Selective C−C Bond Cleavage of Methylene-Linked Lignin Models and Kraft Lignin

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Ⓢ *Supporting Information*

ABSTRACT: Biorefinery and paper pulping lignins, referred hereto as technical lignins, contain condensed C−C interunit linkages. These robust C−C linkages with higher bond dissociation energies are difficult to disrupt under hydrogenolysis conditions, which are generally used for cleaving C−O bonds of native lignin in biomass or model C−O linked compounds. Thus, selective interunit C−C cleavage to release aromatic monomers for high-value applications is a challenge. We report an effective catalytic system to cleave such C−C bonds selectively under mild conditions. A representative methylene-linked C−C model dimer achieves 88% yield of mainly two aromatic monomers within 1.5 h at a reasonably low temperature (250 °C) using a commercial CoS$_2$ catalyst. Aromatic monomers convert to nonaromatic products upon the reaction for a prolonged time. The interunit C−C bond of the dimer become unreactive to cleavage upon dehydroxylation of aromatic rings, while the methoxyl group has little effect on the cleavage. β-1 and 5-5 C−C linked model dimers formed demethoxylated hydroxyl dimers as the major products. Depolymerization of a purified kraft lignin fraction yields five aromatic monomers and lower-molecular-weight soluble products. This study opens up the possibility of valorization of technical lignins using inexpensive catalysts.

KEYWORDS: *technical lignin, kraft lignin, C−C cleavage, model lignin, biorefinery lignin, selective catalysis*
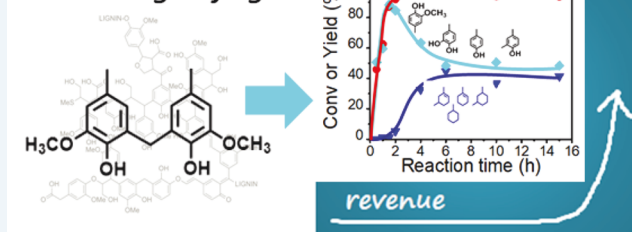
■ INTRODUCTION

Technical lignins, generated by the biorefinery and paper pulping industries, are considered low-value waste streams, and their valorization have intrigued researchers for decades. Researchers have made numerous efforts to disrupt technical lignins into low-molecular-weight (M_w) fragments to upgrade to value-added aromatic products.[1,2] Recent efforts on lignin valorization have been mainly focused on selective cleavage of β-O-4 (β-ether) linkages, which represent the major interunit linkages (50−60%) in native lignin of lignocellulosic biomass,[3−6] with the balance being α-O-4 and various C−C linkages, such as β-5, β-1, and 5-5.[3,7] Hydrolysis,[8] hydrogenolysis,[9−14] and oxidation[15,16] pathways have been widely investigated for lignin depolymerization (Scheme 1). Hydrogenolysis is a selective method to depolymerize lignin to monomers via β-O-4 bond cleavage;[4,9−12] however, the total monomer yield is limited by robust C−C interunit linkages.

In contrast, technical lignin contains mostly interunit C−C bonds, which are formed during biomass pretreatment or pulping processing. Higher bond dissociation energies (BDEs) of C−C bonds (75−118 kcal/mol) in comparison to those of C−O linkages (70 kcal/mol) pose challenges to depolymerize technical lignins selectively under mild conditions (Scheme 1).[17,18] For example, hydrogenolysis depolymerzation of organosolv lignin achieved only 7% monomer yield,[11] while depolymerization of native lignin or uncondensed lignin yielded up to 48% monomers upon cleaving β-O-4 bonds.[3,19,20] Similarly, hydrogenolysis depolymerization of kraft lignin with Pt/Al$_2$O$_3$ at 250−300 °C formed about 7% monomer yield.[21,22] Catalytic pyrolysis of alkali kraft lignins with strong solid acids or solid acid supported catalysts at elevated temperatures (up to 650 °C) was reported to give <10% lignin oil, with the majority being undesired coke (up to 40%) and deactivation of the catalysts.[23,24]

Another common issue of current processes is the very low selectivity of each product, rendering any separation approach energy intensive and expensive. For example, kraft lignin depolymerization in ethanol under pyrolysis conditions (380 °C) produced over three dozen monomers, out of which the total amount of aromatic phenols was only 10%.[25] Efforts have been made to study the cleavage of model compounds featuring 5-5, β-5, and β-1 linkages, but the saturation or disruption of aromatic rings and C−O cleavage were observed, instead of C−C cleavage, under hydrogenolytic and oxidative conditions.[26,27] A CoMo/Al$_2$O$_3$ catalyst was found to be ineffective to cleave the 5-5′ linkage of a model dimer in a prior

Scheme 1. Representative Lignin Structure Featuring Interunit C–O (e.g. β-O-4, Highlighted in Blue) and C–C (e.g. β-β, β-5, and 5-5, Highlighted in Red) Linkages and Current "Lignin-First" Strategy To Produce Monomer in Which C–C Bonds Are Uncleavable
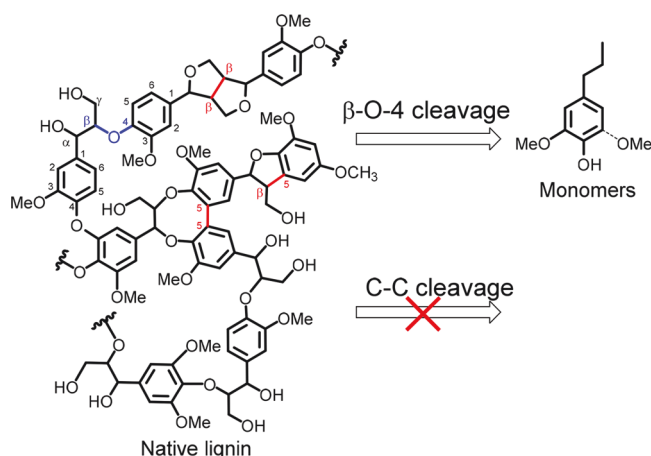
study,[28] while a flowerlike hierarchical MoS_2 composite[29] offered unselective bio-oil yield at higher temperature (310 °C), likely via thermopyrolysis. Because of the rigidity of C–C linkages and the structural complexity, the majority of the 80 million tons of technical lignins annually generated in pulping and biorefinery processes is considered a low-value waste and is burned only for heat recovery.[30]

Efficient conversion technologies to depolymerize technical lignins into high-value fuels and aromatic products are necessary to maximize waste utilization and carbon efficiency in bioproducts and to create additional revenue for pulping and biorefineries. Prior reports suggest that methylene linkages could be formed in technical lignins during self-condensation or in situ generated formaldehyde-induced condensation of depolymerized lignin fragments containing aromatic rings with α-hydroxyl side chain functionalities in acidic and alkaline media.[25,31–33] Herein, we report an effective approach to improve the selective depolymerization of technical lignins using model lignin dimers (dimethylguaiacylmethane, DMGM (Figure 1A) and its dehydroxylated analogues) and purified kraft lignin as representative examples. First, we evaluate the activity of a few types of readily available metal sulfides to

disrupt the methylene linkage of DMGM. The synthesis of DMGM featuring a methylene linkage is shown in Figures S1–S3 in the Supporting Information. The reasons to choose these types of catalysts are as follows. (1) Kraft lignin generally contains 1.5–3% of sulfur which comes from Na_2S, a chemical reagent promoting lignin removal during biomass pretreatment. Metal sulfides are expected to be resistant to sulfur poisoning. (2) Metal sulfides, such as FeS_2, CoS_2, and MoS_2, exist naturally in highly pure forms; therefore, these inexpensive materials are economically suitable for upgrading waste lignin liquor.

■ RESULTS AND DISCUSSION

FeS_2 has been used as a catalyst for hydrocracking of heavy oils containing aromatic units at 300–450 °C. Studies have found that FeS_2 can cleave interunit C–C bridge linkages between aromatic rings.[34] Therefore, we first tested FeS_2 as the catalyst to disrupt the methylene linkage of DMGM at 250 °C and 50 bar of H_2. Monomeric and a small amount of dimeric products are formed (Figure 1A and Figure S4). Some of the resultant monomers having one or two isomers are grouped for simplification, and their retention times are shown in Figure S4. Without FeS_2, DMGM depolymerization at 250 °C and 50 bar of H_2 for 15 h achieves only 15% conversion (Figure S5), likely via thermal pyrolysis. Pyrolysis of lignin to monomers without catalysts and H_2 input has been reported previously.[35] In the presence of FeS_2, a monomer yield of 64% with 97% selectivity is achieved under comparable reaction conditions. This temperature (250 °C) has been widely used in the hydrogenolysis cleavage of β-O-4 linkages of native lignin or model lignin compounds with Ni/C, Ru/C, and Pt/C catalysts,[1,4,5,11,19,36] which allows a fair comparison of the catalytic activities of the two types of catalysts for cleavage of the respective C–C and C–O bonds (vide infra). The reaction is ineffective at 200 °C, giving no conversion of DMGM in the presence of FeS_2. While the results with FeS_2 at 250 °C, giving 64% total monomer yield containing five phenolic products, are more selective in comparison to those of prior studies demonstrating the formation of heterogeneous slates of molecules under pyrolysis conditions, the separation of desired monomer from the five products is still a challenge. In addition, 30% of demethoxylated and dehydroxylated dimeric products with partial ring hydrogenation (Figures S4 and S5) is formed, and these products have been proven to be
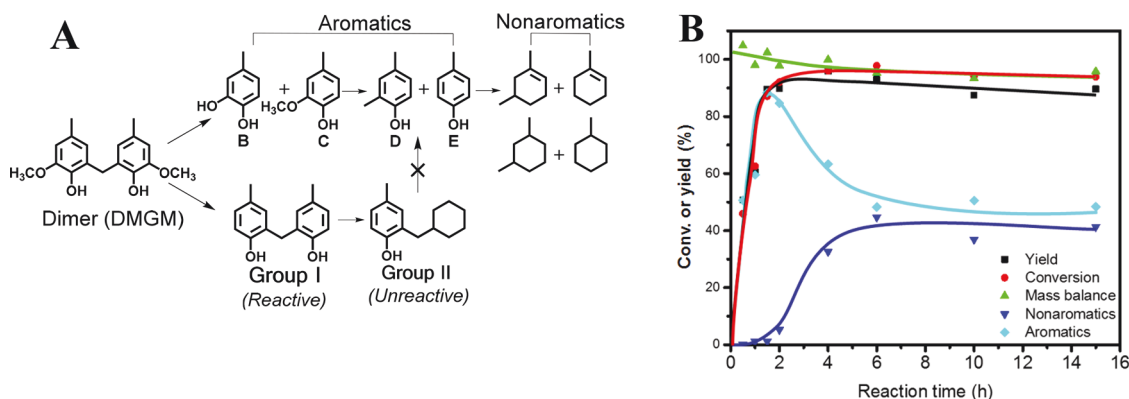

Figure 1. (A) Proposed pathways for metal sulfide catalyzed methylene linkage disruption of dimethylguaiacylmethane (DMGM). (B) Time-course reaction profile for CoS_2-catalyzed DMGM disruption, showing selective formation of aromatic monomers in a short reaction time. Reaction conditions for the time-course experiments: 20 mg of DMGM, 10 mg of CoS_2, 50 bar of H_2, 250 °C, 20 mL of heptane.

uncleavable (vide infra). Therefore, we tested two other metal sulfides, MoS_2 and CoS_2.

The MoS_2-catalyzed reactions under conditions comparable to those for FeS_2 formed a small amount of monomer (8%) and a significant amount of demethoxylated and dehydroxylated dimers with or without partial ring hydrogenation (Figures S4 and S6), which remained uncleaved. In contrast, the initial CoS_2-catalyzed reaction at 250 °C and 50 bar of H_2 for 15 h produced only three monomers (B, D, and E in Figure 1A and Figure S6). The clean dimer region in the GC chromatogram (retention time of 11.7−16.5 min in Figure S6) indicates that the methylene linkage of DMGM was selectively cleaved without formation of uncleavable dimeric products. However, the initial reaction for 15 h gives only a low yield of aromatic monomers. We hypothesize that the low yield could be due to the further conversion of aromatic monomers to other products during a long reaction time of 15 h. Therefore, a time-course experiment was conducted to study the reaction profile of the CoS_2-catalyzed disruption of DMGM.

The time-course results show selective formation of the two aromatic monomers B and C (Figure 1B) at the beginning of the reaction, and the total monomer yield reached 88% within 1.5 h (Figure 1A and Figure S7 and Table S1). B and C convert to other two aromatic monomers, D and E (Figure 1A), through possible dehydroxylation and demethoxylation, when the reaction continued for 4 h. Complete and partial ring hydrogenated nonaromatic products, methyl cyclohexene and cyclohexane (Figure 1A and Figure S7 and Table S1), are formed upon continuing the reaction for 15 h. Small amounts of demethoxylated and dehydroxylated dimeric products are also formed. We hypothesize that the dimers become uncleavable after losing the methoxyl and/or hydroxyl groups of DMGM. To validate the hypothesis, we investigate the C−C cleavage of other model dimers containing a methylene linkage, but without methoxyl and/or hydroxyl groups (Figure S8). The results show the methylene linkage of a model dimer with a phenolic hydroxyl on both aromatic rings but the linkage without methoxyl can still be cleaved with 77% conversion in 1.5 h, suggesting that the methoxyl group has little effect on the cleavage of C−C bonds. Another model dimer with one phenolic hydroxyl group on one ring and no phenolic hydroxyl on the second ring results in low conversion (20%) under comparable reaction conditions. This indicates that the cleavage of the methylene linkage depends on the chemical environments of lignin molecules, especially the vicinal phenolic groups which likely interact with the Co^{2+} sites of cobalt sulfide, and the strong electron-donating effect of the phenolic groups weakens the methylene linkage. This argument becomes more pronounced when an analogous diphenyl model compound without any phenolic hydroxyl group substituent showed no C−C cleavage. Likewise, β-1- and 5-5-linked model dimers formed their corresponding demethoxylated hydroxyl dimers as the major products (Figure S8).

To elucidate the transformation of monomers B and C to monomers D and E, B and C were reacted individually with the CoS_2 catalyst under reaction conditions comparable to those used for the disruption of model dimers. B converts to E through dehydroxylation, but demethoxylation of C formed B and E. A reaction with a mixture of B and C also gives E as the sole product. On the basis of the aforementioned discussion (Figures S7−S9), a proposed reaction pathway for the CoS_2-catalyzed DMGM disruption is shown in Figure 1, although the exact pathway of formation of D is inconclusive.

Next, we tested the role of H_2 for cleavage of the methylene linkage of DMGM. At 10 bar of H_2, DMGM conversion reached only 21% as opposed to nearly 90% at 50 bar of H_2 (Table S2). Another experiment at 10 bar of H_2 but a total pressure of 50 bar using N_2 as an inert gas improved the monomer yield slightly (27%) due to better H_2 solubility in the solvent. Without H_2, DMGM is unreactive, indicating that the C−C cleavage is likely H_2 assisted as reported for C−O cleavage of lignin compounds.[37]

We used Ru/C and Pt/C catalysts to compare their C−C cleavage performance with that of CoS_2. These noble-metal catalysts have been used to selectively cleave β-O-4 linkages of model and native lignins via hydrogenolysis, but C−C cleavage of lignin by these catalysts is rare.[26,27,38] The results in Table 1

Table 1. Comparison of CoS_2- and Noble-Metal-Catalyzed DMGM Disruption and Kraft Lignin Depolymerization[a]

entry	feedstock	solvent	catalyst	catalyst loading (mg)	aromatic monomer yield (%)
1	DMGM	heptane	CoS_2	10	88[b]
2	DMGM	heptane	Ru/C	10	9.9[c]
3	DMGM	heptane	Pt/C	10	4.1[d]
4	lignin[e]	heptane	CoS_2	50	1.2
5	lignin[e]	dioxane	CoS_2	50	11.7
6	lignin[e]	dioxane	CoS_2	100	13.2
7	lignin[e]	THF	CoS_2	50	12.6

[a]Other reaction conditions: 50 bar of H_2, 250 °C, 1.5 h for dimer or 15 h for kraft lignin, 50 mg of kraft lignin or 20 mg of DMGM. [b]Dimer conversion 100%. [c]Dimer conversion 15.3%. [d]Dimer conversion 5%. [e]Kraft lignin (alkali) fraction purified by the ALPHA process.[39] A comparison of breakdown monomer yield from CoS_2, Ru/C, and Pt/C catalysis of DMGM is given in Table S3. Ru/C-catalyzed kraft lignin depolymerized monomer yields in heptane and dioxane are shown in Table S4.

show that CoS_2 exhibits much higher activity to cleave C−C linkages to two monomers (B and C) with 81% yield out of a total molar yield of 88% (entry 1 in Table 1). In contrast, the Ru/C- and Pt/C-catalyzed reactions yield very little monomers (total yields of B and C are 9.9% and 4.1%, respectively; entries 2 and 3 in Table 1), which likely result from a small amount of thermopyrolysis at 250 °C, as observed in the blank experiment without the catalyst (discussed above). The results reveal that CoS_2 is very effective and selective toward aromatic monomers with high yield at high conversion of DMGM in heptane.

Next we evaluate depolymerization of a low-M_w fraction of a kraft lignin with an average M_w value of 1600 Da with the highest M_w species ranging up to 10000 Da (Figure 2) with CoS_2. The kraft lignin fraction was obtained from purification and fractionation of an alkali kraft lignin via the aqueous lignin purification with hot acids (ALPHA) process,[39] followed by a single water wash to remove the acetic acid solvent and reduce the total metals content to <200 ppm and then drying to remove excess water. The ALPHA process had no effect on the original sulfur content of the kraft lignin. Depolymerization with Ru/C was also performed for comparison. The initial results show poor depolymerization of the kraft lignin fraction in heptane (entry 4 in Table 1), which we ascribed to its low solubility in heptane. The solvent screening results suggest that the kraft lignin fraction has higher solubility in dioxane and tetrahydrofuran (THF). In dioxane, CoS_2 catalysis achieves
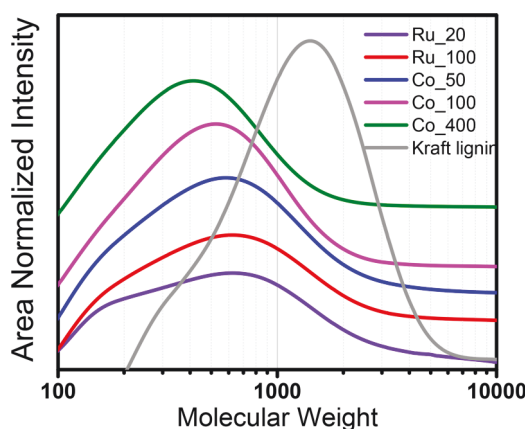
Figure 2. GPC of a kraft lignin fraction before and after depolymerization with CoS_2 and Ru/C.

maximum 13% monomer yield (entries 5 and 6 in Table 1). A reaction in THF yields a similar amount of monomers (entry 7). In contrast, Ru/C-catalyzed reactions in heptane and dioxane at two different catalyst loadings (20 and 100 mg) yield a maximum of 5% aromatic monomers (Figure S10 and Table S4), which are likely formed via cleavage of a small amount of β-O-4 linkages (5−7%[21]) present in the kraft lignin fraction. However, the structural complexity of the condensed kraft lignin makes it difficult to explain which linkages (methylene versus other C−C bonds) were disrupted during the reaction. In addition, M_w species that are outside the detectable range of GC/GC-MS could be formed. Therefore, gel permeation chromatography (GPC) was used to qualitatively characterize the change in M_w of lignin species before and after depolymerization.

Figure 2 shows that the highest M_w species in the kraft lignin fraction before depolymerization ranges up to 10000 Da with an average M_w of about 1600 Da. In contrast, the average M_w of depolymerized lignin is decreased by about 3−5-fold and the M_w distribution range is significantly narrowed. The shape of the peak, M_w distribution range, and average M_w of depolymerized lignin at two different Ru/C loadings are similar, indicating that increasing Ru/C loading could not further cleave interunit C−O or C−C linkages, consistent with similar monomer yields obtained from the two reactions (Table S4). In the case of CoS_2, the M_w distribution range of depolymerized lignin is narrower than that of the Ru/C-catalyzed depolymerization, indicating that a greater degree of depolymerization of kraft lignin occurred. Furthermore, average M_w and the range of the highest M_w of the depolymerized species decreased with an increase in CoS_2 loadings, indicating that C−C cleavage occurred by the CoS_2 catalyst, in addition to any cleavage of the small amount of C−O linkages that are present in kraft lignin. This observation is also consistent with the results of DMGM cleavage, in which the monomer yield increased with CoS_2 loadings.

The CoS_2-catalyzed reaction also generated H_2S (Figure S11), and we hypothesize that CoS_2 could be reduced to CoS by H_2 during the reaction. The XRD pattern of the recovered catalyst validates the hypothesis, which showed the characteristic peaks for CoS (Figure S12). In addition, CoS_2 was treated in heptane and dioxane individually in the absence and presence of H_2 without DMGM or lignin, and the recovered catalyst was characterized by XRD. The recovered catalyst retained characteristic CoS_2 peaks in the absence of H_2;

however it changed to CoS in the presence of H_2 (Figure S13) in both solvents. Thus, CoS_2 may not be the active phase for the C−C cleavage. CoS, synthesized by the reported procedure,[40] yielded 7.7% and 11.1% monomer from the kraft lignin fraction at catalyst loadings of 50 and 100 mg, respectively, which are slightly lower than those from the CoS_2-catalyzed reactions (entries 5 and 6 in Table 1).

A recycling study of CoS_2 shows (Figure S14) that the recovered catalyst is slightly less active and the total monomer yield in the third cycle is 14% lower than that in the first cycle. Compositional analyses of CoS_2 and the recovered catalyst by XRF (for Co and S) and elemental analysis (for S) indicate that the atomic ratio of Co to S in the catalyst before the reaction is 1:1.7, while the ratio decreased to 1:1 in the recovered catalyst after the reaction. The compositional analysis data are consistent with the XRD pattern discussed above and suggest that the catalyst was reduced to CoS by H_2 during the reaction. XPS was employed to examine the surface composition and oxidation states of Co and S of the catalysts before and after C−C cleavage of DMGM (Figure S15). The deconvoluted Co $2p^{3/2}$ band shows peaks for CoS_2, CoS, $Co(OH)_2$, and CoO at binding energies (BE) of ~777.2, 781.5, 784.0, and 786.8 eV, respectively, according to prior assignment.[41−43] The recovered catalyst shows an increased intensity ratio of CoS and a decreased ratio of CoS_2, which is consistent with the changing trend of S in the deconvoluted S 2p band. The S 2p band of the catalyst before the reaction shows BE peaks for $S^{2−}$ (monosulfide), $S_2^{2−}$ (disulfide), $S_n^{2−}$ ($n > 2$, polysulfides), and S^0 (elemental S) at ~161.5, 162.5, 163.7, and 164.4 eV, respectively, according to prior assignment.[44] After the reaction, the ratio of $S^{2−}$ increased and the ratio of $S_2^{2−}$ decreased, indicating that a structural change of the catalyst to CoS occurred during the reaction. A control experiment using a commercial cobalt oxide under reaction conditions comparable to those for Co sulfide formed only 2.4% monomer, indicating that cobalt oxide is not an active species. The recycling experiment and the catalyst characterization results suggest that CoS is formed during the reaction and is active for C−C cleavage; however, the role of CoS_2 cannot be precluded for the reason that the reaction starting with CoS_2 gives slightly higher amounts of monomers.

■ CONCLUSIONS

Selective cleavage of interunit C−C linkages of condensed technical lignins has been a longstanding challenge. This study demonstrates that such selective cleavage of methylene C−C bonds in lignin is possible using an inexpensive cobalt sulfide catalyst. C−C cleavage of a representative methylene-linked lignin motif, dimethylguaiacylmethane (DGMG), gives two aromatic monomers with high yield and selectivity under mild conditions and in a short reaction time. The reaction for a prolonged time forms nonaromatic products. A methoxy substituent has little effect on the C−C cleavage, while the dimer becomes unreactive to C−C cleavage upon dehydroxylation. Depolymerization of a kraft lignin fraction gives lower molecular weight (M_w) soluble lignin species including up to 13% monomer, containing five detected functional aromatic monomers.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.8b00200.

Experimental procedure for DMGM synthesis and catalysis of DMGM and kraft lignin, analytical methodology for analysis of liquid products, quantification of liquid products, characterization of catalysts, ^1H, ^{13}C, and HSQC NMR of DMGM, GC and GC-MS chromatogram and spectra of products, XRD patterns and deconvoluted XPS spectra, controlled experimental data, structures of monomers and dimers from DMGM and kraft lignins, and conversion and yield data (PDF)

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Notes

The authors declare no competing financial interest.

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