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Chemoselective Methylation of Phenolic Hydroxyl Group Prevents Quinone Methide Formation and Repolymerization During Lignin Depolymerization

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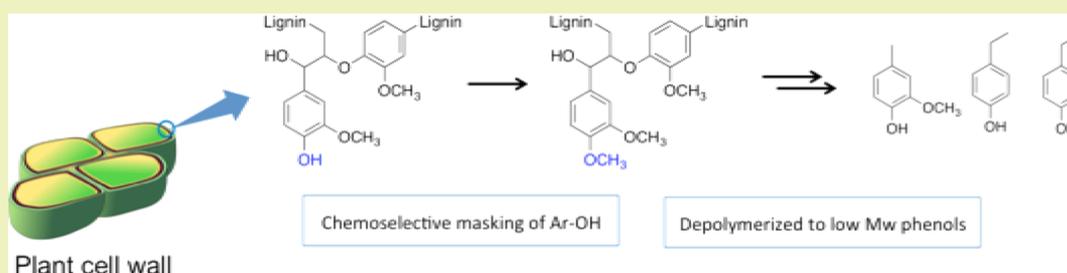
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Supporting Information



ABSTRACT: Chemoselective blocking of the phenolic hydroxyl (Ar–OH) group by methylation was found to suppress secondary repolymerization and charring during lignin depolymerization. Methylation of Ar–OH prevents formation of reactive quinone methide intermediates, which are partly responsible for undesirable secondary repolymerization reactions. Instead, this structurally modified lignin produces more relatively low molecular weight products from lignin depolymerization compared to unmodified lignin. This result demonstrates that structural modification of lignin is desirable for production of low molecular weight phenolic products. This approach could be directed toward alteration of natural lignification processes to produce biomass that is more amenable to chemical depolymerization.

KEYWORDS: Lignin, Depolymerization, Repolymerization, Methylation, Quinone methide

INTRODUCTION

Lignin is the second most abundant naturally occurring polymer next to cellulose, representing a significant share of the organic carbon present on earth. Lignin accounts for approximately 20–30 wt % of the organic matrix of lignocellulosic biomass.¹ Large amounts of technical lignins such as Kraft lignin and liginosulfonate are produced as byproducts in the pulp and paper industries.² In addition, the emerging lignocellulosic biorefinery concept makes lignin more accessible to further utilization as a large amount of organosolv lignin is produced. There has been great interest in and efforts devoted to conversion of technical lignin into green chemicals and fuel precursors. Potential high value products from lignin include carbon fiber, thermoplastic elastomers, and aromatic chemicals such as benzene, toluene, and xylene (BTX).³ Many

approaches have been proposed to convert lignin to value-added products. For example, lignin depolymerization in various solvents in the presence of catalysts^{4–7} and fast pyrolysis of technical lignin^{8,9} have been reported. Most of these efforts have been devoted to the development of efficient lignin decomposition to low molecular weight compounds. However, a scalable biorefinery has not been developed yet due to the structural complexity and recalcitrance of lignin, thus limiting full utilization of lignin as a raw material (Figure 1). Moreover, the multifunctional nature of lignin produces multiple product streams, which require extensive separation

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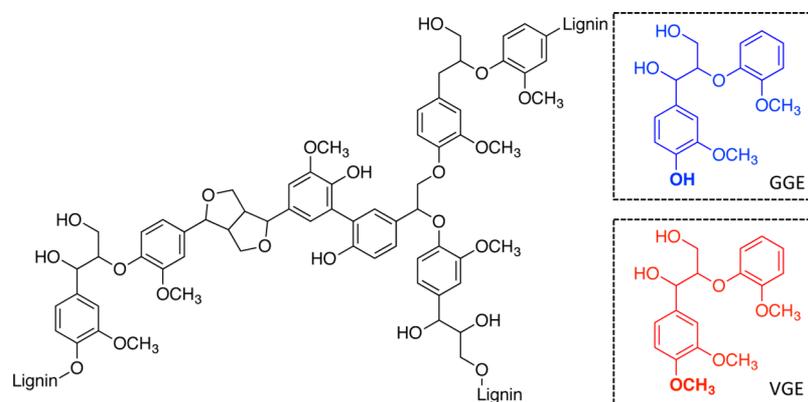


Figure 1. Structure of lignin and representative β -O-4 model dimers [guaiacylglycerol- β -guaiacyl ether (GGE) and veratrylglycerol- β -guaiacyl ether (VGE)].

and purification procedures.³ Also, undesirable reactions such as repolymerization readily occur during lignin depolymerization, which may lead to lower liquid yields and rapid catalyst deactivation. Lignin has striking abilities to self-associate due to the strong electronic stabilization energies between the various intrasubunits.¹⁰ Overcoming these inherent difficulties requires severe reaction conditions as well as the use of the proper catalyst or solvent.

The depolymerized products derived from lignin via thermochemical conversion consist of liquid, char, and gases. Yields and composition of the liquid products depend on the process type and the reaction conditions applied. Additionally, the source of lignin, the extraction method used, and presence or absence of various functional groups also significantly affect the lignin depolymerization reaction and the distribution of products. The functional groups that exert major influences on the reactivity of lignin include methoxyl, phenolic and aliphatic hydroxyl, benzyl alcohol, noncyclic benzyl ether, and carbonyl groups.¹¹ Recently, it was found that more than 60 wt % yield of low molecular mass aromatics result from depolymerization of oxidized lignin under mild conditions.⁵ Although lignin has a complex and heterogeneous structure, selective modifications, even those which are relatively simple, can significantly enhance the degree of depolymerization. For example, Rahimi et al. reported that chemoselective oxidation of the primary alcohol at C_{α} in lignin structure promotes lignin depolymerization in mild reaction conditions.⁵ Shuai et al. pretreated biomass with formaldehyde to extract lignin, which prevented lignin condensation by forming 1,3-dioxane structure with lignin side-chain hydroxyl groups.¹²

Herein, we specifically focused on the Ar-OH group in lignin and studied how the thermal behavior of lignin changes if the Ar-OH groups are chemoselectively blocked by methylation. Because the Ar-OH group is one of the most reactive functional groups in lignin, such blocking groups could confer unique advantages to lignin depolymerization reactions.¹³ Ar-OH groups are reactive toward electrophilic aromatic substitution, and they enable formation of reactive quinone methide intermediates, thereby promoting undesirable condensation reactions in the thermochemical degradation of lignin.¹³ Thus, it is hypothesized that undesirable outcomes such as repolymerization or charring can be reduced by selective methylation of Ar-OH groups, allowing formation of more low molecular weight products during lignin depolymerization.

EXPERIMENTAL SECTION

Methylation of Milled Wood Lignin (MWL). Methylation of MWL was performed according to the literature method.² Briefly, 1 g of MWL was dissolved in 15 mL of aqueous 0.7 M NaOH at room temperature. Also, 10 mmol of dimethyl sulfate was added, and the solution was stirred for 30 min at room temperature. Then the mixture was heated to 80 °C for an additional 2 h. For high degrees of methylation, an aqueous 0.7 M NaOH solution was continually added to the reactants as suggested.

Note that dimethyl sulfate is extremely toxic, carcinogenic, and mutagenic. Please use this chemical with extreme caution. Researchers might want to use alternative methylation reagent (e.g., methyl iodide, etc.).

³¹P NMR. Methylated MWL was analyzed by ³¹P NMR.² Approximately 40–50 mg of lignin samples was dissolved in 500 μ L of anhydrous pyridine/ $CDCl_3$ mixture (1.6:1, v/v). As an internal standard, 200 μ L of an *endo*-N-hydroxy-5-norbornene-2,3-dicarboximide (9.23 mg/mL) was added to the above solution. Also, 50 μ L of a chromium(III) acetylacetonate (5.6 mg/mL) solution was added as a relaxation reagent. Finally, 100 μ L of 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane, a phosphitylating reagent, was added to the solution. NMR spectra were acquired on a 600 MHz Varian Direct Drive (VNMRs) spectrometer (Agilent) with a Varian dual band (AutoXDB) probe. Proton-decoupled ³¹P spectra were collected at 293 K using a 21 μ s nonselective 90° pulse, 285.8 ppm spectral width, 32k complex points, 256 scans, 25 s relaxation delay, and WALTZ decoupling during acquisition. Spectra were referenced to phosphoric acid (0 ppm).

Molecular Weight Distribution of Lignin and Depolymerization Products. The molecular weight distribution of depolymerization products from lignin was investigated using gel permeation chromatography (GPC). The dichloromethane (DCM) soluble fraction was dissolved in tetrahydrofuran (THF) with a concentration of 1 g/L. GPC analysis was performed using a Tosoh Ecosec HLC-8320GPC equipped with a refractive index (RI) and diode array detector (DAD). The column used was an Agilent PLgel 5 μ m Mixed-D. The column flow rate was 1.0 mL/min at 35 °C. The GPC standards, which contained polystyrene ranging from 162 to 29 150 g/mol, were purchased from Agilent and used for calibration. In the case of MWL, it was derivatized using pyridine and acetic anhydride prior to GPC analysis.

Lignin Depolymerization. Lignin depolymerization was performed using a Parr reactor (75 mL, Alloy C276). Approximately 50 mg of lignin was added to the reactor. Also, 20 mL of isopropyl alcohol was added as a reaction medium. After the reactor was purged with nitrogen, it was pressurized to 20 bar with nitrogen and heated to 300 °C. After reaction for 4 h, the reactor was removed and quenched rapidly in an ice bath. Once it was cooled, the products, including liquids and solid residue, were collected and filtered using dichloromethane. The solvents were removed by rotary evaporation and

weighed for calculating the liquid yield. The solids were completely dried under vacuum to determine yield.

GC/MS Analysis of Depolymerization Products from Lignin and Model Compounds. Identification of depolymerization products of lignin and model compounds was carried out using an Agilent 6890N gas chromatography (GC) instrument equipped with Agilent 5973N mass spectroscopy (MS). The GC column used was an Agilent DB-5MS (30 m \times 0.25 mm \times 0.25 μ m). The injection temperature was 280 $^{\circ}$ C, and the split ratio used was 1:20. The GC oven temperature was programmed to hold at 50 $^{\circ}$ C for 5 min, ramp up to 300 $^{\circ}$ C with 5 $^{\circ}$ C/min, and then hold for an additional 5 min.

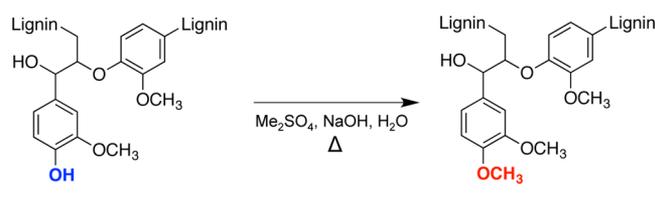
Synthesis of Dimeric Model Compounds. Solvents were distilled from appropriate drying agents under inert conditions prior to use. Unless otherwise stated, all other materials were purchased from commercial sources and used without further purification. Guaiacylglycerol- β -guaiacyl ether (GGE) and veratrylglycerol- β -guaiacyl ether (VGE) were synthesized following previously reported synthetic methodology (see Figure 1 for the structure).^{14–16} The purity of the synthesized products was confirmed by 1 H and 13 C NMR spectroscopy and elemental and mass spectroscopic analyses.

In Situ EPR Reaction. Samples were prepared by dissolving the dimer compounds in isopropanol to a concentration of \sim 135 mg/mL. Samples of these solutions were placed in 2 mm o.d. \times 0.8 mm i.d. quartz capillaries and flame-sealed under vacuum leaving \sim 50% head space. The EPR spectrometer employed a continuous flow VT insert (Bruker ER4131) which maintained the sample temperature at 300 $^{\circ}$ C. The spectrometer is a Bruker Elexsys 580 with an SHQE resonator operating at \sim 9.32 GHz. The field was swept at 200 G in 42 s and modulated 1 G at 100 kHz. Each spectrum had 1024 points, and a time constant of 41 ms was used.

RESULTS AND DISCUSSION

Initially, to test the hypothesis proposed, we prepared structurally modified lignin. Milled wood lignin (MWL) was isolated from Loblolly pine on the basis of the Björkman procedure.¹⁷ MWL is regarded as native biomass lignin that is a good representative lignin for studying the fundamentals of depolymerization. Because technical lignins, such as Kraft lignin and organosolv lignin, undergo structural alteration during extraction and separation depending on the method used, studying the thermal behavior of lignin using native lignin is preferred to develop a fundamental understanding of reaction mechanism. Isolated pine MWL was subjected to methylation for selective blocking of the Ar–OH group. Methylation of MWL was carried out with dimethyl sulfate under basic conditions (Scheme 1).² Methylation of MWL was monitored

Scheme 1. Methylation of Pine MWL with Dimethyl Sulfate under Basic Condition⁸



and analyzed by quantitative 31 P NMR and gel permeation chromatography (GPC) (Figures S1 and S2, respectively). It was confirmed that Ar–OH was selectively converted to the corresponding aryl methyl ether (Ar–O–CH₃) while aliphatic hydroxyl groups remained untouched. The molecular weight distributions of fully methylated lignin (m-MWL) and control were investigated by GPC. The molecular weight distributions of the MWL and m-MWL are almost identical.

Lignin depolymerization was performed at 300 $^{\circ}$ C for 4 h under 20 bar nitrogen pressure with isopropyl alcohol to explore the effect of selective masking of Ar–OH on the chemistry of lignin depolymerization. After the reaction, dichloromethane (DCM) was used to extract the soluble fraction. Figure 2 shows the yields of reaction products after the

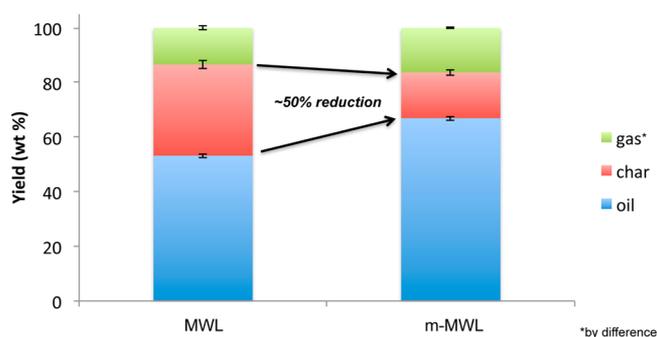


Figure 2. Mass balance for depolymerization of MWL and m-MWL.

depolymerization reaction. The separated soluble fraction corresponded to 53 and 67 wt % from the MWL and m-MWL, respectively. Interestingly, the insoluble fraction (char) was significantly reduced in the m-MWL. The char yield from the MWL accounts for 33 wt % of the original lignin, decreasing to 17 wt % when the Ar–OH group was blocked. Selective structural alterations of lignin, such as the selective methylation of Ar–OH groups described in this work, could substantially reduce formation of undesirable products from lignin decomposition. This finding strongly suggests that the Ar–OH group is one of the most important active groups involved in the addition and condensation reactions which lead to polymerization of primary lignin decomposition products.¹³ Other studies have also suggested that Ar–OH groups are key players in repolymerization and char formation by enabling formation of reactive quinone methide intermediates.^{18,19} When blocked by methyl groups, however, the quinone methide cannot form readily as it would require the methyl ether oxygen to bear a positive charge whereas the phenol can simply release a proton. Prevention of quinone methide formation appears to result in a lower yield of insoluble (polymerized) products.

Although there are other known functionalities that contribute to repolymerization and charring reactions during lignin depolymerization, such as the vinyl ($-C_{\alpha}=C_{\beta}-$) group,²⁰ Ar–OH is believed to play an important role in secondary repolymerization reactions.¹³ It has been found that quinone methide formation, which occurs in the phenolic groups of lignin, is more important than the vinyl condensation in terms of polymerization reactivity.¹⁹ Quinone methide intermediates can participate in further coupling as the polymerization proceeds, not unlike their role in biosynthesis of the lignin polymer in plants. These quinone methides are reactive and readily accept additions of nucleophiles to the double bond, resulting in regeneration of large molecular weight products.²¹ The quinone methide structure also supports resonance stabilization of radicals generated by homolytic bond cleavage (e.g., of the β -O-4 ether linkage) that could contribute to polymerization.

GPC measurement of the DCM soluble fractions obtained from the lignin depolymerization was performed to assess levels of depolymerization. Figure 3 shows chromatograms recorded

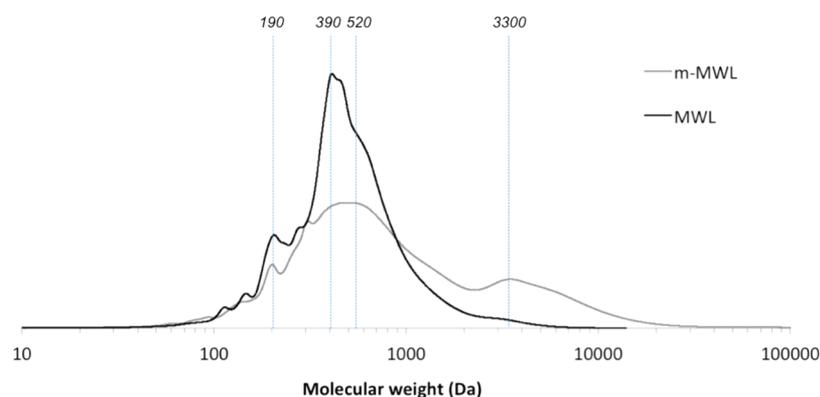


Figure 3. Gel permeation chromatography of the soluble fractions from depolymerization of MWL and m-MWL. Average molecular weight is 608 and 2812 Da from MWL and m-MWL, respectively.

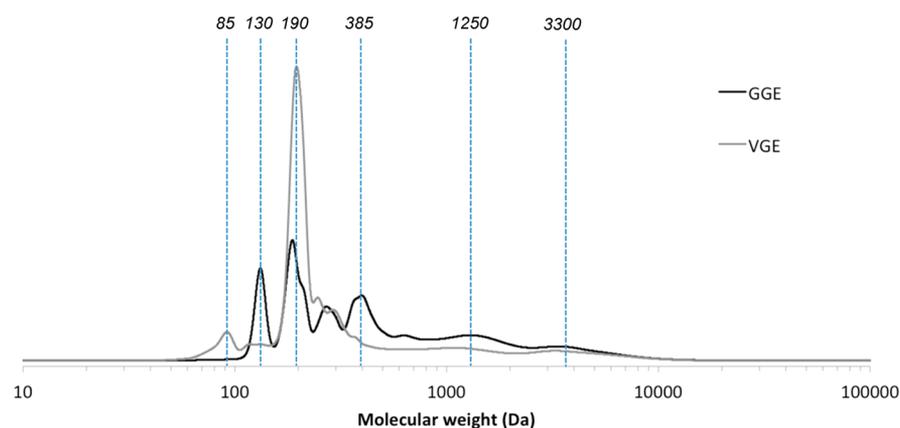


Figure 4. Gel permeation chromatography of the soluble fractions from depolymerization of GGE and VGE. Average molecular weight is 2016 and 1147 Da from GGE and VGE, respectively.

by a differential UV detector at 280 nm. A broad peak with some shoulders was observed from both MWL and m-MWL depolymerization. Considering the molar mass of monolignol (100–200 Da), a small peak around 190 Da can be assigned to monomer, and a broad peak is assigned to oligomers (dimer to pentamer or more). Interestingly, a peak assigned to the high molecular weight at 3300 Da was observed from m-MWL that was not detected from MWL depolymerization. Considering the higher char yield from the depolymerization of MWL, this indicates that the degree of repolymerization was suppressed by methylation of Ar–OH, resulting in more soluble products instead of char. When it comes to the MWL, however, the soluble fraction mainly consists of low molecular weight compounds with the highest peak around 390 Da, which is probably assigned to a dimer or trimer. As the control MWL produced more char than m-MWL above, it is evident that free Ar–OH groups promote secondary repolymerization to insolubles or char unless the products are stabilized to stay in the soluble fraction. GC/MS analysis of depolymerization products of MWL and m-MWL (Figures S3 and S4) shows that 2-methoxy-4-methylphenol, 4-ethyl-2-methoxyphenol, 2-methoxyphenol, and isoeugenol are major compounds from both lignin samples. In-depth analysis of two chromatograms revealed that no distinctive changes of chemical composition in the soluble fractions, i.e., GC detectable monomers, were found between MWL and m-MWL although some new peaks assigned to methylated phenols were observed from m-MWL.

In order to better understand our observations in real lignin samples, we employed two lignin dimeric model compounds (see Figure 1 for the structure). Guaiacylglycerol- β -guaiacyl ether (GGE) is a model dimer with a free Ar–OH group; veratrylglycerol- β -guaiacyl ether (VGE) is a model dimer with the Ar–OH group capped by a methyl group. These two model dimers were subjected to the same depolymerization reaction, and the products were analyzed. Consistent with the trend for m-MWL and MWL, a lower char yield was observed from VGE (~2 wt %), compared to that from GGE (6.7 wt %) (Figure S5). Capping the Ar–OH group suffices to reduce the charring reaction. The char formation from the VGE can be explained because the primary products generated by cleavage of β -ether linkage can dehydrate and undergo repolymerization reactions. However, it is clear that Ar–OH has a much higher reactivity toward polymerization than other functionalities during depolymerization.¹⁹ GPC analysis of the soluble fractions obtained from the two model compounds shows that GGE underwent more repolymerization reactions, as the soluble fraction had some significant peaks assigned to large molar masses (Figure 4). Analysis of the soluble fractions by GC/MS (Figures S6 and S7) revealed that VGE produced more di- and trimers than GGE, although accurate chemical structures cannot be identified due to the limited MS library. This indicates that when the Ar–OH was replaced by Ar–OCH₃ and recondensation reactions through quinone methide intermediates were suppressed, the product distribution shifted

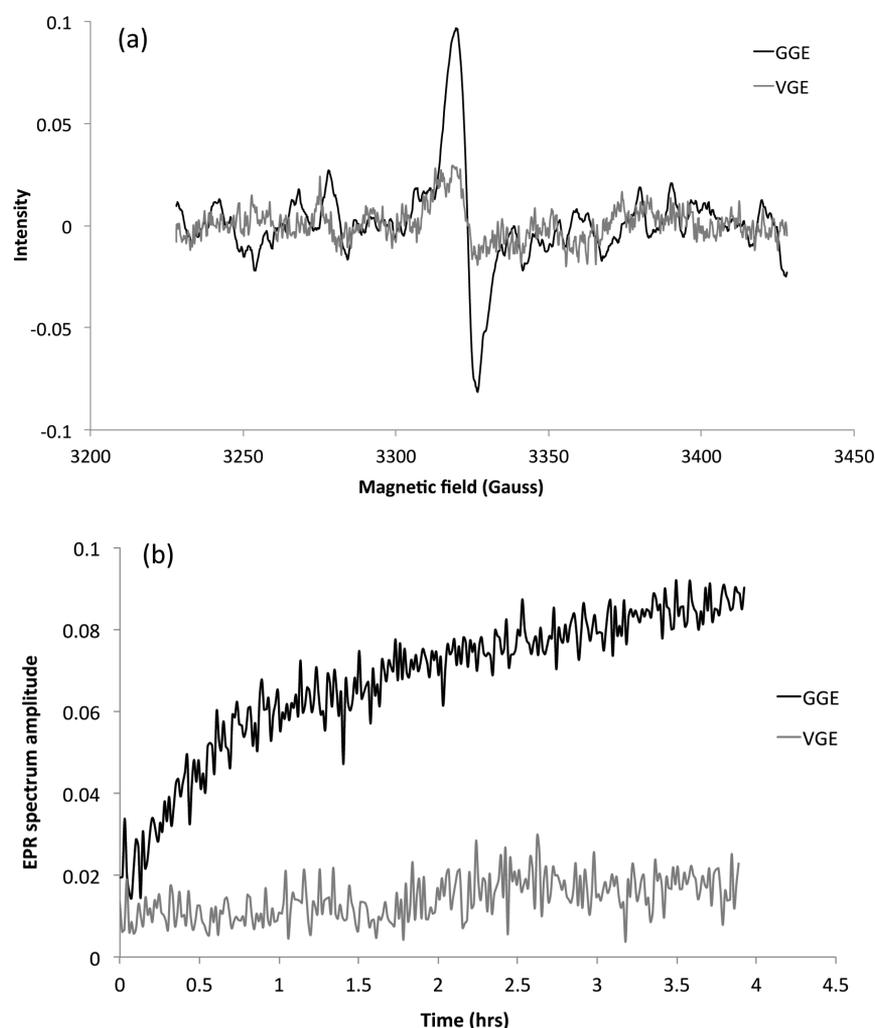
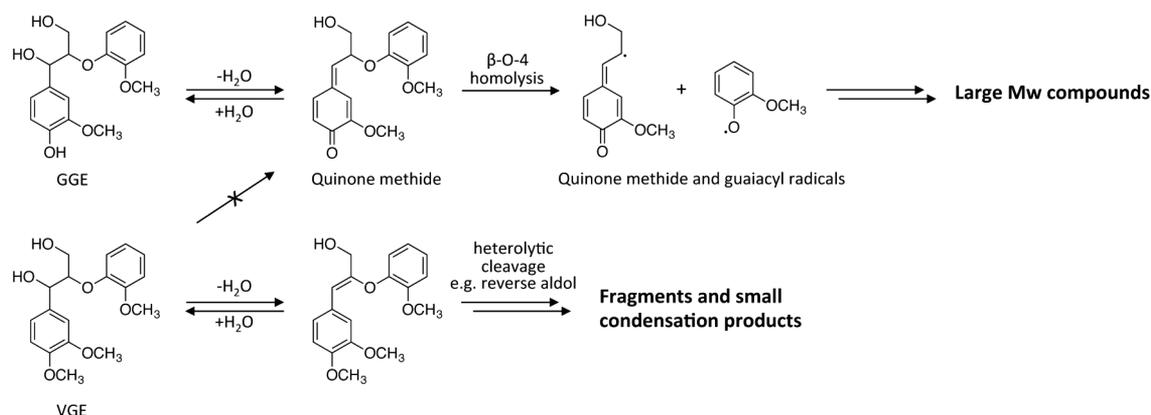


Figure 5. EPR spectra of an *in situ* reaction at 300 °C at the 4 h time point (a) and amplitude of the EPR spectrum during the course of the reaction (b).

Scheme 2. Formation of Quinone Methide Intermediates and Repolymerization To Form Large Molecular Weight Compounds



toward small molecular weight compounds due to the decreased repolymerization.

As discussed above, it was hypothesized that quinone methide intermediates play an important role in repolymerization reactions. If so, quinone methide radical-mediated reactions may be particularly significant in the high temperature reaction conditions used for lignin depolymerization, and observation of free radicals for the GGE but not the VGE

reaction would confirm the centrality of quinone methide intermediates. To test this hypothesis, identical reactions with the two model dimers were conducted within an EPR spectrometer for *in situ* free radical detection. An isopropanol solution of each dimer was flame-sealed in quartz capillaries, leaving approximately 50% head space. The samples were heated in the EPR spectrometer to 300 °C, and spectra were continuously collected for 4 h. Figure 5a illustrates the EPR

spectra of the *in situ* reactions at 300 °C at the 4 h time point. As shown, the EPR spectrum of GGE is isotropic and does not show resolvable hyperfine splitting. This indicates that multiple radicals are present or strong matrix interactions occur between the products.^{22,23} Interestingly, the intensity of EPR spectra obtained from VGE was significantly lower, which implies that the amount of free radicals produced from VGE was negligible during reaction. Figure 5b shows the intensity of the EPR spectrum as a function of reaction time. As expected, the intensity of EPR spectra from GGE continually increased over the reaction time, indicating that radical reactions are significant during the reaction. In the case of VGE, however, no distinctive changes were found during the reaction. Clearly, the reaction of GGE undergoes free radical reactions under the given reaction conditions, whereas VGE did not show any evidence of the presence of free radicals during the reaction. From the structural perspective, the formation of quinone methides is highly expected, which is likely to play an important role in secondary repolymerization to form large molecular weight products. In addition, this striking result suggests that lignin depolymerization occurs by a reaction mechanism involving quinone methide radicals, rather than by an ionic mechanism.

Scheme 2 describes a plausible reaction pathway for bond cleavage and initiation of the repolymerization reaction for dimeric β -O-4 linked model compounds. As discussed above, GGE generated a significant amount of radicals during reactions, and it is believed that resonance-stabilized quinone methide radical intermediates are involved in the reaction pathway, particularly at high temperatures. These radicals likely mediate propagation steps in the polymerization reaction; for example, if a quinone methide radical formed by homolysis of a β -O-4 ether linkage were to add to a double bond in a second (neutral) quinone methide molecule to form a new C–C bond and another radical. The formation of quinone methide intermediates may enhance cleavage of β -O-4 ether linkages by providing a more stable intermediate product (the quinone methide radical)^{24–26} than that resulting from β -O-4 cleavage in VGE, which cannot form quinone methide intermediates due to the blocking of Ar–OH, thereby reducing repolymerization reactions.

CONCLUSION

In summary, we have explored the effect of chemoselective methylation of Ar–OH groups on the reaction chemistry of lignin depolymerization. It was found that Ar–OH groups play an important role in repolymerization or charring reactions, which are undesirable during lignin depolymerization reaction. Selective methylation of Ar–OH groups significantly reduced subsequent repolymerization during thermal degradation of lignin, providing mechanistic insight into the lignin depolymerization. Finally, methylation of Ar–OH groups in model β -O-4 dimers prevented formation of a radical intermediate species, likely a quinone methide radical, suggesting a key role for this intermediate in repolymerization reactions. These findings can be applied to alteration of the natural lignification processes to produce more readily processable biomass structure.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.6b03102.

³¹P NMR spectra and gas chromatogram (PDF)

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Notes

The authors declare no competing financial interest.

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