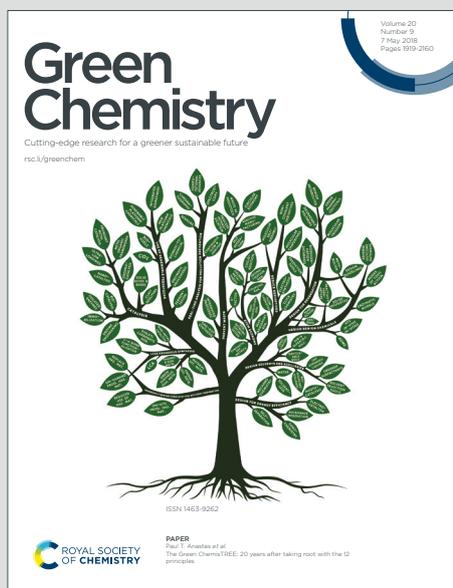


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Profiling of the Formation of Lignin-derived Monomers and Dimers from *Eucalyptus* Alkali

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Lignin

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Lignin is renewable and the most abundant aromatic sources that can be used for extensive chemicals and materials. Although approximately 50 million tons of lignin are produced annually as a by-product of the pulp and paper industry, it is currently underutilized. It is important to know the structural features of technical lignin when considering its application. In this work, we have demonstrated the formation of low-molecular-weight constituents from hardwood (*Eucalyptus*) lignin, which produces much more low-molecular constituents than softwood (spruce) lignin, after a chemical pulping process, and analyzed micromolecular compositions in the alkali lignin after fractionation by dichloromethane (DCM) extraction. By applying analytical methods (gel-permeation chromatography, 2D NMR and GC-MS) with the aid of evidence from authenticated compounds, a great treasure trove of lignin-derived phenolic compounds from *Eucalyptus* alkali lignin were disclosed. Except for some common monomeric products, as many as 15 new lignin-derived monomers and dimers including syringaglycerol, diarylmethane, 1,2-diarylethanes, 1,2-diarylethenes, (arylvinyl ether)-linked arylglycerol dimers and isomeric syringaresinols were identified in the DCM-soluble fraction. Regarding to the formation and evolution of C α -condensed β -aryl ether structure, a novel route that is potentially responsible for the high content of β -1 diarylethenes and diarylethanes in lignin low-molecular fraction, in addition to the β -1 (spirodienone) pathway, was proposed. This work not only provides novel insights into the chemical transformation of S-G lignin during alkali pulping process, but also discovered lignin-derived phenolic monomers and dimers that potentially can be used as raw materials in chemical or pharmaceutical industries.

Keywords: Structural characterization; Model compound; Depolymerization; Condensation; 2D HSQC NMR; Phenolic compounds.

1. Introduction

Lignin is the largest renewable aromatic source that has great potential to produce extensive chemicals, biofuels, functional materials and bioactive molecules.¹⁻⁵ It principally occurs in natural plants in the form of linear biomacromolecules with the main building blocks of *p*-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) units, and the chemical linkages of C-O and C-C bonds.⁶⁻¹⁰ The block units of lignin vary from wood species; for example, softwood lignin consists mostly of G unit and very low levels of H unit, whereas hardwood lignin is primarily composed of S and G units with traces of H unit.⁶ Among the interunit linkages, β -aryl ether bond (β -O-4) is most abundant and is relatively labile, providing a basis for chemical and industrial processes to convert lignin to low-molecular-weight value-added chemicals.^{4,11,12}

As for pulp and paper production, chemical pulping targets the manufacture of high-quality cellulosic fiber during chemical pulping processes, in which lignin is abundantly produced as a byproduct (approximately 50 million tons every year).¹³ During these processes, the harsh conditions applied result in a massive and intricate structural alteration of lignin, from depolymerization, condensation, and redox reactions.^{14,15} The majority of native ether bonds are destroyed, producing low-molecular-weight aromatic fragments as well as large polymers with various new unknown moieties. Degradation and condensation reactions during the pulping processes make the technical lignins even more inhomogeneous and structure-complicated; consequently, technical lignin valorization becomes more challenging.¹⁶⁻¹⁸

Many efforts, including employing various model compounds aided with advanced analytical techniques, have been directed toward unraveling the structural characteristics of technical lignins. These efforts have elucidated some of key pathways associated with the chemical evolution of lignin native structures (β -O-4 and β -5 and β - β) during pulping process,^{14,19,20} and provided many significant perspectives on the structural features of technical lignins, especially on the identification of various new chemical structures (styryl ethers, stilbenes, diarylmethanes, biaryl, diarsinol, arylglycerol, arylpropanol, reduced aryl ether, and condensed lactone etc.).^{15,16,21-24} Such findings are very helpful for lignin post-processing and valorization strategies. However, efficient valorization of lignin remains the most challenging part of biomass utilization. Thus, a deeper fundamental understanding of the characteristics of technical lignins, in particular with regard to the degradation products of lignin during pulping process, is of crucial importance.

Nowadays, lignin fractionation by using organic solvents prevails at the research stage.^{10,15,25,28,30-32} Such a strategy can fractionate the complicated lignin mixtures into relatively homogeneous fractions (in terms of molecular weight and structural functionality),²⁹ and have realized some proof-of-concept applications in polymer materials, pyrolytic oils and nano particles.³⁰⁻³² These works have provided some information on molecular weight, interunit linkages, end-groups, and the content of functional groups of different fractions. However, very limited research, only one literature reported so far, has touched on the small-molecular fraction (molecular weight <600 g/mol) from hardwood technical lignin.²⁷ Based on our knowledge of lignin structural studies, such fraction is presumably consists of lignin-derived monomeric and dimeric products, although the authors haven't mentioned that. If so, it will be of great importance for lignin valorization on account of their potential uses as functional chemicals or valuable precursors for the production of pharmaceuticals.

In this study, as a continuation of our alkali lignin structural studies, and to address the issues presented, we fractionated low-molecular-weight (low-Mw) material from *Eucalyptus* alkali lignin by an optimized organic solvent (dichloromethane, DCM) extraction, and then analyzed the lignin-derived monomers and dimers in this fraction via analytical techniques (detailed methods can be seen in Supplementary Information). In addition, several model compounds were designed and synthesized, and then used these model compounds as substrates to conduct pulping studies. The degradation products were then analyzed and identified to reveal the formation of such products during the pulping process.

2. Results and discussion

2.1 Structural fundamental for the formation of low-Mw fraction from hardwood lignin during chemical pulping processes

Lignin subunit composition and structure in plants varies from species. In general, hardwood lignins are composed of S and G units, whereas lignin in softwoods are made up of G units and small amounts of H units. Hardwood and softwood lignins are therefore highly different in their subunit compositions, thereby the interunit linkages and their consequent reactivities. In consideration of the valorization of technical lignin, it is of great importance to understand the variation in the nature of such lignins that originate from their inherent natural variation in lignin subunit composition and structure, as well as the production process. In this work, four different organic solvents (ethanol, acetone, ethyl acetate, and DCM) were employed to optimize the extraction process for low-Mw constituents from *Eucalyptus* alkali

lignin. By comparison, DCM showed a better selectivity for the extraction of low-Mw constituents (shown in Table 1). Thus, DCM was used for fractionation of low-Mw constituents in the following study. Interestingly, it was found that the *Eucalyptus* technical lignins contain a much higher content of DCM-soluble low-Mw fractions than the spruce (softwood) technical lignins (28.2% vs. 1.8% for alkali lignins and 43.7% vs. 2.4% for kraft lignins) (shown in Table 2). This difference can be interpreted by a different reactivity caused by the structural difference of hardwood and softwood lignins during chemical pulping process (Scheme 1).

Table 1 Content (wt.%) and molecular weights of the soluble fractions of *Eucalyptus* alkali lignin isolated by using various organic solvents.

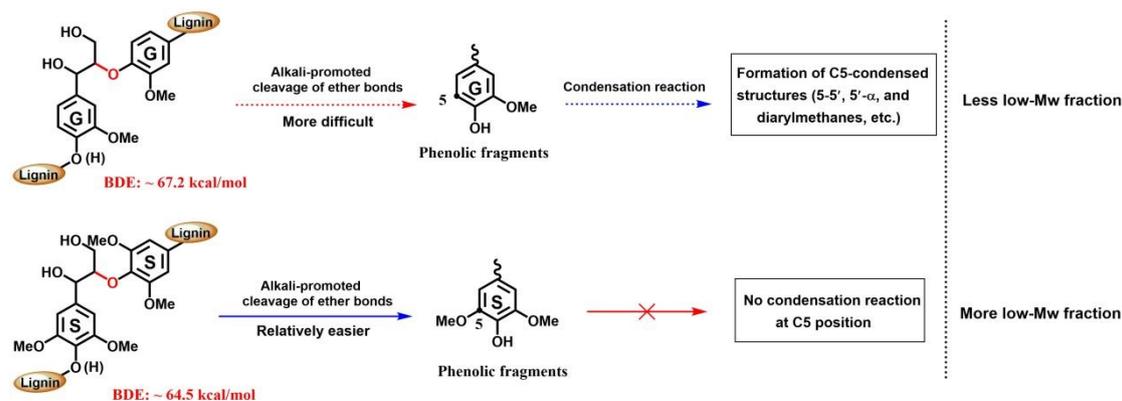
Solvents	Content	Molecular weight		
		Mw	Mn	PDI
Ethanol	74.8%	1821	951	1.91
Acetone	66.0%	1889	927	2.04
Ethyl acetate	43.5%	997	666	1.50
Dichloromethane	28.2%	780	569	1.37

Table 2 Content (wt.%) of DCM-soluble low-Mw fractions from alkali and kraft lignins.

Feedstock	Alkali lignin	Kraft lignin
Spruce	1.8%	2.4%
<i>Eucalyptus</i>	28.2%	43.7%

Despite of the much higher content of β -ether in hardwood lignins, two more reasons could be drawn forth (Scheme 1). First, the hardwood lignin is more easily depolymerized to produce more lignin-derived fragments in comparison to softwood lignin, due to the fact that β -aryl ether bonds formed by S units are easier to be cleaved than those composed of G units;^{33,34} This is supported by the result from density functional theory (DFT) calculation that the bond dissociation energy (BDE) of (S-S)-type β -aryl ether bond is lower than that of (G-G)-type β -aryl ether bond.^{35,36} On the other hand, S-type fragments are relatively stable as the C5 positions are substituted by methoxy groups, whereas the G-type fragments can be consumed by condensation reactions to form recalcitrant C-C linkages (5-5', 5- α' and

diarylmethanes) under alkaline pulping conditions.^{15,16,37} Hence, under the same pulping processes, technical lignins from hardwood should contain more low-Mw lignin-derived degradation products than those from softwood lignins.



Scheme 1 Schematic illustration for the different yields of the low-Mw aromatics from softwood and hardwood lignins after alkaline pulping process. Bond dissociation energies (BDEs) of β -O-4 units determined by density functional theory (DFT) were reported in the literature.³⁶

2.2 Structural features of low-Mw fractions of *Eucalyptus* alkali lignin

Molecular weight and molecular weight distribution. The gel-permeation chromatography (GPC) molecular weight distributions of *Eucalyptus* alkali and kraft lignins DCM-soluble/insoluble fractions are shown in Figure 1. Nine reference polystyrene samples with weight-average molecular weight in the range of 208-49000 g/mol were used for the molecular weight calibration of fractional lignins (Figure 1a). The Mw of DCM-soluble fractions extracted from alkali and kraft lignin were 780 g/mol and 694 g/mol, respectively. In contrast, the Mw of DCM-insoluble fractions were much higher, which were 5331 g/mol for alkali lignin and 1959 g/mol for kraft lignin, respectively. In the chromatogram of the DCM-soluble fraction from alkali lignin, two individual peaks at the retention time of 16.1 min and 16.6 min can be observed (Figure 1b) and the corresponding Mw values of these two peaks were 487 g/mol and 315 g/mol, indicating that the DCM-soluble fraction of alkali lignin is rich in monomeric and dimeric lignin compounds.³⁸ In addition, similar results are observed for the DCM-soluble fraction of kraft lignin, consistent with the above-mentioned mechanism (Scheme1).

For the DCM-soluble fraction of *Eucalyptus* kraft lignin, in spite of the higher content, it is normally highly sulfurized and its composition is difficult to authenticate by currently available techniques.^{2,39} Hence, the following work is focused on understanding the lignin small molecules from *Eucalyptus* alkali lignin, which is sulfur free and structurally much closer to the degradation products of native lignins.

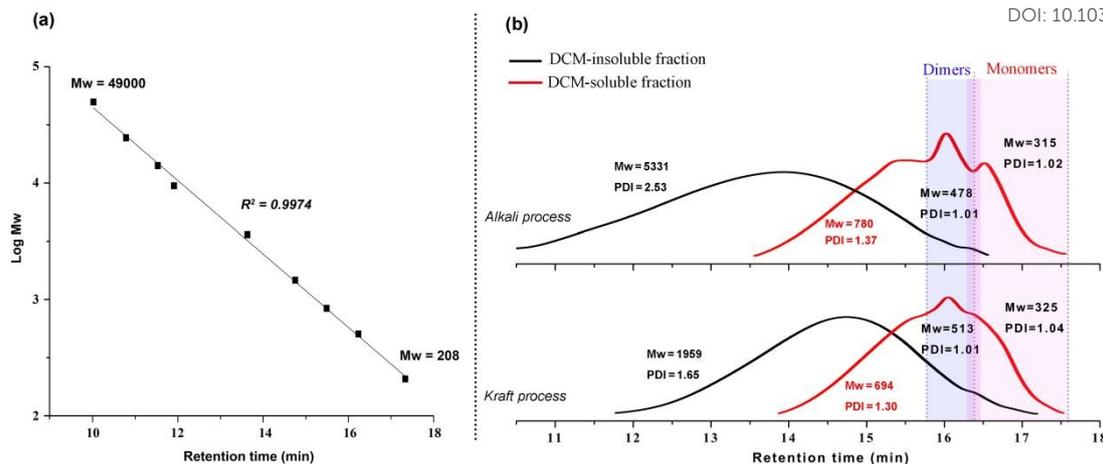


Figure 1 Molecular weight analysis of DCM-soluble/insoluble fractions from *Eucalyptus* alkali and kraft lignins. (a) The standard curve of polystyrenes for molecular weight calibration of lignin fractions; (b) the molecular weight distribution of DCM soluble/insoluble fractions.

Chemical linkages and end-groups. Cellulolytic enzyme lignin (CEL) was isolated from *Eucalyptus* and then analyzed by NMR to represent the native lignin of Eucalypts (Figure S1). The relative abundance of the substructures were calculated by integrating the contour volumes of the corresponding correlations in the HSQC spectra, and the percentages of each linkage were β -O-4 (**A**, β -aryl ether, 59.6%), β -5 (**B**, phenylcoumaran, 3.8%), β - β (**C**, resinol, 10.5%), and β -1 (**D**, spirodienone, 3.5%) linkages. In addition, low levels of cinnamyl alcohol (**CA**) and cinnamaldehyde (**J**) end-groups were also found in the CEL spectra, at around 1%. The S/G ratio was 2.6. It is obvious that the structure of the *Eucalyptus* lignin was significantly modified after the alkaline pulping process. Figure 2 shows the 2D HSQC NMR spectra of the high-Mw fraction (DCM-insoluble) and low-Mw fraction (DCM-soluble) from the alkali lignin. Apart from some remaining lignin substructures including β -O-4, resinol and cinnamyl alcohol, many new structures were observed and identified according to ^1H - ^{13}C cross peak assignment (Table S2).^{16,21,23,24,40-42} These structures include isomeric epiresinols (**C'**) and diarsinol (**C''**), arylglycerol (**Gly**), enol ethers (**E**), β -1/5 stilbenes (**SB**, or β -1/5 diarylethenes), β -1 diarylethane (**DE**), aryl propanol (**P**), and aldehyde and ketone end-groups. The semi-quantitative analysis of characteristic correlations was performed based on volume integration to indicate the relative abundance of structural units. Aromatic $S_{2,6}$ and G_2 peaks were chosen as the reference.

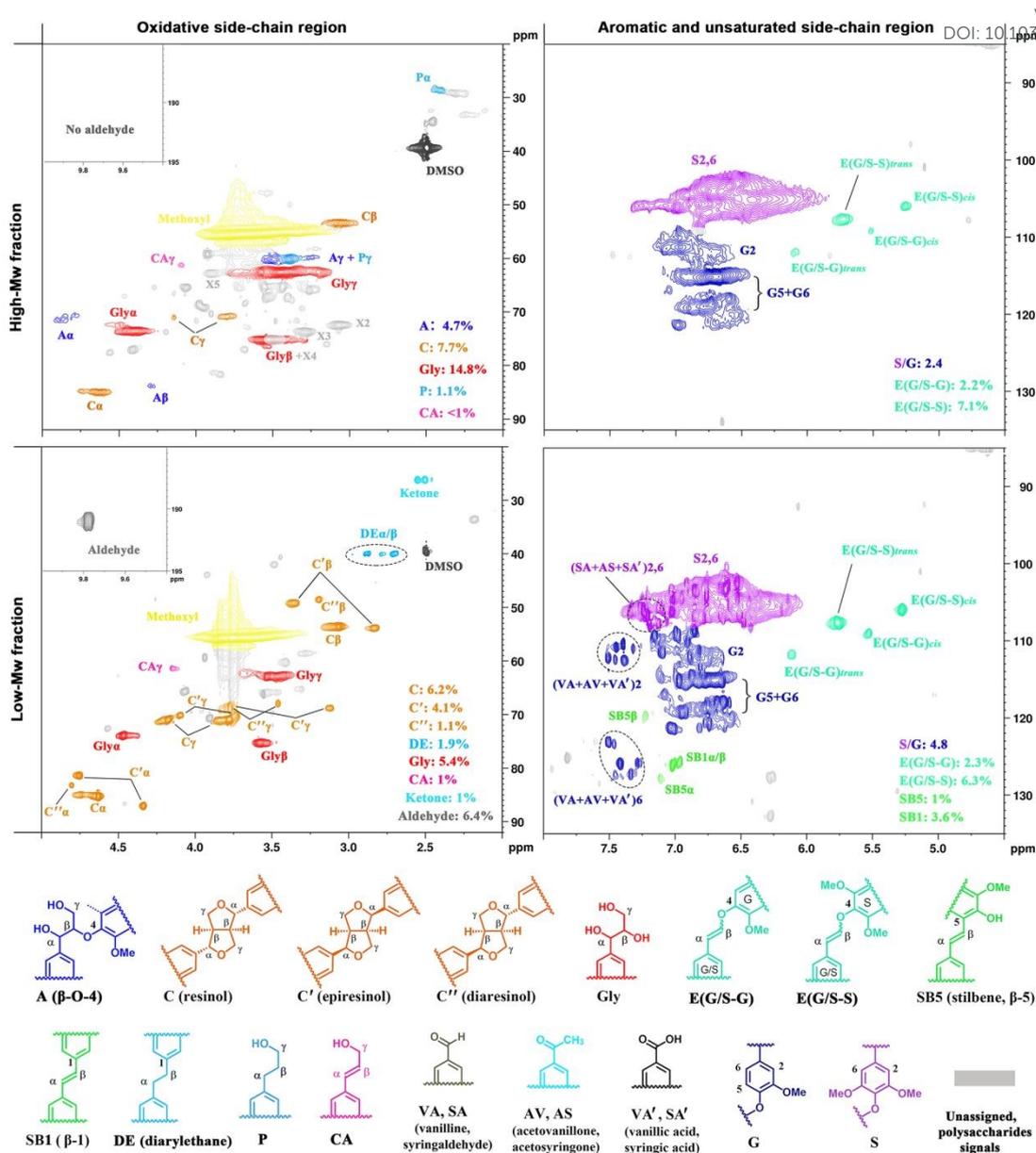


Figure 2 2D HSQC NMR spectra of high-Mw (DCM-insoluble) and low-Mw (DCM-soluble) fractions from *Eucalyptus* alkali lignin.

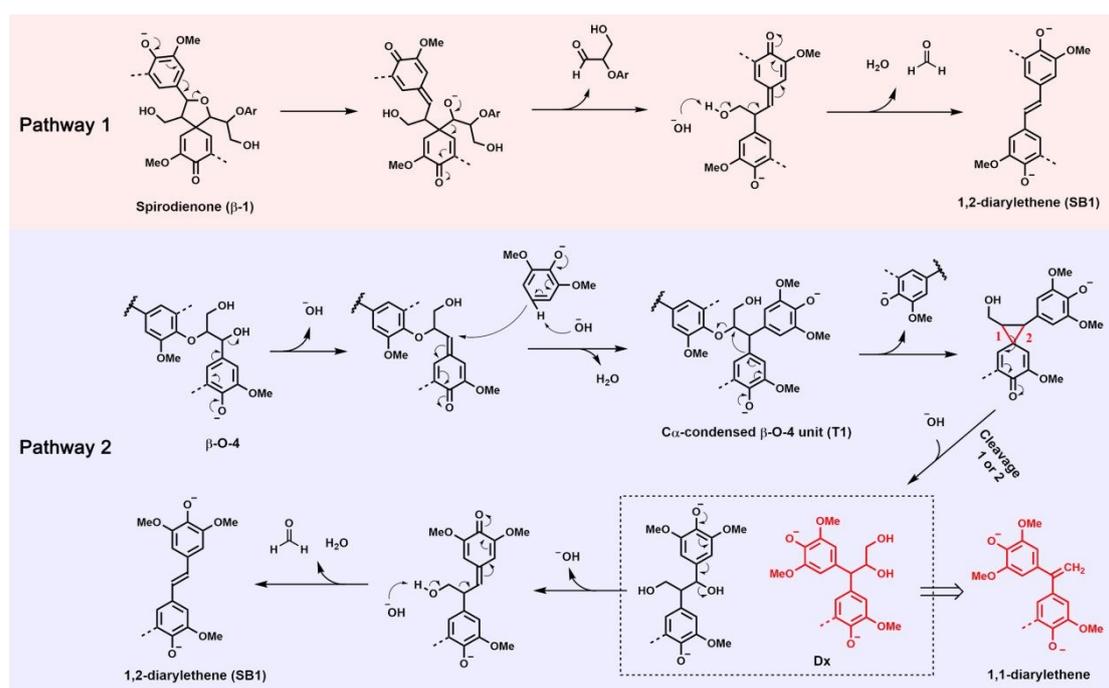
As shown in Figure 2, a very low level of native β -O-4 linkage was detected in high-Mw fraction of alkali lignin that accounts for 4.7% of all aromatic groups, whereas it was absent in the low-Mw fraction. Resinol structures are relatively stable in the alkaline media that can be observed in both high- and low-Mw fractions, although some of them were transformed into epiresinols and diarsinols. Such alkali-catalyzed epimerization occurs only when the associated phenolic groups are free.^{16,22} The epimers are easily identified in the spectrum of low-Mw fraction, but hardly observed in the high-Mw fraction. The total content of β - β -linked structures (resinol, epiresinol, and diarsinol) was 11.4% in low-Mw

fraction, which is much higher than that of the high-Mw fraction (7.7%). The possible reason is that these resinol-related units are easy to be released with the base-promoted depolymerization of hardwood lignin.

Gly and vinyl ether (or enol ether, **E**) structures come from the derivation of β -O-4 linkages through different reaction pathways based on the etherified or free nature of associated phenolic groups.^{20,39} These structures are significant, and prominently higher in alkali lignins than that of normal kraft lignins.²³ In line with the previous report,¹⁶ much more **Gly** presented in high-Mw fraction (14.8%) than that in low-Mw fraction (5.4%). This is because the stability of this end-group highly depends on the etherified phenolic nature whereas the high-Mw fraction contains more aryl ether bonds.²⁴ Except for *cis-trans* isomerism, vinyl ether linkages in hardwood alkali lignins have four different structural forms based on different combinations of G and S units. Unfortunately, it is difficult to distinguish these correlations from each other, the correlations of **E(G-G)** overlaps with the signals of **E(S-G)**, and the correlations of **E(G-S)** overlaps with the signals of **E(S-S)**.²⁴ Based on the analysis of the spectra, the content of vinyl ether linkage was in a comparable value (~9%) in two fractions, while the content of (G/S-S)-linked vinyl ethers was two times higher than that of (G/S-G)-linked vinyl ethers.

As condensed structures, β -1/5 diarylethenes (**SB1** and **SB5**) and β -1 diarylethane (**DE**) were identified in the low-Mw fraction, but are totally absent in the high-Mw fraction. **SB5** is formed by the degradation of phenylcoumaran,²⁵ and its content is very low due to the low levels of phenylcoumaran in hardwood native lignin. **SB1** accounts for 3.6% of all aromatics in the low-Mw fraction, which can be produced by β -1 unit (spirodienone) (Pathway 1 in Scheme 2).²⁵ Normally, it is found to be more in the highly-depolymerized lignin fraction, and is considered to be quite easily released from lignin polymer during chemical processes, potentially due to the quinoid end-group in spirodienone that restricts the chain branching.^{7,16} It is worth noting that a novel pathway differing from Pathway 1 might occur that accounts for the formation of **SB1** and **DE** structures. In this pathway, the (β -1)-condensed C-C linkages can be generated from β -O-4 linkages after formation of C α -condensed structure (**T1**) in alkali media (Pathway 2 in Scheme 2). A part of this pathway was proved previously.¹⁹ This pathway is supported by the reaction products of synthesized model compounds (simplified β -O-4 and C α -condensed model compounds) (Figure S2, S3 and S4). Although it is still difficult to distinguish the dominant pathway guiding the formation of **SB1** in hardwood alkali lignin, the pathway 2 can be an explanation for the high content of this structure in some softwood kraft lignins (4-7%),²⁵ because the content of spirodienone in softwood lignin is quite low.⁴³ β -1 diarylethanes (**DEs**), to the best of our knowledge, is first assigned in

the alkali lignin fraction (the dimeric diarylethane products also are identified by GC-MS in follow-up analysis). The methylene groups “-CH₂-” in **DEs** with different aromatic substituent groups have inverse cross signals (versus “=CH-” and “-CH₃”) at the ¹³C-¹H correlation of 39.8/2.74-2.29 ppm according to the synthesized reference compounds in literatures (Figure 2).^{40,41} Similar with **SB1**, this structure mainly distributes into the low-Mw fraction, accounting for about 2% of all aromatics. The presence of **DEs** implies that the formal reduction of quinone methide or **SB1** structure is possible in the complicated alkaline pulping system.



Scheme 2 Two possible pathways for the formation of diarylethenes during alkali pulping process.

Pathway 1 was previously proposed;²⁵ Pathway 2 is proposed based on the analysis of the products from related model compounds. 1,1-diarylethene was identified in the products of simplified $\text{C}\alpha$ -condensed model compound (Figure S3 and S4), whereas it was not observed neither in the 2D HSQC NMR spectra (according to the NMR data of its structural analogs⁴⁴) of all lignin fractions nor by the GC-MS analysis of the low-Mw lignin fraction (Section 2.4).

Aldehyde and ketone end-groups in alkali lignin are derived from alkali-catalyzed oxidation of aromatic side-chains.^{2,25} These groups are primarily present in the low-Mw fraction that are related to the vanillin (**VA**), syringaldehyde (**SA**), acetovanillone (**AV**) and acetosyringone (**AS**) identified in the HSQC spectrum of low-Mw fraction.

In comparison to the *Eucalyptus* CEL, the low-Mw fraction has a very high S/G ratio (4.8), whereas

the S/G ratio of high-Mw fraction (2.4) is slightly lower than that of CEL (2.6). This supports the point that the S-incorporated lignin fragments are more facile to depolymerize compared to G-incorporated lignin fragments during the chemical pulping process, as discussed above.

2.4 Identification of lignin-derived monomers and dimers in low-Mw fraction

The low-Mw fraction was subjected to acetylation to analyze the lignin monomers and dimers by GC-MS. Figure 3 shows the primary aromatic monomers identified in the low-Mw fraction. These monomers include guaiacol (**G1**), vanillin (**G2**), and acetovanillone (**G3**) constituted by G units, and syringol (**S1**), syringaldehyde (**S2**), acetosyringone (**S3**), and syringylglycerol (**S4**) constituted by S units. The S-type monomers had a significantly higher content than the G-type monomers. The total content of identified S-type monomers was 19.85 mg/g DCM-soluble fraction, whereas the total content of identified G-type monomers was 5.13 mg/g (Table S3). **G1** and **S1** can be produced by retro-aldol reaction of hardwood lignin in alkali media.¹⁵ **G2**, **G3**, **S2** and **S3** are the common products from the oxidative depolymerization of hardwood lignin.⁴⁵⁻⁴⁹ Vanillin has been reported to be isolated from kraft lignin.⁵⁰ **S4**, as a monomer with glycerol side-chain, was first identified in the hardwood alkali lignin with the aid of a reference compound. However, in consideration of its instability at high temperature under base conditions due to the presence of free-phenolic group, this compound was potentially generated after the pulping process (see the discussion below).

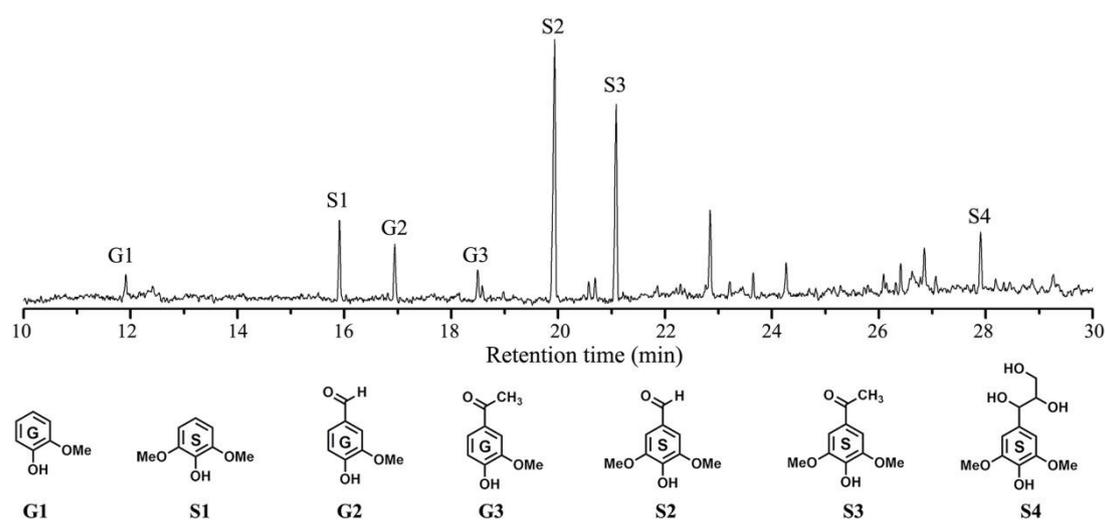


Figure 3 Aromatic monomers identified in the low-Mw fraction from *Eucalyptus* alkali lignin by GC-MS.

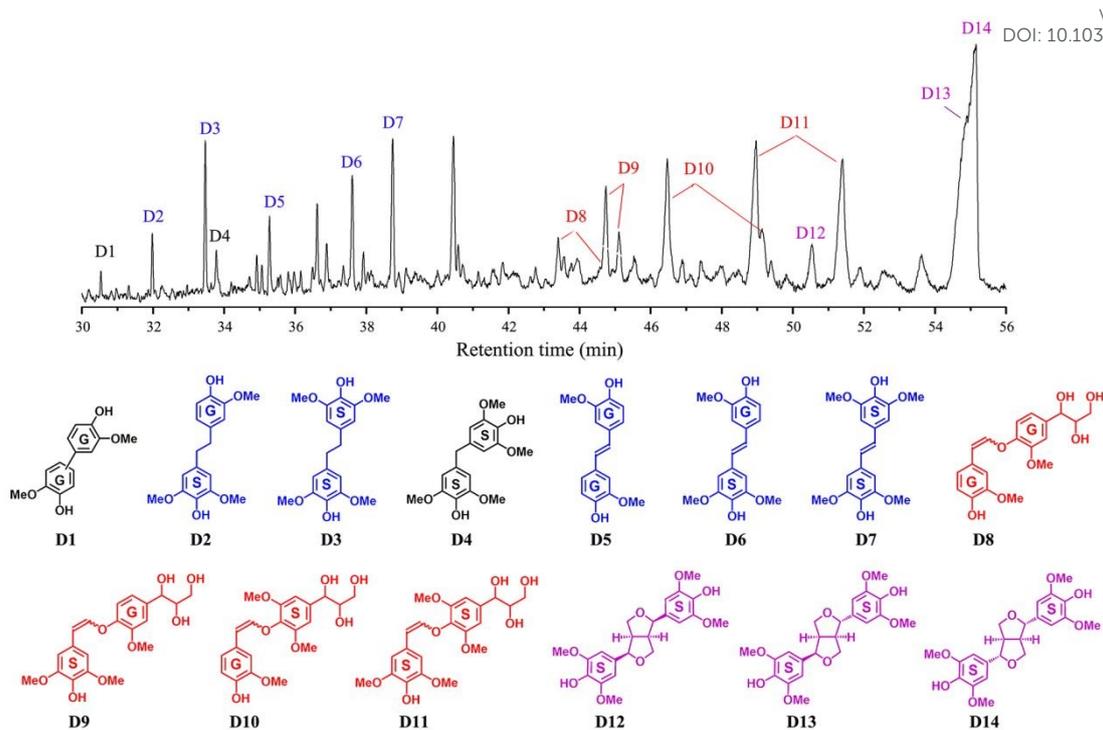
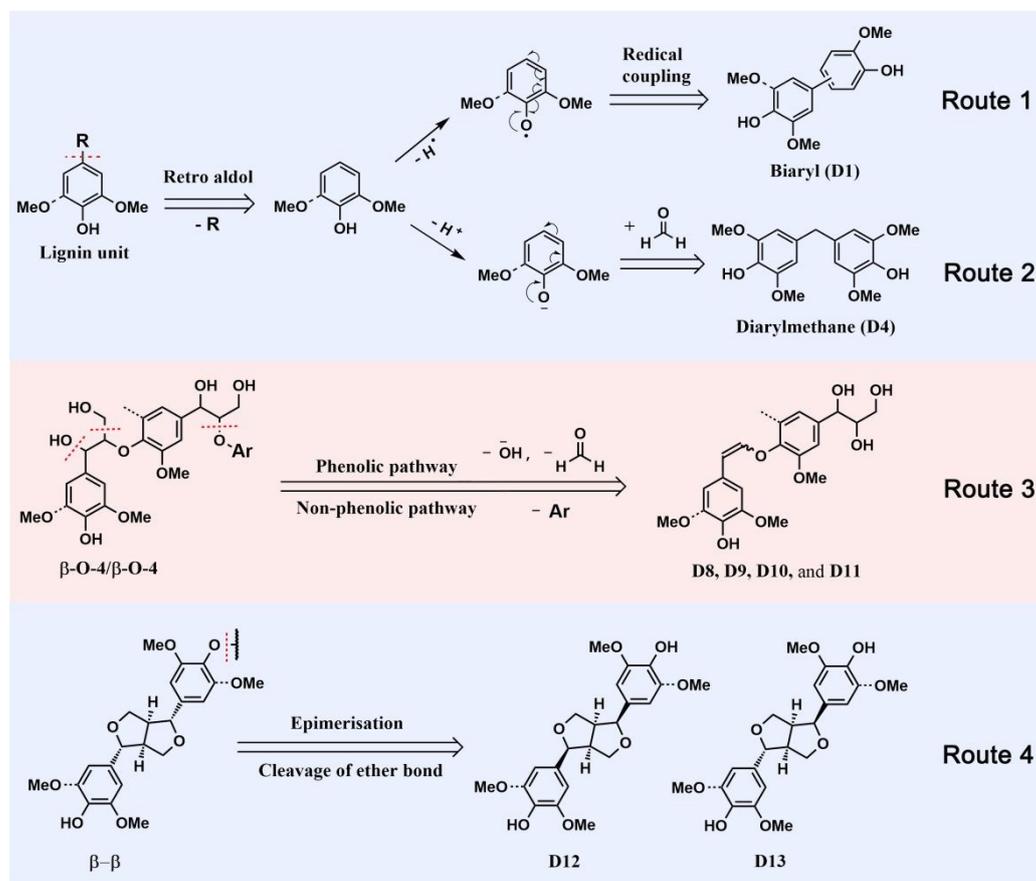


Figure 4 Lignin dimers identified in low-Mw fraction of the *Eucalyptus* alkali lignin by GC-MS.



Scheme 3 Possible routes for the formation of lignin-derived dimers during alkaline pulping process.

As shown in Figure 4, a total of fourteen lignin-derived dimers were identified in the low-Mw fraction of *Eucalyptus* alkali lignin (MS information seen in Section 2.2 in supplementary material). These compounds including biaryl compound (**D1**), 1,2-diarylethanes (**D2** and **D3**), diarylmethane (**D4**), diarylethenes (**D5**, **D6** and **D7**), (arylvinyl ether)-linked arylglycerols (**D8**, **D9**, **D10** and **D11**), and isomeric syringaresinols (**D12**, **D13** and **D14**). **D1** is produced by the radical coupling reaction of guaiacols produced by retro-aldol reaction of lignin under alkaline condition, in which the C1 and C5 positions are preferred for coupling reaction (Route 1, in Scheme 3).^{15,51} Diarylmethane is formed by the phenol-formaldehyde reaction,⁵² of which the formaldehyde can be produced by elimination of γ -CH₂OH in phenolic β -O-4 or β -5 structure. *trans*-(β -1)-Diarylethene and (β -1) diaryethane structures have been proved to be present in low-Mw fraction lignin by 2D HSQC NMR. The formation of these structures is related to two distinct pathways that have been discussed above (Scheme 2). Four (arylvinyl ether)-linked arylglycerols have a similar structure that contains vinyl ether linkage and glycerol side-chain, with different aromatic units. Apparently, the content of S-S enol ether linked dimer (**D11**) is the dominant component in four types of dimers, which is much higher than that of the dimers incorporating G units (**D8**, **D9** and **D10**), in agreement with the results from 2D HSQC NMR. Each dimer consists of *cis* and *trans* isomers that can be clearly identified in the chromatogram according to the MS information (Section 2.2, in supplementary material). These structural dimers can be produced by phenolic tandem β -aryl ether fragments (β -O-4/ β -O-4), in which one of the β -O-4 units undergoes the phenolic reaction pathway to form arylvinyl ether linkage, whereas the other β -O-4 unit suffers degradation reaction to produce a glycerol terminal unit following the non-phenolic pathway (Route 3). Although these dimers are notably identified, they are labile and tend to be degraded under acidic conditions or in air owing to the presence vinyl ether bonds,²⁴ which also explains the presence of phenolic arylglycerol monomer (**S4**) in the low-Mw fraction lignin. The original β - β units can undergo base-catalyzed epimerization to generate epiresinol and diaresinol once the associated phenolic group is generated from lignin depolymerization.¹⁶ From the GC-MS analysis, only isomeric syringaresinols were substantially identified, which can be interpreted by that (1) S monomers are more prone to form β - β linkage rather than G monomers during lignification;⁷ (2) The β -aryl ether bonds incorporating with S units are more sensitive to chemical processing.⁵³ In three resinol products, the syringaresinol (**D14**) is most abundant, followed by episyringaresinol (**D13**) and diasyringaresinol (**D12**), in accordance with the result from semiquantitative analysis by 2D NMR. Quantitative analysis by GC-MS shows that the content of

syringaresinol, episyringaresinol, and diasyringaresinol is 36.85 mg, 23.3 mg, and 5.69 mg of per gram DCM-soluble fraction, respectively (Table S3). View Article Online
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Overall, we have identified a series of lignin-derived monomers and dimers in low-Mw fraction isolated from *Eucalyptus* alkali lignin. It is meaningful not only for the fundamental understanding of chemical transformation of hardwood lignin during alkaline processing, but also for the potential industrial and medical applications for these identified aromatic small molecules. For instance, syringaresinols, which are normally obtained by chemical/biological synthetic strategies or by isolation from some special natural plants, are promising for preparation of epoxy-amine resins, and have anti-inflammatory and anti-microbial activities;^{54,58} Guaiacol, acetovanillone, vanillin, syringol, syringaldehyde, and acetosyringone are basic chemical raw materials with antioxidative/antibacterial properties;⁵⁹ Arylglycerols, diarylethanes, and diarylethenes with featured structures potentially can be used as pharmaceutical precursors.

Although this work hints a sustainable and low-cost supplementary source for these valuable chemicals and raw materials, the isolation and separation of these compounds are still challenging. DCM has shown a high selectivity for extraction of low-Mw fraction from technical lignins, whereas it is normally associated with acute and/or chronic toxicity in humans, and long-time half-life in environment.⁶⁰ These issues make it important to reduce the use of this undesirable solvent, and look for some greener alternative solvents, in consideration of the large-scale implementation in industry. In addition, the low-Mw fraction of alkali lignin is a quite complex product mixture (Figure 4), due to the structural complexity of lignin and the non-specificity of reactions involved in pulping process. The separation and purification of individual compound, to some extent, in a relatively pure form, is high-cost in consideration of diversiform constituents. Nevertheless, further fractionation protocols to screen the lignin-derived small molecules into a series of mixtures with various functionalities would be cost-efficiency to pave the way for more efficient valorization of this by-product.

3. Conclusion

Hardwood lignin, in comparison with softwood lignin, with abundant S units is more facile to be depolymerized during alkaline pulping, and also undergoes relatively low levels of condensation reaction due to the presence of the C5 substituent on S units. In this work, *Eucalyptus* alkali lignin was fractionated by dichloromethane extraction to afford a low-Mw fraction and a high-Mw fraction, and these two

fractions were analyzed. It was found that the substructures: epiresinol and diarsinol (with β - β linkages), β -1 condensed diarylethane and diarylethene units, as well as aldehyde and ketone end-group-derived units, were primarily present in the low-Mw fraction, whereas the content of arylglycerol was much higher in high-Mw fraction and the content of enol ether units were comparable in two fractions. A new pathway related to the formation and chemical production of α -condensed β -aryl ether structures was proposed that potentially explained the high content of β -1 type of diarylethane and diarylethene structures in the low-Mw fraction, in addition to the traditional reaction pathway from native spirodienone structures. By further analysis of the low-Mw fraction, a series of novel lignin-derived phenolic monomers (syringaglycerol) and dimers (including a biaryl dimer, a diarylmethane dimer, 1,2-diarylethanes, 1,2-diarylethenes, (arylvinyl ether)-linked arylglycerol dimers, and isomeric syringaresinols) were identified. The disclosure and identification of these lignin-derived phenolic products in quite substantial amounts in low-Mw fraction isolated from hardwood alkali lignin provides new insights of technical lignins, and thereby aids the development of efficient valorization strategies for the production of valuable chemicals or materials from industrial byproducts.

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Conflict of interest statement

There are no conflicts to declare.

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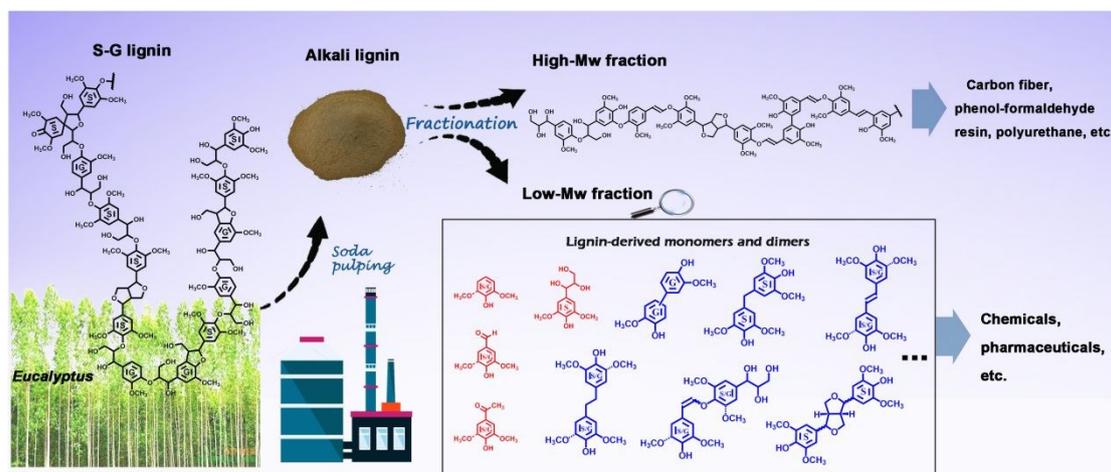
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Identification and mechanism study of lignin-derived monomers and dimers from fractionation of eucalyptus alkali lignin provide new insights into lignin valorization.