.3	0.3	0.3	0.1	0.0	0.0	1.6
Syringol	n.c.	4.1	1.0	0.1	0.0	0.0	3.0
Syringaldehyde	n.c.	4.0	4.3	3.4	0.0	0.0	7.3
Acetosyringone	n.c.	3.8	1.5	0.0	0.0	0.0	1.9
Total selectivity	13.3[a]	13.3	8.1	4.8	0.0	0.3	17.9
Total monomer yield	8.0[a]	3.1	2.3	1.0	0.0	0.15	9.2
S:G Ratio (mol/mol)	–	6.6	4.4	2.2	–	–	1.7

[a] Depolymerization products from SKL also included a significant amount of homovanillic acid (Selectivity = 4.2%, Total monomer yield = 2.5% additional) which is not included in this table because it was obtained in negligible amounts for the rest of the lignins studied. n.c. = not conclusive.

Table 5
Net yield of light oil and monomers upon SCW depolymerization. It is calculated as the difference between the yield of the experiment and the blank.

	KL-EC	OS	WS	BL-EC
Light oil	11.8	24.4	19.5	*20.1*
Guaiacol	0.16	**0.06**	**0.15**	1.19
Creosol	0	0	0	**0.41**
Vanillin	*0.01*	0.12	0.08	*0.02*
Acetovanillone	0.04	**0.09**	0.02	0.75
Syringol	0.68	**0.28**	0.02	nd
Syringaldehyde	*0.54*	1.01	**0.71**	nd
Acetosyringone	0.72	0.43	0	0.63
TOTAL	2.15	1.99	0.98	8.29[a]

nd: non determined.

[a] not accounting for Syringol and Syringaldehyde blank yield. Font code: Yield by SCW depolymerization relative to blank yield. **Bold:** >20 times. Normal: 2–20 times. *Italic*: <2 times. Grey: Non calculated, values too low or zero.

vanillin formation.

The main monomers obtained after depolymerization of SKL (softwood) were creosol (2.0%), guaiacol (3.9%) and vanillin (4.1%). From SKL a significant proportion of homovanillic acid was also obtained (4.2%) [13] and this compound was present in negligible amounts for the rest of the lignins studied. Thus, the origin of it is not fully clear and for comparison purposes it has not been considered in Table 4 and Fig. 6. In any case, this would not alter the conclusions reached.

The main compounds from the depolymerization of KL-EC, OS and the black liquor (hardwoods) were the counterparts syringyl-based units syringol, syringaldehyde and acetosyringone. No aromatic polyols (catechol, pyrogallol, methoxycatechol, etc.) are obtained as in other reports [17,40] probably because the reaction time is too short for the hydrolysis of the methoxy group.

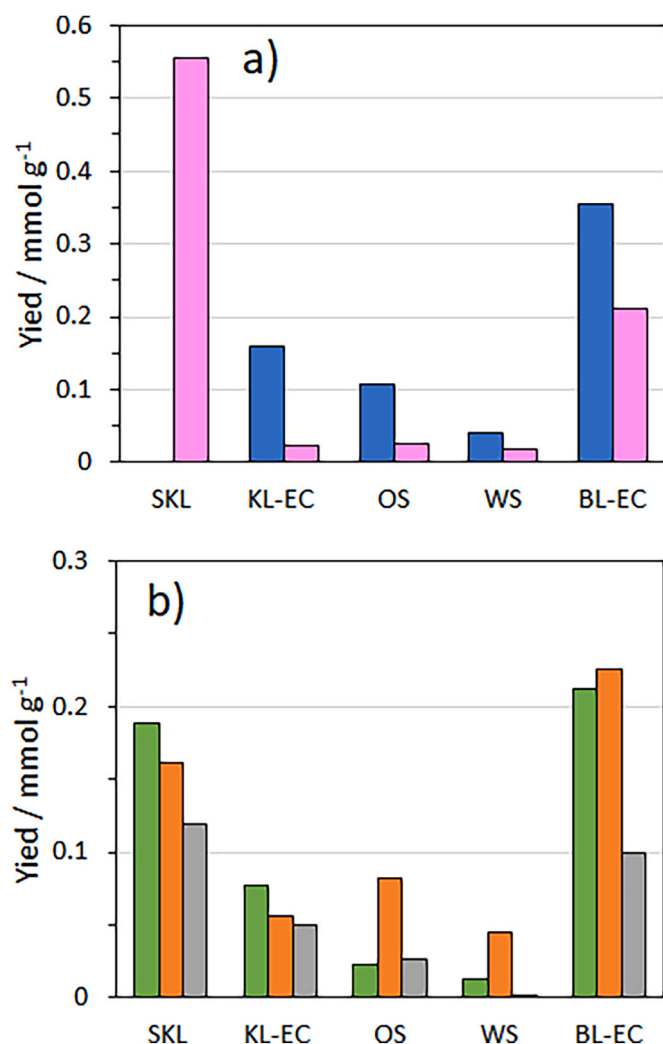In Fig. 6a guaiacyl and syringyl-based monomers are grouped. The

monomers by a factor of 3.2 (KL-EC) or higher. Table 5 shows the net yield of each monomer (subtracting the yield of the blank experiment). For most of the cases, the increment is significant (>×2), except for the vanillin and the syringaldehyde for the lignin and black liquor obtained by ENCE, where the supercritical process does not seem to favour much

Fig. 6. Monomeric yield from the depolymerization of SKL, KL-EC, OS, WS and BL-EC. a) according to the aromatic ring, (■): G-units, (■): S-units and b) according to the 4- substituent, (■): H substituted, (■): CHO substituted, (■): COCH₃ substituted. SKL also yielded a significant amount of homovanillic acid (not included).

substituted (guaiacol and syringol), –CHO substituted (vanillin and syringaldehyde) and –COCH$_3$ substituted (acetovanillone and aceto-syringone), following the order: H > -CHO > -COCH$_3$. For OS and WS the proportions of –H and –COCH$_3$ substituted monomers is much lower. The black liquor also yields similarly –H and –CHO substituted monomers than the other two Kraft lignins, but the –COCH$_3$ monomers decreases slightly.

Although more experimental evidences are necessary, these results tentatively suggest that the proportion of G-units and S-units available for depolymerization depends more on the starting biomass of lignin (as it is mainly responsible of the proportion G:S units) while the 4- substituent for the monomers obtained is more dependent on the pulping method (as it mainly alters the aliphatic backbone). This hypothesis is plausible according to the proposed mechanisms of SCW lignin depolymerization [13,14]. According to them, the α-carbonyl moiety in monomers is generated by an α-hydroxyl, while H- substituted ones are originated from radical scission of R–Ar. Since KL-EC contains less aliphatic –OH (confirmed by ^{31}P NMR and ^{13}C NMR, see Fig. 2 and Table 2, oxygenated aliphatic), the monomers obtained are preferentially –H substituted. In pyrolysis of lignin it has also been detected a preponderance of these monomers for the lignins extracted at more severe conditions [43].

For the lignins isolated from non-wood the results obtained were different from one another being the highest light oil yield achieved by BP with 75.0%, followed by TOB and WS. However, no lignin gave high selectivity or yield in aromatic monomers (negligible for TOB and BP and moderate for WS). The same tendency in light oil is seen in the amount of sugars (see Table 1) so, it is possible that light oil was mainly formed by sugar di-trimers or derived compounds instead of aromatic monomers from lignin. One must consider that the sugar conversion reactions also has a fast reaction kinetics in the conditions studied [44].

Additional analyses of the changes in chemical functionality upon BC-SCWD were presented in the Supplementary Information. FTIR results (Figs. S7 and S8) strengthen what had been observed in a previous work [13]: whatever transformations are occurring in the SCW reactions they do not alter significantly the aromatic structure. ^{31}P NMR of the depolymerized fractions showed that starting lignin, greatly affects not only the yields of the oils obtained but also its chemical structure (Table S6 and Fig. S6). The amounts of aliphatic –OH decrease while that for –COOH increases, which has been observed before, under similar conditions [12,14]. Also, the generation of organic acids is a common phenomenon in high-temperature treatment of organic matter [45] including lignin [13].

3.3. Comparison between a black liquor and isolated lignin

In a previous report we demonstrated that KL-EC is a suitable stream to be upgraded [13] giving a yield of products comparable to the corresponding lignin. With new data presented in this work, a more complete discussion can be done to elucidate the differences between lignin and black liquor as starting materials for ultra-fast BC-SCWD. The production of light oil and monomers from KL-EC is comparable to the rest of the lignins studied (Table 4). Comparing to literature, our results are promising in terms of monomeric selectivity, for example, the best reported case of SCW processing of black liquors was a light oil containing 5 wt % of monomers obtained after 1 h of reaction time [46].

BC-SCWD of KL-EC and its corresponding black liquor, BL-EC differ significantly in terms of yield of fractions and monomers. In both cases the char production is low and the proportion of S-monomers is high, as expectable from a hardwood lignin but there are some remarkable differences: a) The amount of light oil is higher when the black liquor is used while the heavy oil is lower, b) the yield of total monomers is almost three times higher for the black liquor, c) the proportion S:G of the monomers is significantly higher for KL-EC than for BL-EC (see Fig. 6a). The isolation step selectively precipitates the largest fragments, leaving smaller ones in the solution [36]. Moreover, the latter have a

former are the only ones present in softwood lignin whereas the latter are higher in hardwood lignins. The S:G ratio follows the trend: KL-EC > OS > WS. This trend can be related to the ratio 5-substituted units to 3,5-substituted units detected by ^{31}P NMR (see Fig. 2). It must be clarified that OH functionality is not indicative of the real proportion of S or G units (because some Ar-OH can be etherified and condensed units give a biased value of S units). However, it seems to be qualitatively related. Notice that ^{13}C NMR also provides a higher S:G ratio for KL-EC than for OS.

It is worth noting that S:G is higher for the monomers obtained (6.6, 4.4, 2.2 for KL-EC, OS and WS respectively) than for the functionality of the starting lignin (3.5-substituted:G units = 3.3, 2.2, 1.1 for KL-EC, OS and WS, respectively). Thus, it seems that a higher proportion of S units than expected is obtained upon BC-SCWD, i.e., this process could be selective towards S units. Although the reaction mechanisms are nor fully elucidated, it is clear that the composition of the starting lignin influences the proportion of the different type of monomers obtained. It has been observed that the proportion S:G increases upon Kraft pulping [41] so it is possible that something similar is occurring in high-temperature water [42].

If the monomers are classified according to the aliphatic substituent in 1 (Fig. 6b), the two Kraft lignins contain significant proportions of H-

higher proportion of CHO groups. These smaller and more oxidized soluble fragments present in the black liquor seem to be more prone to depolymerize than KL-EC (see Fig. 4).

Summarizing, not only the direct SCWD would be more efficient in terms of energetical demand and technical investment but also the depolymerization products would be of a higher quality. Then, this ultrafast BC-SCWD seems a promising methodology that could be incorporated into a Kraft process to valorise the black liquors.

4. Conclusions

Six lignins and one black liquor obtained from different sources and by different pulping methods were compared as starting material for an ultra-fast base catalysed supercritical water depolymerization. The composition and structure of these feedstocks are very different and they have a great effect on the depolymerization products. However, two technical lignins which had similar origin, purity and molecular weight distribution (Kraft and organosolv from hardwood) yielded similar results.

Repolymerization could be controlled due to the low reaction time applied, and as result, the amount of char formed was low in all cases, however the distribution of heavy and light oils is very variable, being the former more favoured for hardwood lignins. The S:G ratio is mainly dependent on the biomass origin and this tendency also remains in the monomers obtained with the difference that the depolymerization tends to increase the proportion of S-units. The best lignin in terms of light oil and monomer yield is the commercial sulfonated Kraft lignin. Herbaceous lignins obtained by different steps of high-temperature and/or enzymatic hydrolysis were not satisfactory to obtain aromatic low-molecular-weight compounds, probably because the isolation step yields lignin of a different structure and the presence of residual cellulose. Molecular weight decreases upon depolymerization to bio-oil but also the chemical functionality changes, decreasing the proportion of aliphatic –OH and increasing the –COOH groups.

Comparing the results of a black liquor and its corresponding lignin allows concluding that the ultra-rapid BC-SCWD treatment is a promising methodology to be integrated into a Kraft mill operation, since the yield of light oil and monomers is higher for the black liquor. Results also suggest that the isolation of the lignin from the black liquor is not only an unnecessary, but also a detrimental step if the dissolved Kraft lignin is intended to be valorised by BC-SCWD.

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Data availability

No data was used for the research described in the article.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.biombioe.2022.106536.

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