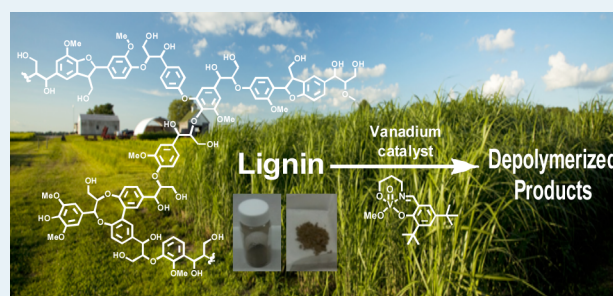


Studies on the Vanadium-Catalyzed Nonoxidative Depolymerization of *Miscanthus giganteus*-Derived LigninJulian M. W. Chan,^{†,‡,⊥} Stefan Bauer,[‡] Hagit Sorek,[‡] Sanil Sreekumar,^{†,‡} Kun Wang,^{†,§} and F. Dean Toste^{*,†,‡}[†]Department of Chemistry, University of California, Berkeley, Berkeley, California 94720, United States[‡]Energy Biosciences Institute (EBI), Berkeley, California 94720, United States[§]Institute of Biomass Chemistry and Technology, Beijing Forestry University, Beijing 100083, China

S Supporting Information

ABSTRACT: Lignin samples isolated from *Miscanthus giganteus* using organosolv processes were treated with vanadium catalysts that were previously developed in our group. We demonstrate that the catalyst with high β -O-4' bond-cleaving activity in dimeric lignin models was also effective in depolymerizing actual lignin. Molecular weight-lowering was evidenced by gel permeation chromatography (GPC), whereas 2D NMR experiments showed that β -O-4' linkages were selectively cleaved in the degradation process, just as in the case of lignin models. Monophenolic degradation products were also formed, and the individual molecules were identified and quantified by GC/MS.

KEYWORDS: lignin, vanadium, depolymerization, lignocellulose, biofuels



INTRODUCTION

The development of biorenewable chemicals and fuels from nonfood sources is of great interest because of the escalating global demand for energy, diminishing petroleum reserves, and a concern over rising CO₂ emissions.¹ Lignocellulosic biomass, often described as a recalcitrant material that is resistant to degradation,² is composed mostly of cross-linked polysaccharide networks, glycosylated proteins, and lignin. The challenge in efficiently breaking down lignocellulosic biomass remains an impediment to its utilization as an ideal carbon-neutral energy source. Although major improvements have been recently achieved in the bioconversion of cellulose to ethanol using enzyme technology,³ the fact that only 38–48% of the total plant biomass can be used renders the entire process inefficient and uneconomical. On the basis of the principles of biorefining,⁴ the ability to efficiently extract the intrinsic energy content of a given substrate is crucial for favorable process economics.

Lignin is a complex plant-derived biopolymer that accounts for ~20% of all terrestrial biomass, with a molecular structure largely composed of phenylpropanoid residues (*p*-hydroxyphenyl, guaiacyl, and syringyl) derived from three hydroxycinnamyl alcohol-based monomers: *p*-coumaryl, coniferyl, and sinapyl alcohols (Figure 1).

Although the exact monolignol content of lignin is species-dependent, the interunit linkages that connect monomer units tend to be common to all, and these include: the β -O-aryl ether (β -O-4'), resinol (β - β'), phenylcoumaran (β -5'), biphenyl (5-5'), diaryl ether (4-O-5'), and 1,2-diaryl propane (β -1') linkages (Figure 2). The β -O-4' moiety accounts for a significant

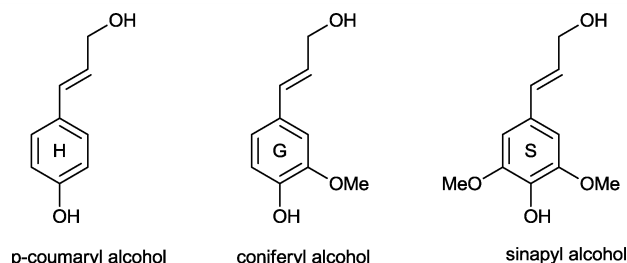


Figure 1. The three major precursor building blocks of lignin. (The substituted aromatic cores derived from these alcohols are referred to as H (*p*-hydroxyphenyl), G (guaiacyl), and S (syringyl).)

percentage of all the linkages in lignin and also happens to be one of the weakest and most abundant bonds within the structure, thus presenting itself as an obvious target with regard to lignin depolymerization. Thus, a catalyst that can effectively cleave β -O-4' bonds will significantly lower the overall molecular weight of the lignin. Furthermore, if such a process could be carried out under mild and inexpensive conditions, the utilization of lignin for high-value applications⁵ may become practical.

Although much research has dealt with the general degradation of lignin,⁵ less attention has been focused on the selective cleavage of specific linkages within the polymer.^{6–8} In addition, extending model system chemistry to actual lignin has in many cases been fraught with obstacles. For example, Binder

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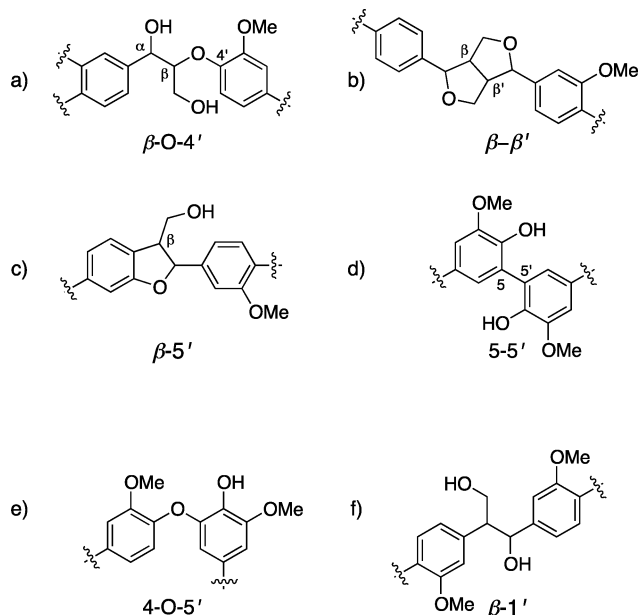


Figure 2. Various linkages between monolignol units in lignin: (a) β -O-4' (β -O-aryl ether); (b) β - β' (resinol); (c) β -5' (phenylcoumaran); (d) 5-5' (biphenyl); (e) 4-O-5' (diaryl ether); (f) β -1' (1,2-diarylpropane).

and co-workers have successfully used Brønsted acid catalysts to degrade 2-phenoxyanisole in an ionic liquid, but they were unable to achieve the same results with organosolv lignin under identical conditions.⁹ The recently developed transition metal-catalyzed depolymerization of lignin model compounds¹⁰ may have to contend with the issue of lignin having limited solubility in the aromatic hydrocarbon solvents employed in these processes. Although the efforts of Lercher and co-workers have resulted in successful catalytic lignin depolymerization, harsh conditions such as high temperatures and pressures were required.¹¹

Despite the difficulties, several catalyst systems, both heterogeneous¹² and homogeneous,¹³ have been tried on actual lignin, with varying degrees of success. Recently, our group investigated the reactivity of a series of vanadium complexes with dimeric lignin model compounds and discovered catalysts that can effectively and selectively cleave β -O-4' bonds in these lignin substructures.¹⁴ In the present paper, we demonstrate that this vanadium-based chemistry can be applied to degrade lignin extracted from *Miscanthus giganteus*. Using GPC and 2D NMR analysis, clear evidence of depolymerization resulting from selective β -O-4' bond cleavage was obtained. The results of these lignin degradation studies resemble the data obtained with lignin models in terms of the relative activities of the different catalysts, selectivity for β -O-4' bonds and the type of functional groups obtained from the reaction. Last, we also identify and quantify the volatile phenolics produced in the reaction using GC/MS.

RESULTS AND DISCUSSION

Degradation of Lignin Models. Our recent work on the degradation of lignin model compounds¹⁴ investigated a series of vanadium complexes bearing Schiff base ligands (Figure 3) as catalysts for C–O bond cleavage. Catalyst **5** was empirically found to be the most active of the series, converting 95% of the dimeric lignin model **7** under optimal conditions to give various degradation products via β -O-4' bond cleavage and a small degree of benzyl alcohol oxidation (Scheme 1). By contrast,

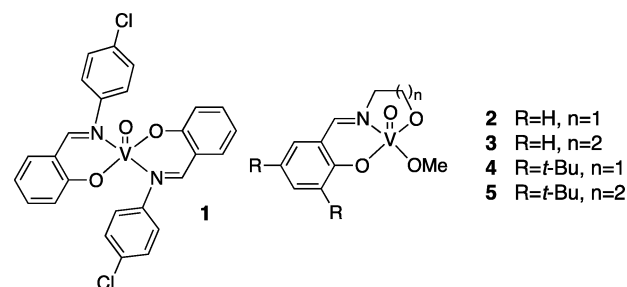


Figure 3. Structures of our recently developed vanadyl-based complexes.

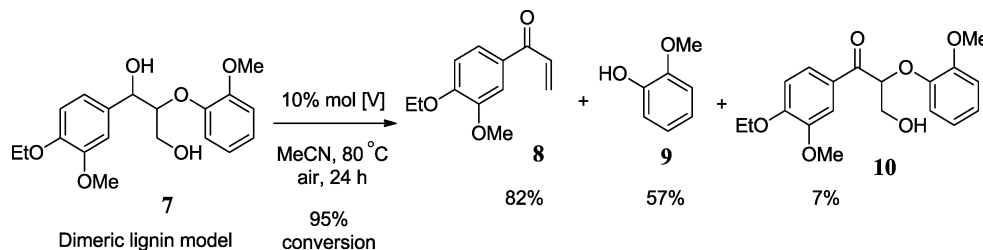
complex **1** was the least effective in β -O-4' bond cleavage and preferentially catalyzed benzylic oxidation instead. In general, the catalysts with tridentate ligands favored C–O bond cleavage over benzylic oxidation, with higher selectivities corresponding to larger bite angles. The increased reactivity of catalyst **5** can be attributed to its bulky *tert*-butyl substituents, which allow the ensuing vanadium-based intermediates to remain as catalytically active monomeric species instead of being shunted toward insoluble inert aggregates. The aryl enone **8** obtained in our model studies was interesting not only for its novelty, but also because it is a product of a redox-neutral transformation.

In an effort to elucidate the mechanism of this nonoxidative β -O-4' bond cleavage, several degradation experiments on various lignin model derivatives were subsequently carried out. A plausible mechanism based on a one-electron process was proposed (Scheme 2). The initial step in this mechanism involves ligand exchange at the vanadium center and requires the benzylic hydroxyl group to be unalkylated. The benzylic hydrogen is abstracted from the intermediate to give a ketyl radical that eliminates an aryloxy radical to generate an enolate species. Breakdown of this enolate gives rise to the observed enone product as well as a vanadium(IV) complex that is reoxidized to vanadium(V) by the aryloxy radical, completing the cycle. Molecular oxygen was found to be unessential for catalyst turnover, although it did increase the reaction rates. As such, these catalytic degradations can be conveniently conducted in the presence of air.

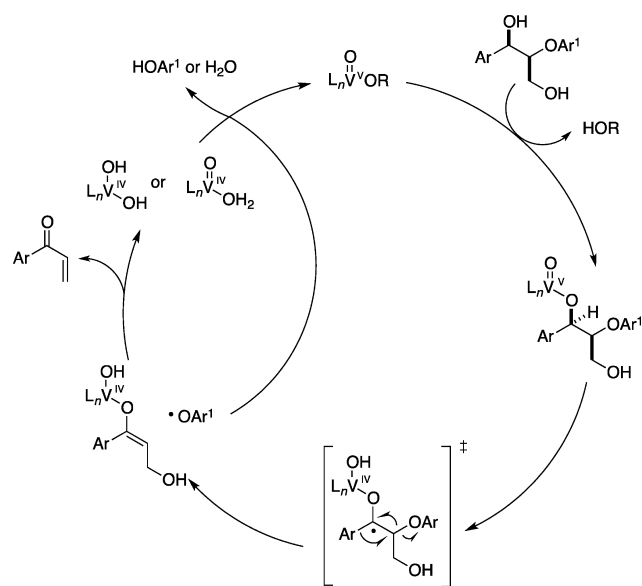
Additional experiments involving lignin substructures focused on the more complex systems, such as the trimeric model compound **11** (Scheme 3). This compound also underwent the vanadium-catalyzed β -O-4' bond cleavage reaction upon treatment with catalyst **5**. The dimeric lignin model compound **7** featured in Scheme 1 could also be degraded under identical reaction conditions in the presence of cellobiose (a model compound for cellulose), proceeding with the same selectivity and efficiency as without the cellobiose. Moreover, the cellobiose itself was unaffected by the reaction conditions. The encouraging results obtained with these complex systems suggested that the vanadium catalysts might be able to degrade plant-derived lignin, as well. On the other hand, the complex three-dimensional structure of lignin could inhibit any of the steps in the catalytic cycle, including access of the catalyst to the β -O-4' benzylic alcohol or preventing the required geometry for elimination of the aryloxy group. To assess these possibilities, we undertook a series of studies on the reactivity of our vanadium catalysts toward lignin extracted from *M. giganteus* with various solvents.

Lignin Degradation Studies. For the degradation studies involving an actual plant-derived substrate, lignin was extracted from *M. giganteus* using dioxane, acetone, and ethanol to give samples of dioxasolv lignin, acetosolv lignin, and ethanosolv

Scheme 1. Vanadium-Catalyzed Degradation of a Lignin Model Compound



Scheme 2. Proposed Mechanism for the Nonoxidative Vanadium-Catalyzed Cleavage of a Dimeric Lignin Model Compound



lignin, respectively (see the Experimental Section for details). Degradation reactions were carried out by treating the organosolv lignins with vanadium catalysts at 80 °C over 24 h in sealed vials (Scheme 4), using 10:1 acetonitrile/THF and 8:1 ethyl acetate/THF mixtures (and also acetone in the case of acetosolv lignin)¹⁵ as the solvents.

Control experiments, in which catalyst was absent, were conducted simultaneously. Upon completion, each of the resulting mixtures was evaporated to dryness and analyzed by GPC and 2D NMR to characterize changes in molecular weight distribution and functional groups, respectively. In the case of dioxasolv lignin, 24-h treatment with catalyst **5** resulted in the lowering of the overall molecular weight distribution based on GPC analysis (Figure 4a). The same extent of degradation was not observed in the controls where the catalyst was absent.¹⁷ Both solvent mixtures were found to be equally effective. Both acetonitrile and ethyl acetate were optimal solvents in lignin model studies; however, in the case of the lignin itself, THF had

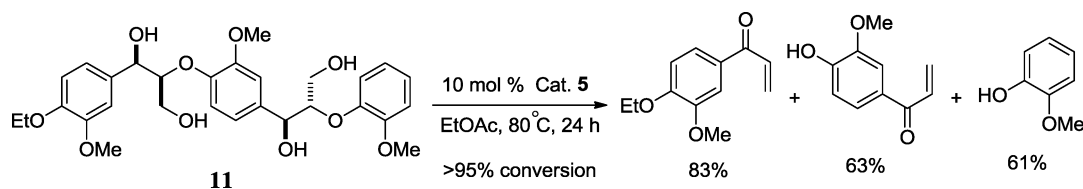
to be added to bring about complete miscibility of all the reaction components. Degradation experiments with acetosolv lignin also produced a moderate shift toward lower molecular weight species upon catalytic treatment (Figure 4b). As a solvent, acetone performed as well as MeCN/THF and ethyl acetate/THF mixtures.

Negligible depolymerization was again observed in the control where the catalyst had been deliberately omitted. In the third set of experiments involving ethanosolv lignin, GPC analysis showed less pronounced reduction in molecular weight distribution after catalytic treatment (Figure 4c). This was expected because ethanosolv lignin contains a large percentage of ethylated benzyl alcohol groups as a result of the pretreatment process that uses acidified ethanol. These modified β -O-4' linkages are inert to our vanadium catalyst because the protected OH groups cannot coordinate to the vanadium metal centers. The small percentage of β -O-4' linkages with free benzylic OH groups meant that there were fewer susceptible sites on the lignin to be cleaved, and as a result, the change in overall molecular weight distribution was less significant.

To investigate the role of β -O-4' bond cleavage in lowering the lignin molecular weights, a similar set of degradation experiments using catalyst **1** (structure shown in Figure 3) in place of catalyst **5** were conducted. Compared with **5**, the vanadium complex **1** had previously been shown to be a poor catalyst for β -O-4' bond cleavage in lignin models, and we thus expected the extent of lignin degradation to be much smaller with **1**. As expected, the reaction of **1** with dioxasolv and acetosolv lignins resulted in minimal reduction in the lignin molecular weight, as measured by GPC (Figure 5 and Supporting Information Figure S4). Moreover, ethanosolv lignin remained completely unaffected on treatment with catalytic amounts of **1** (Supporting Information Figure S5). Complex **1** does catalyze the cleavage β -O-4' to a small extent and is also able to oxidize free benzylic alcohols, accounting for its minor effect on overall molecular weight of dioxasolv and acetosolv lignins. With ethanosolv lignin, no effect was observed since the majority of benzylic OH groups are ethylated and thus not susceptible to either β -O-4' cleavage or alcohol oxidation.

Hanson et al.,¹⁸ recently reported that 8-quinolate vanadium complex **6** catalyzed selective C–C bond cleavage in phenolic lignin model compounds. Therefore, in addition to testing the

Scheme 3. Vanadium-Catalyzed Degradation of a Trimeric Lignin Model



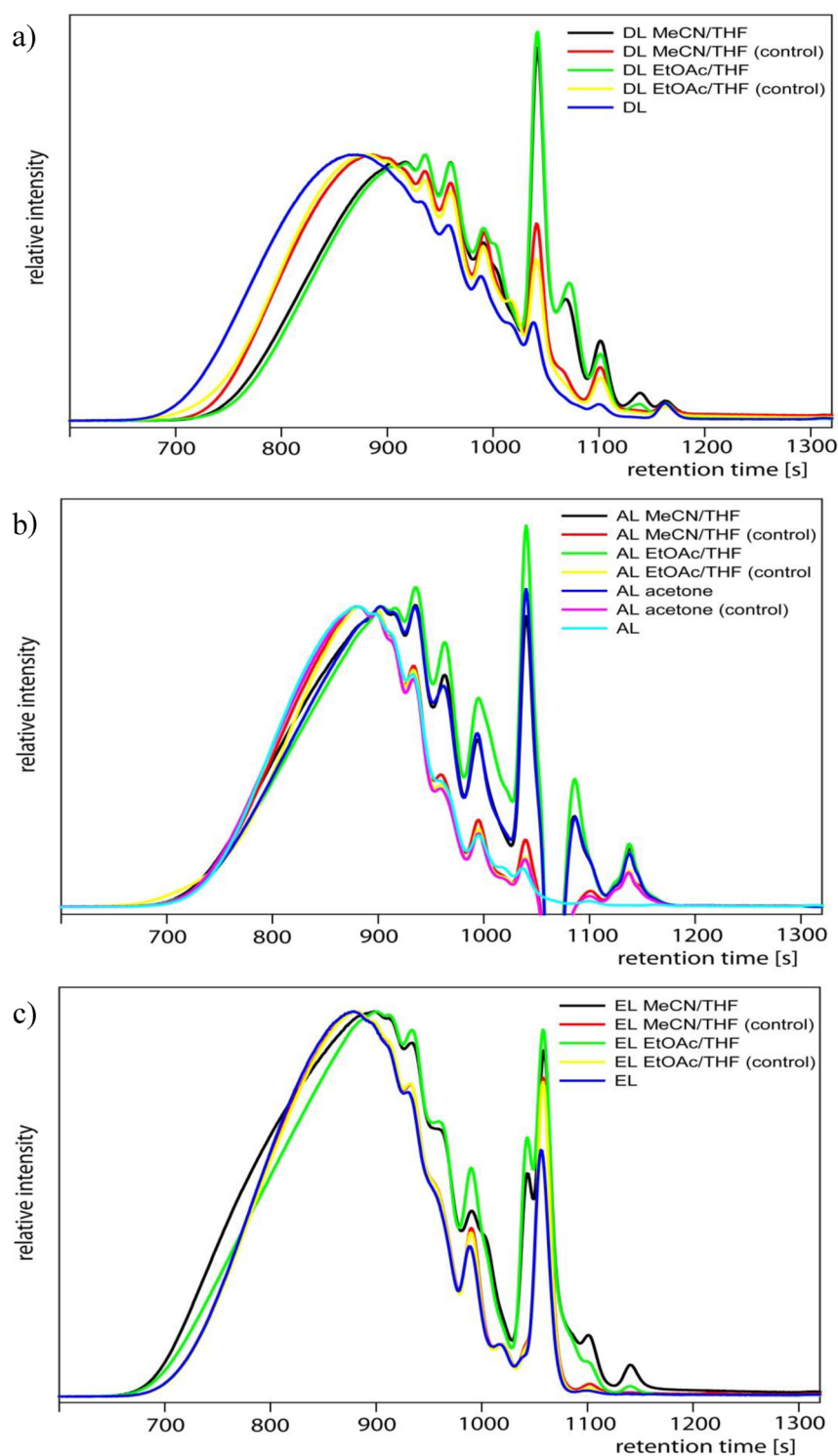
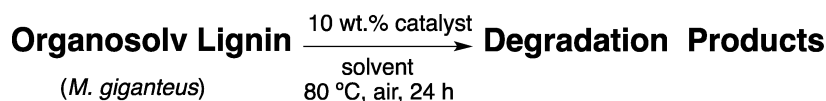
Scheme 4. Treatment of Organosolv Lignin (from *M. giganteus*) with Vanadium Catalyst¹⁶

Figure 4. GPC chromatographs showing the molecular weight distributions of untreated (a) dioxasolv, (b) acetosolv, and (c) ethanosolv lignins vs corresponding controls and postreaction product mixtures resulting from treatment with catalyst **5** in different solvent systems.

catalysts developed by our group, we also investigated the effect of catalyst **6** (Scheme 5) on the organosolv lignins. The reactions with complex **6** were conducted under conditions similar to

those above, and the resulting degradation mixtures were likewise analyzed by GPC (see Supporting Information, Figure S3), with the observation that catalyst **6** lowers the molecular

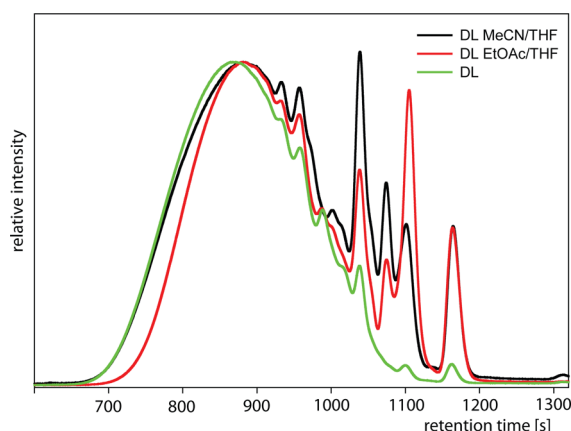


Figure 5. GPC chromatograph showing the molecular weight distributions of untreated dioxasolv lignin vs postreaction product mixtures resulting from treatment with catalyst **1** in different solvents. Chromatographs for acetosolv and ethanosolv lignins are available in the Supporting Information (Figures S4 and S5).

weights of the organosolv lignins to a similar degree as catalyst **5**. In light of these results, we envisioned that the combining β -O-aryl ether and C–C bond cleavage reactions would produce a greater degree of lignin depolymerization. However, using a combination of both catalysts **5** and **6** did not enhance the extent of degradation of organosolv lignins, as judged by GPC.

2D NMR Studies. Results of the catalytic reactions are most readily visualized from the oxygenated side chain region in the NMR spectra, particularly the two-dimensional ^{13}C – ^1H correlation (HSQC) spectra. The lignin subunits in the oxygenated side chain region were assigned by comparison with the literature.¹⁹ As has been established previously, the β -O-aryl ether (β -O-4') is a dominant linkage in lignin. The three different types of lignin used in our study are all rich in β -aryl ether units (A) with more modest amounts of resinol (B) and phenylcoumaran (C), as is typical for *M. giganteus* lignin.²⁰ The ethanosolv lignin spectrum (Figure 6a) depicts a typical lignin containing the β -O-4' (A) cross-peaks; C_α – H_α correlations observed at $\delta_\text{C}/\delta_\text{H}$ 71–72/4.8–4.9 ppm; C_β – H_β correlations observed at $\delta_\text{C}/\delta_\text{H}$ 83/4.3 and 86–87/4.0–4.1 ppm for substructures linked to G and S units, respectively; and C_γ – H_γ correlations observed at $\delta_\text{C}/\delta_\text{H}$ 59/3.5 and 3.7 ppm. Ethanosolv lignin is also rich in α -ethylated β -O-4' units (A') that are not normally reported, but they become apparent due to pretreatment under acidic conditions with EtOH.^{21,22}

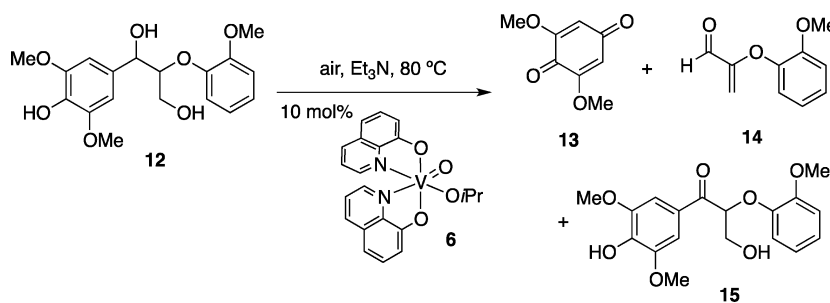
The treated ethanosolv lignin reflected almost the same side chain signals as those observed in the spectrum of untreated lignin (Figure 6a, b), except for two distinct differences. First, there are no apparent β -O-4' (A) cross-peaks. Second, signals

from resinol (β - β') substructures (B) that were observed in both spectra, with their C_α – H_α , C_β – H_β , and the double C_γ – H_γ correlations at $\delta_\text{C}/\delta_\text{H}$ 85/4.7, 53/3.1, and 71/3.8 and 4.2, respectively, were present in the treated lignin but with a slight decrease in their intensity. Both spectra showed the presence of phenylcoumaran (β -5') substructures (C), with their signals for their C_α – H_α and C_β – H_β correlations being observed at $\delta_\text{C}/\delta_\text{H}$ 86–87/5.4–5.6 and 53/3.5, respectively, and that of the C_γ – H_γ correlation overlapping with other signals around $\delta_\text{C}/\delta_\text{H}$ 62/3.6.

The α -ethylated β -O-4' linkages (A') were not attacked by the vanadium catalyst, presumably because a free OH group is required for coordination to the vanadium center, as indicated in the proposed mechanism of C–O bond cleavage. However, this linkage is a product of the pretreatment and does not exist in the native lignin.^{21,22} Since there was no postreaction separation between the catalyst and the reaction products, several cross-peaks arising from residual catalyst were observed in the spectrum (Figure 6b, in red). In addition, small new signals appeared in both treated lignin spectra. Efforts to elucidate the source of those new correlations revealed the presence of aryl enones that are the major β -O-4' cleavage products arising from lignin model degradation (Scheme 1), and these give rise to the correlations at $\delta_\text{C}/\delta_\text{H}$ 129/5.9, 6.3; 132/7.5 (confirmed by HMBC experiments, see the Supporting Information). The HSQC spectrum of the dioxane lignin reflected the same side chain signals observed in ethanosolv lignin (β -O-4' (A), resinol (B), and phenylcoumaran (C)), and there was also no modification of the β -O-4' substructures (A). Consequently, the disappearance of β -O-4' linkages from the HSQC spectrum of treated lignin was quite noticeable (Figure 6d). Regarding the other substructures, no significant change was detected. The HSQC spectra of the acetone lignin before and after catalytic reaction revealed the most significant changes (Figure 6, d, e). Some of these changes (most likely in the carbohydrate moieties) were observed in the spectrum of the control reaction (Figure S1, in the Supporting Information); however, the relevant β -O-4' (A) linkage remained unaffected in the control experiment, as did the resinol (B) and the phenylcoumaran (C) substructures.

GC/MS Studies. Although GPC and 2D NMR spectroscopy are useful in elucidating changes in molecular weight distribution and functional groups, respectively, they are not ideal ways to characterize or quantify individual degradation products. In particular, volatile small molecules released by the process would escape analysis. From the standpoint of being able to eventually utilize lignin as a renewable aromatic chemical feedstock, these small molecules (e.g., monophenolics) are especially important because they represent highly functionalized monobenzenoid species that could serve as precursors to numerous commodity bulk chemicals/materials. Therefore, in addition to GPC and 2D

Scheme 5. Selective C–C Bond Cleavage in Lignin Model Systems Catalyzed by 8-Quinolate-Based Vanadium(V) Complex **6**¹⁸



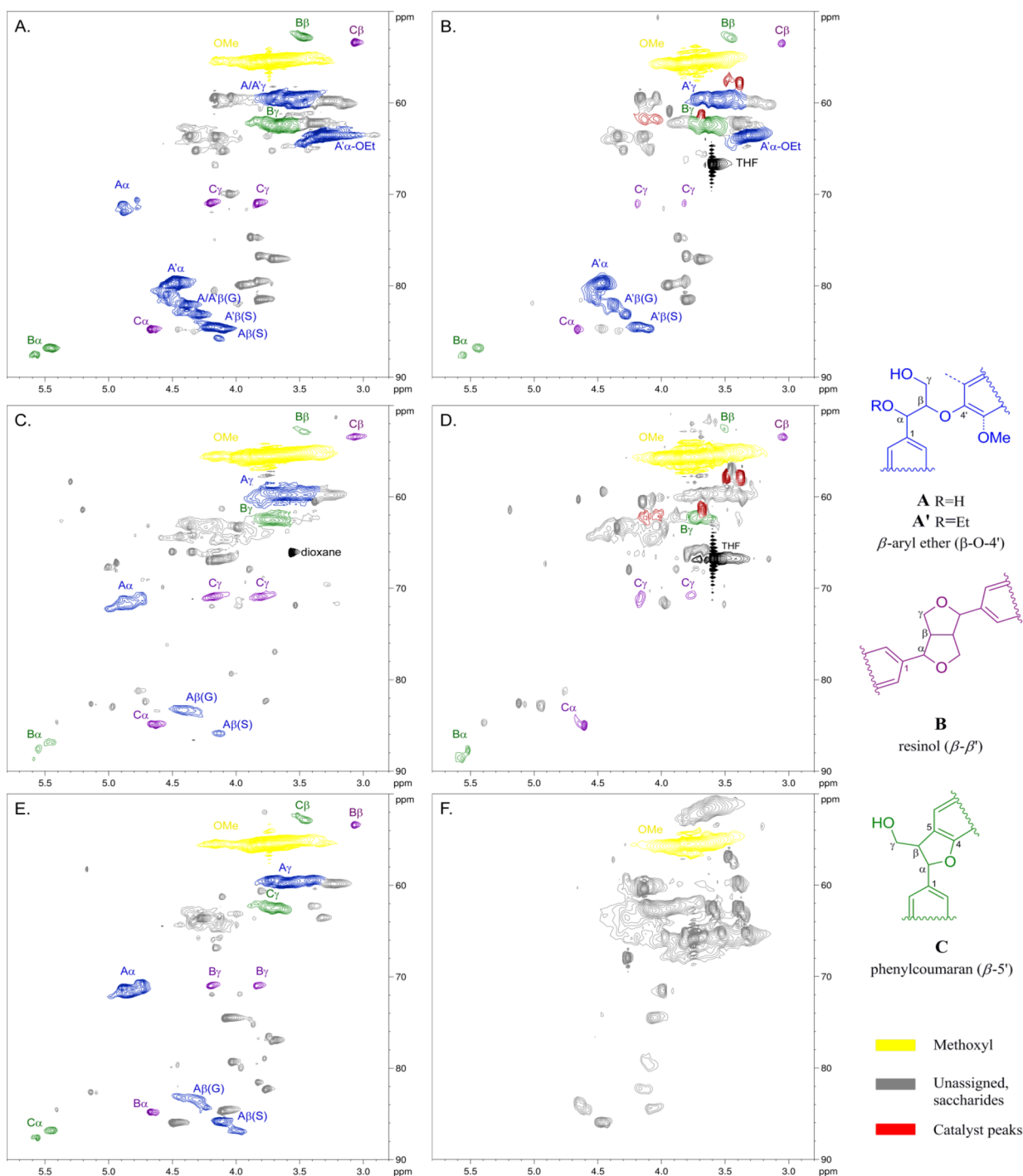
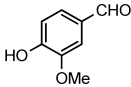
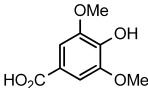
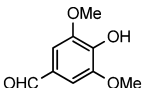
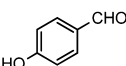
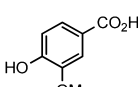
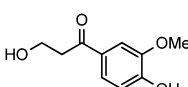
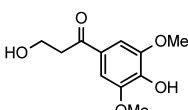
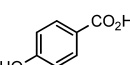


Figure 6. The HSQC spectra of the oxygenated aliphatic part (δ_C/δ_H 50–90/2.8–5.8) of three different untreated lignins (left) and the resulting mixture after treatment with catalyst **5** (right): (a) ethanosolv lignin, (b) treated ethanosolv lignin, (c) dioxasolv lignin, (d) treated dioxasolv lignin, (e) acetosolv lignin, and (f) treated acetosolv lignin.

NMR characterizations, GC/MS analysis was also performed on the product mixture arising from vanadium-treated dioxasolv lignin (i.e., the lignin that degraded the most according to GPC). For this, the catalytic degradation was conducted in an identical manner, except that the final mixture was not evaporated to dryness prior to analysis. The omission of this workup step was to avoid the loss of any volatile products. Control experiments containing no added catalyst were also run alongside under identical conditions. Precise experimental details are described in the Experimental Section. The main phenolic

products that were formed are shown in Table 1, in descending order of quantity detected. Vanillin, syringic acid, and syringaldehyde were found to be the three most prevalent degradation products, resulting from the G and S units of lignin respectively. All other products are also consistent with fragments that could arise from the cleavage of β -O-4' carbon–oxygen bonds in lignin.

Table 1. The Identity and Yield of the Volatile Monophenolic Compounds Released by the Vanadium-Catalyzed Degradation of Dioxasolv-Lignin (1.0 mg in 0.50 mL of solvent), as Determined by GC/MS

Entry	Degradation product	Quantity formed (μg)
1	 Vanillin	7.8
2	 syringic acid	6.7
3	 syringaldehyde	5.9
4	 4-hydroxybenzaldehyde	3.3
5	 Vanillic acid	3.1
6	 3-hydroxy-1-(4-hydroxy-3-methoxyphenyl)propan-1-one	1.2
7	 3-hydroxy-1-(4-hydroxy-3,5-dimethoxyphenyl)propan-1-one	0.8
8	 4-hydroxybenzoic acid	0.5

CONCLUSIONS

Lignin model systems are often employed as surrogates for the more complex polymer to simplify the development of novel processes for the depolymerization of lignin. However, the complex three-dimensional structure of natural lignin can raise concerns about the validity of these model systems and whether the chemistry discovered employing them will translate to lignin. In this study, we show that the reactivity observed in the vanadium-catalyzed nonoxidative degradation of organosolv

lignins from *M. giganteus* closely emulates that originally observed for the cleavage of β -O-aryloxy bonds in simple models for the β -O-4' linkage.

GPC analysis showed that dioxasolv and acetosolv lignins treated with catalyst **5** had lower molecular weight distributions compared with control experiments in the absence of catalyst. The reactivity of **5** toward these lignins parallels that uncovered in the model studies in several ways. First, two-dimensional NMR studies (HSQC and HMBC experiments) revealed that correlations due to β -O-4' linkages either diminished significantly or disappeared completely following catalytic treatment, as a result of β -O-aryloxy bond cleavage. In addition, these NMR studies revealed that, as in the model studies, enones are formed as a result of this C–O bond cleavage. Second, a lesser degree of depolymerization was observed for lignin samples treated with catalyst **1** that was also less active in the model systems. Third, ethanosolv lignin was significantly less reactive toward vanadium-catalyzed depolymerization. This lower reactivity could be correlated to a prevalence of ethylated benzylic hydroxyl groups in ethanosolv lignin resulting of the acidic pretreatment and is consistent with the requirement for a free benzylic alcohol in the reactive model compounds. This latter finding highlights that pretreatment and isolation can dramatically alter the structure and, in turn, reactivity of lignin toward catalysts. Ideally, for future development of catalysts, the results obtained in model studies can potentially be used to inform the appropriate isolation lignin method. Finally, using GC/MS, we also identified and quantified the formation of various highly functionalized monophenolic compounds that could prove useful as part of a renewable aromatic chemical feedstock.

EXPERIMENTAL SECTION

General Considerations. All commercial solvents and chemicals of ACS-certified grade were purchased from Fisher Scientific and used as received. The vanadium complexes **1** and **5** were synthesized by Dr. Sunghye Son.¹⁴ Lignin samples were prepared according to the procedure described below.

Preparation of Organosolv Lignin from *Miscanthus*. The isolation was carried out according to Bauer et al.²² In brief, *M. giganteus* was ground up using a SM200 rotor mill (Retsch, Haan, Germany) passing through a sieve of 2 mm pore size. The ground biomass was extracted with water and ethanol at 100 °C using an ASE350 (Automated Solvent Extractor, Dionex, Sunnyvale, CA). The extracted biomass was further ground using a ZM200 rotor mill (Retsch, Germany) passing through a sieve with a 0.5 mm pore size and refluxed with either 95% ethanol/5% 4 M HCL (v/v) or 95% acetone/5% 4 M HCL (v/v) (using a nitrogen atmosphere for dioxane extraction) for 4 h. After filtration through a glass microfiber filter, the filtrate was concentrated, and the dissolved lignin was precipitated in acidified water; collected by centrifugation (3200g); washed with water; and finally, freeze-dried.

Molecular Weight Analysis (GPC). Lignin samples were dissolved in THF and analyzed on a PolymerLabs GPC 50 system (Agilent Technologies, Santa Clara, CA) with a UV detector and autosampler. The samples were injected onto a series of two MesoPore columns (300 \times 7.5 mm, Agilent Technologies) including a guard column (50 \times 7.5 mm), eluted at 30 °C with 1 mL/min THF, and detected at 280 nm. The system was calibrated using polystyrene standards in the range of M_p 38 640–162 Da (EasiVial PS-L, Agilent Technologies).

NMR Spectroscopy. The NMR spectra were acquired on a Bruker Avance 600-MHz spectrometer equipped with a CPTXI cryoprobe. Lignin (10 mg) was dissolved in 0.6 mL of DMSO- d_6 ; the solvent peak was used as an internal reference (δ_C 39.5, δ_H 2.49 ppm). We used the standard Bruker implementations of 2D NMR (COSY, HSQC, HMBC, and HSQC-TOCSY) experiments for structural elucidation and assignment authentication. HSQC experiments (Figure 6) had the following parameters: acquired from 12 to 0 ppm in F2 (1H) by using 2048 data points for an acquisition time (AQ) of 143 ms, 210–0 ppm in F1 (^{13}C) by using 256 increments (F1 acquisition time 4.0 ms) of 48 scans with a 1 s interscan delay (D1). Squared cosine-bell apodization function was applied in both dimensions. HSQC cross-peaks were assigned by combining the results and comparing them with the literature.

GC/MS Analysis. To 50 μ L of reaction mixture, 50 μ L of internal standard (isopropylphenol, 50 μ g/mL in THF) was added, and the mixture was incubated with 100 μ L of *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) containing 1% trimethylchlorosilane (TMSCl) at 70 $^{\circ}C$ for 30 min. A 1 μ L portion was injected in splitless mode onto a VF5-ms capillary column (30 m \times 0.25 mm \times 0.25 μ m, Varian, Palo Alto). An Agilent 7890A gas chromatograph coupled to an Agilent 5975C single quadrupole mass spectrometer with the following settings was used: injector temperature, 280 $^{\circ}C$; carrier gas, helium at 1 mL/min; temperature program, 75 $^{\circ}C$ 3 min isocratic, 5 $^{\circ}C$ /min to 150 $^{\circ}C$, 0.5 to 160 $^{\circ}C$, 2 to 190 $^{\circ}C$, 5 $^{\circ}C$ /min to 240 $^{\circ}C$, 70 $^{\circ}C$ /min to 325 $^{\circ}C$, 3 min isocratic; ions were detected in full scan mode m/z 35–500. Identification of compounds was achieved by comparing mass spectra with the National Institute of Standards and Technology (NIST) database entries or by interpretation of the mass spectra and comparison to literature data and was further confirmed by the retention time of standards if available. Quantitation was performed using selected extracted ions for the compounds in internal standard calibration mode (m/z 193 for isopropyl phenol). Background levels of phenols in an unheated, unreacted mixture of dioxane-lignin and catalyst in solvent were controlled and accounted for.

■ ASSOCIATED CONTENT

■ Supporting Information

Additional 2D NMR spectra (HSQC and HMBC) and GPC traces from the lignin degradation experiments. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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(15) In addition to these conventional organic solvents, we also explored nonvolatile green solvents for the lignin degradation. The ionic liquids 1-ethyl-3-methylimidazolium (emim) acetate, 1-butyl-3-methylimidazolium (bmim) hexafluorophosphate, and 1-ethyl-3-methylimidazolium (bmim) tetrafluoroborate were tested for compatibility with our vanadium-based chemistry. As expected, [emim][acetate], which has a nucleophilic anion, was incompatible with the vanadium complexes. On the other hand, [bmim][PF₆] and [bmim][BF₄], both of which feature noncoordinating and relatively inert anions, proved to be excellent solvents for the vanadium-catalyzed cleavage of β -O-4' bonds in dimeric lignin models, yielding results as favorable as those obtained previously with acetonitrile.¹⁴ Unfortunately, ethanosolv lignin was found to be insoluble in [bmim][PF₆], and although the lignin did dissolve readily in [bmim][BF₄], degradation experiments showed the ionic liquid to be inferior to the much less expensive conventional organic solvents.

(16) Typical experimental procedure: A 5-mL glass vial containing organosolv lignin (10.0 mg), vanadium catalyst (1.0 mg), solvent mixture (0.5 mL), and a small magnetic stir-bar was sealed with a screw cap, then shaken and sonicated for 15 min before being heated with vigorous stirring in an oil bath at 80 °C for 24 h (with air occupying the headspace above the reaction mixture). The reaction mixture was cooled to room temperature, and all the solvents were removed by rotary evaporation, after which the resulting residue was characterized by GPC and 2D NMR. For GC/MS studies, rotary evaporation was not done; the reaction mixture was directly analyzed.

(17) The slight but apparent decrease in molecular weights for the dioxasolv lignin controls was due to an artifact rather than actual degradation in the absence of catalyst. Unlike ethanosolv and acetosolv lignins, heating dioxasolv lignin for prolonged periods produced a small amount of THF-insoluble residue that likely resulted from the highest molecular weight polymer chains reacting and combining, causing them to escape subsequent GPC analysis.

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