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Chemical Modifications of Lignin for the Preparation of Macromers Containing Cyclic Carbonates

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Abstract. An epoxidized lignin derivative was prepared directly inserting epichlorohydrin on the phenolic functionalities. The epoxidized lignin was then converted to cyclic carbonates through the coupling reaction of CO_2 with the oxirane rings. Imidazolium based ionic liquids, acting both as solvents and catalysts, were successfully employed in the carbonation reaction. Moreover, the ionic liquid was reused up to three times without significant loss in activity. Finally, an exhaustive spectroscopic characterization was carried out on the epoxidized and carbonated lignin by quantitative ^{31}P and ^{13}C NMR analysis.

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Introduction

Lignin is described as an irregular and tridimensional polymer whose structure depends on the botanical source. The main functional groups encountered in lignin chemistry are hydroxyl (both aliphatic and phenolic), methoxyl, carboxyl, and carbonyl moieties in different amount, depending upon the type of extraction employed. As the principal side-stream of the papermaking, bioethanol, and agro industries, alternative uses of lignin have been sought by the whole scientific community since the early ‘70s.[1] Even if the specific process to which lignocellulose is subjected causes a modification of the polymer characteristics, the abundance of lignin of different type as a waste product has made such material an attractive proposition for the preparation of value-added products.

The valorization of lignin through integrated approaches is of crucial importance to match the requirements of the biorefinery concept, which is a comprehensive utilization of all those lignocellulosic materials consisting of the residual non-food parts of current crops or other non-food sources (known as second-generation feedstock) by converting these biomass into fuels, energy, chemicals and materials.[2]

Nowadays, the most explored fields for a convenient industrial application of lignin are the incorporation into polymer compositions as a physical additive[3,4] and, especially, the use of the lignin carbon skeleton as a building block. Among the plethora of examples reported in literature, lignin as a macromer has been introduced in phenol-formaldehyde and epoxy resins, as well as in polyurethane and natural polyesters formulations[5-9]. At present, the methods to synthesize lignin-based resins consist of: modifying lignin derivatives directly and modifying lignin derivatives in order to improve their reactivity.

Epoxidized lignin is a remarkably reactive derivative, useful both as a green substitute for epoxy resins components and as intermediate in the synthesis of other lignin-based macromer by means of nucleophilic addition and insertion reactions.[10,11] For example, the synthesis of cyclic carbonates through the addition of CO_2 to epoxy groups is an atom-economical reaction approach, and

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provides value-added monomers for the preparation of poly(hydroxy)urethanes, avoiding the use of toxic isocyanates[12]. The introduction of cyclic carbonate groups in the lignin macromolecule is so far not reported in literature.

In this work, two technical lignins, namely a soda pulping herbaceous lignin (HBL) and a hardwood kraft lignin (HWKL), were modified through the direct insertion of epoxide groups by reaction between lignin phenolic groups and epichlorohydrin. The epoxide groups were then converted to cyclic carbonates through the fixation of CO_2. Different solvents and experimental conditions were tested to optimize the conversion to cyclic carbonates. In particular, in agreement with recent reports, the use of ionic liquids was successfully investigated. In fact, the use of ionic liquids as both solvent and catalyst, or their combination with metal salts, has been exploited for the synthesis of cyclic carbonates[13,14]. Currently, imidazolium based ILs, are reported as the best choice for the synthesis of cyclocarbonates from epoxide and CO_2 due to the high solubility of CO_2 observed in this kind of ILs[15,16]. In this study, 1-allyl-3-methylimidazolium based ionic liquids were selected as solvents of choice as they are widely exploited for the dissolution of lignin and lignocellulose in general[17,18].

An exhaustive spectroscopic characterization was finally performed on the epoxidized and carbonated lignin samples. ^{31}P NMR spectroscopy was used for a quantitative measurement of the epoxide groups bonded to lignin after reaction with epichlorohydrin. The characteristic IR absorption band of the cyclic carbonate moiety at 1790 cm^{-1} was used to qualitatively evaluate the extent of cyclic structures formed after reaction with CO_2. Several qualitative ^{13}C NMR analyses were performed to confirm the formation of both the glycidyl and cyclic carbonate lignin derivative. Once established the best set of experimental conditions for the carbonation reaction, quantitative ^{13}C NMR spectra were acquired in the presence of an internal standard (dimethyl carbonate) to retrieve the actual amount of cyclic structures formed. Moreover, glycidyl and cyclic carbonate derivatives of lignin model compound (i.e., phenol, guaiacol, 2,6-dimethoxyphenol, 4-hydroxy-3-methoxybenzyl alcohol, and vanillic acid) were prepared and spectroscopically characterized to

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evaluate the ^{13}C NMR absorbance range of aliphatic alcohol, *p*-hydroxyphenyl, guaiacyl, syringyl, and carboxylic acid moieties, respectively.

Experimental

Reagents and Materials. All reagents and solvents used were purchased from Sigma-Aldrich and used as received without further purification. Lignin specimens were supplied during the project ProLignin, EraNets WoodWisdom/Bioenergy, 2012-14. The samples under investigation are a herbaceous lignin (purity 98.2%, total phenolic content 3.55 mmolg^{-1}) obtained from a soda pulping process sold under the trademark Protobind1000®, and a hardwood lignin recovered after a kraft pulping process (purity 96.7%, total phenolic content 3.90 mmolg^{-1}).

General Procedure for the Epoxidation of Model Compound. 1g of a specific phenolic model compound (phenol 10.6 mmol, guaiacol 8.0 mmol, 2,6-dimethoxyphenol 6.5 mmol, 4-hydroxy-3-methoxybenzyl alcohol 6.5 mmol, and vanillic acid 5.9 mmol) was dissolved in acetone (15 mL) in the presence of epichlorohydrin (1:5 molar ratio of total hydroxyls moiety to epoxide; 4.2, 3.1, 2.6, 5.1, and 4.6 mL of epichlorohydrin for the reaction with phenol, guaiacol, 2,6-dimethoxyphenol, 4-hydroxy-3-methoxybenzyl alcohol, and vanillic acid, respectively). The mixture was warmed to 70°C and then 50 mL of an aqueous solution of NaOH (1:5 molar ratio of hydroxyls moiety to hydroxide; 2.12, 1.6, 1.3, 2.6, and 2.4 g NaOH for phenol, guaiacol, 2,6-dimethoxyphenol, 4-hydroxy-3-methoxybenzyl alcohol, and vanillic acid, respectively) was added dropwise under stirring. After 3 hours the mixture was allowed to cool to room temperature. Epoxidized phenol[19], epoxidized guaiacol[20],and epoxidized 2,6-dimethoxyphenol were extracted in petroleum ether (2 times, 30 mL each). Epoxidized 4-hydroxy-3-methoxybenzyl alcohol and epoxidized vanillic acid were instead extracted in diethyl ether (2 times, 30 mL each). The collected organic phase was washed with deionized water, anhydrified over Na_2SO_4, and filtered. After rotary evaporation of the solvent a thick oil was left in the case of mono-hydroxy compounds and vanillic acid, whereas a solid was obtained from 4-hydroxy-3-methoxybenzyl alcohol. Epoxidized vanillic acid was purified

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on silica column chromatography (Merck, pore size 60Å , 230-400 mesh) by elution with ethyl acetate-petroleum ether 1:1. Yields were included between 30-40% for epoxidized mono-hydroxy model compounds and 4-6% for epoxidized 4-hydroxy-3-methoxybenzyl alcohol and vanillic acid. Structure and purity of epoxidized model compounds were assessed by IR and ^{1}H NMR analysis. Characteristic absorptions of the different epoxide chains were recognized by ^{13}C NMR analysis.

2-(2,6-dimethoxybenzyl)oxirane. Colourless oil, > 90% purity, yield 33%. ^{1}H NMR ($CDCl_3$, 100 MHz): δ = 6.98 (t, J = 8.42 Hz, 1H, Ar), 6.57 (d, J = 8.42 Hz, 2H, Ar), 4.10 (dd, J = 4.10 and 11.29 Hz, 1H, OC*H*HCH), 3.99 (dd, J = 5.85 and 11.29 Hz, 1H, OCH*H*CH), 3.83 (s, 3H, OCH_3), 3.36 (m, 1H, $CH_2C\mathit{H}CH_2$), 2.79 (dd, J = 4.39 and 4.74 Hz, 1H, CHC*H*HO), 2.61 (dd, J = 2.67 and 5.03 Hz, 1H, CHCH*H*O) ppm . ^{13}C NMR (DMSO-d_6, 125 MHz): δ = 153.4 (C_q OMe), 136.8 (C_q), 123.9 (C_{Ar}), 105.2 (C_{Ar}), 74.0 ($O\mathit{C}H_2CH$), 56.0 (OMe), 50.4 ($CH_2\mathit{C}H$), 44.6 ($CH\mathit{C}H_2O$) ppm.

*Oxiran-2-ylmethyl-3-methoxy-4-(oxiran-2-ylmethoxy)benzoate.*Colourless oil, > 90% purity, yield 4.3%. ^{1}H NMR ($CDCl_3$, 100 MHz): δ = 7.67 (d, J = 1.97 Hz, 1H, Ar), 7.56 (dd, J = 1.97 and 8.45 Hz, 1H, Ar), 6.93 (d, J = 8.50 Hz, 1H, Ar), 4.63 (dd, J = 3.09 and 12.29 Hz, 1H, OCH*H*CH PhOH), 4.33 (dd, J = 3.29 and 11.35 Hz, 1H, OCH*H*CH Acid), 4.13 (dd, J = 6.27 and 12.29 Hz, 1H, OC*H*HCH PhOH), 4.07 (dd, J = 5.68 and 11.41 Hz, 1H, OC*H*HCH Acid), 3.92 (s, 3H, OCH_3), 3.40 (m, 1H, $CH_2C\mathit{H}CH_2$ PhOH), 3.33 (m, 1H, $CH_2C\mathit{H}CH_2$ Acid), 2.90 (m, 2H, CHC*H*HO PhOH and CHC*H*HO Acid), 2.77 (dd, J = 2.65 and 4.92 Hz, 1H, CHCH*H*O PhOH), 2.71 (dd, J = 2.65 and 4.93 Hz, 1H, CHCH*H*O Acid) ppm. ^{13}C NMR (DMSO-d_6, 125 MHz): δ = 166.1 (C=O), 152.3 (C_q PhOH), 149.2 (C_{Ar}), 123.6 (C_q OMe), 112.6 (C_{Ar}), 69.8 ($O\mathit{C}H_2CH$ PhOH), 65.3 ($O\mathit{C}H_2CH$ Acid), 56.0 (OMe), 49.8 ($CH_2\mathit{C}H$ PhOH), 49.5 ($CH_2\mathit{C}H$ Acid), 44.7 ($CH\mathit{C}H_2O$ PhOH), 44.6 ($CH\mathit{C}H_2O$ Acid) ppm.

General Procedure for the Carbonation reaction of Model Compounds. 200 mg of a selected epoxidized model compound was solubilized with dimethyl formamide (10 mL) and gently loaded into the pressure vessel. After purging the reactor with CO_2 for 10 minutes the pressure was brought up to 20 bar and the reactor heated to 80°C. After 20 hours reaction time, carbonated model

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compounds of phenol[21], guaiacol[22], 2,6-dimethoxyphenol, and vanillic acid were recovered by extraction in methylene dichloride (2 times 30 mL each). The organic phase was washed twice with deionized water, anhydrified over Na_2SO_4, filtered, the solvent removed by rotary evaporation and finally exsiccated under vacuum. All yields were included between 50-60%. Structure and purity of carbonated model compounds was evaluated by IR and ^{1}H NMR analysis. Characteristic absorption of the different cyclocarbonate chains were established through ^{13}C NMR analysis.

4-(2,6-dimethoxy benzyl)-1,3-dioxolan-2-one. Colourless oil, > 90% purity, yield 58%. ^{1}H NMR ($CDCl_3$, 100 MHz): δ = 6.95 (t, J = 8.26 Hz, 1H, Ar), 6.52 (d, J = 8.15 Hz, 2H, Ar), 4.85 (m, 1H, $CH_2C\mathit{H}CH_2$), 4.72 (dd, J = 6.41 and 8.38 Hz, 1H $CHC\mathit{H}HO$), 4.51 (t, J = 8.43 Hz, 1H, $CHCH\mathit{H}O$), 4.11 (dd, J = 4.44 and 9.26 Hz, 2H, $OC\mathit{H_2}CH$), 3.77 (s, 3H, OCH_3) ppm. ^{13}C NMR (DMSO-d_6, 125 MHz): δ = 155.1 (C=O), 153.2 (C_q OMe), 136.4 (C_q), 124.4 (C_{Ar}), 105.2 (C_{Ar}), 75.1 ($OCH_2\mathit{C}H$), 71.3 ($CH_2CH\mathit{C}H_2$), 66.3 ($O\mathit{C}H_2CH$), 56.0 (OMe) ppm.

(2-oxo-1,3-dioxolan-yl)methyl-3-methoxy-4-[(2-oxo-1,3-dioxolan-4-yl)methoxy]benzoate. Yellowish oil, > 90% purity, yield 35%. ^{13}C NMR (DMSO-d_6, 125 MHz): δ = 166.2 (C=O Acid), 155.0 (C=O cyclic carbonate PhOH), 154.6 (C=O cyclic carbonate Acid), 150.4 (C_q PhOH), 147.6 (C_q OMe), 128.7 (C_q Acid), 122.5 (C_{Ar}), 115.6 (C_{Ar}), 112.3 (C_{Ar}), 74.5 ($OCH_2\mathit{C}H$ PhOH), 74.0 ($OCH_2\mathit{C}H$ Acid), 68.7 ($CH_2CH\mathit{C}H_2$ PhOH), 66.2 ($O\mathit{C}H_2CH$ Acid), 66.1 ($O\mathit{C}H_2CH$ PhOH), 63.7 ($CH_2CH\mathit{C}H_2$ Acid), 56.0 (OMe) ppm.

General procedure for the reaction of lignin with epichlorohydrin. Lignin (1 g, total phenolic content 3.55 and 3.90 mmolg^{-1} for herbaceous and hardwood kraft lignin, respectively) was solubilized under vigorous stirring into 40 mL of NaOH aqueous solution (1:20 molar ratio of phenolic moiety to hydroxide; 2.9 and 3.1 g NaOH for herbaceous and hardwood kraft lignin, respectively). 10 mL of acetone was then added, along with epichlorohydrin (1:20 molar ratio of phenol moiety to epoxide; 5.6 and 6.1 mL of epichlorohydrin for herbaceous and hardwood kraft lignin, respectively). The mixture was heated to 70°C and reacted for 3 hours. After cooling to room temperature, epoxidized lignin was precipitated out in cold acidic water (0.2 M HCl, 250 mL,

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additional concentrated HCl was added if needed to reach slightly acidic pH), filtered on a sintered glass crucible (size 4), thoroughly washed with deionized water and lyophilized. Mass recovery was about 70-75% for both the technical lignin.

General Procedure for the Carbonation reaction of Lignin. In a typical experimental procedure, 200 mg of epoxidized lignin was dissolved in a suitable amount of a specific solvent (20 mL of organic solvents, 4 g of ionic liquid). When an ionic liquid (IL) was employed as solvent, epoxidized lignin and the IL were placed into a screw top glass vial equipped with a magnetic stirrer and the mixture heated with a heat gun (metabo H 16-500, 2 heating cycles of approximately 45 sec) and stirred overnight at 40°C to achieve complete solubility. The sample was then gently loaded into the pressure vessel and the reactor purged with CO_2 for 10 min. The pressure was loaded up to 20 bar and the reactor heated to 80°C. After 20 hours reaction time, carbonated lignin was precipitated out in excess cold water, filtered on a sintered glass crucible (size 4), thoroughly washed with deionized water, and finally lyophilized. Carbonated lignin mass recovery was around 90% for both the herbaceous and hardwood kraft lignin.

Ionic Liquid Recycling. The IL 1-allyl-3-methyl imidazolium chloride (amimCl) collected after the carbonation reactions was regenerated according to the following procedure. The aqueous phase containing amimCl was extracted with ethyl acetate (2 times, 40 mL each), and water first rotary evaporated at 80°C and then exsiccated under vacuum for 2 h at 90°C, to give an extremely thick gel. The required amount of regenerated ionic liquid (4 g) was further exsiccated under vacuum for 2 h at 90°C into the screw top vial used for the carbonation reaction, conveniently equipped with a screw cap with pierced aperture and a glass stopcock.

FTIR Analysis. Fourier Transform Infrared Spectroscopy was used for a rapid screening of the reactions outcome and to evaluate the relative yield of different lignin carbonation experiments by the % absorbance of the characteristic cyclic carbonates band at 1790 cm^{-1} after spectrum normalization. The analyses were performed on a Nicolet iS10 spectrometer (Thermo Scientific) equipped with a Smart iTR™ Total Attenuated Reflectance (ATR) sampling accessory (total scan

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16, range 4000-700 cm^{-1}, resolution 1 cm^{-1}). The data reported for the estimation of the cyclocarbonation yield are the mean of 4 to 6 experiments; maximum standard deviation 0.010 a.u., maximum standard error 0.005 a.u.

^{31}P-NMR Analysis. Accurately weighed lignin samples (30 mg) were dissolved in a pyridine-deuterated chloroform stock solution (1.6:1 v/v, 700 µL) containing 1 mg/mL of chromium(III) acetylacetonate, [Cr(acac)$_3$] as relaxation agent. 100 µL of an internal standard solution of endo-N-hydroxy-5-norbornene-2,3-dicarboximide (e-HNDI, 121.5 mM, CDCl3/pyridine 4.5:0.5) was then added. 2-chloro-1,3,2-dioxaphospholane (RI, 100 µL) was used as phosphorus derivatizing agent for the detection and quantification of primary and secondary aliphatic alcohols[23], whereas 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (RII, 100 µL) was used for the detection and quantification of phenolic and acidic moieties[24]. ^{31}P-NMR spectra were recorded on 800 µl samples with a Bruker Avance 500 MHz instrument at room temperature. The chemical shifts were referred to the water-phosphytilating agent adduct signal (121.5 ppm) when RI was used, and to the internal standard signal (152 ppm) when RII was employed. Relaxation delay of 5 s was used between the scans (90° pulse angle). Line broadening of 3 Hz was applied to FIDs before Fourier transform. For each spectrum, typically 100 scans were accumulated.

^{13}C NMR Analysis. Broadband decoupled ^{13}C-NMR spectra were recorded on a Bruker Avance 500 MHz spectrometer at room temperature on 800 µl samples dissolved in deuterated dimethylsulfoxide (DMSO-d$_6$). The chemical shifts were referred to the methoxyl group signal (56 ppm). For qualitative evaluations relaxation delay of 4 sec was used between the scans (90° pulse angle). Line broadening of 0.8 Hz was applied to FIDs before Fourier transform. For each spectrum, typically about 6'000 scans were accumulated. Quantitative ^{13}C NMR spectra were acquired for carbonated herbaceous and hardwood kraft lignin in the presence of dimethyl carbonate (25 ul, ≥99%) as internal standard. Relaxation delay of 10 sec was applied and approximatively 10’000 scans were accumulated. The assignment of predominant signals was based on the chemical shift data obtained from the synthesized lignin model compounds and from literature data[25,19].

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Results and Discussion

Synthesis and Characterization of Epoxidized Lignin

A soda pulping herbaceous lignin (HBL) and a hardwood kraft lignin (HWKL) were subjected to epoxide derivatization through nucleophilic substitution in the presence of excess epichlorohydrin. The large excess of epichlorohydrin employed is dictated by need to achieve a thorough epoxide functionalization of the lignin molecule minimizing undesired side reactions such as the formation of high molecular species.[26] Lower phenols:epichlorohydrin ratios were tested but they were found to be not adequate to achieve the required epoxidation degree.

The formation of the glycidyl derivative was at first assessed by ATR-FTIR analysis (Fig.1, middle). The presence of oxirane rings is confirmed by the appearance of weak to medium band at 760 and 835 cm^{-1}, by the higher intensity of the C-H stretching vibrations, and by the modification of the -OH stretching profile.

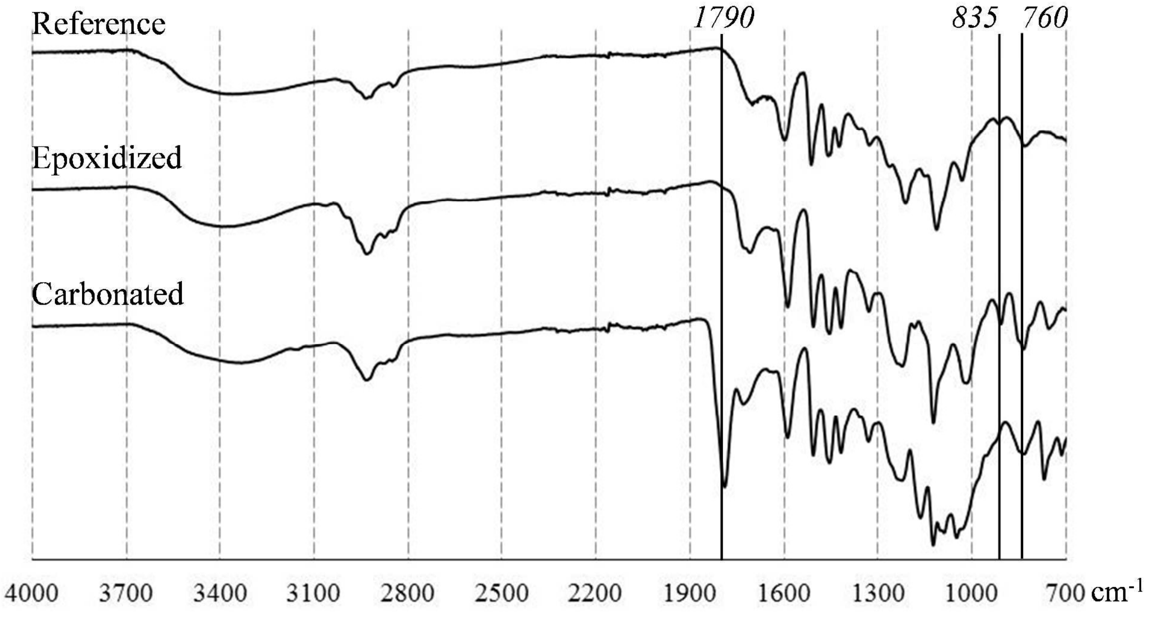

Figure 1 Top to bottom: ATR-FTIR spectra of reference, epichlorohydrin epoxidized, and carbonated herbaceous lignin.

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^{31}P NMR analyses were carried out on reference lignin and after treatment with epichlorohydrin. Since a general underestimation of aliphatic hydroxyls groups was observed using 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (RII), labile hydroxyls quantification was accomplished in duplicate on each sample: RII was dedicated to the quantification of phenolic and acidic moieties, whereas 2-chloro-1,3,2-dioxaphospholane (RI) was exploited for the quantification of aliphatic alcohols. Moreover, RII affords a better resolution of the phenolic signals whereas RI provides a better resolution of the peaks originated by reaction with primary and secondary alcohols.

For both the herbaceous and hardwood kraft lignin, a complete functionalization of the phenolic moiety was achieved (Fig. 2, phosphorus reagent RII, below). More interestingly, the phosphorus derivatizing agent is also able to react with the epoxide groups on lignin as it is evident by the presence of two different strong and broad signals in the aliphatic region of the ^{31}P NMR spectrum (Fig. 2, phosphorus reagent RI, above). The signal recorded between 134.5 and 133 ppm lie in the same region as the preponderant primary alcoholics groups in the reference lignin, but it is more populated on account of the formation of hydroxypropylic structure after reaction with RI. On the other hand, the signal recorded at lower fields between 137.0 and 134.5 ppm, in the secondary alcohols region, should be exclusively attributed to the hydroxypropylic derivative[27]. It is worth noticing that after phosphorus derivatization the formation of both a primary and a secondary phosphitylated alcohol derivative is possible, indeed.

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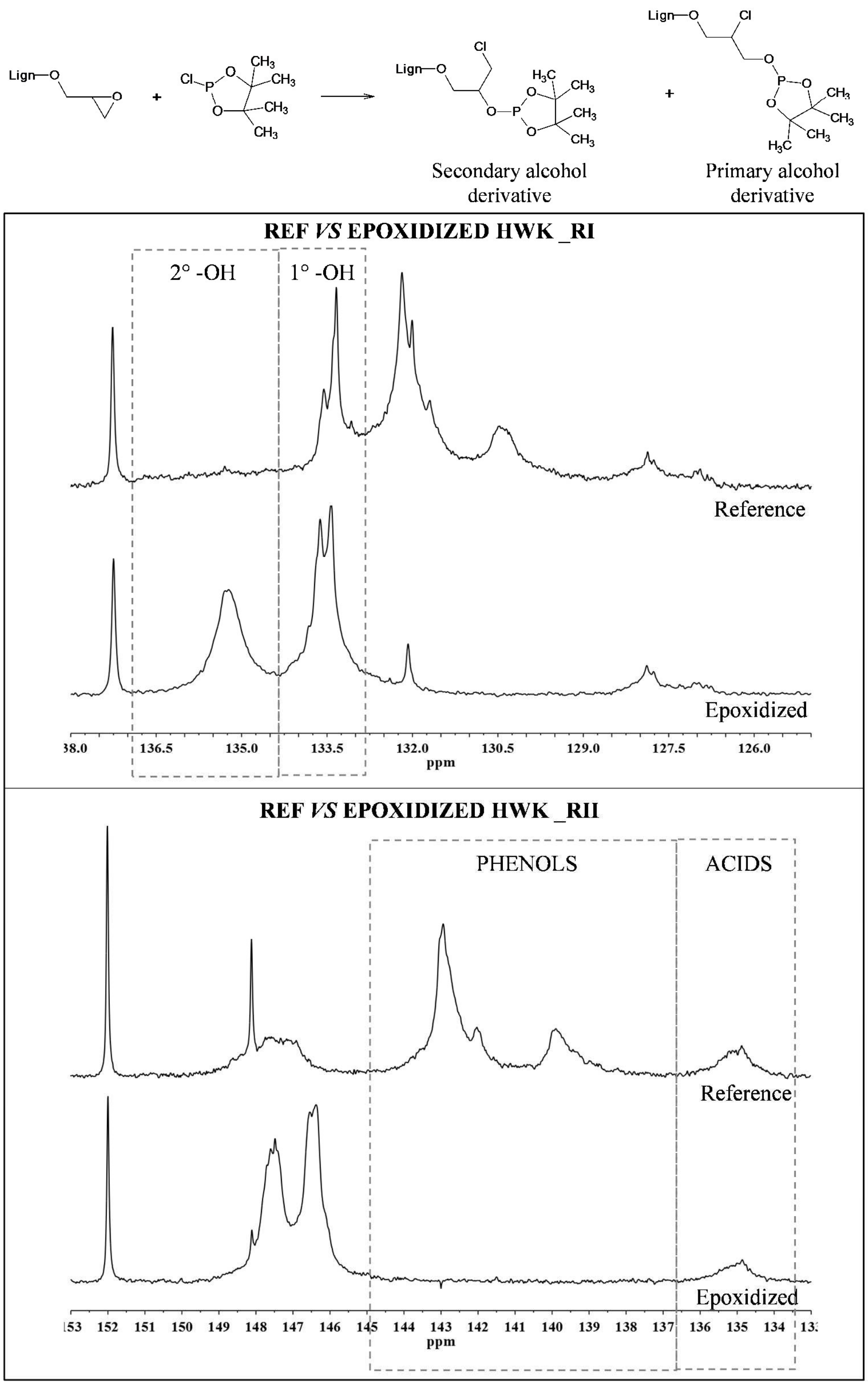

Figure 2 Comparison between ^{31}P NMR spectra of reference and epichlorohydrin epoxidized hardwood kraft lignin after reaction with 2-chloro-1,3,2-dioxaphospholane (RI, above) and 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (RII, below).

The upper part of Table 1 reports the distribution of labile hydroxyls for reference and epoxidized HBL and HWKL as found by ^{31}P NMR analysis. After the epoxidation phenolic groups were no longer detected, whereas the amount of primary and, especially, secondary aliphatic alcohols dramatically increased. As mentioned above, two different kinds of aliphatic hydroxyl moieties can be discerned: naturally occurring side-chain aliphatic hydroxyls and hydroxypropylic alcohols ensuing from epoxide rings opening after phosphitylation. The quantification of the hydroxypropylic moiety is given in the penultimate line of Table 1. It was obtained by subtracting to the total amount of aliphatics detected for the epoxidized lignins an opportunely corrected value of the total amount of aliphatics found for the reference lignins. The aforementioned correction has to be intended as a percentage mass correction accounting for changes in the molecular weight of lignin C_9 units after chemical functionalization. For the purpose of this work, a C_9 unit containing a methoxyl group, a phenolic hydroxyl, and a primary and a secondary aliphatic hydroxyl was considered. The empirical formula of the illustrated structure is $C_{10}H_{15}O_4$ and its molecular weight is ca. 197 gmol^{-1}; the corresponding epoxidized unit is described by the formula $C_{13}H_{19}O_5$ and its molecular weight is ca. 253 gmol^{-1}. Corrected values of total aliphatics in reference lignins are reported in the third to last line of Table 1. The resulting quantification of hydroxypropylic moieties attained for the herbaceous and hardwood kraft lignin was 2.25 and 2.47 mmolg^{-1}, respectively.

As a rule of thumb, it could be stated that the amount of oxirane rings introduced is nearly the same as the disappeared phenols, i.e., the total amount of phenolic groups quantified in reference lignin. It is reminded that also this value has to be conveniently corrected according to lignin molecular weight variation after the epoxidation reaction (Table 1, last line). The values associated to this correction are 2.77 and 3.04 mmolg^{-1} for HBL and HWKL, respectively. Moreover, it is highlighted that all the hydroxypropylic units are associated to phenols functionalization. In fact, as confirmed by the study of lignin model compounds, no reaction with epichlorohydrin was observed at the aliphatic hydroxyls sites whereas a negligible yield in epoxidized carboxylic acids was achieved. Discrepancies between theoretical (HBL 2.77 and HWKL 3.04 mmolg^{-1}) and experimental (HBL

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2.25 and HWKL 2.47 mmolg^{-1}) values for the ensuing hydroxypropylic units and the reduced amount of carboxylic acid detected after reaction with epichlorohydrin are caused by the of low molecular weight lignin fractions during the purification process. In fact, intrinsic disadvantages connected to lignin multifunctional nature and possible side reactions, such as oxirane ring opening, confers an enhanced hydrophilic character to the substrate resulting in a limited mass recovery (approximately 75% of the starting mass).

^{31}P NMR Assignment (mmol/g)	HBL	HBL Epoxy	HWKL	HWKL Epoxy
Total aliphatics (RI)	1.31	3.27	1.73	3.82
1° alcohol (RI)	0.92	1.50	1.20	2.24
2° alcohol (RI)	0.39	1.77	0.53	1.58
Total PhOH (RII)	3.55	n.d	3.90	n.d
S-OH + Cond. (RII)	1.96	n.d.	2.87	n.d.
G-OH (RII)	1.05	n.d.	1.03	n.d.
P-OH (RII)	0.54	n.d.	n.d.	n.d.
COOH (RII)	1.04	0.18	0.63	0.33
Tot aliph reference (mass corrected)	1.02	-	1.35	-
Hydroxypropylic alcohols	-	2.25	-	2.47
Tot PhOH (mass corrected)	2.77	-	3.04	-

Table 1 ^{31}P NMR quantification of labile hydroxyl groups for reference and epoxidized herbaceous and hardwood kraft lignin (phosphorus derivatizing agent used in brackets). Epoxide groups quantification is labelled as “hydroxypropylic alcohols”. Mass correction accounts for the effect of molecular weight variations after the epoxidation reaction on lignin hydroxyls distribution.

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^{31}C-NMR analysis also confirmed the accomplishment of lignin epoxidation. In fact, strong absorptions at about 44, 50, and 70-75 ppm were diagnostic for the presence of oxirane rings (*vide infra*).

Carbonation Reaction of Epoxidized Lignin, Synthesis and Characterization

The feasibility of the insertion reaction of CO_2 on the epoxidized lignin was then assessed.

At first, different organic solvents suitable for lignin dissolution, i.e., dimethylformamide (DMF), dimethylsulfoxide (DMSO), methyl acetoacetate (Meacac), dioxane, and methylethyl ketone (MEK) in association with a commonly employed salt catalyst (potassium iodide, KI) were tested. Typical reaction conditions applied for carbonation reactions in organic solvent medium are, if not otherwise stated: 20 bar pressure, 20 hours reaction time, 80°C as reaction temperature, 10% w/w catalyst loading, and 1% w/w consistency[28]. For a rapid screening of the reaction outcome, the % absorbance of the cyclic carbonate peak at 1790 cm^{-1}, as detected from ATR-FTIR analysis, was considered (Fig. 1). ^{13}C NMR analyses were performed on selected samples to evaluate the reaction progress by the disappearance of characteristic epoxides carbon signal (spectra not reported). As a general observation, IR absorbance of the characteristic cyclic carbonates peak (1790 cm^{-1}) above 0.30 a.u. means a complete conversion of epoxides groups according to ^{13}C NMR analysis.

Results of the carbonation experiments are reported in Table 2. No significant conversion occurred without the presence of any catalyst under these reaction conditions (entry 1). Dioxane and MEK (entries 5 and 6) were not able to solubilize epoxidized lignin. Among DMF, DMSO, and Meacac, in all cases in association with KI as catalyst (entries 2-4), the best performance in term of carbonation yield was obtained with DMF, which was therefore selected as organic solvent of choice for further investigation. Other catalysts were then tested: 1,8-diazabicyloundec-7-ene (DBU) and N,N-dimethylaminopyridine (DMAP) were selected as metal- and halide-free catalysts[29] while the onium salt tetrabutylammonium bromide (TBAB) was assayed both in its pure form and in association with a Cobalt(II) salt[30]. With the exception of the trials involving DBU and DMAP as catalysts (entries 7 and 8), the outcome of the CO_2 fixation experiments using KI, pure TBAB, or

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the TBAB-$CoCl_2$ system were roughly the same (entries 2, 9, and 10). However, a slight increase in the catalytic activity was observed in presence of $CoCl_2$.

Given the prominent role of halide- and onium-based catalysts in epoxidized lignin carbonation, the catalytic capabilities of two imidazolium-based ionic liquids, i.e., 1-allyl-3-methylimidazolium chloride (amimCl) and 1-allyl-3-methylimidazolium bromide (amimBr) in DMF medium was investigated. The ILs were tested in their pure form and in the presence of $CoCl_2$. Both the ILs were found to be active catalysts but amimBr demonstrated superior performances over amimCl (entries 11 and 13). Furthermore, the addition of $CoCl_2$ as co-catalyst remarkably improved the yield in cyclic carbonates in both cases (entries 12 and 14). The high catalytic activity of $CoCl_2$ appears to be linked to the high Lewis acidity of the metal ion. It was demonstrated that when $CoCl_2$ and an ammonium salt such as TBACl or an imidazolium-based IL were mixed together, a new ion pair, $[\text{onium}]^+[CoCl_3]^-$, was formed[31,32]. These ion pairs are believed to be the catalytically active species in the synthesis of cyclic carbonates. In the particular case of ILs, the coordination of both cationic and anionic moieties is believed to promote the reaction by dual activation of the epoxide and carbon dioxide[33]. Another crucial factor is the good leaving ability of the IL counteranion that is essential for ring closure and can also explain the lower activity of amimCl compared to amimBr.

The ability of imidazolium-based ILs to act as powerful catalyst in the fixation of CO_2 to epoxides is already well documented on simple molecules such as propylene oxide[14,34] but it has never been reported on epoxidized lignin.

Finally, the weight loading (w/v%) of epoxidized lignin in DMF in the presence of amimBr as catalyst was forced to its limit. The solubility was assessed by eye inspection. The conversion to cyclic carbonates was in line with previous experiments involving the same IL (entry 15).

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Entry	**Solvent**	**Catalyst (w/w%)**	**Weight loading (w/v%)**	**IR Abs (a.u.)**
1	DMF	None	1	0.09
2	DMF	KI (10%)	1	0.58
3	DMSO	KI (10%)	1	0.48
4	Meacac	KI (10%)	1	0.34
5	Dioxane	KI (10%)	1	Not soluble
6	MEK	KI (10%)	1	Not soluble
7	DMF	DBU (10%)	1	0.44
8	DMF	DMAP (10)	1	0.38
9	DMF	TBAB (10%)	1	0.53
10	DMF	TBAB-$CoCl_2$* (10%)	1	0.62
11	DMF	amimCl (10%)	1	0.49
12	DMF	amimCl-$CoCl_2$* (10%)	1	0.63
13	DMF	amimBr (10%)	1	0.59
14	DMF	amimBr-$CoCl_2$* (10%)	1	0.66
15	DMF	amimBr (10%)	6.7%	0.62

*TBAB-$CoCl_2$, amimCl-$CoCl_2$, and amimBr-$CoCl_2$ 1:1 mol/mol

Table 2 List of carbonation experiments performed on HBL lignin at 20 bar for 20 hours at a fixed temperature of 80°C, reporting: adopted solvent, % weight loading, catalyst type and loading, pressure, reaction period, and absorbance of the cyclic carbonate peak at 1790 cm^{-1}.

The natural continuation of the previously described results is the exploitation of the sole IL as both reaction medium and catalyst. Table 3 shows the effect of different ILs and experimental conditions. Typical conditions applied for carbonation reactions in IL medium are, if not otherwise

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stated: 20 bar pressure, 20 hours reaction time, 80°C as reaction temperature, and 5% w/w consistency.

amimCl was the first IL chosen for this investigation due to its widely spread use in the dissolution of lignocellulosic materials. The obtained outcome (entry 16) was in line with trials performed in DMF medium in the presence of amimCl, proving its catalytic activity even under different experimental conditions. As previously discussed, the IL counteranion nature plays a crucial role in promoting CO_2 fixation with epoxides. Accordingly, amimBr was selected as an IL bearing a better leaving group than amimCl for further experiments. According to IR analysis, the attained result was the best among all the trials presented in term of cyclic carbonates yield (entry 20). It is highlighted that, when ILs are used as proper solvent, the addition of $CoCl_2$ to the reaction mixture did not result in an increased catalytic activity, as was instead observed in DMF medium (entries 19 and 21).

Additional experiments involving the use of recycled amimCl were also performed to evaluate the catalytic and solvating efficiency of the IL after purification. At the third run, neither a minor conversion nor a decrease in selectivity of cyclic carbonates formation was observed according to IR and ^{13}C NMR analysis (entries 16-18).

Furthermore, others commercially available imidazolium-based ILs bearing chloride counteranions were tested for the cycloaddition reaction: 1-butyl-3-methylimidazolium chloride (bmimCl) and 1-benzyl-3-methyl-imidazolium chloride (BzmimCl). In agreement with the scarce influence of the cation nature reported in literature[25], their efficiency in promoting the formation of cyclic carbonates was the same to that observed for amimCl (entries 16,22,and 23).

Again, the weight loading of epoxidized lignin was increased to evaluate the catalytic activity of the IL in extreme reaction conditions. The solubility was assessed by eye inspection. Going from 5 to 20% lignin loading, epoxides conversion to cyclic carbonates was only slightly affected (entries 20, 24, and 25). It is worth noticing that the corresponding limit in DMF medium was 6.7%. Even if the recovery process is similarly smooth (water precipitation followed by filtration), the use of ILs

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allows for the use of minimal amount of solvent and, as direct consequence, antisolvent if compared to DMF. Moreover, as organic salts with negligible vapor pressure, imidazolium-based ILs are far more easily regenerated by high-vacuum water distillation.

Entry	Solvent & Catalyst	Additional Catalyst (w/w%)	Consistency (w/v%)	IR Abs (a.u.)
16	amimCl	-	5	0.57
17	amimCl cycle 2	-	5	0.51
18	amimCl cycle 3	-	5	0.55
19	amimCl	$CoCl_2$ (10%)	5	0.60
20	amimBr	-	5	0.68
21	amimBr	$CoCl_2$ (10%)	5	0.58
22	bmimCl	-	5	0.57
23	BzmimCl	-	5	0.56
24	amimBr	-	10	0.62
25	amimBr	-	20	0.61

Table 3 List of carbonation experiments performed on HBL lignin at 20 bar for 20 hours at a fixed temperature of 80°C, reporting: adopted solvent, **%** weight loading, type and % of catalyst, pressure, reaction period, and absorbance of the cyclic carbonate peak at 1790 cm^{-1}.

Besides, ^{13}C NMR spectra acquired on epoxidized and carbonated specimens of herbaceous and hardwood kraft lignin were thoroughly interpreted. More interestingly, quantitative ^{13}C NMR spectra were acquired on carbonated HBL and HWKL in the presence of dimethyl carbonate as internal standard to provide a reliable quantification of the cyclic carbonate moiety. Carbonated specimens were prepared according to the best experimental conditions found, i.e., pure amimBr as

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reaction solvent. Epoxidized and carbonated lignin was not subjected to acetylation (traditionally performed in a pyridine/acetic anhydride solution) in order to avoid degradation of glycidyl and cyclic carbonate moieties.

Accurate assignment of epoxides and cyclic carbonates Carbon nuclei, as a function of the type of labile hydroxyl (phenolic or from carboxylic acid) and degree of *ortho*-substitution of the phenolic moiety (not substituted, mono-, and di-substituted), was based on spectroscopic data obtained by ^{13}C NMR analyses of epoxidized and carbonated lignin model compounds (Table 4). As already reported for allylated lignin[35], the C_1 position of the epoxide chain is the most affected by the surrounding chemical environment ($\Delta C_1 \approx 8.7$ ppm, $\Delta C_2 \approx 0.9$ ppm, $\Delta C_3 \approx 0.4$ ppm). Surprisingly, this is no longer true for carbonated derivatives, in which the most perturbed site is the C_3 position and the least influenced the C_1 ($\Delta C_1 \approx 0.2$ ppm, $\Delta C_2 \approx 1.1$ ppm, $\Delta C_3 \approx 7.6$, $\Delta C_4 \approx 0.6$ ppm).

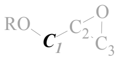
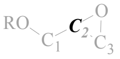
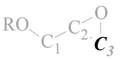
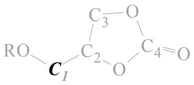
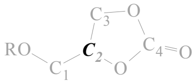
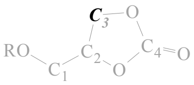
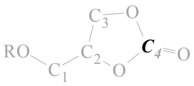
Assignment (ppm)	Phenol	Guaiacol	2,6-dimethoxy phenol	Vanillic acid (phenol)	Vanillic acid (acid)
	68.3	70.4	74.0	69.8	65.3
	50.2	50.3	50.4	49.8	49.5
	44.7	45.0	44.6	44.7	44.6
	66.3	66.3	66.3	66.1	66.2
	74.3	74.9	75.1	74.5	74.0
	67.0	69.4	71.3	68.7	63.7
	154.8	155.2	155.1	155.0	154.6

Table 4 ^{13}C NMR assignment for the epoxide and cyclic carbonate side chain in representative model compounds of lignin after labile hydroxyls functionalization.

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Figure 3 reports the ^{13}C NMR spectra acquired for epoxidized and carbonated herbaceous (top) and hardwood kraft (bottom) lignin. In the NMR spectrum of epoxidized HBL, partially overlapped signals located at 43.5 and 50.4 ppm were assigned to the C_3 and C_2 positions of condensed and syringyl derivatives, while peaks at 43.9 and 49.9 ppm were attributed to the C_3 and C_2 positions of guaiacyl and *p*-hydroxyphenyl derivatives, respectively. In the case of epoxidized HWKL, partially overlapped signals at 43.4 and 50.4 ppm were assigned to the C_3 and C_2 positions of condensed and syringyl derivatives, while peaks located at 43.9 and 49.9 ppm were attributed to the C_3 and C_2 positions of guaiacyl derivatives, respectively. In agreement with labile hydroxyls distributions in the two lignin under investigation (Table 1), the relative intensity of signals pertaining to condensed and syringyls (C&S) compared to guaiacyls and *p*-hydroxyphenyls (G&H) is similar for the herbaceous lignin (C&S ≈ G&H) whereas favorable to disubstituted phenols for the hardwood kraft lignin (C&S › G&H).

The accurate assignment of the C_1 Carbon of the epoxide chain was more challenging. A number of different and weak signals were indeed detected, as a consequence of the strong influence of the surrounding chemical environment to which this position is subjected. Anyway, it is for certain that downfielded peaks have to be attributed to condensed and syringyl derivatives, whereas upfielded peaks have to be related to guaiacyl and *p*-hydrophenyl derivatives (in agreement with the study performed on model compounds). The broad signal in the aromatic region (not entirely reported) is characterized by a single well-defined peak related to quaternary aromatic Carbon linked to methoxyl groups.

After CO_2 fixation, no signal pertaining to the C_2 and C_3 position of the epoxide chain (around 50 and 44 ppm, respectively) was detected for both the lignins examined, proving a total conversion of the glycidyl group. On the other hand, the appearance of well-defined peaks at 65.9 and 155.1 ppm were unambiguously attributed to the C_1 and C_4 position of the cyclocarbonate structure, respectively. C_2 and C_3 Carbon signals were numerous and scattered along a broad ppm range.

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Approximately, their position lay between 73-76 and 68-72 ppm, respectively, being in both cases the more downfielded peaks attributed to condensed and syringyl derivatives, and the more upfielded peaks related to guaiacyl and *p*-hydrophenyl derivatives (in agreement with the study performed on model compounds).

^{13}C NMR spectra of carbonated lignins were also recorded in the presence of dimethyl carbonate (25 µl) as internal standard to provide a reliable quantification of the cyclic carbonate moiety. The carbonyl group Carbons of the internal standard (155.9 ppm) and carbonyls groups of cyclic carbonates on lignin (155.1 ppm) were used as reference signals for the quantification. The strong signal detected at 54.8 ppm is related to methyl groups in dimethyl carbonate.

Table 5 reports the experimental (first line) and theoretical (third line) quantification of the cyclic carbonates groups for HBL and HWKL, expressed as mmolg^{-1}. The theoretical data were calculated starting from the quantification of epoxides groups, as obtained by ^{31}P NMR analysis (Table 1). The amount of hydroxypropylic alcohols ensuing from phosphorus derivatization (penultimate line, Table 5) ought to be conveniently corrected according to lignin molecular weight variation after CO_2 fixation. In this case, the C_9 lignin unit, already described in the section concerning the epoxidation reaction, is illustrated by the empirical formula $C_{14}H_{17}O_7$ and its molecular weight is ca. 297 gmol^{-1}. Corrected values for hydroxypropylic alcohols are reported in the last line of Table 5 (1.91 and 2.10 mmolg^{-1} for HBL and HWKL, respectively).

According to ^{13}C NMR analysis, the cyclic carbonates moiety quantification is 2.01 and 1.78 mmolg^{-1} for the herbaceous and hardwood kraft lignin, respectively, in very good agreement with calculated theoretical values.

The occurrence of degradation phenomena leading to cyclic carbonates ring opening was excluded by both IR and NMR analyses. IR spectra of carbonated lignin specimens did not evidenced the presence of peaks around 1750 cm^{-1}, which is the typical absorption region of linear carbonates. On the other hand, ^{13}C NMR spectra acquired for qualitative purposes, i.e., without dimethyl carbonate,

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never did displayed absorption around 156 ppm, which is the characteristic signal of linear carbonates.

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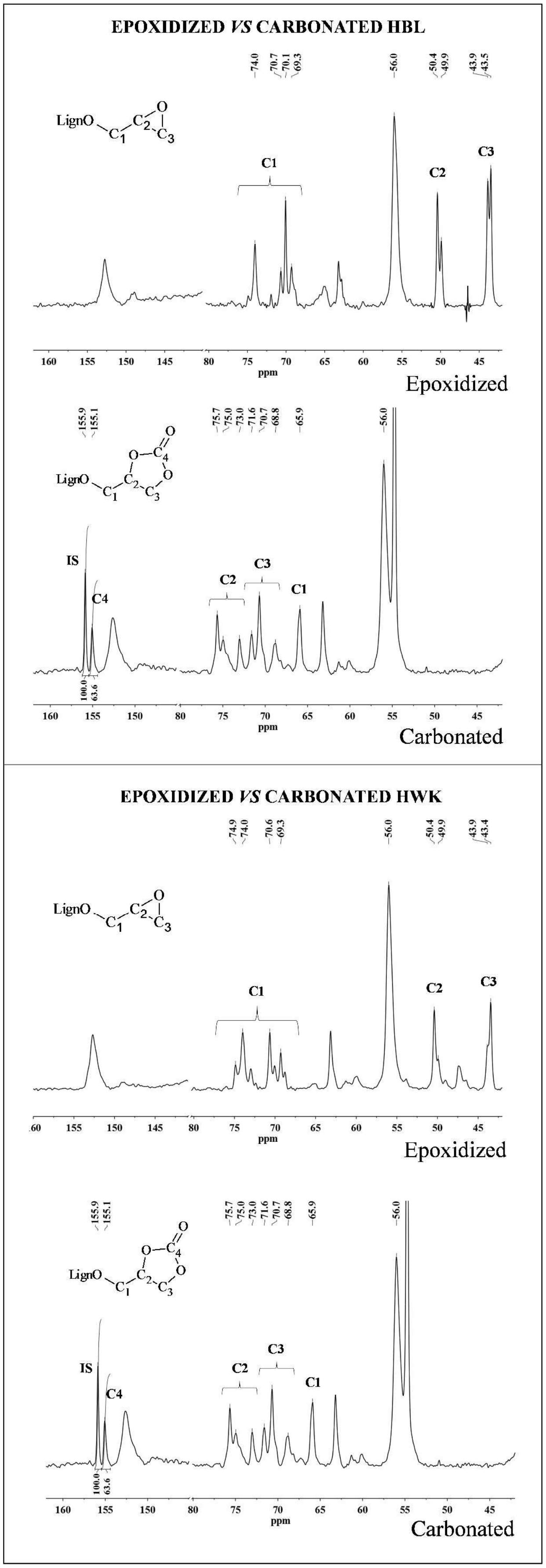

EPOXIDIZED *VS* CARBONATED HBL

EPOXIDIZED *VS* CARBONATED HWK

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Figure 3 ^{13}C NMR spectra depicting epichlorohydrin epoxidized and carbonated herbaceous and hardwood kraft lignins. Spectra normalized on methoxyls signal (56 ppm). Epoxidized and carbonated lignins were not subjected to acetylation to avoid degradation of glycidyl and cyclic carbonate moieties.

Quantification (mmol/g)	**HBL**	**HWKL**
Experimental		
Cyclic carbonates (^{13}C NMR)	2.01	1.78
Theoretical		
Hydroxypropyl –OH (^{31}P NMR)	2.25	2.47
Hydroxypropyl –OH (mass corrected)	1.91	2.10

Table 5 Theoretical and experimental quantification of cyclic carbonates groups in herbaceous and hardwood kraft lignin, calculated according to ^{31}P and ^{13}C NMR analysis, respectively. Mass correction considers the effect of molecular weight variations after the carbonation reaction on lignin hydroxyls distribution.

Conclusion

Lignins from different sources were directly reacted with epichlorohydrin, providing a pure epoxidized derivative. A quantitative evaluation of the epoxide groups inserted was attained through ^{31}P NMR analysis. The addition reaction of CO_2 to the epoxide groups was for the first time reported on lignin. Ionic liquids were successfully used as both solvent and catalyst for the reaction. With the aid of conveniently functionalized model compounds, epoxidized and carbonated lignin was fully characterized by ^{13}C NMR analysis. A precise determination of the cyclic carbonate structures formed was also given by quantitative ^{13}C NMR.

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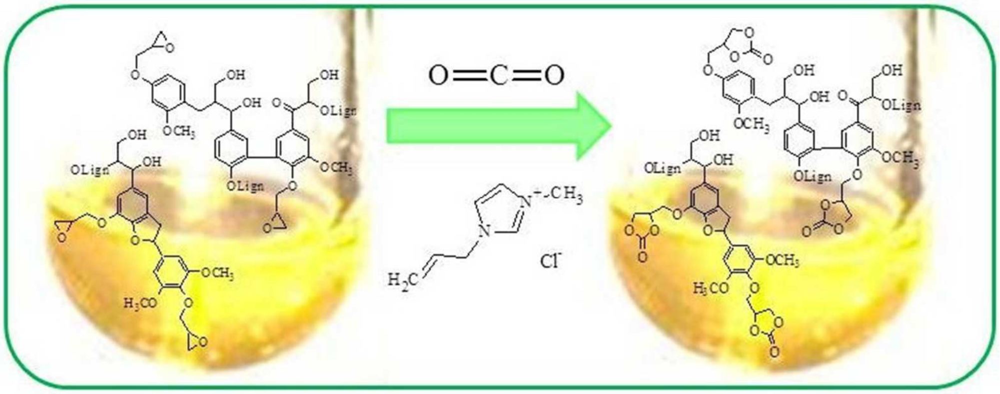

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