

Supporting Information

Selective C–C Bond Cleavage of Methylene-linked Lignin Models and Kraft Lignin

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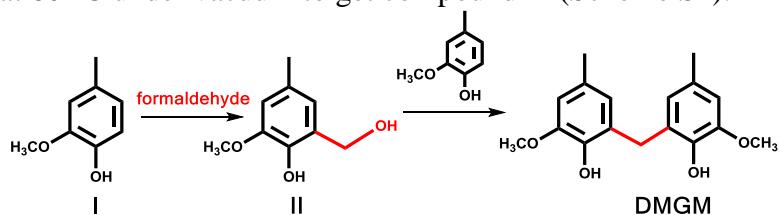
Chemicals and materials

All commercial chemicals were analytical reagents, and were used without further purification. 5% Ru on Carbon (Ru/C), 5% Pt on Carbon (Pt/C), CoS₂ ($\leq 10 \mu\text{m}$), FeS₂ (44 μm), MoS₂ ($< 2 \mu\text{m}$), methyl guaiacol (2-methoxy-4-methylphenol), 2,2'-methylenebis(4-methyl phenol), diphenylmethane, 2-benzyl-4-methylphenol, methylcatechol, pyridine (anhydrous, 99.8%), decane (>99%), N,O-Bis(trimethylsilyl)trifluoroacetamide (98%), fuming hydrochloric acid (37 %), formaldehyde solution (37%) were purchased from Sigma Aldrich. Ultrapure and fractionated Kraft lignin (alkali) fraction was obtained from collaborator at Chemson University.¹

Experimental

(1) Preparation of model dimers

1.40 g monomer Methyl guaiacol (**A**), 1 ml of formaldehyde (FA) solution (37 w% in water) and 0.40 g NaOH were dissolved in 10 mL water in a 100-mL flask and reacted at 60 °C for 15 h. The mixture was neutralized with hydrochloric acid to a PH of 7 followed by extraction with 30 mL ethylacetate (EA) twice. The organic phase was transferred to a flask and was dried with a rotary evaporator at 60 °C under vacuum to get compound **II** (Scheme S1).



Scheme S1. C-C linked model lignin dimer synthesis featuring a methylene linkage.

The compound **B** was mixed with additional 2.00 g methyl guaiacol and 0.40 g NaOH in 20 mL dioxane/water co-solvent (50/50) and the mixture was reacted at 90 °C for 40 h. The mixture was neutralized to a PH of 7 followed by extraction with 30 mL EA. The organic phase was transferred to a flask and was dried with rotary evaporator to get a mixture of methyl guaiacol (**I**) and the dimer (dimethylguaiacylmethane DMGM). The mixture was distilled at 200 °C under vacuum to remove methyl guaiacol (**I**). The residue after distillation was DMGM. The purity of

DMGM was determined to be 76%. The GC chromatogram, MS spectra and NMR spectra of DMGM are shown in Figures S1 and S2. The low purity is mainly caused by moisture.

(2) C-C cleavage of model dimers

20 mg of synthesized DMGM was dissolved in 20 mL heptane in a 50-mL high-pressure Parr reactor along with calculated amount of catalysts. The reactor was stirred with a magnetic stir bar and heated with high-temperature heating band (Omega) equipped to a variable power supply controlled by a PID temperature controller (Omega) with a K-type thermocouple to measure the reaction temperature through a thermowell. Once closed, the reactor was purged three times with ultrapure H₂ and then pressurized with 50 bars of H₂ for the reaction. The reactor was heated to the desired temperature and then held at that temperature for the specified residence time. After the reaction completed, the gas phase in the reactor was released and the reactor was cooled in an ice bath to room temperature. 2 mL of standard solution (1 mg/mL decane in heptane) was added to the reaction mixture. Decane was used as an internal standard for quantification of products from GC analysis. The resulting liquid was filtrated through a nylon membrane filter (Whatman[®], 0.8 µm, 47mm). Similarly, the C-C cleavage of other model dimers (2,2'-methylenebis(4-methyl phenol), diphenylmethane, 2-benzyl-4-methylphenol) were also performed.

The recycling experiments of the catalyst for the C-C cleavage of DMGM were conducted at 250 °C and 50 bar H₂ for 1.5 h. In the first cycle, the reactor was loaded with 30 mg DMGM, 20 mg catalyst and 30 mL heptanes. After the reaction and cooling down the reaction mass, the catalyst was separated by filtration, washed with heptane and dried. A small loss of catalyst mass (~15%) was observed during the recovery. Therefore, we decreased the scale of the reaction in the subsequent cycles to keep the ratios of catalyst, substrate and solvent same. For example, the 2nd cycle was conducted using 23.6 mg DMGM, 16 mg recovered catalyst and 25 mL of heptane at comparable reaction conditions as the 1st cycle. The products after each cycle was analyzed following the method discussed below.

(3) Depolymerization of kraft lignin

50 mg of kraft lignin fraction was dissolved in 20 mL solvent (Table 1) in a 50-mL high-pressure Parr reactor along with certain amount of catalysts (Table 1). The reactor was stirred with a magnetic stir bar and heated with high-temperature heating jacket connected to a variable power supply controlled by a PID temperature controller and a K-type thermocouple to measure the reaction temperature through a thermowell. Once closed, the reactor was purged three times and then pressurized with 50 bars of H₂. The reactor was heated to the desired temperature and then held at that temperature for the specified residence time. After the reaction completed, the gas phase in the reactor was released and the reactor was cooled in an ice bath to room temperature. 2 mL of standard solution (1 mg/ml decane in heptane) was added to the reactor as an internal standard. The resulting liquid was filtrated through a nylon membrane filter (Whatman[®], 0.8 µm, 47mm) and the filtrate was analyzed.

(4) Synthesis of CoS

CoS was synthesized by a precipitation method according to a reported procedure.² A Na₂S solution (12.0 g Na₂S·9H₂O in 50 mL water) was poured into a 500 mL beaker and mixed with a

$\text{Co}(\text{NO}_3)_2$ solution (14.6 g $\text{Co}(\text{NO}_3)_2$ in 50 mL water). The mixture was stirred at 300 rpm for 20 min using a magnetic bar and then filtered. The pellet was washed with 500 mL water followed by 500 mL acetone. After washing, the pellet was redispersed in acetone and dried at 80°C under vacuum with a rotary evaporator.

Analytical methods

(1) Monomer and dimer analysis by GC-MS

0.5 mL of aliquot, 0.25 mL pyridine and 0.25 mL N,O-Bis(trimethylsilyl)trifluoroacetamide was added into a GC vial and then incubated at 50 °C for 30 min. The prepared sample was analyzed by GC-MS using an Agilent 7890B series GC equipped with a HP5-MS capillary column and an Agilent 5977A series Mass Spectroscopy. The following operating conditions were used: injection temperature at 250 °C, a column temperature program of 50 °C (1 min), ramp at 15 °C/min to 300 °C and hold at 300 °C (7 min), and a detection temperature of 290 °C.

(2) Monomer and dimer quantification by GC-FID

The prepared sample was analyzed with a GC (Agilent 7890B series) equipped with an HP5-column and a flame ionization detector (FID). The injection temperature was 300 °C. The column temperature program was: 40 °C (3 min), ramp at the rate of 30 °C/min to 100 °C, ramp at the rate of 40 °C/min to 300 °C and hold at 300 °C (5 min). The detection temperature was 300 °C. The peaks in the GC-FID chromatogram appear in the same orders as those in GC-MS chromatograms due to the use of a similar capillary column.

Due to the difficulty to obtain standard monomers and dimers, we used a quantification based on an internal standard (decane) and the effective carbon number (ECN) method. The monomer yield was calculated based on the area of the monomer and the area of decane in the GC chromatograms. The detailed calculation was as follows:

$$n_{\text{decane}} = \frac{W_{\text{decane in sample}}}{MW_{\text{decane}}} = \frac{2 \text{ mg}}{142 \text{ mg/mmol}} = 0.014 \text{ mmol} \quad (\text{S1})$$

$$n_{\text{monomer}} = \frac{A_{\text{monomer in sample}}}{A_{\text{decane in sample}}} \times 0.014 \text{ mmol} \times \frac{ECN_{\text{decane}}}{ECN_{\text{monomer}}} \quad (\text{S2})$$

$$Y_{\text{monomer}} = \frac{n_{\text{monomer}}}{n_{\text{monomer_theoretical}}} \times 100\% \quad (\text{S3})$$

In the equations,

$W_{\text{decane in sample}}$ (mg): the weight of decane used as an internal standard in each analyzed sample;

MW_{decane} (mg mmol⁻¹): the molecular weight of decane (142 mg mmol⁻¹);

n_{decane} (mmol): the molar amount of decane in each analyzed sample;

n_{monomer} (mmol): the molar amount of monomer in each analyzed sample;

$A_{\text{monomer in sample}}$: the peak area of monomer in the GC-FID chromatogram;

$A_{\text{decane in sample}}$: the peak area of decane in the GC-FID chromatogram;

ECN_{decane} : the effective carbon number (10) of decane;

ECN_{monomer} : the effective carbon number of the lignin monomer molecule;

Y_{monomer} : the molar yield of monomer. W_{lignin} (mg): the weight of the dimer or lignin;

$n_{\text{monomer_theoretical}}$: The theoretical yield for 20 mg dimer is: $\frac{20 \text{ mg}}{288 \text{ mg/mmol}} * 2 = 0.139 \text{ mmol}$; the theoretical yield for 50 mg lignin is estimated to be: $\frac{50 \text{ mg}}{220 \text{ mg/mmol}} = 0.227 \text{ mmol}$.

(3) Gel permeation chromatography (GPC) analysis

GPC analysis was conducted on a Waters 2695 HPLC equipped with a refractive index detector ((RID); Waters model 2414) and two Waters Styragel columns (dimensions: 4.6 x 300 mm with packing size of 5 μm) connected in series (Models: HR 3 and HR 4). Polystyrene was used as a standard. Tetrahydrofuran (THF) was used as the mobile phase at a flow rate of 0.3 mL/min. The column compartment and the RID temperature was set at 25 °C.

(4) Instrumentation

XRD patterns of the reduced and used catalysts were recorded by a diffractometer (Bruker D8) equipped with a $\text{CuK}\alpha$ radiation source ($\lambda=0.154 \text{ nm}$) at 40 kV and 40 mA. Elementar Vario EL Micro cube was used for elemental analysis (CHNS) using Helium as flushing gas and 1150 °C combustion temperature. Thermal conductivity detector was used to measure CHNS composition of sample based on Sulfanilamide standard. Wavelength Dispersive X-ray Fluorescence (WDXRF) Spectrometer (Rigaku Supermini200) was used for XRF measurements. Analysis was performed using both flow-proportional and scintillation detectors. A Thermo-Fisher K-alpha+ X-ray photoelectron spectrometer equipped with a monochromatic aluminum K-alpha X-ray source (400 nm) was used for XPS.

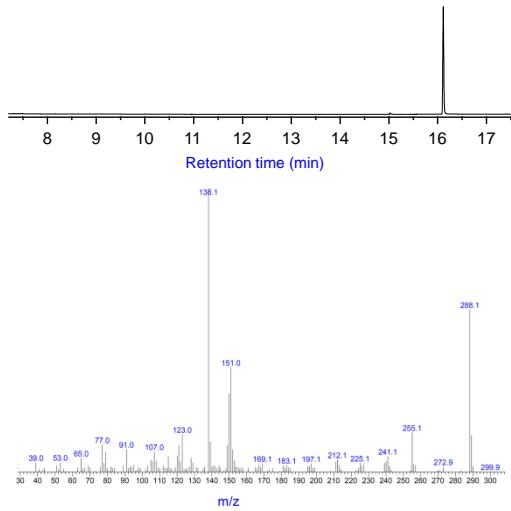


Figure S1. GC chromatogram and GC-MS spectrum of the synthesized dimethylguaiacylmethane (DMGM).

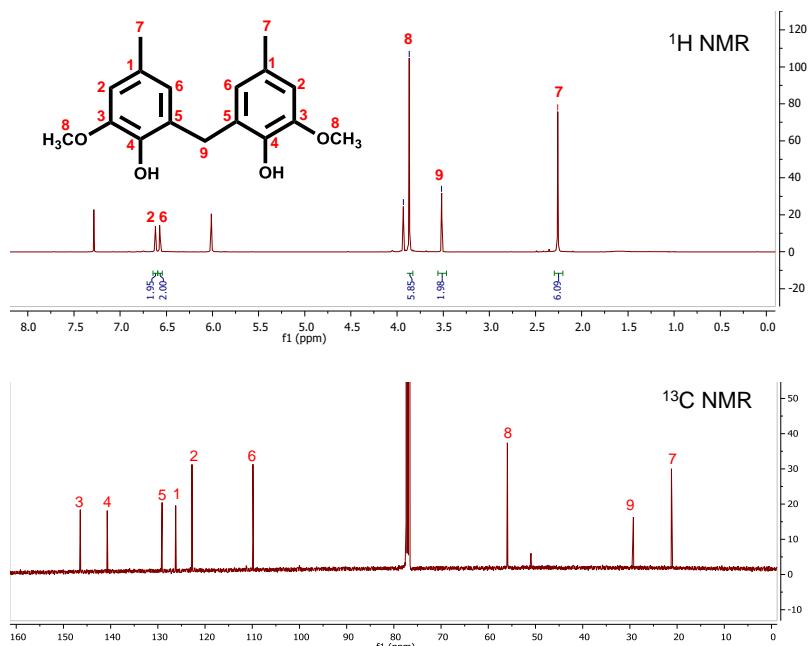


Figure S2. NMR Spectra of the synthesized dimer, DMGM.

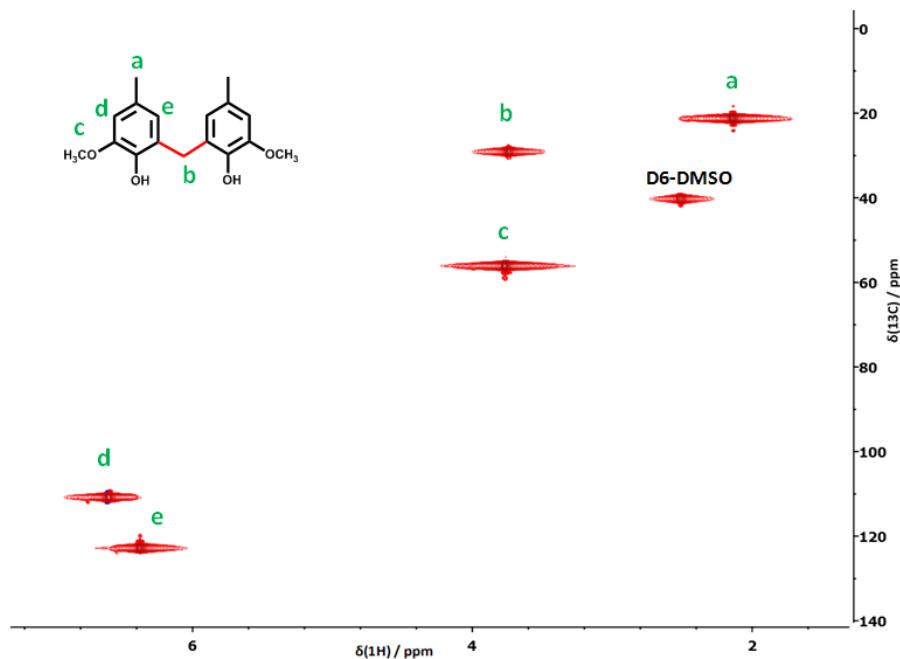


Figure S3. HSQC NMR spectrum of the synthesized dimer, DMGM.

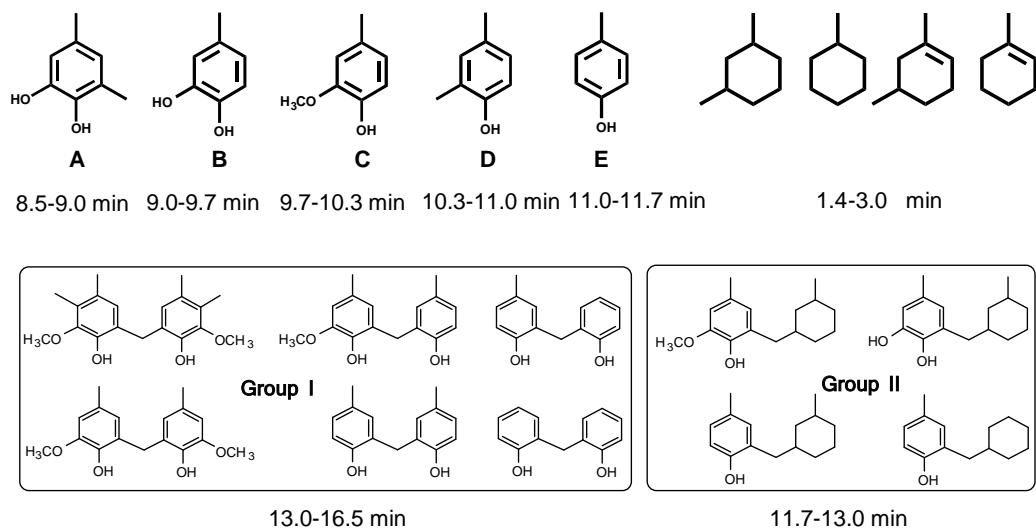


Figure S4. Chemical structures of monomeric and dimeric products from the disruption of DMGM.

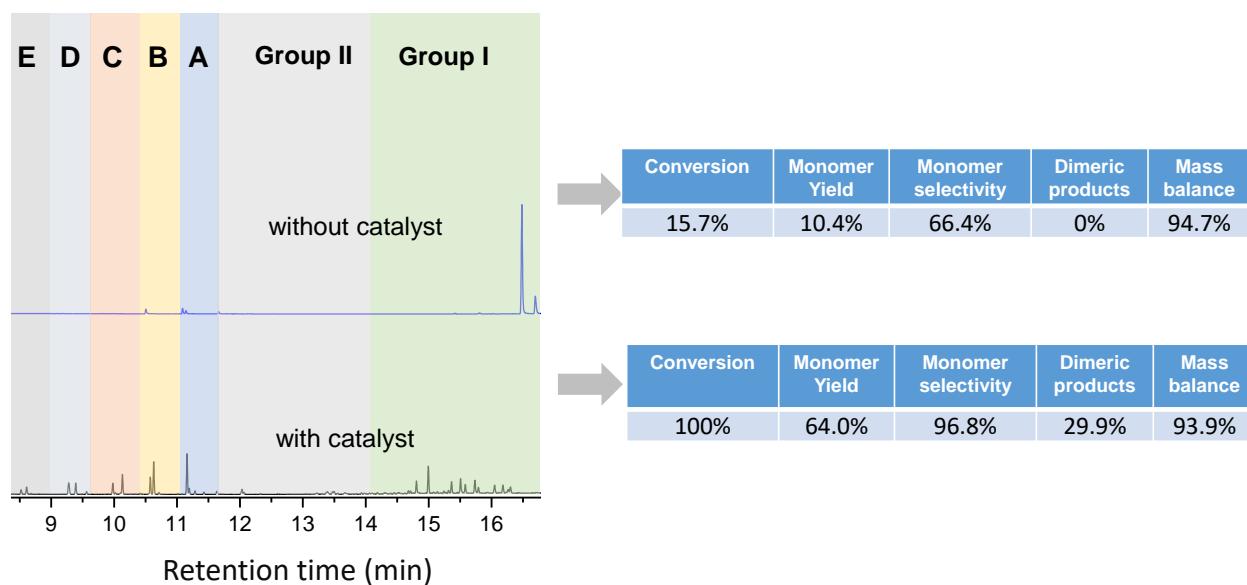


Figure S5. FeS_2 -catalyzed DMGM disruption at 250 °C. Reaction conditions: 20 mg DMGM, 20 mL heptane, 100 mg FeS_2 , 250 °C, 50 bar H_2 , and 15 h reaction time. Monomer selectivity was calculated for monomers A to E on the basis of all identified monomers.

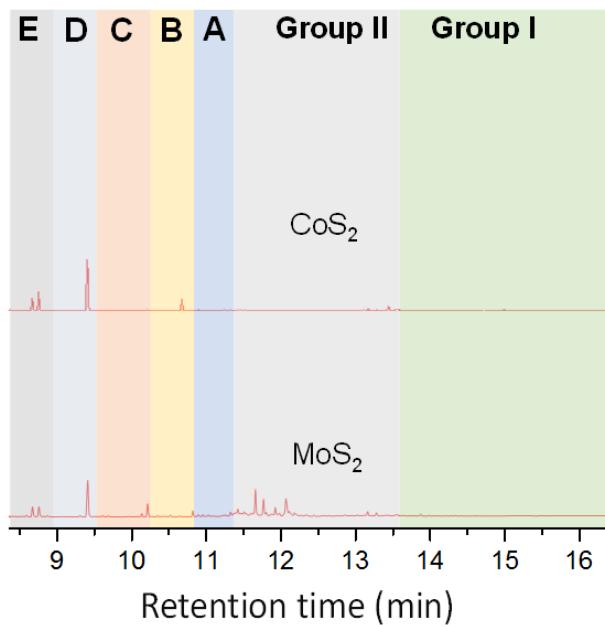


Figure S6. CoS_2 - and MoS_2 - catalyzed DMGM disruption at 250 °C and 50 bar H_2 for 15 h. Other reaction conditions: 20 mg DMGM, 20 mL heptanes and 200 mg MoS_2 or 50 mg CoS_2 .

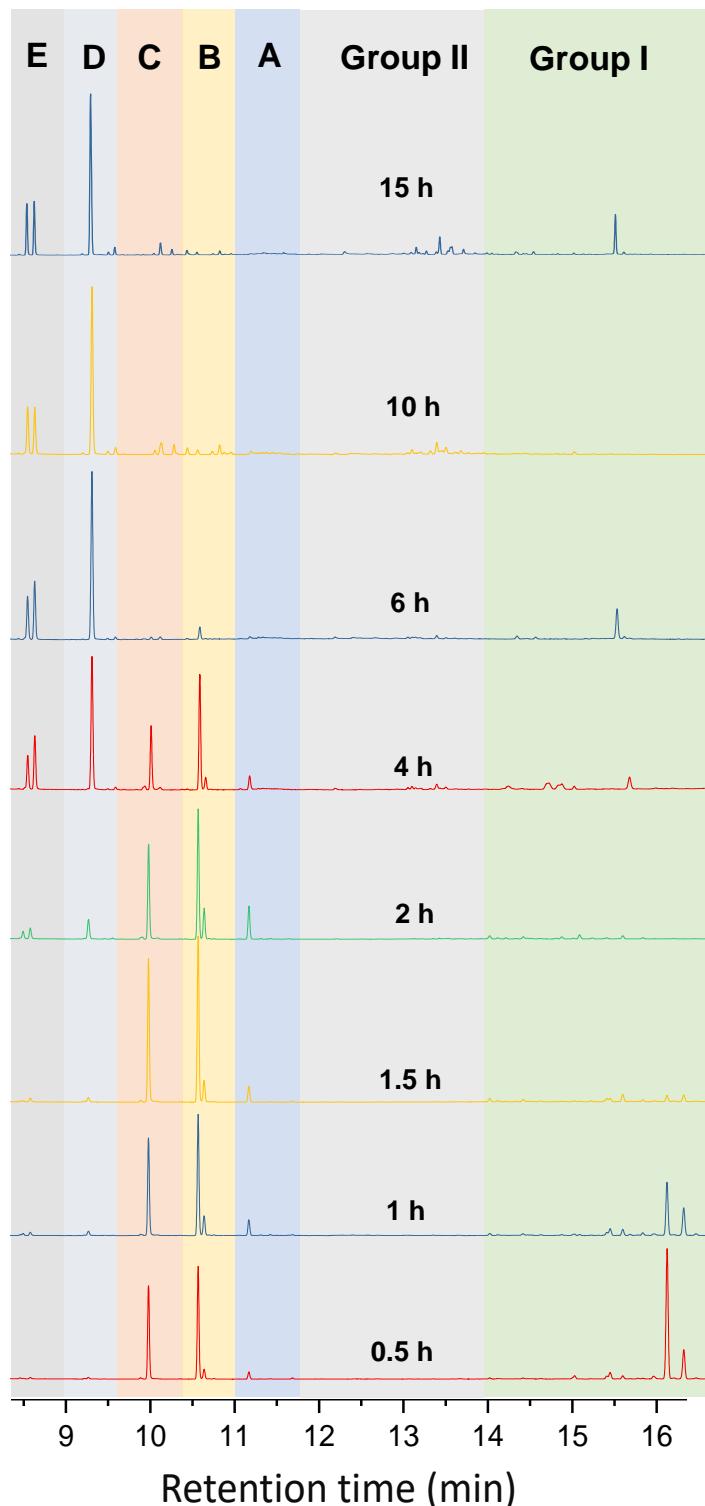


Figure S7. Time-course reaction profiles for CoS_2 -catalyzed DMGM disruption at $250\text{ }^\circ\text{C}$. The yields of each monomer and total monomer are shown in Table 2. Other reaction conditions: 20 mg DMGM, 50 bar H_2 , 20 mL heptane and 10 mg CoS_2 .

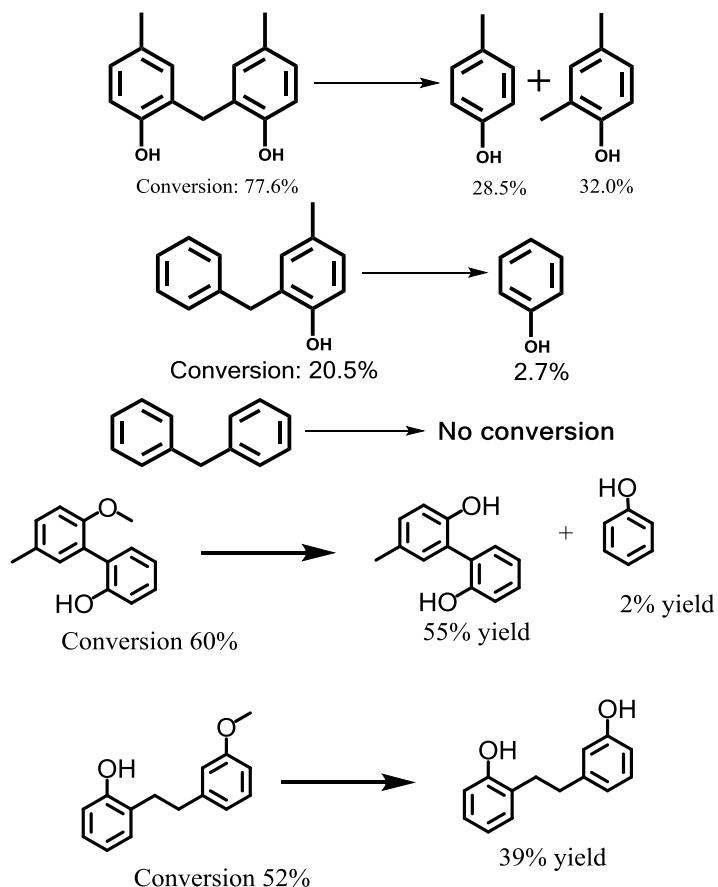


Figure S8. Comparison of CoS_2 -catalyzed disruption of model dimers with different C-C linkages and different numbers of hydroxyl and methoxyl substituents. Reaction conditions: 20 mg dimer, 20 mL heptane, 10 mg CoS_2 , 250 °C, 50 bar H_2 and 1.5 h reaction time.

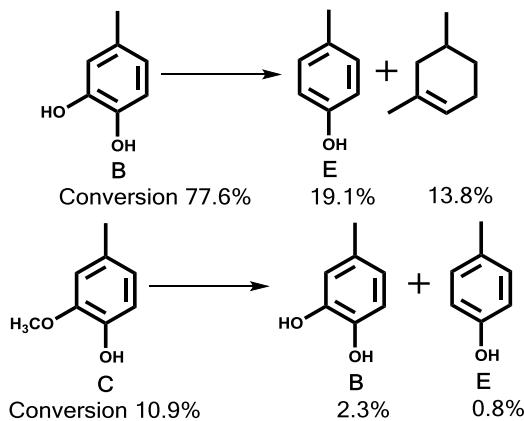


Figure S9. Controlled experiments using monomers B and C as the starting substrates to understand formation of monomers D and E that are formed during DMGM disruption with CoS_2 . Reaction conditions: 10 mg monomers, 20 mL heptane, 10 mg CoS_2 , 250 °C, 50 bar H_2 and 1.5 h reaction time. The numbers for the products represent their yields. There could be other products,

which are either in the vapor phase or in the liquid phase but their retention times overlapped with the retention time of the solvent peak (heptane). Such products were not detected and quantified. Thus, there is a carbon loss in the detected products.

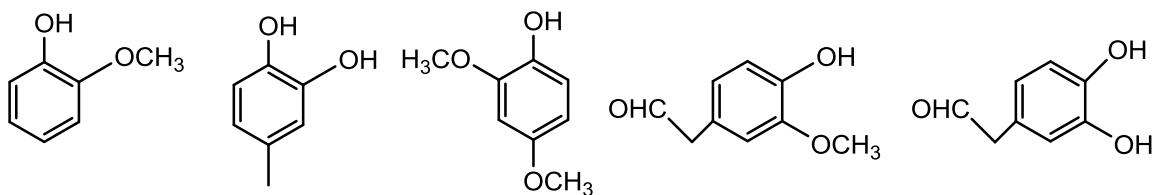


Figure S10. Identified monomers result from CoS_2 -catalyzed depolymerization of kraft lignin.

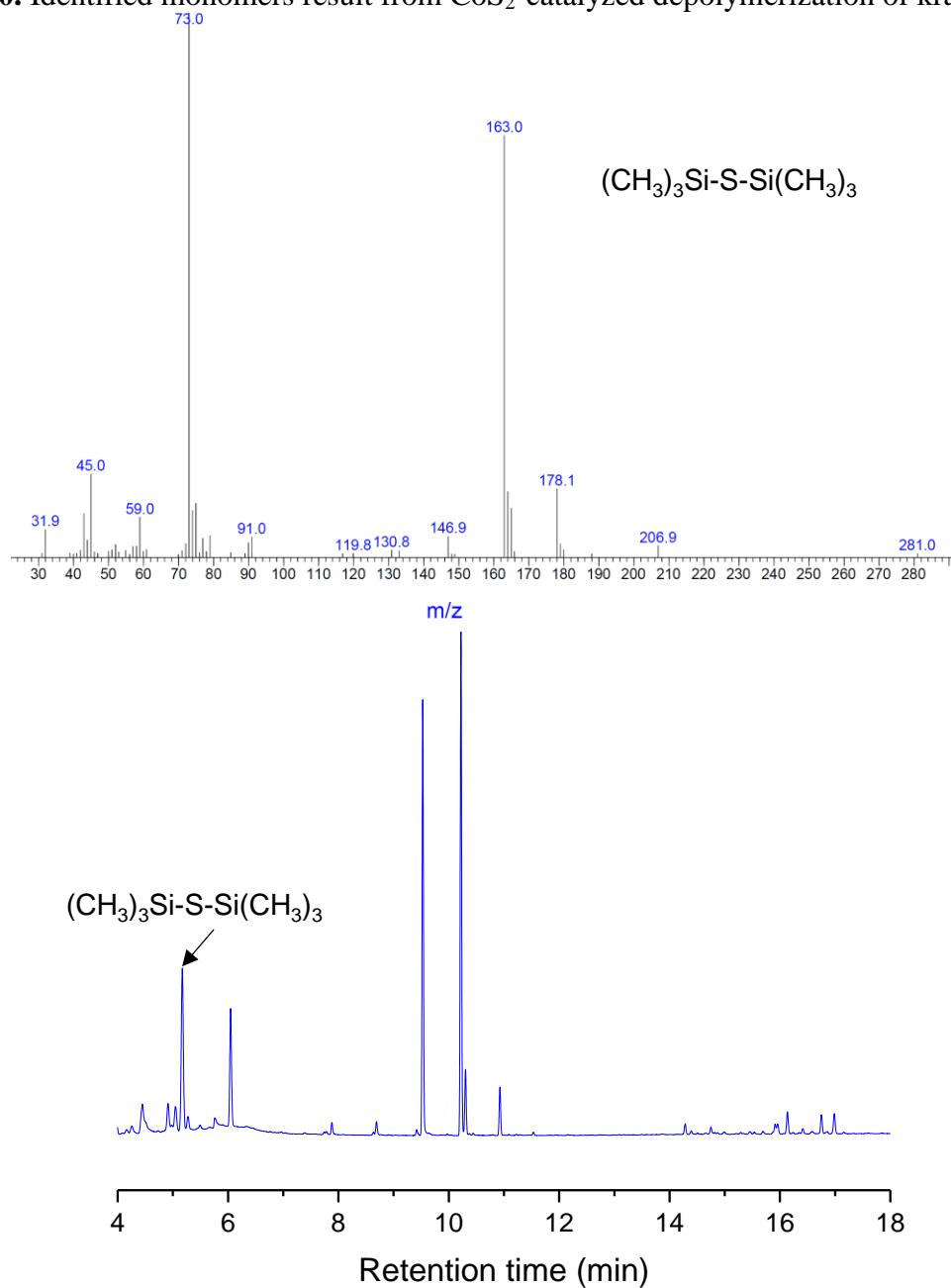


Figure S11. Identification of H_2S in the form of silane compound that is formed by the reaction between H_2S and the silane compound added to the product solution prior to GC analysis.

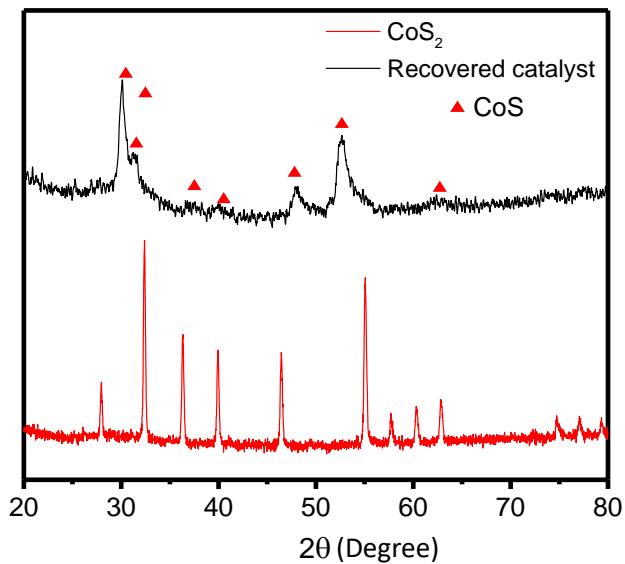


Figure S12. XRD patterns of CoS_2 before and after depolymerization of DMGM. These patterns showing characteristic peaks for CoS and CoS_2 are consistent with previous reports.²⁻³

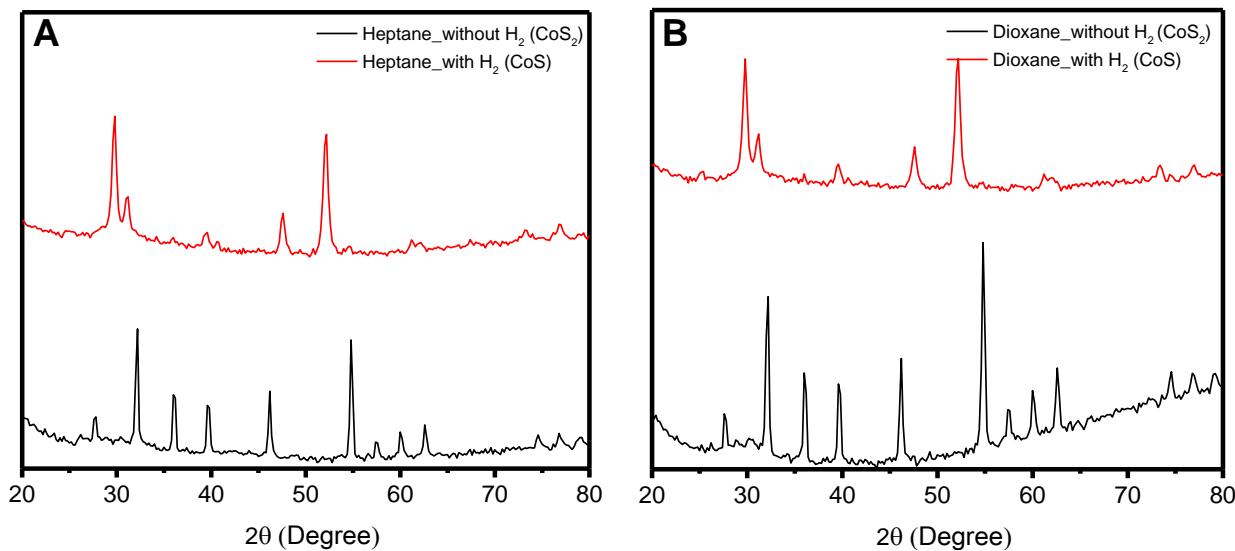


Figure S13. XRD patterns of CoS_2 before and after treatment in the absence and presence of H_2 ; (A) in heptane and (B) in dioxane.

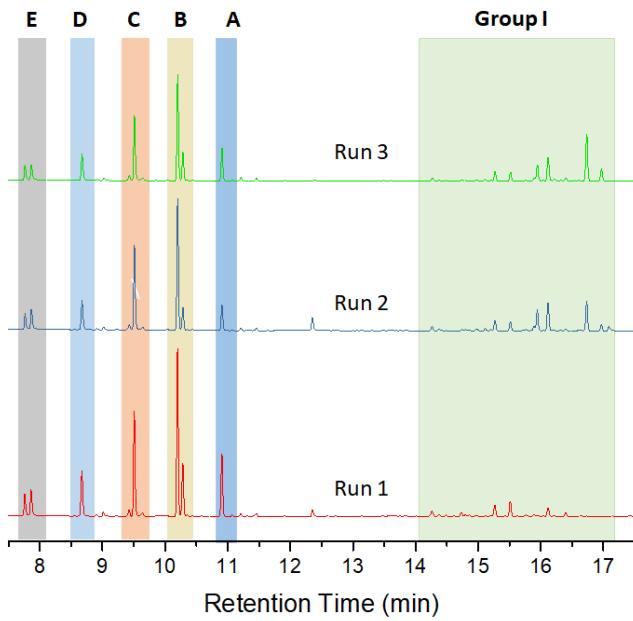


Figure S14. Recyclability results for CoS_2 -catalyzed DMGM disruption at 250 °C. Other reaction conditions: 20 mg DMGM, 50 bar H_2 , 20 mL heptanes and 10 mg CoS_2 .

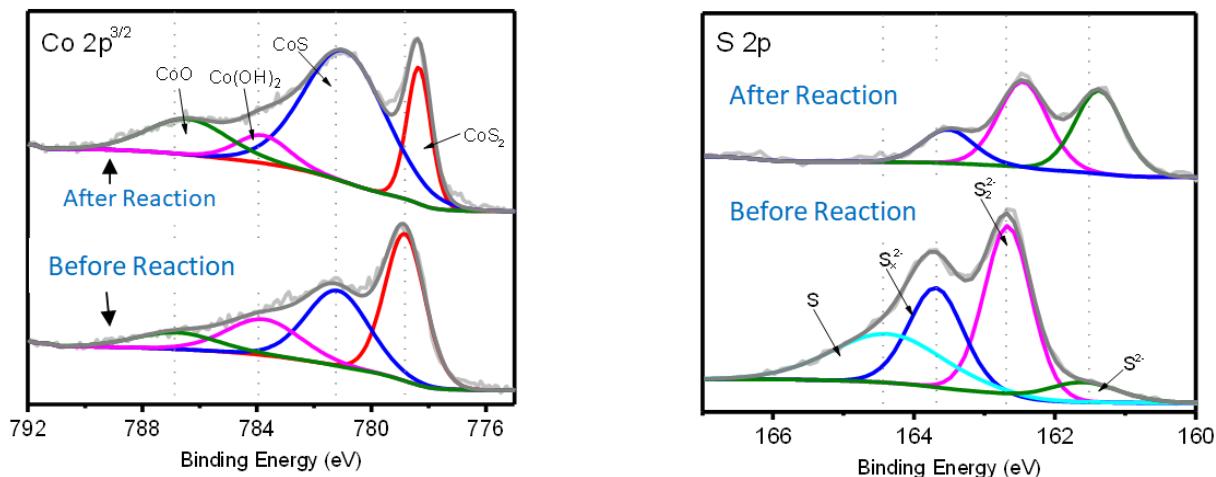


Figure S15. XPS deconvoluted spectra of $\text{Co 2P}^{3/2}$ and S 2P of CoS_2 and the recovered catalyst before and after depolymerization of DMGM.

Table S1. Time-course reaction profiles for CoS₂-catalyzed DMGM disruption.

Reaction Tim (h)	DMGM Conversion (%)	Aromatic monomers (%)					Non-aromatic monomers (%) (Cyclohexane and cyclohexane)	Total monomers (%)
		A	B	C	D	E		
0.5	46	1	24	24	1	1	0	51
1	63	4	28	25	1	2	1	61
1.5	89	3	41	40	2	2	1	88
2	92	7	36	29	6	6	5	90
4	96	1	15	11	21	14	33	96
6	98	1	2	1	27	17	45	93
10	94	1	2	7	26	14	37	87
15	94	0	4	1	25	13	41	84

Reaction conditions: 20 mg DMGM, 20 mL heptane, 10 mg CoS₂ and 250 °C.

Table S2. The effect of H₂ pressure on CoS₂-catalyzed DMGM disruption.

H ₂ pressure (bar)	DMGM conversion (%)	Monomer yield (%)
50	89	88
10	23	21
10 ^a	32	27
0	0	0

Reaction conditions: 20 mg DMGM, 10 mg CoS₂, 20 mL heptane, 250 °C, 1.5 h reaction time.
Total pressure was kept at 50 bar using an inert gas, N₂.

Table S3. Comparison of CoS₂, Ru/C and Pt/C catalyzed DMGM disruption.

Reaction Tim (h)	Conversion (%)	Aromatic monomers (%)					Non-aromatics monomers (%) (Cyclohexane and cyclohexane)	Total monomers (%)
		E	D	C	B	A		
CoS ₂	89	3	41	40	2	2	0	88
Ru/C	15	2	1	2	3	2	0	10
Pt/C	5	0	2	2	0	0	0	4

Table S4. Kraft lignin depolymerisation using Ru/C in heptane and dioxane solvents.^[a]

Entry	Feedstock	Solvents	Catalysts	Catalyst loading (mg)	Aromatic monomer yield (%)
4	Lignin	Heptane	Ru/C	50	1.3
6	Lignin	Dioxane	Ru/C	20	4.9
7	Lignin	Dioxane	Ru/C	100	5.0

[a] Other reaction conditions: 50 bar H₂, 250 °C, 15 h, 50 mg Kraft lignin. Kraft lignin (alkali) fraction purified by ALPHA process.^{1b}

Reference

1. (a) Klett, A.; Chappell, P.; Thies, M. Recovering Ultraclean Lignins of Controlled Molecular Weight from Kraft Black-Liquor Lignins. *Chemical Commun.* **2015**, *51*, 12855-12858; (b) Klett, A. S.; Payne, A. M.; Thies, M. C. Continuous-Flow Process for the Purification and Fractionation of Alkali and Organosolv Lignins. *ACS Sus. Chem. Eng.* **2016**, *4*, 6689-6694.
2. Kumar, N.; Raman, N.; Sundaresan, A. Synthesis and Properties of Cobalt Sulfide Phases: CoS₂ and Co₉S₈. *Zeitschrift für anorganische und allgemeine Chemie* **2014**, *640*, 1069-1074.
3. Ahn, S.; Yang, J.; Lim, H.; Shin, H. S. Selective Synthesis of Pure Cobalt Disulfide on Reduced Graphene Oxide Sheets and Its High Electrocatalytic Activity for Hydrogen Evolution Reaction. *Nano Converg.* **2016**, *3*, 5.