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Perspective on oligomeric products from lignin depolymerization: their generation, identification, and further valorization†

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The present contribution emphasizes the formation of oligomeric products in various depolymerization approaches of lignin, namely reductive catalytic fractionation, oxidative catalytic fractionation, and pyrolysis. Three possible routes to form such oligomers in these depolymerization processes are summarized and compared from various studies conducted on model compounds. Next, the main identification techniques for characterizing oligomeric products are highlighted. Particular focus is given to 2D-HSQC-NMR, GPC, Maldi-TOF-MS and FT-ICR-MS, which represent the state-of-art characterization of lignin. Special attention was paid to the transferability of these techniques for depolymerized oligomeric lignin. Finally, both the existing and expected potential lignin valorization routes are discussed for these oligomers, and technical hurdles and recommendations are provided in an attempt to catalyze the development of new discoveries and enabling technologies.

Keywords: Lignin oligomer; Reductive and oxidative depolymerization; Biofuels; Characterization techniques; Lignin valorization.

1 Introduction

With the emphasis on transitioning away from fossil fuels and petroleum-based products, more and more research has moved toward exploiting renewable natural resources, and great interest has grown in applying the principles of "green chemistry" to valorize these materials, particularly *via* conversion to chemicals.[1,2] Among the four source-independent categories of renewable materials (polysaccharides, lignin, triglycerides, and proteins), lignin is challenging to break down into chemically useful fragments, while the rest are relatively easy to decompose into their constituent building blocks.[1,3–5] It is believed that natural lignin is an amorphous three-dimensional polymer comprising methoxylated phenylpropane structures, crossed-linked by C–O–C (β-O-4, α-O-4, 4-O-5) and C–C (β-1, β–β, 5–5) bonds.[6] This structure intrinsically presents a unique challenge regarding its characterization, which then significantly hampered the establishment of lignin chemistry (*e.g.* radical-induced repolymerization). However, a progressive development of relative conversion technologies has been accomplished over the years;[7–9] this is motivated by the fact that around 100 billion tons of lignin are naturally synthesized among plants in the biosphere, and approximately 1 billion is industrially produced per year as the side products.[10,11] According to the existing pathways, various valuable chemical compounds can be produced through chemical treatments that aim to break down the lignin into low-molecular fragments; therefore, these depolymerization processes have recently drawn increasing attention in the field of lignin valorization.[2,3,12,13]

Common targeted products from lignin depolymerization are monomeric phenols, aromatics, cycloalkanes, and dicarboxylic acids.[12,14,15] The large-scale of one such process can be exemplified by the industrial production of vanillin through oxidative catalytic depolymerization (OCD).[13,16] The relatively low-cost of the substrate and the ease of operation counteract the fact that the yield of vanillin is often not high,[3,17,18] which overall still makes this process economically viable.[18] The same logic, however, may not be well applied to other lignin-valorization routes, such as reductive catalytic depolymerization (RCD), which is often a pre-treatment of lignin (*via* hydrogenolysis) if the final products are fuel-ranged cycloalkanes.[19–21] A similar dilemma also exists in the thermochemical treatment of lignin, from

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which the pyrolysis process can yield only less than 15 wt% of monomeric phenolic compounds, leading to the rest of the products full of oligomeric phenols that are not GC-detectable.[22,23] Regardless of the chemical treatments, oligomeric fractions from any lignin depolymerization are inevitably formed as the side products, and in many cases, can be the major products as well (Fig. 1). The inherent causes, although not very clear so far, have been extensively discussed in many studies.[9,24–27] One of the commonly agreed viewpoints is the unavoidable participation of the crosslinking/repolymerization reactions during the proceeding of various lignin depolymerizations.[28,29] Major efforts have been made to mitigate the rate of repolymerization for the individual process by 1) enhancing the efficiency of hydrogen transfer for RCD, 2) lowering the temperature for OCD, and 3) reducing the residence time for pyrolysis.[30–36] All these attempts, however, could not eliminate the oligomers as the side products and therefore diverted our attention from studying pristine lignin to depolymerized lignin oligomers.

Currently, the available instrumental analysis of the oligomeric products from lignin depolymerization is usually inadequate because such products are neither volatile enough to be detected by gas chromatography techniques nor inherently heterogenous enough to be identified through the combined column separation and spectroscopy systems. A similar issue was previously identified to initialize the characterization of native lignin (*e.g.* lignin biosynthesis) but later circumvented by introducing the NMR techniques, in which a well-accepted protocol for analyzing the most common six interunit linkages in natural lignin was established.[37,38] It is still ambiguous, however, whether such methods are well suited to characterizing the oligomeric products after depolymerization. As evidenced by model compound studies, there should be new chemical bonds presented in these oligomers based on the hypothesis that many of them are re-coupling and re-condensation products during depolymerizations. Therefore, in this short review, the current state-of-art instrumental analysis of these oligomeric products from lignin depolymerization is detailed, and our discussion focuses on the transferability of the techniques for natural lignin to the depolymerized oligomers in various processes. In addition, the current and existing valorization routes for the oligomers are listed and compared. Products that are derived from any other processes that are not designed for the depolymerization of lignin, such as industrial lignin generation and black liquor from the pulp industry, are beyond this scope and are not discussed in this review.

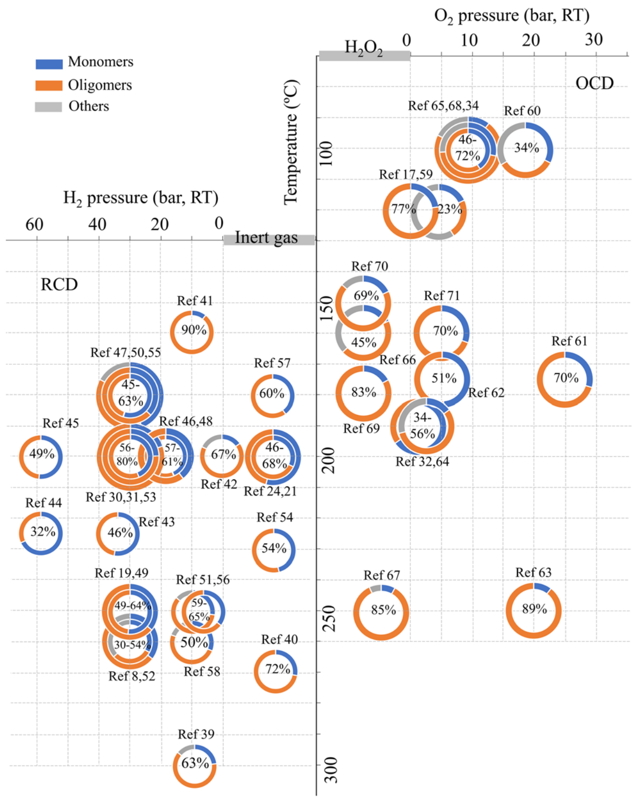

Fig. 1 The yields of oligomeric products (orange-colored, the weight percentages of the oligomeric fractions are indicated inside the pie charts) from various reported depolymerization processes of lignin.[8,17,19,21,24,30–32,34,39–71]

2 The generation of oligomeric products

2.1 Comparison between petro-based hydrocracking and lignin-based cracking and depolymerization

In the petro-based sector, the thermal cracking or hydrocracking-induced reactions were ensembled similarly to lignin depolymerization and were put together for comparison. The process is used to convert larger hydrocarbon molecules into smaller molecules under high hydrogen pressure and high temperature.[72,73] Hydrocracking of saturated hydrocarbons could proceed by several mechanisms depending on the catalyst functionality.[74,75] Even without a catalyst, thermal cracking occurs in chain reactions *via* radicals, in which β-scission is widely identified as the initiation step.[76,77] Similar techniques were applied to lignin cracking or hydrocracking, in which fast pyrolysis and reductive catalytic fractionation or hydrogenolysis were developed. Under hydrocracking conditions, the aryl ether and unstable C–C bonds from the lignin structure are cleaved, often followed by hydro-dealkylation leading to the rupture of the alkyl side chain groups linked to the aromatic rings. A peculiarity in the lignin structure, however, is the pronounced presence of the hydroxyl group.[78] Efficient oxidation leads to the formation of carbonyls that could result in the depolymerization of lignin, which is not derived from the petro-sector.[3,79] The redox-neutral depolymerization is another noteworthy approach for lignin because it is a tandem catalytic dehydrogenation (oxidation)/C–O bond cleavage (reduction) that requires no added reagent.[80] Several pioneered studies have indicated that the redox-neutral approach could also cleave the C–C bond (evidenced by lignin model compounds) with proper metal catalysts and ligands.[81,82] Such a catalytic system has been applied to depolymerize dioxasolv lignin and alkaline lignin, affording aromatic ketones as the major monomer products.[82,83]

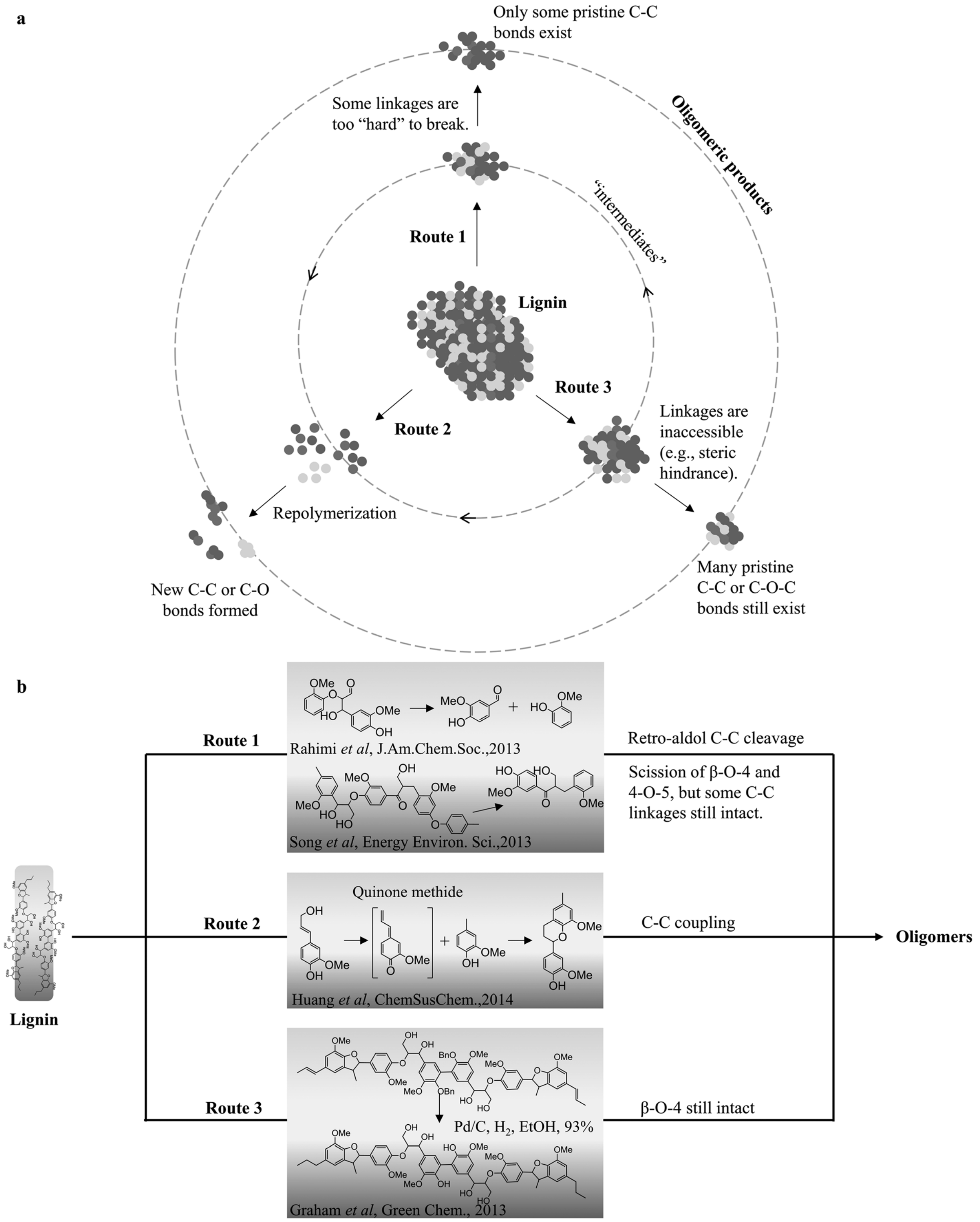

Fig. 2 The proposed routes for the formation of oligomeric products during lignin depolymerization (a), evidenced by the respective model compound studies (b).[24,39,79,90]

2.2 The chemistries during the formation of oligomeric products (thermally, reductively, oxidatively and redox-neutrally)

Extensive studies have reported that solid residues/char from various lignin depolymerization results from the repolymerization of the active lignin intermediates (monomers or oligomers). It is generally believed that lignin repolymerization occurs through the reaction of the lignin intermediate with electron-rich carbon atoms, such as the C-2 and C-6 of guaiacyl and syringyl rings, promoting the formation of new C–C linkages.[24,37,47] However, it is not that explicit if the formation of tar-like lignin products (*e.g.* lignin oil and bio-oil) is solely due to the repolymerization as char; or simply a stabilization of those intermediates with the desired active agents, such as hydride, hydroxyl radical; or other small radical components (alkyl groups). Huang *et al.* investigated the effect of reaction time on the possible repolymerization during the catalytic depolymerization of alkali lignin in ethanol.[39] The results indicate that the yield of the monomers and non-monomeric lignin oil (THF soluble tar) significantly increases with the extended reaction time, implying that tar is more likely from the forward depolymerization instead of the repolymerization. Studies from pyrolysis also suggest that both the phenolic hydroxyl group and unsaturated side chains are the most reactive structures present in the primary tar fraction.[35,84–86] These chemical structures play an important role in repolymerization chemistry.[39,86] It was particularly pointed out that the new carbon–carbon bonds are normally formed on the *ortho*- and *para*-positions *via* nucleophilic attack to the quinone methide intermediates during the condensation of many phenolic model compounds.[84,86,87] The steric hindrance plays a role in oxidative cleavage reactions. Several possible routes that may lead to the formation of lignin oligomers are summarized in Fig. 2. Depending on the conditions, the final pathway for the formation of these oligomers can be a combination of various routes. For instance, under pyrolysis conditions, lignins are more likely to undergo all the routes and form the pyrolytic lignin, while route 1 or 3 is more often proposed in oxidative and the redox-neutral depolymerization of lignin depending on the reaction severity. In the case of RCD of lignin, route 3 is likely to prevail under low temperature, while higher temperature reportedly induces more of route 1 during depolymerization. Figueirêdo *et al.* used principal component analysis to confirm that temperature is a crucial parameter for the depolymerization of pyrolytic lignin.[88] Using various wet chemical and spectroscopic methods, the pyrolytic lignin structure was elucidated by Bayerbach *et al.*, who concluded that these oligomers emerge because of both recombination reactions (route 2) and thermal ejection of intact lignin fragments (route 3).[89] For the oligomeric products from either RCD or OCD, it is still a debatable topic on exactly how they are generated at various reaction conditions, and advanced techniques are needed for detailed characterization to gain a better understanding of the types and nature of these oligomers.

3 Identification of oligomeric products

3.1 The state-of-art

The state-of-the-art methods for characterizing these oligomeric products are Two-dimensional Heteronuclear Single Quantum Coherence nuclear magnetic resonance (2D-HSQC-NMR), gel permeation chromatography (GPC), matrix-assisted laser desorption/ionization-time of flight mass spectrometry (Maldi-TOF-MS), LTQ Orbitrap mass spectrometry (Elite) and Fourier-transform ion cyclotron resonance mass spectrometry(FT-ICR-MS), combined with other less informative instrumental analyses, such as UV/vis, UV-florescence, pyrolysis gas chromatography mass spectrum (py-GCMS), elemental analysis, thermogravimetric analysis (TGA) and Fourier-transform infrared spectroscopy(FTIR). It is desirable to identify each oligomer in the depolymerization products. A detailed comparison of the advantages and disadvantages of each technique has been thoroughly discussed in previous reviews. This paper focuses specifically on the recent developments in the characterization of oligomeric lignin products in this section.[91,92]

3.1.1 Chromatographic techniques (HPLC-MS, GC × GC–MS). Owing to the large molecular weights of various lignin substrates, there are so far no identification techniques available that can provide complete structural information on these natural polymers. However, the depolymerization products of lignins, although diverse, can sometimes be a mixture of small monomers (such as phenol or guaiacol), which can be readily identified and even quantified by gas or liquid chromatography when attached to a mass spectrometer (such as GC–MS or HPLC–MS). The basic idea is that the depolymerized product mixture undergoes an effective separation through a column, and then each separated compound is transferred into the mass spectrometer for subsequent fragmentation. The fragmentation induced by the ionization of the molecule results in the formation of a characteristic mass spectrum for each compound with the information of the respective ionic fragment. In theory, such mass spectrum for each molecule should be unique and therefore offer the feasibility of identifying an unknown by solely comparing it with a known spectrum database. The comparisons are normally achieved using a database or library established with the mass spectrums of all the relevant commercially available chemical references. The higher the matching probability between the unknown and a known chemical, the more reliable the identification. Because most oligomeric products from lignin depolymerization are commercially unavailable, further identification can only rely on interpreting their mass spectrums, which can be very challenging owing to the complexity of the fragmentation chemistry of the oligomers. These techniques are therefore only limited to mostly lignin dimers, while the molecular size larger than a trimer is normally not detected by the GC–MS system. More often, a pre-derivatization *via* trimethylsilylation is used to improve the volatility needed to make the dimers GC-detectable.[19]

Until recently, GC × GC-MS or FID had been extensively applied in determining the dimers and trimers of lignin depolymerization products, but this technique is unsuitable for larger oligomers, which remain unidentified.[27,39,88] LC–MS or HPLC–MS systems can separate oligomers to identify any known compounds. In practice, however, many unfamiliar molecular ion profiles are detected for the oligomeric lignin products, hampering their further identification. Synthetic model compounds are required to establish a database of oligomeric MS to make this analysis possible. Contrary to conventional liquid chromatography, supercritical fluid chromatography (SFC) uses supercritical CO_2 as the mobile phase.[93] To efficiently separate lignin oligomers, the SFC is often combined with reversed phase liquid chromatography.[94] More recently, the newest protocol using the SFC to characterize lignin dimers has been developed and validated. The chromatogram showed baseline separation of all reference compounds in less than 10 min, and the response factors of the tested dimers did not differ significantly from one another, suggesting that this strategy is well suited for quantifying lignin dimers and oligomers.[95]

3.1.2 Molecular weight characterization (GPCMaldi-LC-MS, LTQ-Orbitrap Elite, ESI-MS, and FT-ICR-MS). Another important index for characterizing these oligomeric products is the profile of their molecular weight (or molecular mass) distribution. The resulting average molecular weight is often used to measure the extent of depolymerization. Although several approaches, including GPC, Maldi-TOF, ESI-MS, and FT-ICR-MS, are often used for such purposes, so far, there is no census as to which approach would provide the most representative molecular weight of the lignin and its depolymerized oligomers. Both ESI-MS and Maldi-TOF are based on "soft ionization" methods in which ion formation does not lead to a significant loss of sample integrity. In general, mass spectrometry can provide structural information for many large molecules, such as peptides, and it is possible to determine known compounds quantitatively, especially when combined with chromatography. Owing to the complex nature of the lignin matrix, the resulting oligomers are often unknown; therefore, it is more common to conduct a semiquantitative evaluation with these mass spectrometry-based techniques.

The GPC has also been used extensively to characterize the molecular weight distribution although the mechanism differs from the MS-based techniques. In general, a set of standards is needed to calibrate the peaks arising from the GPC of an unknown sample. Often, a series of polystyrene standards are well accepted for use for such purposes, although they may not simulate the targeted lignin oligomers because of the distinct polarity and topological structure. For oligomeric lignin, the solvents are used to recover the product matter in terms of the resulting molecular weight that is reflected by the GPC. Van den Bosch *et al.* characterized the resulting oligomeric products that are recovered by dichloromethane from the RCD of Birch lignin. The GPC showed two major signals at *circa* 200 and 450 g mol^{-1} (based on polystyrene standards), suggesting successful depolymerization as the signal of the proto birch lignin appears above at least 1000 g mol^{-1}.[19] Huang *et al.* found that their oligomeric products recovered with THF (tetrahydrofuran) showed a molecular weight of around 900 g mol^{-1}.[39] One of the advantages of analyzing the oligomers is the avoided pre-derivatization step that is required for the natural lignin to increase the sample solubility in the eluent. It was proven that the THF can dissolve oligomers with a wide range of molecular weight, as evidenced by the work from Joffres *et al.*[96] They characterized the oligomeric products (THF soluble) from depolymerization of a wheat straw soda lignin and concluded a bimodal distribution that the oligomers on average comprise 13 phenyl units compared to 27 units for the initial lignin.[96] Similar bimodal distribution was also confirmed by the work from the Rinaldi group; the apparent molecular weight of the oligomeric lignin products was centered at approximately 300 and 1250 Da compared with the wide monomodal distribution for the original lignin with the M_w greater than 3000 Da.[97] In addition to the main contribution to the reductively produced oligomers, GPC analysis also confirmed the presence of similar-sized molecules as the side products in oxidative and pyrolysis processes. For instance, Hafezisefat *et al.* used GPC to demonstrate the effectiveness of their oxidative depolymerization route in which the average molecular weight of the products could decrease from 511 Da to 287 Da, whereas the one from the reference (inert gas environment) increased from 505 Da to 661 Da.[63] In addition, the oligomers from lignin pyrolysis had also been characterized by GPC, and many results indicated that the average molecular weight of the oligomeric products was in the range of 200–1000 g mol^{-1}.[98–101] Owing to the usage of other calibrants (high MW lignin oligomers are not commercially available), there are some uncertainty in the reported MW values from GPC analysis, and sometimes the results are merely comparative.[102] This is because the separation in the GPC is not only driven by size exclusion but also by other interactions occurring because of lignin's heteropolymer nature and diverse functional groups.[103–105] Therefore, the usage of the polystyrene standards cannot emulate the non-size-specific interactions and thus may result in a misleading calibration.

Unlike GPC, which relies heavily on the standards to calibrate, MS-based techniques are mostly considered direct measurements because each molecule can be individually estimated in theory. The accuracy and precision of the MS-based method, however, highly depend on the completeness of the ionization of all the oligomeric products. The ionization of lignin and its depolymerized products is significantly affected by the ionization interface, as pointed out in the work by Finch *et al.*[106] They found that intense responses were obtained under positive APCI or negative ESI conditions. This result agrees with other similar studies in which only the negative ESI mode mass spectrometry was used to represent the lignin oligomers derived from the pyrolysis route.[107,108] Kong *et al.* also discussed the limitation of using APPI ionization for the FT-ICR-MS characterization because only the species with molecular weights between 150 and 700 Da were counted from lignin depolymerization. This was due to the limited boiling point of the APPI.[109] To compare the effect of depolymerization conditions, many reported ESI-MS data generally suggest that there is no distinct distribution in molecular weight for the oligomeric products from oxidative and reductive route.[20,70] More recently, FT-ICR-MS and Maldi-TOF have received more attention for the characterization of the lignin depolymerization products because of their improved accuracy or enhanced reliability.[110] Owing to the accuracy of the FT-ICR-MS, results can often be used to derive the molecular formula of components; then, the weighted average of carbon atom number, hydrogen atom number, oxygen atom number, and sulfur atom number can be calculated to form van Krevelen diagrams or other plots, such as heat maps, Kendrick mass defect, and carbon number *versus* double bond equivalent (DBE), to enhance the processing of the acquired data.[91,111] Huber's group recently used the FT-ICR-MS data to plot the carbon number *vs.* DBE of the lignin oligomeric products and identified four main clusters corresponding to dimers (20 C, 10 DBE), trimers (30 C, 15 DBE), tetramers (39 C, 21 DBE), and pentamers (49 C, 25 DBE).[112] Paananen *et al.* conducted a base-catalyzed oxidative depolymerization of Kraft lignin (softwood), and the FT-ICR-MS of the oxidation products showed the disappearance of signals over *m*/*z* 500, implying the efficient depolymerization of high-mass oligomers.[110] A similar phenomenon was also reported by Zhang *et al.* in which catalytic transfer hydrogenolysis (RCD) was employed instead of oxidative depolymerization. Their FT-ICR-MS showed that the signal at *m*/*z* was over 500 and weakened after the hydrogenolysis of the Kraft lignin.[113] Song *et al.* employed the Maldi-TOF technique to analyze oligomeric fractions from lignin alcoholysis (methanol) and indicated that the depolymerized products with molecular weight from *m*/*z* *ca.* 1100 to *ca.* 1600.[24] In addition, Liu *et al.* detected oligomers with molecular weight mainly located from 248 to 496 *m*/*z* by Maldi-TOF from isopropanol-assisted lignin depolymerization.[114] The molecular weight of the products from various depolymerization processes of lignin is displayed in Fig. 3. No direct relationship was observed between the temperature and the average molecular weight of the oligomers. For both techniques, the limitation of elucidating the structural information of the oligomers is due to the lack of standards for various lignin fragments. An attempt has been made to address the issue by some pioneer studies, in which a computational stochastic method was proposed to generate a molecular library for lignin that was used for supporting the assignment of potential candidate structures to compounds detected during FT-ICR-MS analysis.[25] More recently, the LTQ orbitrap mass spectrometer is considered an alternative to FT-ICR-MS owing to its low operating cost. Although the mass resolution of orbitrap mass spectrometers is lower than that of FT-ICR-MS, the resolution for both Orbitrap Velos and Orbitrap Elite is sufficient to characterize the oligomers from pyrolysis oil.[115]

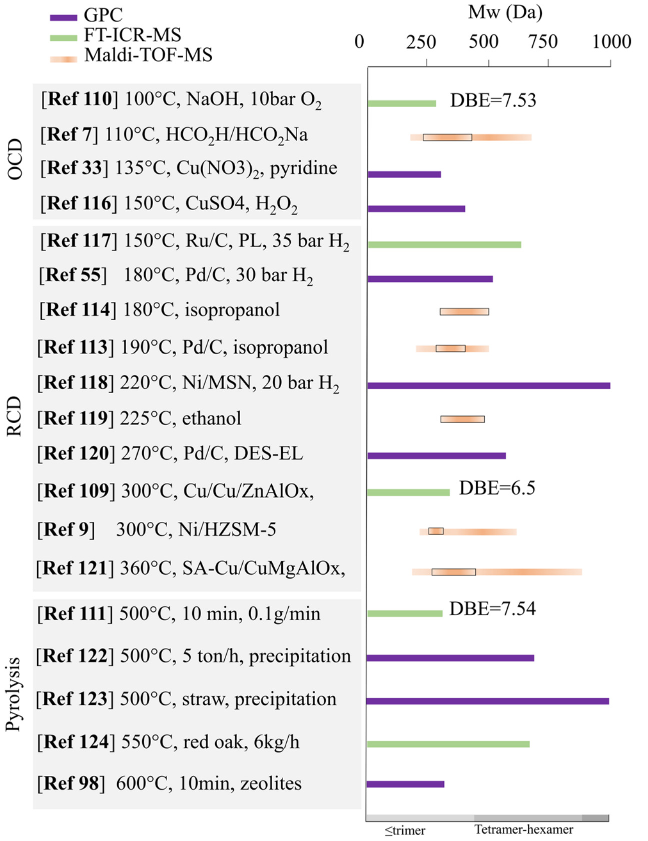

Fig. 3 Molecular weight distribution (Maldi-TOF-MS) or the average molecular weight (GPC or FT-ICR-MS with the double bond equivalent value) for the products from various lignin depolymerization processes.[7,9,33,55,98,109–111,113,114,116–124]

3.1.3 2D-NMR. As the most useful technique, 2D-^{1}H–^{13}C NMR, specifically their HSQC, has been extensively used to characterize the interunit linkages of many lignin oligomers.[67,120,125,126] Ideally, the 2D-HSQC spectra provide some information on the bond linkage between ^{1}H and ^{13}C. However, ^{13}C has a natural abundance of just over 1%, and the major isotope (^{12}C) is not NMR active, so very little proton signal is coupled.[127] Owing to the weak sensitivity of the ^{13}C nuclei, a very long relaxation delay is needed, and the signal-to-noise often remains poor even with very long acquisition times, thereby jeopardizing attempts to obtain reliable quantitative data.[127] However, the 2D-HSQC is still considered state-of-the-art because it is the main technique used to identify the major interunit linkages, mainly β-O-4, β–β, β-5 and α-O-4, which had been confirmed by the respective model compounds. Additionally, this method is believed to be more effective in semi-quantifying the individual G/S/H unit and also G/S ratio in various lignins.[128] For absolute quantification of the linkages and pendant units of lignin by 2D HSQC NMR spectra, it is still challenging as the signal integrations can be influenced by many parameters, such as T1 and T2 relaxation rates, carbon pulse offset effects, and multiplicity and magnitude of coupling constants.[129,130] Fig. 4 indicates the general identification of the interunit linkages in real lignin and the products from depolymerization by the 2D-NMR-HSQC method that was reported recently. For the oligomers from lignin depolymerization, many 2D-HSQC data suggest that within the oligomeric structures, more C–C bonds are presented with less C–O–C, and the repositioning of several functional groups (mainly methoxyl and hydroxyl) is also commonly observed in the newly formed oligomers. However, Ren *et al.* pointed out that new alkane C–C bonds were formed at the beginning of their hydrogenolysis reaction of the lignin but then decreased over time.[131] Under pyrolysis conditions, it has been reported that β-O-4 in lignin is preferentially cleaved into small fragments that are then transformed into more stable C–C linkages.[123] As recently reported for the RCD process, a clear correlation is observed between monomer distribution and the main linkages and aromatic unit constituents of the original lignin, as determined by 2D-HSQC-NMR samples.[130] This correlation has also been well recognized in other lignin pyrolysis studies.[87,132] It is noteworthy that the disappearance of β–β and β-5 signals in HSQC spectra does not necessarily imply depolymerization because, sometimes, the scission only occurs at their neighboring C–O–C positions (*i.e.*, α-O-γ and α-O-4, respectively) with the C–C remain.[96,97] Moreover, other new linkages, except for the well-known ones, have not been thoroughly reported but were possibly present in oligomeric production after lignin depolymerization. Ralph *et al.* mentioned three more interunit linkages in their papers, including 5–5 in the dibenzodioxocin type subunit, α-O-4 in the benzodioxane type, and β-1 in the spirodieneone type.[37,38] However, these linkages have not been well reported elsewhere for various oligomeric lignin products.[125,126,130]

3.1.4 Other techniques. Other techniques that could be used in characterizing the lignin oligomers, such as FTIR, TGA, UV-fluorescence and elemental analysis, are often considered to be auxiliary. These techniques can sometimes provide similar information from different perspectives or provide completely different dimensions. For instance, elemental analysis that provides the overall weight percentage of the carbon, hydrogen, nitrogen, and oxygen has been frequently conducted to form the van Krevelen plot to make the reaction pathways more indicative.[135,136] It could also turn out to be a key piece in identifying an oligomer structure, especially when NMR and molecular weight had already been obtained. The fluorescence spectrum, however, is another technique to characterize polyphenols that are abundant in the oligomeric products of lignin

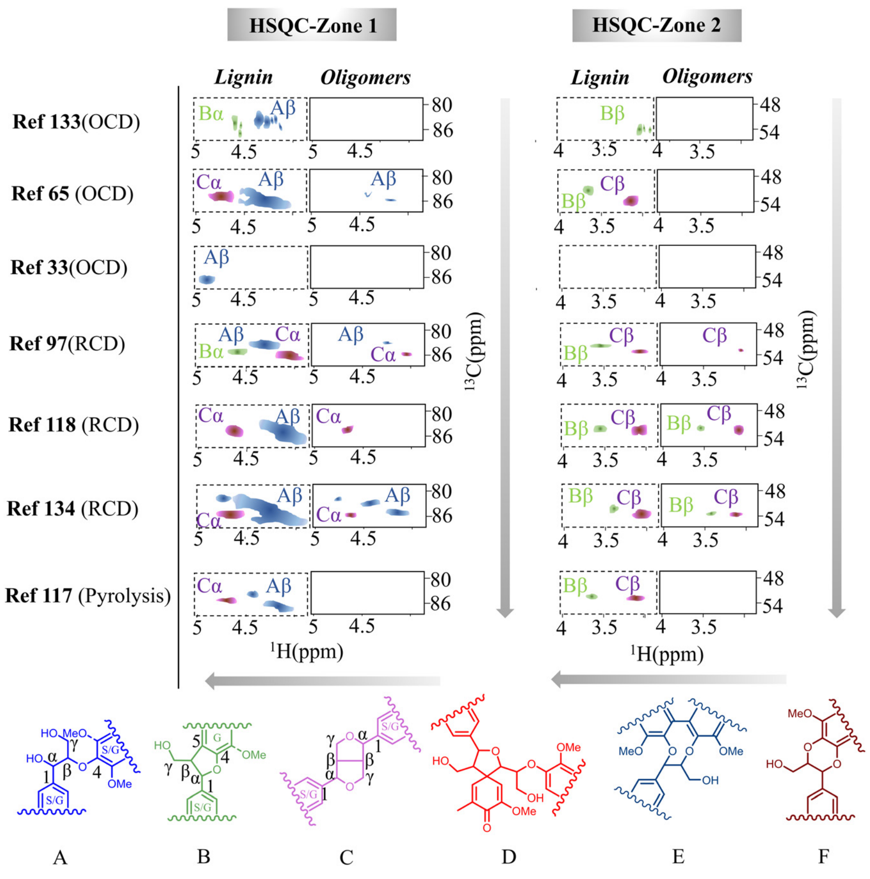

Fig. 4 Characterization of the oligomeric products from various lignin depolymerization processes by 2D-HSQC-NMR analysis (the contour plots were adapted and normalized from each reference).[33,65,97,117,118,133,134]

depolymerization.[137,138] This method is fast and effective in distinguishing oligomers with different molecular sizes although the corresponding quantification is still challenging. In addition, TGA is also a useful technique for displaying the boiling point curve of oligomeric products.[121,139] Generally, the boiling point ranges of lignin monomer, dimer, and trimer were defined as 180–280 °C, 280–400 °C, and 400–500 °C, respectively, as referenced by the corresponding model compounds.[139] A growing application of phosphitylation followed by ^{31}P NMR can also be observed in the lignin characterization field to quantitatively analyze lignin structure, especially for the hydroxyl group.[140,141]

3.2 Challenges in identifying oligomeric products

Although many studies on characterizing lignin oligomers have been reported in the literature, key questions remain unresolved, particularly concerning our collective understanding of the exact structure of each oligomer. The major challenges in identifying the oligomers from various lignin depolymerization lie in the fact that most oligomers are mixed with the monomers in the produced lignin oils. Classical molecular weight characterization may not well represent the oligomeric class of interest owing to the relative difficulty in separating the monomers from the oligomers. Conventional liquid–liquid extraction, regardless of the solvents being used, ubiquitously recovered both components in one fraction. Recently, Stahl group attempted to push this boundary using centrifugal partition chromatography, offering access to isolated oligomers from the products.[71] In addition, the resulting oligomeric products may have weak stability and react with each other to induce the aging phenomenon, as extensively reported in various bio-oils,[85,142,143] posing an obstacle to fully understanding the intrinsic structure of the oligomers. Additionally, all the state-of-the-art techniques combined are still inadequate for distinguishing and then quantifying each oligomer. More efforts are needed on this aspect in the future, which is pivotal in utilizing these oligomeric products in many other applications.

4 Further valorization options for oligomeric products

Conventionally, depolymerization is considered to be one of the valorization routes for lignin by producing monomers as the only goal. With the development of this process, however, more efforts have been made in recent years to explore the valorization path for the side-produced oligomers.[26,144] Possibly owing to the intrinsic nature of depolymerization, oligomeric products derived from different processes often have different fates in terms of their further valorization. For example, oligomers from RCD or OCD of lignin are often reported to be the precursors of polymer synthesis, while tar materials from pyrolysis are more likely to undergo thermal/catalytic decomposition for the production of smaller fragments.[145–149] The reported pathways for the valorization of the oligomeric products can be generally categorized into three: 1) further depolymerization for more phenolic/aromatic monomers, 2) modification of lignin oligomers into value-added materials, and 3) decomposition to short-chain dicarboxylic acids or even hydrogen gas.

4.1 Enhancing the yield of monomers

Monomeric phenols derived from various lignin depolymerization processes can be readily converted into respective aromatics or cycloalkanes, which could potentially serve as renewable-carbon alternatives in chemical, materials, and fuel applications.[150] As the side products, lignin oligomeric products can be valorized *via* a further depolymerization process. Huber's group conducted multistep hydrogenation of pyrolytic lignin, in which the oligomeric product was separated from the spent catalyst; then, a new hydrogenation step was repeated with fresh catalyst.[125] A successful depolymerization process of the oligomeric products from the 1st step was observed in the next steps, resulting in an increase in monomer yield from 15.9% to 26.7%. This study perfectly exemplified the idea that many oligomeric lignins can be further fragmented to yield more monomers but not at their full scale. Even when undergoing multiple steps of hydrogenation, decent amounts of oligomers still exist in the final product.[125] Evidenced by the ^{13}C-NMR analysis, the final form of the oligomers exhibited more aliphatic C–C but fewer aromatics.[125] The mechanism of the intrinsic transformation to oligomers after multiple hydrogenations is still unclear. According to the previously summarized mechanisms that accounted for the generation of oligomeric products, many chemical routes (*i.e.*, hard bond, repolymerization, or yet incomplete depolymerization) could cause such issues, and more informative identifications are still needed to confirm accurate mechanisms. Wang *et al.* proposed a method to calculate the theoretical maximum yield of the monomer from lignin hydrogenolysis, as listed below:[55]

$$\text{Theorectical monomer yields} = \frac{(N-2)\times 0.6^2 + 2\times 0.6}{2!}\times 100\%,$$
$$\text{where } N = \frac{M_\mathrm{n}}{226.23},$$

where M_n represents the average molar weight obtained from GPC analysis and N represents the polymerization degree calculated by M_n and theoretical general formulas for angiosperms (226.23 g mol^{-1}).[55] Experimentally, the yield of monomers from further hydrogenolysis of pyrolytic lignin (oligomers) was reported to be as high as 33 wt%.[88] Song *et al.* optimized their nickel-based RCD and achieved a 48.5 wt% monomer yield from birch wood lignin.[24] Additionally, many studies have been carried out to explore new possibilities for the cleavage of the relatively refractory carbon–carbon (C–C) interunit linkages under different conditions, aiming to maximize the monomer yield during depolymerization. For instance, Kim *et al.* had effectively activated the C–C bond cleavage in β-alkoxyl and β-1 lignin model dimers *via* copper-catalyzed oxidation although the same strategy had been tested with raw lignin.[151] Ren *et al.* tested a similar approach for alkaline lignin at room temperature, and the 2D-HSQC-NMR results suggested a selective cleavage of the aliphatic C–C bond from the lignin although the dimeric-trimeric aromatic acids and aldehydes were identified as the main products.[133]

4.2 Modification of lignin oligomers into value-added materials

The chemical structure endows lignin oligomers with great potential as core components for functional materials.[152,153] For instance, lignin oligomers can generate interesting photo physicochemical properties, attributed to the incorporated aromatic structures.[154,155] More recently, Wan *et al.* developed an auto fabrication strategy to convert lignin into afterglow room temperature phosphorescence materials.[156] Because the key step of the process was to oxidize lignin to aromatic chromophores, it offers the possibility that such a method could be implanted into the oligomeric lignin as well. In addition, owing to the lower molecular weight and dispersity index with high phenolic content, the depolymerized lignin oligomers could also serve as a great candidate to replace petroleum-derived aromatic precursors at least partially in the industrial synthesis of polymers. Among various depolymerization processes, the RCD of lignin has been widely accepted as a technology to effectively reduce the degree of lignin branching and the molecular weight of natural lignin.[58,157] The resulting oligomeric lignin products, once coupled with an epoxide (such as epichlorohydrin), could readily transform a brown oily prepolymer, which is the main precursor for obtaining the epoxy resin adhesive.[157] The low molecular weight lignin oligomers derived from the RCD process were also tested to fully replace the petroleum-based bisphenol A diglycidyl ether (hard to recycle) for synthesizing bio-based epoxy resins.[158] In addition, oligomers from OCD routes have been discussed recently, and the resulting oligomers were used in epoxy resin synthesis or as adsorbents without further functionalization.[149] Except for the direct use of the produced oligomers, some synthesis paths can be integrated into the depolymerization and produce phenolic foam *in situ* as evidenced by the work of Wang *et al.*[159] A synergetic effect was proposed in this coprocessing that significantly inhibits lignin condensation and therefore enhanced the yields of the polymers. Xue *et al.* claimed that the oligomeric products from their lignin depolymerization are bio-polyols for the preparation of a bio-based rigid polyurethane foam.[160] Chen *et al.* pointed out that the oligomeric products from their reductive depolymerization of lignin acted as the more active phenolic oil preferentially polymerized with formaldehyde compared to phenol.[161] More recently, O'Dea *et al.* demonstrated the utility of the oligomeric products from the RCD of lignin in high-performance additive manufacturing *via* stereolithography 3D printing and highlighted its economic advantages over the conventional process.[162]

4.3 Decomposition into dicarboxylic acids or gaseous products

Valorization of oligomeric lignin products into dicarboxylic acids is another route to produce value-added chemicals. Interestingly, most related studies have used pyrolytic tar materials as the substrate for various decomposition processes. For example, Figueirêdo *et al.* demonstrated the concept of the ozonation of pyrolytic lignin for low molecular weight dicarboxylic acids and esters.[163] In their study, the high reactivity of ozone in depolymerizing pyrolytic lignin was reported under mild conditions (0 °C, atmospheric pressure), and the optimized yield of dicarboxylic acids/esters was 45 wt% of the original pyrolytic lignin, implying the attractiveness of such a valorization route. As they pointed out, however, this approach requires a substrate that can be readily dissolved in methanol, which thus may not offer the same level of straightforwardness as any solid industrial lignin owing to its poor solubility in this solvent. However, the oligomeric products after the depolymerization could potentially serve as the ideal substrate because of the better solubility of oligomeric products in methanol.[30,31,164] Additionally, the decomposition of tarry material over nickel-based catalysts has been extensively studied to improve the gas quality for biomass gasification. This offers an alternative path to utilize the oligomeric products from various lignin depolymerization processes, not limited to thermochemical conversion. According to Duc *et al.*, enhanced depolymerization of the tar over nickel catalyst could result in a five-times increase in hydrogen gas yield after gasification.[145] The tarry material in their work was just one form of oligomeric lignin being discussed in this study. Yang *et al.* applied the biochar-based nickel catalyst to lignin oligomers and successfully converted them into syngas with high purity.[165] Therefore, it is reasonable to see this route as a promising valorization path for these oligomeric products although studies on this aspect are still very rare.

Several new ideas have recently been proposed and tested for utilizing lignin or its oligomers. For instance, Kim *et al.* recently reported the use of Kraft lignin as a photocatalyst that forms H_2O_2 by O_2 reduction and H_2O oxidation under visible light.[166] It is, therefore, an attractive idea to implement a similar concept to the depolymerized lignin oligomer and test their performance in terms of the radical-scavenging activity and redox reactivity and to evaluate its potential as a photocatalyst as well. In addition, the low molecular weight lignin oligomers derived from solvent extraction showed high resistance to oxidative degradation, demonstrating the potential for utilizing depolymerized lignin oligomers as antioxidants.[167] Another example to valorize lignin material is to use it as a battery binder, which normally requires materials that maintain a great insulation capability. This could also be a new research field to be developed for oligomeric products from lignin in the future. In addition, these aromatic bio-oligomers derived from lignin depolymerization offer many other striking properties, such as biodegradability, UV-blocking, antioxidant, and antimicrobial activities.[26] Utilization that stems from any of these features could also be a promising path for the valorization of oligomeric products from lignin in the future.

5 Overview of addressing technical hurdles

The depolymerization of lignin provides access to a new dimension of the utilization of lignin-based materials. During the fractionation process, it is highly desirable to control the lignin structure, molecular weight, branching, and functional complexity to adapt lignin to various valorization processes. However, one of the biggest technical hurdles in achieving this potential is the difficulty in identifying all depolymerization products. The oligomers are indispensable pieces if one wants to gain an insightful mechanistic view of the process or to valorize them. Such difficulty could mainly be attributed to the fact that, as a natural biopolymer, the structural heterogeneity of lignin could significantly diversify the derived oligomeric products compared to the depolymerization of those petro-based polymers (*e.g.*, polyethylene, polystyrene). Most of these oligomers are often classified as "unknown" compounds in the literature because there are no references that could be used to justify their characteristic index (*e.g.* retention time, chemical shift, and wavenumbers) analytically. It is, therefore, reasonable and pivotal to establish structural databases for identifying these oligomers in the future. One feasible route is to develop protocols for synthesizing various synthetic compounds as standards by the polymerization of individual monomers. Ciofi-Baffoni *et al.* initially successfully synthesized the β-O-4 containing oligomers to mimic the lignin structure for their enzymatic degradation tests.[168] Kiyota *et al.* established a simple way to synthesize many lignin oligomers by mimicking the natural polymerization of lignin and used LC–MS to determine their structures and to build a library of lignin oligomer data.[169] Later, Forsythe *et al.* developed an efficient synthetic method to prepare the model lignin hexamers and octamers containing three of the most common connectivity motifs found in native lignin (*i.e.*, β-O-4, 5–5′, and β-5′).[90] It is noteworthy that all these available standards may not well simulate the oligomeric products from lignin depolymerization because these oligomers often contain only a minor amount or none of the β-O-4, as reported in the literature.[113,126,170] Therefore, more efforts should be made to establish databases specially designed for depolymerized oligomers, in which computational simulations are needed to generate hypothetical structures.

Another parallel effort should be made on lignin analytics, where major improvements in separation efficiency and fast but accurate interpretation are highly desired. The current state-of-art instruments include 2D-NMR and various high-resolution MS analyses but address the issue that the analytes cannot be well separated before the identification index is generated. The resulting structural information cannot be further translated to each compound, and more often, chromatography techniques are combined as complimentary separation processes to characterize individual oligomer. Even with more sophisticated LC–MS, it is still challenging to interpret each oligomer with high accuracy. Sometimes, one could circumvent such a dilemma if the goal is to interpret the reaction pathways. Data visualization techniques could facilitate the elucidation of the structural elements of lignin species. This could be exemplified by interpreting the FT-ICR-MS data using the concept of Kendrick mass defect plots, which provide systematic line-ups of the different lignin linkages to reveal hidden information from the MS analyses.[25,137]

In summary, the classical and most recent lignin depolymerization approaches are discussed in this perspective with the main emphasis on the formation, identification, and valorization of oligomeric products. Three major routes are summarized in this review to illustrate the generation of these oligomeric products from various depolymerization processes. According to the state-of-art characterization, these oligomeric products often contain minor or no aryl ether bond and are extensively present in the lignin. In addition, the molecular weight of the oligomers ranged from 250 to 1600 Da, implying a structure with up to 13 phenyl units. However, the lack of standards to identify the lignin oligomers is a challenge for the analysis of complex oligomeric products, especially when distinguishing each of the oligomers is an essential requirement. The establishment of a library for various possible lignin oligomeric structures is highly desirable.

Conflicts of interest

The authors declare no conflict of interest.

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