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Simultaneous extraction and controlled chemical functionalization of hardwood lignin for improved phenolation†

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Lignin is a promising candidate for the replacement of fossil-based materials, due to its natural abundance and aromatic structure. This same structure poses major challenges to lignin's exploitation for material development. The harsh conditions generally needed for its isolation make it susceptible to uncontrollable side reactions that limit its further upgrading and/or functionalization. Here, by using aldehyde-assisted fractionation (AAF), we have extracted lignin while avoiding condensation reactions and, at the same time, introduced new functional groups on the lignin in a single step. By using a multifunctional aldehyde such as terephthalic aldehyde (TALD), we used acetal functionalization to prevent the dehydration and condensation of lignin's β-O-4 linkage and introduced an aldehyde on the lignin backbone. By tuning the amount of TALD during the extraction process, we were also able to precisely control the degree of chemical functionalization. We then exploited the reactivity of the newly functionalized biopolymer to increase phenolation reactions yields in both acid and basic environment, in order to provide better lignins for incorporation in phenol formaldehyde resins. These TALD-lignins were more reactive than Kraft lignin or mild organosolv lignin extracted in an acid solution of 80% ethanol in water, which could facilitate their use for developing more sustainable resins and materials.

Introduction

Lignin, together with cellulose and hemicellulose, is one of the main components of lignocellulosic biomass and is the most abundant renewable source of aromatic functionalities present in nature. Because of this, lignin is generally considered a promising sustainable alternative for producing aromatic fuels and materials that are currently derived from fossil sources.[1] One of the most promising uses of lignin is the partial substitution of phenol and formaldehyde in PF resins, given the similarities between lignin's structure and that of phenolic resins.[2] However, this same lignin structure poses important challenges that ultimately hinder the use of this biopolymer in material applications. Specifically, the two main challenges are given by its irregularity, especially when isolated, which makes consistent incorporation in these PF thermosets difficult, and the low reactivity of its phenolic groups, which limits crosslinking compared to pure phenol.[3,4]

Lignin is biosynthesized from three different C_9 aromatic monolignols, namely coniferyl, sinapyl and *p*-coumaryl alcohols, that give rise to a heterogenous polymer formed respectively by guaiacyl, syringyl, hydroxyphenylpropane units, where the final composition of these units can vary depending on the plant species.[5] The heterogeneity of lignin arises not only from to the different monolignol composition, but also from the variety of functional groups and chemical linkages that bind these subunits together (Fig. 1a). Amongst these linkages, the β-O-4 is the most abundant and, thus, the most targeted for the depolymerization or for the chemical modification of lignin.[6] In fact, aliphatic hydroxy groups, together with residual phenolics, are prone to a variety of chemical reactions that are widely used for targeted lignin functionalization but also lead to condensation.[7]

Specifically, these hydroxy groups act as reactive species in the strong acid or basic environments which are commonly used to isolate lignin from the rest of the biomass.[8] This is the case for organosolv lignin (OSL) extraction conducted in organic solvents with acid catalysts,[9] or of Kraft lignin (KL) which is generally separated from the rest of the biomass by using a solution of sodium sulfide and sodium hydroxide at temperatures between 150 °C and 180 °C.[10] In these conditions, lignin tends to condense, beginning with dehydration reactions that remove the α hydroxy groups in the β-O-4 lin-

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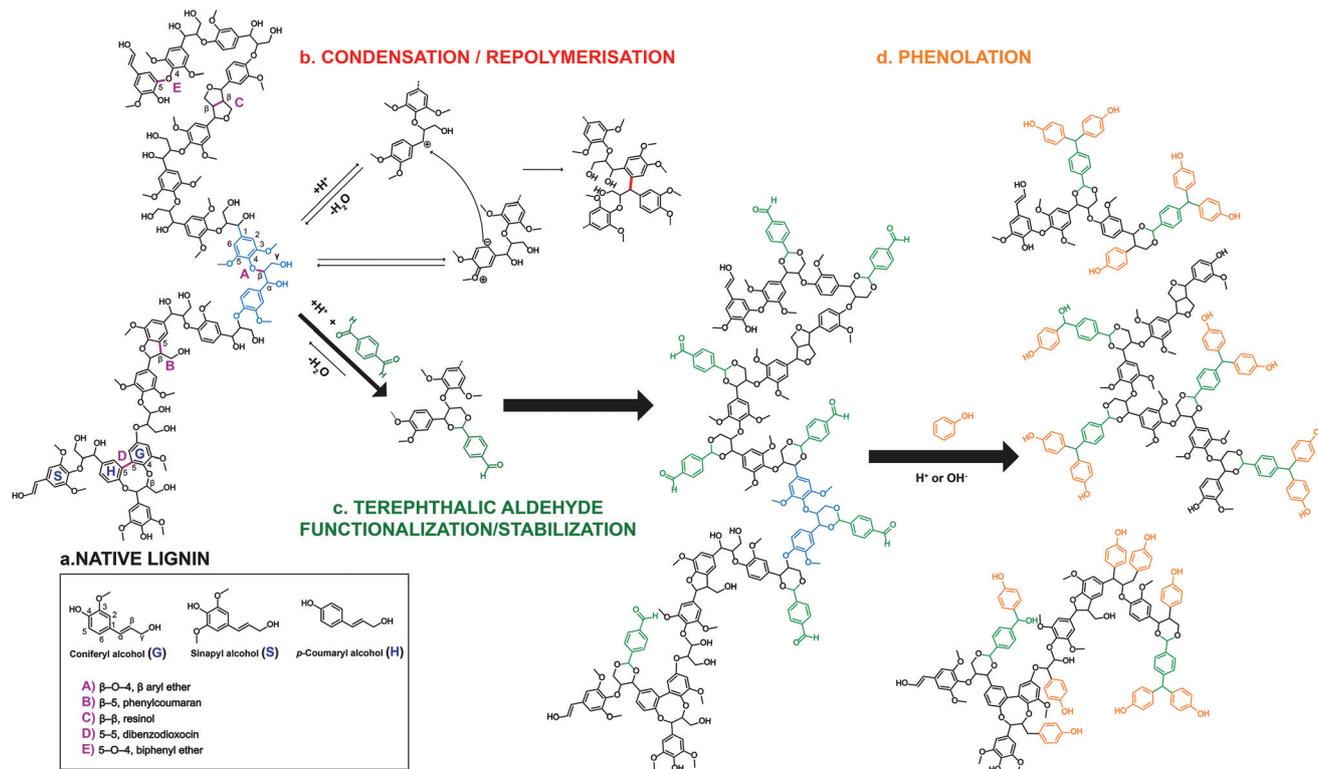
Fig. 1 The structure of hardwood lignin and overview on the functionalization process of this paper. (a) Proposed structure of native lignin in hardwood. (b) The mechanism of condensation and repolymerization reactions of lignin treated in strong acid conditions. (c) The TALD assisted fractionation mechanism and lignin structure described in this work. (d) The phenolation reactions of lignin performed in this paper.

kages. This dehydration causes the formation of reactive carbocations that are prone to electrophilic substitution on the phenolic rings. These resulting repolymerization reactions lead to the formation of strong and new C–C linkages which are highly recalcitrant to further upgrading, *i.e.* they are very difficult to break selectively or selectively functionalize[11] (Fig. 1b). This recondensation, that occurs almost systematically with chemical lignin isolation, makes it very challenging to control the chemical structure of the final isolated lignin and ultimately the degree of functionalization that can be achieved on the polymer.

The structure of native lignin and to an even greater extent, that of isolated lignin, leads to low reactivity when used as a phenol substitute in PF resins.[12] This low reactivity mainly occurs because the positions on the phenolic ring are more occupied in isolated lignin and, to a lesser extent, native lignin, compared to simple phenol.[13] For this reason, functionalizing conventionally isolated lignins to increase their reactivity towards certain type of reactions is an approach that has been extensively used to valorise this sustainable biopolymer and make it more suitable to incorporation in materials.[14]

In particular, to increase the compatibility and reactivity of lignin towards the synthesis of PF thermosets, while decreasing its recalcitrance, many researchers have attempted to maximize the number of reactive sites of the biopolymer.[15] A well-known reaction used to achieve this goal is phenolation

(Fig. 1d). Generally, the preferred catalysts for phenolation are strong acids, due to the possibility of performing electrophilic aromatic substitution between phenol and the carbocations that forms on the α or γ position of the lignin, after dehydration at low pH (Fig. 1). A drawback of this approach is that most of the PF resin are currently synthesized at high pH, which requires a neutralization and/or lignin isolation step necessary after acid-catalyzed phenolation.[16,17]

In this context, we sought an avenue to both prevent the condensation of lignin during isolation to provide a more regular structure and create an avenue for improved lignin functionalization. We have recently introduced a novel process for extracting lignin, where we have shown that by simply adding formaldehyde during the isolation of lignin, almost all the β-O-4 bonds present in the biopolymer could be preserved in the form of stable acetals.[18] Lan *et al.* then further demonstrated that the same process could be extended to a variety of other aldehydes.[19] By further taking advantage of the process versatility, we wanted to develop the simultaneous isolation and functionalization of the lignin using multifunctional aldehydes.[20] Such aldehydes could stabilize the β-O-4 bonds *via* the formation of acetals, and at the same time introduce novel functional groups on the lignin scaffold (Fig. 1c).[20] In this regard, the multifunctional aldehyde that is chosen should carry functional groups that do not degrade under the acidic condition of lignin isolation. Specifically, they should not

react/condense *via* aldol condensation due to the presence of protons in the alpha position with respect to the aldehyde.[21]

One possibility would be to use terephthalic aldehyde (TALD), which cannot undergo aldol condensation due to the presence of the aromatic group. TALD can also be sustainably sourced or be easily synthesized from renewable precursors. Indeed, Goulas *et al.* have recently reported that TALD could be produced *via* the heterogeneously catalysed oxidation of di-(hydroxymethyl) benzene, a molecule that can be synthesized from 5-hydroxymethyl furfural (5-HMF) derivatives and therefore from renewable carbohydrates.[22] Furthermore, Foyer *et al.* showed that it was possible to obtain thermoset resins of phenol with high thermal properties by substituting formaldehyde with TALD and conducting the reaction at high pH, demonstrating the reactivity of this dialdehyde towards phenol in basic conditions.[23]

Therefore, in this work, we sought to use TALD to extract lignin at high yields while, at the same time, avoiding its condensation and precisely controlling the quantity of aldehydic functionalization on the scaffold of the biopolymer. Moreover, we performed phenolation reactions in both acid and basic catalysis, comparing the result obtained with commercial Kraft Lignin (KL) and a mild organosolv lignin (OSL) extracted in a solution 80 : 20 ethanol : water for 5 h and using HCl as the acid catalyst.

Results and discussion

Lignin extraction and characterization

TALD functionalized lignins (TALD-lignins) were extracted from birch (*Betula Pendula*) wood chips based on a modified procedure of our previously published aldehyde-assisted protocol.[24] In this process, lignocellulosic biomass was mixed with TALD at concentrations between 12.6 and 0.85 mmol g^{-1} dry biomass in an acid environment at 80 °C. These conditions favoured acetal formation and led to the stabilized lignin being solubilized into the organic solvent. Purified cellulose remained as an insoluble fraction, which was easily isolated by filtration. TALD-lignin could then be separated from the carbohydrates and the unreacted aldehyde by precipitation in diethyl ether. To perform control experiments, a OSL was also extracted in 80% ethanol in water for 5 h at reflux using HCl as a catalyst, following a protocol published by Zijlstra *et al.*[25] (see S2.3 in ESI†), while KL was obtained from a commercial source.

After the extraction, and without further treatments, isolated TALD-lignin, OSL and KL were all subjected to hydrogenolysis to evaluate the effectiveness of the lignin extraction, as the resulting monophenolic molecules yield is an indirect indicator for the lack of condensation during extraction.[26,27] The hydrogenolysis results, reported on the basis of the Klason lignin content in the original biomass, were then compared to those of the direct hydrogenolysis of native birch wood (Fig. S4 and section S3.2 in ESI†). Direct hydrogenolysis of untreated birch wood in THF produced 44.8 wt% of aromatic monomers.

In comparison, the hydrogenolysis of TALD, OSL and KL lignins led to the production of monomer yields of 39.4 wt%, 7.2 wt% and 1.7 wt%, respectively. The monophenolic content is far superior when using TALD-lignin, despite both OSL and TALD-lignin having a high β-O-4 linkage content. However, OSL lignin, when extracted at such mild conditions, could only be obtained with a yield of 28 wt%, while TALD lignins could be extracted with yields ranging from 81 to 100 wt%. In comparison, KL were generally efficiently isolated from the biomass at high yields, but the very condensed structures, with few ether linkages and a high content of uncleavable C–C bonds, resulted in a low yield of monophenolic molecules after hydrogenolysis.

After extraction and purification, we first characterized the TALD-lignin through Nuclear Magnetic Resonance (NMR) (Fig. 2). To confirm lignin functionalization and identify possible side reactions, we synthesized a mixture of simple model compounds starting from TALD and ethylene glycol, that we then analysed by ^{1}H NMR (Fig. 2a). These model compounds mimic the acetal formation between the aromatic dialdehyde and the α and γ hydroxy groups in the β-O-4 bonds of lignin. In particular, from the ^{1}H NMR spectrum of the mixture of model compounds, we observed that TALD in presence of ethylene glycol (or lignin) can produce three distinct products: unreacted TALD (Fig. 2a, first model compound), TALD that has reacted with one diol (Fig. 2a, second model compound), or TALD that has reacted with two diols (Fig. 2a, third model compound) to form new acetal rings. We then compared the obtained ^{1}H NMR spectrum of the mixture of model compounds to the spectrum obtained from isolated functionalized lignin (Fig. 2b), which revealed the close alignment between functionalized lignin peaks and their corresponding model compound structures. Moreover, we also noted that the functionalized lignin's peaks broaden, as a result of the increase of the transverse relaxation time (T_2), which is typical of large molecules such as polymers and lignin oligomers. Therefore, this broadening suggested that TALD was successfully bound to the biopolymer.

We also characterized the structure of the isolated lignin by Heteronuclear Single Quantum Coherence NMR spectroscopy (HSQC-NMR). This technique allowed the identification of the signals assigned to the lignin scaffold such as the β-O-4 and β–β bonds, the C–H bonds of the syringyl and guaiacyl aromatic rings, and the signal assigned to the TALD functionalization (Fig. 2c).

Despite the extensive purification that included a Soxhlet extraction step and washing with diethyl ether, signals assigned to functionalized xylose (TALDX) were still found in the HSQC spectra. Since the presence of such a significant amount of impurities present on the lignin after purification was unlikely, we hypothesized that the TALD could also partly act as a cross-linking agent between xylose and the lignin β-O-4 bonds. To confirm this hypothesis, we performed Diffusion Ordered SpectroscopY-NMR (DOSY-NMR). This technique allows the resolution of molecules present in a system based on their capacity for diffusion in solution, which reflects
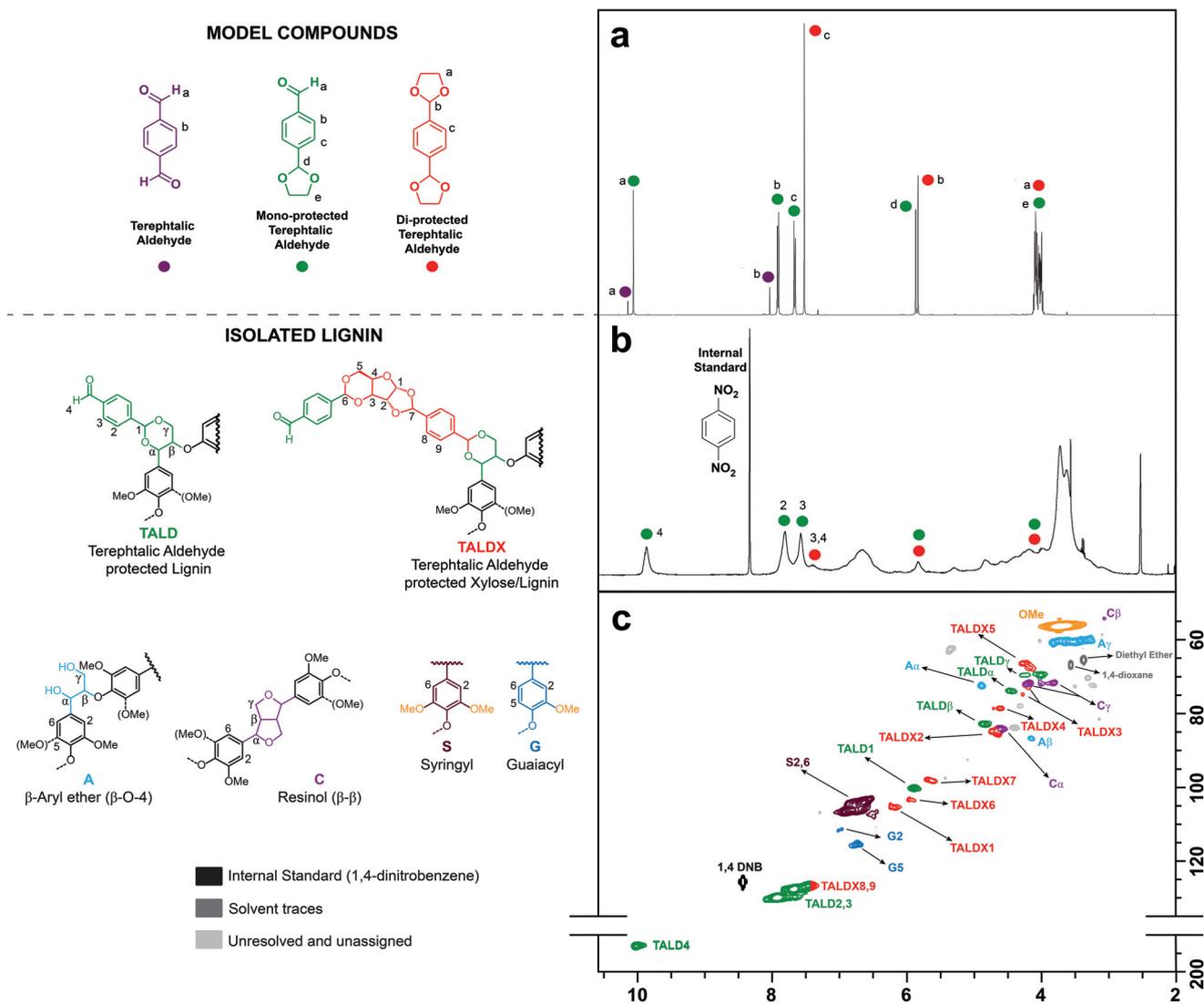
Fig. 2 (a) The chemical structure of the synthesized model compounds and its ¹H NMR spectrum. (b) The chemical structure of the main structural features of lignin functionalized with terephthalic aldehyde (TALD-lignin) and its ¹H NMR and (c) HSQC NMR spectra.

their difference in molecular weight. The spectra obtained for the TALD-lignin in DMSO-d_6 (Fig. S3 ESI†) suggested that all these aforementioned signals present in the sample, in the region of interest, are thus likely part of the same molecular system. This result indicated that TALD functionalized xylose was likely directly bound to the lignin. The exact amount of this carbohydrate impurity however could not be quantified by standard or quantitative HSQC-NMR due to the variable differences in relaxation time and intensity of the signals. In fact, some of the carbohydrate signals were barely detectable after using a longer relaxation time during spectra acquisition. In such samples, the signal to noise ratio was low enough to cause substantial errors, which prevented reliable quantification. GPC measurement and DOSY NMR measurements also indicated that cross-linking between different lignin oligomers was unlikely to occur. We did not observe significant differences in measured molecular weights or diffusion behaviours

in lignin samples, regardless of the amount of TALD used during the extraction or even when using a lignin extracted with propionaldehyde—an aldehyde that cannot facilitate crosslinking (Table S3 in ESI†).

We further characterized the structure of TALD-lignin *via* Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectroscopy (Fig. 3). Infrared techniques are a useful tool for the characterization of functional groups, and particularly for the detection of carbonyls, being that these functional groups have generally a strong transmittance signal at around 1700 cm⁻¹. We therefore compared the spectra of TALD-lignin extracted with a high (12.6 mmol g⁻¹ dry biomass) or low (0.85 mmol g⁻¹ dry biomass) amount of TALD with the spectrum of a lignin extracted in the presence of formaldehyde. The spectra of TALD-lignin showed a strong signal at 1702.5 cm⁻¹ corresponding the carbonyl stretch. This signal, as expected, was not present in formaldehyde-stabilized lignin,
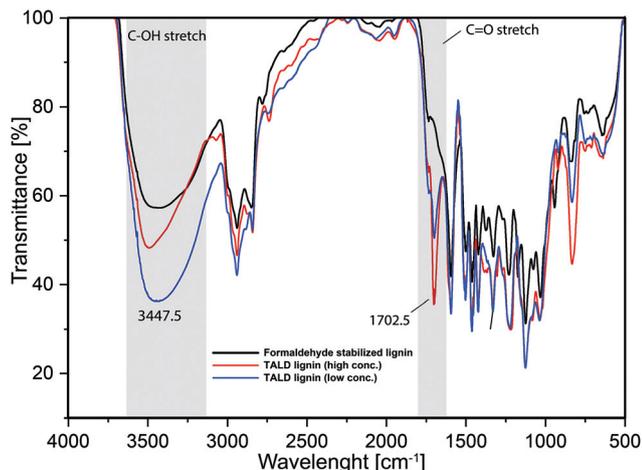
Fig. 3 DRIFT spectra of formaldehyde and lignin functionalized with terephthalic aldehyde (TALD–lignin).

since its carbonyl group disappears in the formation of the acetal. Noticeably, the relative intensity of the carbonyl stretch compared to the hydroxyl stretch at 3447.5 cm^{-1} was higher for the lignin that was extracted at a higher concentration of TALD than that for the lignin isolated with a lower concentration of the same aldehyde. This suggested a strong correlation between the concentration of TALD introduced during the extraction process and the amount of functionalization achieved on the lignin.

Controlling and quantifying the degree of TALD functionalization on isolated lignin

The structure of isolated lignins doesn't usually allow for quantitative or even qualitative determination of functional groups *via* ^{1}H NMR due to overlapping of the proton signals. However, in the ^{1}H NMR and HSQC-NMR spectra of TALD-lignin, the signals of bound TALD's free aldehyde group (δ_H/δ_C 10.01/193.4 ppm) did not overlap with any other peak, which could allow its straightforward quantification by ^{1}H NMR. To do so, we used 1,4-dinitrobenzene (1,4-DNB) as an internal standard, because it did not react with lignin under analysis conditions and its ^{1}H NMR signal is a single peak at 8.42 ppm that did not overlap with other peaks associated with TALD-lignin (Fig. 2b). We then performed Inversion Recovery experiments on the signals of the free aldehyde at 10.01 ppm and of the internal standard at 8.42 ppm, in order to measure their longitudinal relaxation time constant (T_1) and assure full recovery of the peaks in between spectra acquisitions. The results (Fig. S2 in ESI†) showed that the T_1 values were 2.33 s for the free aldehyde and 2.62 s for 1,4-dinitrobenzene. From these values we then decided to acquire spectra with a minimum delay time of 14 s. This method was then used to quantify the degree of functionalization of a series of lignins isolated using increasing concentration of TALD (Fig. 4, ESI S3.1†).
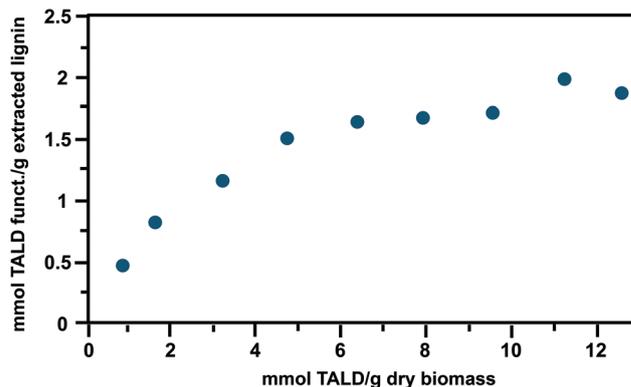
Fig. 4 Effect of initial TALD concentration over final functionalization.

The concentration of TALD added to the reaction correlated with the quantity of residual free aldehyde groups on the corresponding extracted lignin, increasing from a minimum of 0.47 mmol g^{-1} of aldehyde groups to a plateau at 1.85 mmol of aldehyde functionalities per gram of isolated lignin. This correlation demonstrates that the concentration of TALD used during the isolation process can be tuned to precisely control the degree of functionalization of lignin.

Phenolation of TALD-lignin

Exploiting the versatility of the aldehyde functionalities and their reactivity with phenol in both acid and base conditions, we conducted phenolation reactions in both of these environments on TALD-lignin with an aldehyde content of 1.89 mmol g^{-1} (Fig. 5a).[13,28] We compared the results to those obtained with a commercial KL and a OSL under the same conditions. The phenol was used as both the reagent and solvent during phenolation. Acidic phenolation (APH) of lignin was conducted following a procedure previously reported by Podschun *et al.*,[29] with some modification. Basic phenolation (BPH) was performed with the same ratio of lignin to phenol but catalysed by an aqueous solution of NaOH (ESI S2.4†).

After isolation, lignins were structurally characterized by HSQC-NMR to confirm the success of the reactions. We observed increases in peak volumes within the aromatic region of the HSQC spectrum after acid (TALD-APH lignin) and basic (TALD-BPH lignin) phenolation (Fig. 5b–d). After reaction of TALD-lignin with phenol, the signal of the aromatic proton in the *ortho* and *meta* position of TALD shifted form δ_H/δ_C 7.66/127.44 and δ_H/δ_C 7.91/129/95 ppm to higher fields at δ_H/δ_C 6.96/129.44 ppm. Furthermore, a new signal corresponding the phenol units bound to the lignin appeared at δ_H/δ_C 6.68/115.35 ppm, indicating the success of the reaction in both catalytic conditions. The DRIFT spectra of these lignins further confirmed phenolation due to the signal of carbonyl stretch disappearing in both APH- and BPH-TALD-lignins, while the relative intensity of the hydroxyl stretch increased in both cases (Fig. 5e). This change suggested that a higher quantity of phenolic groups was successfully bound to the lignin
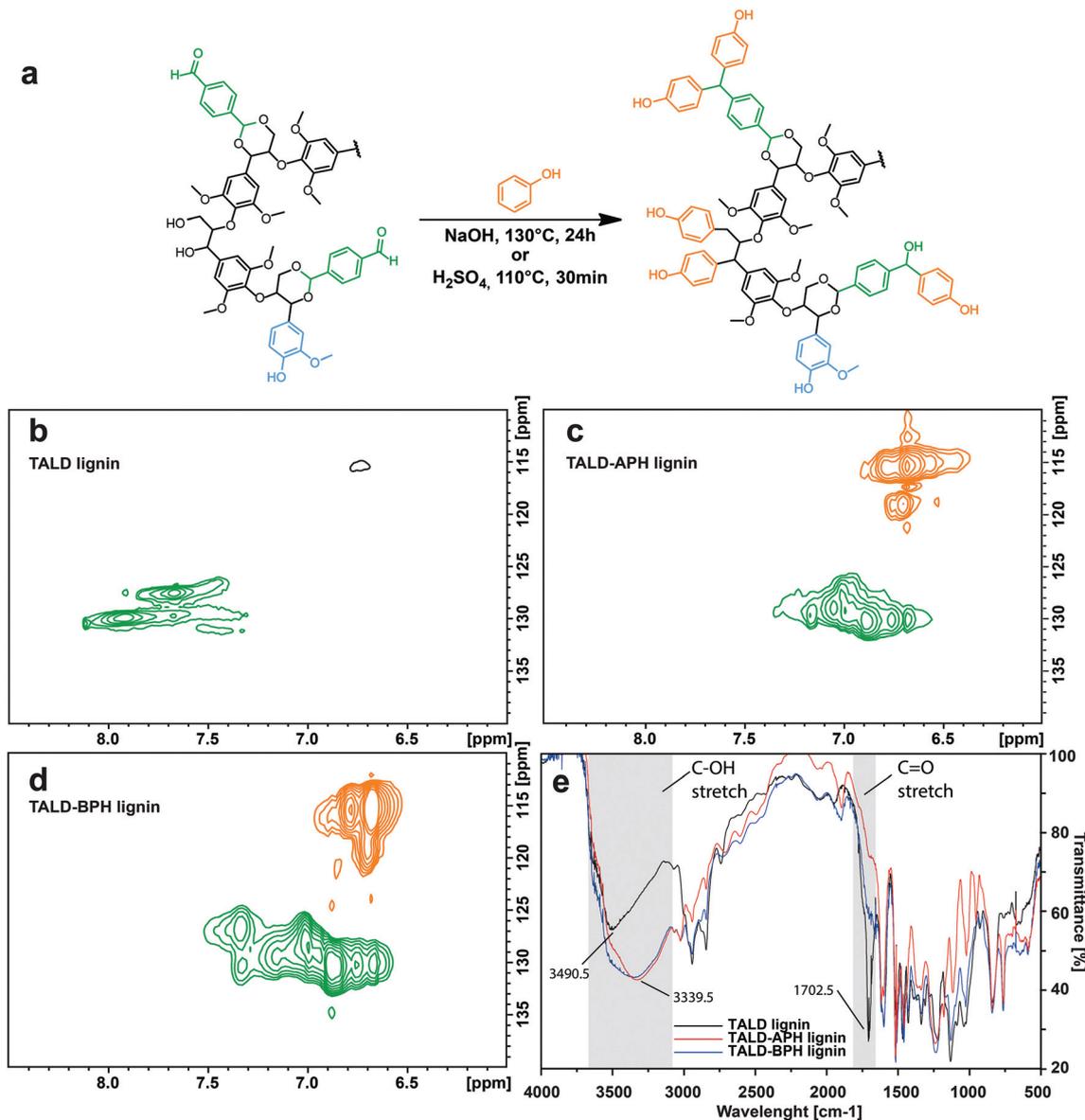
Fig. 5 Acid and basic phenolation of lignin functionalized with terephthalic aldehyde (TALD–lignin). (a) Presumed reaction mechanism. Peak growth in the aromatic region of the HSQC spectra before (b) and after phenolation in acid (c) and basic (d) conditions. Peak colours in panels (b–d) correspond to functionalities depicted in (a). (e) DRIFT spectra of TALD-lignin before and after phenolation.

and that the aldehyde was consumed as hypothesized in the mechanism (Fig. 5a).

We then used ^{31}P NMR to quantify the amount of aliphatic and aromatic hydroxy groups, and thus quantitatively compare the added phenol in both acid and basic conditions.[30] When comparing spectra before and after reaction, we observed a clear decrease in the signal assigned to aliphatic hydroxy groups and a corresponding increase of the signal assigned to phenolic units (Fig. 6a). The quantitative comparison of phenolic groups per effective extracted lignin (where "effective" indicates that the weight of the TALD functionalization was subtracted from the weight of TALD-lignin in order to have comparable results between the three lignins) shows that both

TALD-lignin and Mild-Acidolysis organosolv lignin have a higher and similar content of aliphatic hydroxy groups (respectively 3.21 mmol g^{-1} and 3.10 mmol g^{-1}) compared to KL (Fig. 6b). The similar content of aliphatic units in TALD and OSL lignin could be explained by the fact that for the first lignin a certain degree of beta-O-4 will be non-functionalized by the acetal formation with TALD, but still sterically protected by adjacent functionalized β-O-4, which will prevent condensation. A confirmation of this could be seen in HSQC spectra of TALD-Lignin (Fig. 2c) where it is possible to clearly see the signals of unfunctionalized α and β hydroxy groups (δ_H/δ_C 4.87/74.2 ppm for OH$_\alpha$, δ_H/δ_C 4.12/86.9 ppm for OH$_\beta$). On the other hand, OSL will see less functionalisation but likely
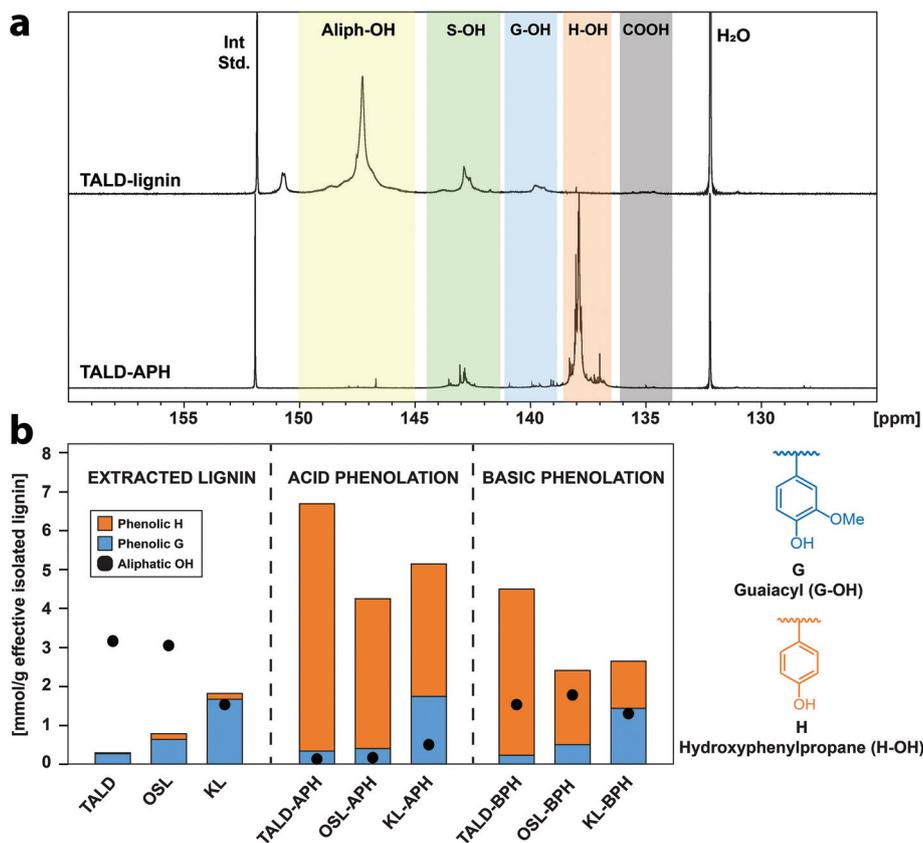
Fig. 6 Characterization of phenolated lignins. (a) ^{31}P NMR spectra of lignin functionalized with terephthalic aldehyde (TALD-lignin) before and after acid phenolation using TMDP as phosphorylating agent. (b) Yields of phenolation for different lignins in acid and basic conditions.

undergo a certain degree of condensation even at mild conditions of extraction, as shown by the lower overall yields, which would result in a decrease of hydroxy groups compared to the native lignin. In the case of KL, the aliphatic content is 1.55 mmol g^{-1}, which indicates a more condensed structure, which was expected due to harsh extraction conditions. Isolated KL had a higher amount of guaiacyl units (1.84 mmol g^{-1}) than the other two lignins because the commercial KL used in this study was derived from softwood, which contains only guaiacyl units, while birch contains a higher fraction of syringyl units. Second, the high temperature and basicity used during Kraft pulping favoured condensation reactions, but also a partial depolymerization of the lignin, which consequently could have led to an elevated number of phenolic end groups.[31]

After acid and basic phenolation, all lignin presented an increase of phenolic units and a decrease in aliphatic hydroxy groups regardless of the catalyst used (Fig. 6b). Phenolation conducted in presence of concentrated sulfuric acid was the most effective in introducing new hydroxyphenyl units in the lignin. OSL and KL showed a 5.47 and 2.83 fold increase in their respective quantity of total phenolic units, with a final phenolic content of 4.31 mmol g^{-1} and 5.22 mmol g^{-1} of lignin, respectively, which was in line with previously reported results.[29] In comparison, the functionalization of TALD-lignin

increased the aromatic hydroxyl content 23.4-fold with a total phenolic amount of 6.79 mmol g^{-1} of effective isolated lignin, which, to the best of our knowledge, is the highest phenolation value reported in literature. Furthermore, in the case of TALD-lignin and OSL, two lignins with a higher content of β-O-4 bonds, the phenolation in acid conditions also favoured partial depolymerization of the biopolymer (Table S4 in ESI†), which was not the case for KL, which lacked β-O-4 linkages even before phenolation as evidenced by the low yields obtained after hydrogenolysis.

The aldehyde functionality also proved to be beneficial during phenolation in presence of NaOH. When functionalized in basic conditions, TALD-lignin showed a 15-fold increase of total phenolic units, with a final content of 4.57 mmol g^{-1}. Interestingly, both mild organosolv and KL showed an increase in hydroxylphenyl units after phenolation in basic condition with a respective total phenolic content of 2.44 mmol g^{-1} and 2.69 mmol g^{-1}, even though aldehyde groups were not present in the original scaffold of these two aromatic polymers. This increase could be explained by these lignins forming intermediates and reactive species that react with phenol to form covalent bonds at harsh basic conditions. Alternatively, this phenol may not have been covalently bound to the lignin, and instead been physically attached with the biopolymer through non-covalent interactions. However,

DOSY-NMR of the lignins (ESI Fig. S3†) showed that in DMSO-d_6, a solvent that forms strong hydrogen bonds with phenolic molecules and thus disfavours intermolecular interactions between lignin and phenol,[32] all phenolated lignins showed a unique diffusion behaviour in solution, suggesting that phenol was covalently bound to the polymeric scaffold and not just interacting with it physically.

Conclusions

We demonstrated that the aldehyde stabilization process previously used to maximize the production of monomers from lignin is also an effective tool for the controlled and simultaneous extraction and chemical modification of lignin. Furthermore, this process allows us to introduce functional groups on the lignin scaffold that were not originally present on the biopolymer and that could then be further modified. We notably demonstrated that this method offers the unique possibility to functionalize lignin with free aldehyde groups. This aldehyde functionalization could be used to strongly increase the reactivity of lignin towards phenolation in both acid and base-catalysed systems. The use of any fossil-based phenol as a solvent for phenolation reactions creates health and sustainability drawbacks. However, efforts are being made in order to minimize the impact of phenol by either sourcing the molecule from biobased feedstocks[33] or by developing resins where the phenolic part of said polymers are substituted by more sustainable and bio-based alternatives.[34–36] The increased reactivity of TALD-lignin in phenolation resins suggests that this kind of functionalization could be beneficial for the subsequent integration of a higher fraction of lignin into phenolic resins, which would not eliminate the use of fossil-based phenol but at least contribute to reducing its use. Because aldehydes are versatile chemical functionalities that can react under mild conditions to obtain a variety of other important functional groups such as amines, carboxylic acids and hydroxy groups, we believe that this work could expand lignin functionalization possibilities, and ultimately enable substituting fossil-based materials with renewable alternatives.

Conflicts of interest

SB and JSL are inventors on a European patent application (EP19202957) that was submitted by EPFL and covers the isolation of functionalized lignins *via* the aldehyde assisted process. JSL is co-founder and part owner of Bloom Biorenewables Ltd that aims at commercializing the aldehyde assisted fractionation process.

Acknowledgements

References

1 F. G. Calvo-Flores and J. A. Dobado, *ChemSusChem*, 2010, **3**, 1227–1235.
2 S. Kalami, N. Chen, H. Borazjani and M. Nejad, *Ind. Crops Prod.*, 2018, **125**, 520–528.
3 M. Lettner, F. Hesser, B. Hedeler, P. Schwarzbauer and T. Stern, *J. Cleaner Prod.*, 2020, **256**, 120520.
4 J. Li, J. Zhang, S. Zhang, Q. Gao, J. Li and W. Zhang, *Polymers*, 2017, **9**, 428.
5 J. Ralph, C. Lapierre and W. Boerjan, *Curr. Opin. Biotechnol.*, 2019, **56**, 240–249.
6 X. Wu, X. Fan, S. Xie, J. Lin, J. Cheng, Q. Zhang, L. Chen and Y. Wang, *Nat. Catal.*, 2018, **1**, 772–780.
7 A. E. Kazzaz and P. Fatehi, *Ind. Crops Prod.*, 2020, **154**, 112732.
8 A. Tribot, G. Amer, M. Abdou Alio, H. de Baynast, C. Delattre, A. Pons, J.-D. Mathias, J.-M. Callois, C. Vial, P. Michaud and C.-G. Dussap, *Eur. Polym. J.*, 2019, **112**, 228–240.
9 R. El Hage, N. Brosse, P. Sannigrahi and A. Ragauskas, *Polym. Degrad. Stab.*, 2010, **95**, 997–1003.
10 F. S. Chakar and A. J. Ragauskas, *Ind. Crops Prod.*, 2004, **20**, 131–141.
11 L. Shuai, M. Talebi Amiri and J. S. Luterbacher, *Curr. Opin. Green Sustainable Chem.*, 2016, **2**, 59–63.
12 M. Ghorbani, F. Liebner, H. W. G. van Herwijnen, L. Pfungen, M. Krahofer, E. Budjav and J. Konnerth, *BioResources*, 2016, **11**, 6727–6741.
13 M. Wang, M. Leitch and C. Xu, *Eur. Polym. J.*, 2009, **45**, 3380–3388.
14 S. Bertella and J. S. Luterbacher, *Trends Chem.*, 2020, **2**, 440–453.
15 F. Taleb, M. Ammar, M. ben Mosbah, R. ben Salem and Y. Moussaoui, *Sci. Rep.*, 2020, **10**, 11048.
16 M. Zhou, H. Shi, C. Li, X. Sheng, Y. Sun, M. Hou, M. Niu and X. Pan, *Ind. Eng. Chem. Res.*, 2020, **59**, 14296–14305.
17 J. Podschun, B. Saake and R. Lehnen, *Eur. Polym. J.*, 2015, **67**, 1–11.
18 L. Shuai, M. T. Amiri, Y. M. Questell-Santiago, F. Héroguel, Y. Li, H. Kim, R. Meilan, C. Chapple, J. Ralph and J. S. Luterbacher, *Science*, 2016, **354**, 329–333.
19 W. Lan, M. T. Amiri, C. M. Hunston and J. S. Luterbacher, *Angew. Chem., Int. Ed.*, 2018, **57**, 1356–1360.
20 G. R. Dick, S. Bertella and J. S. Luterbacher, Production of fragments of lignin with functional groups, EP19202957, 2019.
21 C. L. Perrin and K.-L. Chang, *J. Org. Chem.*, 2016, **81**, 5631–5635.
22 K. A. Goulas, M. Shiramizu, J. R. Lattner, B. Saha and D. G. Vlachos, *Appl. Catal., A*, 2018, **552**, 98–104.
23 G. Foyer, B.-H. Chanfi, D. Virieux, G. David and S. Caillol, *Eur. Polym. J.*, 2016, **77**, 65–74.

24 M. Talebi Amiri, G. R. Dick, Y. M. Questell-Santiago and J. S. Luterbacher, *Nat. Protoc.*, 2019, **14**, 921–954.

25 D. S. Zijlstra, A. de Santi, B. Oldenburger, J. de Vries, K. Barta and P. J. Deuss, *J. Visualized Exp.*, 2019, 58575.

26 S. Wang, W.-X. Li, Y.-Q. Yang, X. Chen, J. Ma, C. Chen, L.-P. Xiao and R.-C. Sun, *ChemSusChem*, 2020, **13**, 4548–4556.

27 M. M. Abu-Omar, K. Barta, G. T. Beckham, J. S. Luterbacher, J. Ralph, R. Rinaldi, Y. Román-Leshkov, J. S. M. Samec, B. F. Sels and F. Wang, *Energy Environ. Sci.*, 2021, **14**, 262–292.

28 M. Sultania, J. S. P. Rai and D. Srivastava, *Eur. Polym. J.*, 2010, **46**, 2019–2032.

29 J. Podschun, A. Stücker, B. Saake and R. Lehnen, *ACS Sustainable Chem. Eng.*, 2015, **3**, 2526–2532.

30 X. Meng, C. Crestini, H. Ben, N. Hao, Y. Pu, A. J. Ragauskas and D. S. Argyropoulos, *Nat. Protoc.*, 2019, **14**, 2627–2647.

31 C. Crestini, H. Lange, M. Sette and D. S. Argyropoulos, *Green Chem.*, 2017, **19**, 4104–4121.

32 V. G. Kontogianni, P. Charisiadis, A. Primikyri, C. G. Pappas, V. Exarchou, A. G. Tzakos and I. P. Gerothanassis, *Org. Biomol. Chem.*, 2013, **11**, 1013–1025.

33 X. Huang, J. M. Ludenhoff, M. Dirks, X. Ouyang, M. D. Boot and E. J. M. Hensen, *ACS Catal.*, 2018, **8**, 11184–11190.

34 A. E. Vithanage, E. Chowdhury, L. D. Alejo, P. C. Pomeroy, W. J. DeSisto, B. G. Frederick and W. M. Gramlich, *J. Appl. Polym. Sci.*, 2017, **134**, 44827.

35 W. Yang, L. Jiao, X. Wang, W. Wu, H. Lian and H. Dai, *Int. J. Biol. Macromol.*, 2021, **166**, 1312–1319.

36 L. Granado, R. Tavernier, S. Henry, R. O. Auke, G. Foyer, G. David and S. Caillol, *ACS Sustainable Chem. Eng.*, 2019, **7**, 7209–7217.