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COMMUNICATION

In situ trapping of enol intermediates with alcohol during acid-catalysed de-polymerisation of lignin in a nonpolar solvent

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Processes that can de-polymerise lignin efficiently to yield low molecular mass compounds have received considerable attention in recent years owing to their potential in generating aromatic compounds from a renewable resource. Widely employed protocols for the acidolysis of lignocellulosic biomass can generate numerous products owing to the recondensation of enol ether intermediates formed during the decomposition of structures containing β -O-4 linkages. Here, we show that the acid-catalysed degradation of lignin in Japanese cedar and *Eucalyptus globulus* wood samples in the hydrophobic solvent toluene, containing a small amount of methanol at 140 °C–170 °C by microwave heating, yield the lignin monomers homovanillyl aldehyde dimethyl acetal and homosyringaldehyde dimethyl acetal selectively. The maximum combined yield of lignin monomers and oligomers is > 10%, based on the weight of the wood sample. Furthermore, when de-polymerisation is performed in hydrophobic media, hydrolysis and hydroxylation of cellulose and lignin fragments is suppressed, wherein methanol serves as an *in situ* trapping agent for the enol ether intermediate, generating oligolignols and the dimethyl acetal derivatives.

Lignocellulosic biomass has recently garnered the interest of researchers as a carbon neutral energy resource owing to its abundant and widespread availability, non-competitiveness with food supply and potential as a platform for the production of green chemicals, significantly reducing green-house gas emissions. Lignocellulosic biomass predominantly consists of cellulose, hemicellulose and the heterogeneous aromatic polymer, lignin. Lignin, which accounts for 10%–35% of the total lignocellulosic biomass in lignified plants, hinders the enzymatic degradation of cellulose and hemicelluloses. In bioethanol production, the effective removal or destruction of the lignin crust has been a major challenge

overcoming which can pave the path towards increased yield of sugars from lignocellulosic biomass by enzymatic saccharification and fermentation. To facilitate the replacement of petroleum refineries with biorefineries along with the identification of protocols that effectively decompose lignin, processes that accommodate the use of lignin as an aromatic feedstock and convert (hemi)cellulose to fuels or functional materials also need to be identified to ensure multiple revenue streams. Numerous approaches to decompose lignin for the production of biofuels, chemicals and paper have been reported. However the selective degradation of lignin to low molecular mass products remains challenging owing to the heterogeneity of the molecular structures and the ability of lignin fragments to recondense during chemical degradation.¹ In acid-catalysed reactions, electrophilic aromatic substitutions or aldol reactions interfere with the degradation processes. It has been reported that the recondensations of enol ether intermediates yield various degradation products when acidolysis is performed in water-miscible solvent.

In this study, we propose a protocol for obtaining low molecular mass lignin fragments in high yield and selectivity directly from wood by adopting a strategy of trapping the enol intermediates with alcohol in water-immiscible solvent.

Wood particles (1 g, 1.5 ϕ) of Japanese cedar (*Cryptomeria japonica*) are suspended in toluene/methanol mixture in the presence of 0.1 % sulphuric acid and heated by microwaves. Addition of water to the cooled reaction mixture yields a solid that is readily separated by filtration. The components of the filtrate are partitioned between organic and aqueous layers by extraction with toluene. Combined organic layer is dried over MgSO₄ and evaporated. GC-MS analysis of the compounds in the organic fraction reveals the presence of homovanillyl aldehyde dimethyl acetal (**2a**) and compound **4a** predominantly. The proposed reaction mechanism, depicted for the de-polymerisation of lignin via cleavage of the β -O-4 ether and C β -C γ bonds, is shown in Fig. 1. In the presence of an acid, γ carbon is released as formaldehyde (top pathway), providing the enol intermediate **1**.² On hydrolysis, **1** gives homovanillyl

aldehyde, which, however, is susceptible to re-condensation via acid catalysed aldol reactions or electrophilic aromatic substitutions, yielding a large number of reaction products. In contrast to the reactions in aqueous media, when the reactions are performed in a water-immiscible solvent system, e.g. toluene/methanol, the enol intermediate **1** is trapped by the methanol (solvolysis) to give compound **2a**. The acetal formation protects the unstable aldehyde, increasing the reaction selectivity. Similarly, when the reaction progresses through the enol intermediate **3** (formed by elimination of β -proton during dehydration),² the ether linkage in **3** is cleaved by hydrolysis and the resulting benzyl cation is trapped with methanol yielding compound **4a**. Thus, the use of toluene/methanol as the reaction solvent inhibits the re-condensation of lignin fragments during the de-polymerisation of lignin, yielding products with high selectivity and conversion efficiency.

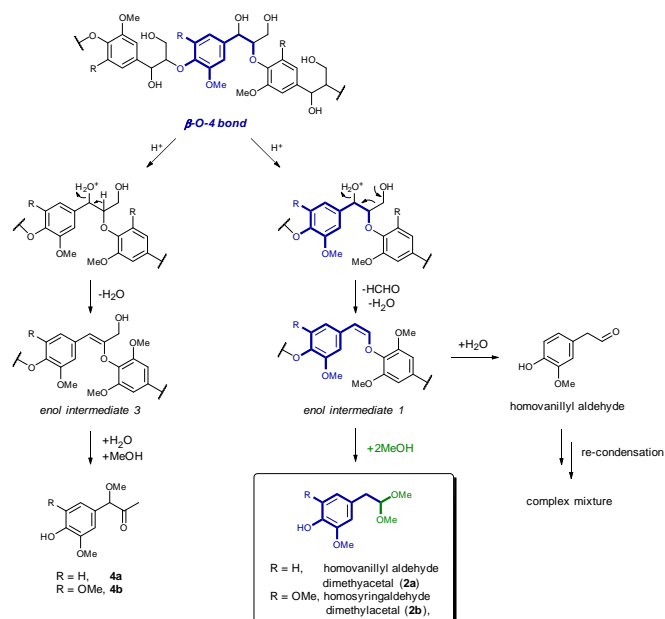


Fig. 1 Mechanism for the de-polymerisation of lignin showing the intermediacy of enol ethers.

The toluene/methanol system is found to suppress the degradation of cellulose, reducing the production of undesirable hydrophobic products. The combined yield of these products, such as methoxymethyl furfural (MMF), levoglucosenone, levulinic acid methyl ester and acetal product of MMF (DMMF) account for a mere 4% of the total yield (unless mentioned otherwise, all yields are based on the weight of the original wood) when the reaction is performed at 170 °C (Fig. 2). Insignificant amounts of these compounds are observed when the temperature is lowered (e.g. 140 °C) or when the methanolic content of the mixture is increased (see Fig. 2). Under the conditions employed, no clear relationship between the amount of degradation products and reaction time can be established. Therefore, the optimized reaction conditions are: a reaction temperature of 140 °C, a reaction time of 20 min and the use of toluene:methanol (12:3) mixture as the solvent.

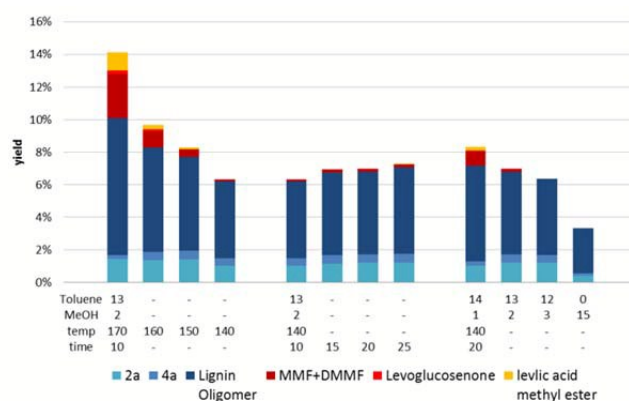


Fig. 2 Dependence of the yield of lignin degradation products on reaction conditions (Japanese cedar)

When the reaction is conducted in toluene with methanol as the trapping agent for the enol ether intermediate, high yields of low molecular mass lignin fragments are obtained. Yields as high as 10% can be obtained; this corresponds to a 30% yield when considering the content of lignin in the wood.

Next, we evaluated the effect of different solvents and trapping agents on the yield and nature of the products (Fig. 3). When ethanol is used instead of methanol, low molecular mass products were obtained in a high yield (8%). Furthermore, as predicted by the proposed mechanism, the obtained product is diethyl acetal. Replacement of toluene with xylene gave the degradation products in a yield exceeding 5%. Not surprisingly, when the reaction is conducted in water/methanol mixtures, the yield of degradation products decreases significantly; furthermore, the compounds **2a** and **4a** are not observed. Thus, reactions performed in the mixture of hydrophobic solvent and alcohol are effective in the selective degradation of lignin. From these observations, it is evident that the choice of the solvent mixture can further expand the applications of the ligninolytic reactions yielding low molecular mass degradation products with the desired substitutions.

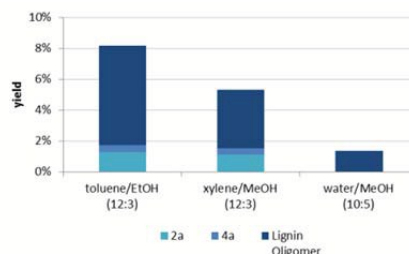


Fig. 3 Degradation of Japanese cedar (*Cryptomeria japonica*) wood in mixtures of different solvents. Reaction conditions: 140 °C, 20 min.

Reactions of hardwood *Eucalyptus globulus* give low molecular mass lignin fragments in a yield higher than that observed for the softwood (Fig. 4). In addition to compounds **2a** and **4a** with guaiacyl nucleus, hardwood yields homosyringaldehyde dimethylacetal (**2b**) and compound **4b**. In the absence of water induced side-reactions, the yield of degradation products increases when dry wood is used.

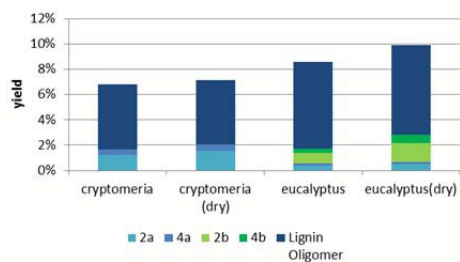


Fig. 4 Yields of acid-catalysed lignin degradation products in toluene/methanol from Japanese cedar (*Cryptomeria japonica*) and *Eucalyptus globulus* wood samples with different water contents. Water contents of the softwood (*C. japonica*) and hardwood (*E. globulus*) before drying were 6% and 9%, respectively.

Considering the heterogeneity inherent in the structure of lignin and potential for the reactions between intermediates of different structures, the formation of diverse degradation products is unavoidable during chemical degradation. In particular, reactions of softwood lignin give more denatured degradation products; these include re-polymerized products formed by the condensation of guaiacyl nuclei at C5 position. GPC analysis of the products reveals that similar molecular weight distributions, spanning the gamut of monomer-to-oligomer structures, are similar for reactions of softwood and hardwood (Fig. 5). M_n and M_w of Japanese cedar were 338 and 490 and those of *E. globulus* were 347 and 508, respectively. 70% of the total area in the GPC profiles is accounted for the peaks corresponding to the degradation products, i.e. monomers, dimers and trimers. This demonstrates that even during the depolymerisation of softwood lignin, condensation reactions are suppressed. Interestingly, the analysis of low molecular mass products over three GPC columns connected in tandem partially resolves the peaks attributed to monomers, dimers and trimers in the two wood species. Three peaks are discernible in the chromatogram of the products resulting from the reaction with *E. globulus* (Fig. 5, left panel), while in the case of Japanese cedar, in addition to three peaks, an additional peak located between monomer and dimer peaks is observed. Origins of this peak requires further studies.

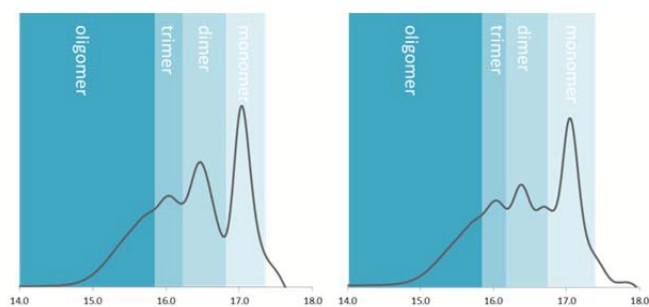


Fig. 5 GPC of lignin degradation products (RI, left; *E. globulus*, right; Japanese cedar). Conditions for degradation: toluene:methanol, 12:3; 140 °C; 20 min.

Several recent efforts have been directed towards the conversion of lignin into functional polymers.³ Owing to the heterogeneous nature of aromatic polymer as component of resins, it becomes necessary to understand the composition of different structural motifs within the polymer, in particular those of phenolic and aliphatic hydroxyl groups. Therefore, the amount of hydroxyl groups is determined using ^{31}P NMR after

the phosphorylation of the lignin degradation products.⁴ Fig. 6 shows ^{31}P NMR spectrum of the phosphorylated lignin degradation products from Japanese cedar wood. Distinct signals attributed to phosphoryl group on the phenolic hydroxyl in guaiacyl nuclei are observed at 130.6–129.1 ppm. Signals from the phosphoryl group on primary hydroxyl group appear at 133.7–132.4 ppm. The amounts of phenolic and primary hydroxyl groups were determined to be 2.9 and 1.3 mmol/g, respectively. Signals due to phosphoryls on secondary hydroxyl groups are barely noticeable, and those attributed to carboxylic group are below background noise levels because carboxylic groups are esterified with methanol in our reaction conditions. The observed profile of phenolic and aliphatic hydroxyl groups, molecular weight distribution and high solubility in organic solvents ensures the use of the reaction products as raw feedstock for the generation of functional resins.

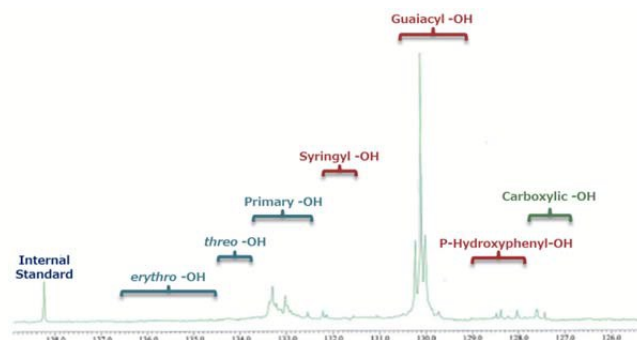


Fig. 6 ^{31}P NMR spectrum of phosphorylated lignin degradation products (Japanese cedar). Conditions for degradation: toluene:methanol, 12:3; 140 °C; 20 min.

Conclusions

Poor selectivity for low molecular mass products during the chemical degradation of lignin has been the major bottleneck for the industrial use of the aromatic polymer. During aqueous acidolysis of lignin, the occurrence of enol ether intermediates result in the formation of numerous products, thereby precluding their use as feedstock for the production of fine chemicals. In this study, we have identified reaction conditions that suppress the undesirable reactions of the enol ether intermediates. By treating wood with catalytic amount of acid in a mixture of hydrophobic solvent (e.g. toluene) and alcohol (e.g. methanol), the intermediate enol ether can be trapped in its acetal form, yielding homovanillyl aldehyde dimethyl acetal and homosyringaldehyde dimethyl acetal selectively. These chemicals are widely used as monomers in polymer synthesis. When ethanol is used as the alcohol component of the mixture, the corresponding diethyl acetal is formed. The described reaction protocol converts wood particles directly to the lignin-derived monomers and oligomers which display high solubility in organic solvents. Furthermore, the formation of degradation products such as furfural, HMF and levulinic acid from carbohydrates is suppressed significantly. The selective degradation of lignin in wood to low molecular mass products fosters the potential applications of various wood resources in polymer synthesis and other chemical applications.

Notes and references

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