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ARTICLE

Catalytic Conversion of High S-Lignin to a Sustainable Tri-epoxide Polymer Precursor†

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More than 40 million tons of thermosetting plastics are produced annually and 70% of those are epoxy polymers. The synthesis of bio-based epoxide provides a pathway for making renewable thermoset plastics. We describe in this study the use of a genetically modified high-S poplar lignin to produce 4-propyl-2,6-dimethoxyphenol (DMPP), which is converted to the tri-functional compound propylpyrogallol (DMPPO) by a reaction catalysed by N_2O_5 in the green solvent water. The resulting DMPPPO can be converted to a novel tri-epoxide by reaction with epichlorohydrin. Native high-S lignin as well as several organosolv lignins extracted from this poplar biomass were investigated as feedstocks. Notably, direct reductive catalytic fractionation (RCF) of the high-S poplar wood over Pd-Zn/C catalyst with Pd:Zn ratio 1:10 at 225 °C under 35 bar H_2 in methanol gave the highest yield of biophenol monomers from the lignin present, the major product being DMPP. Under optimized conditions, conversion of DMPP to DMPPPO over the Nb_2O_5 was nearly quantitative (96% yield), and this conversion could be made using without extensive prior purification of the DMPP. The Nb_2O_5 catalyst could be recycled several times before significant deactivation. This sequence of two catalytic reactions demonstrates that the production of epoxides from lignin-derived DMPPPO is a realistic strategy for making renewable polymer building blocks from biomass.

Introduction

Plastics are ubiquitous in modern living and are found in products ranging from automobiles to clothing and packaging.¹⁻⁴ Since plastics largely stem from petrochemicals, there is an imperative to develop renewable alternatives given increasing concerns about greenhouse gas emissions from their production.⁵⁻¹² However, the lack of economic incentives and the scarcity of renewable monomers have maintained the status quo of petroleum-based plastics dominance.

Lignin is an important component of lignocellulosic biomass and is the most abundant renewable source of aromatic carbon. The world annually produces around $\sim 10^8$ metric tons of lignin which is valued at $\sim \$7$ /metric ton, significantly less than petroleum.¹³ Thus, lignin is a cheap, abundant and renewable feedstock that has the potential to provide building blocks for polymers, resins, and adhesives.¹⁴⁻¹⁶

Depolymerization of lignin can result in a broad range of chemicals.¹⁷ Many of those are phenolic molecules, which can be further upgraded to lignin-based polymers such as epoxy thermosetting plastics.¹⁸⁻²² Zhao et al. have demonstrated the use of the lignin monomer, dihydroeugenol (DHE, Figure 1), as a starting material for making biobased epoxies.¹⁸ DHE was first converted into 4-propylcatechol (DHEO, Figure 1), and the resulting catechol subsequently reacted with epichlorohydrin to give a di-epoxide structure that can be cured into a thermosetting polymer. Another important lignin monomer is 4-propyl-2,6-dimethoxyphenol (DMPP, Figure 1), which has a structure similar to DHE but having one more

methoxy substituent on the aromatic ring. DMPP is derived from the syringyl unit (S unit) of lignin. To our knowledge, there have been no reports regarding the production of a novel tri-epoxide from lignin derived DMPP. Thus, in this study, we targeted a genetically modified high-S poplar biomass (content of S unit up to 85% compared to 64% in wild-type) as the feedstock to produce DMPP.^{23, 24} Pd/C was the catalyst used for the lignin depolymerization reactions.^{25, 26}

Klein et al. reported that loading Zn^{2+} on Pd/C to give a bifunctional Pd-Zn/C catalyst was essential for selectivity to phenolic products.²⁷ The Zn^{2+} catalyses the dehydroxylation of the propyl side chain, so that DHE and DMPP are prepared from lignin using this catalyst. In contrast, DHE-OH and DMPP-OH (Figure 1) result from the reactions with the Pd/C catalyst without Zn^{2+} . Therefore, the combination of Pd-Zn/C and high-S poplar lignin favors the formation of DMPP in the present study.

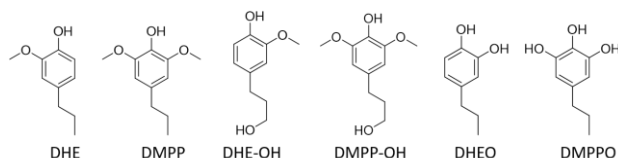


Figure 1. Illustration of chemical structures of phenolic monomers derived from lignin: dihydroeugenol (DHE), 4-propyl-2,6-dimethoxyphenol (DMPP), 4-(3-hydroxypropyl)-2-methoxyphenol (DHE-OH), 4-(3-hydroxypropyl)-2,6-dimethoxyphenol (DMPP-OH), 4-propylcatechol (DHEO), and 5-propylpyrogallol (DMPPPO).

Once DMPP was prepared from high-S lignin, it was converted to 5-propylpyrogallol (DMPPPO, Figure 1) by hydrolysis of the aryl methoxy groups. Since DMPPPO is a highly functional molecule with

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three phenolic hydroxyl groups, a tri-epoxide can be prepared, which constitutes an interesting building block for biobased epoxy polymers.^{20,28} However, clean production of DMPPO from DMPP has been challenging, since the complex mixture from depolymerized lignin typically contain impurities that hinder reactions with the HBr or BBr₃ commonly used to convert DHE to DHEO.^{16, 18} Furthermore, the use of these highly corrosive and toxic halogenated reagents is undesirable. To overcome these significant and practical problems, we developed a greener, halogen-free method to convert DMPP made directly from lignin to DMPPO over a Nb₂O₅ catalyst that does not require extra purification of the biomass-derived DMPP product and that can be carried in water as a green solvent. As noted below, the resulting DMPPO can be upgraded to the tri-epoxide, a monomer for forming renewable polymers.

Experimental

Reagents and feedstocks

All commercial chemicals were purchased and used as received. 2-Methoxy-4-propylphenol ($\geq 99\%$), 4-allyl-2,6-dimethoxyphenol, *p*-dioxane, formaldehyde (37%), zinc chloride, palladium (5 wt%) on activated carbon, and epichlorohydrin were purchased from Sigma-Aldrich. Dichloromethane (ACS reagent grade), methanol (ACS reagent grade), and ethyl acetate (ACS reagent grade) were purchased from Fisher Chemical. Cetyltrimethyl ammonium bromide (CTAB 98%) and *n*-dodecane (99%) were purchased from Alfa Aesar. Niobium (V) chloride ($\geq 99\%$) was purchased from Strem Chemicals. Dimethyl sulfoxide-*d*₆ (99.5%) and dichloromethane-*d*₂ (99.9%) were purchased from Cambridge Isotope Laboratories Inc. Hydrochloric acid (ACS reagent grade) was purchased from EMD Millipore Corporation. Hydrogen gas (5.0 grade) and nitrogen gas (99.998%) were purchased from Praxair. Water was obtained from a A10 Milli-Q water purification system by Millipore. The dry high-S poplar biomass was provided by Drs. Clint Chapple and Richard Meilan from Purdue University. The high-S poplar was made through biosynthesis by over-expressing the F5H gene to increase the content of the S unit up to 85.2% in poplar wood.²⁴ The poplar biomass was milled to small particles by ACE Hardware Lumberyard, Santa Barbara, CA. Lignin was extracted from poplar shavings by organosolv methods. High-S poplar lignin extracted by methanol and HCl was named as OPL lignin;²⁹ lignin treated with formic acid and acetic acid was called FA/AA lignin;³⁰ lignin isolated by co-solvents of methanol-H₂O system with the acids of HCl and H₂SO₄ were named as H₂O/HCl and H₂O/H₂SO₄ lignin, respectively;³¹ while the lignin extracted by formaldehyde and *p*-dioxane was named as FPL lignin.³² These extraction methods are summarized in the Supporting Information (SI) Table S-1. The DMPP standard was synthesized from commercial 4-allyl-2,6-dimethoxyphenol by reduction over Pd/C under hydrogen pressure.

Catalyst preparation

Nb₂O₅ was synthesized using a modified hydrothermal method from our previous work.²² Typically, a 20 mmol portion of the precursor NbCl₅ (5.4 g) was dissolved in 20 mL ethanol with rigorous stirring for 10 min. This solution was then added to an aqueous solution of CTAB (1 g in 15 mL distilled water) dropwise with 300 rpm magnetic stirring. The mixed solution was stirred for 0.5 h followed by adding 20 mL of aqueous HCl (pH 1), and stirred for another 1.5 h. The resulting solution was put into a Teflon-lined autoclave and aged at 160 °C for 24 h. Subsequently, the precipitate was separated and washed with distilled water and dried at 60 °C overnight. After that,

the sample was ground and packed for calcination in air in a Thermolyne F6020 1200C Muffle furnace. The ramping rate of the furnace was pre-set to 1 °C/min. After 6 h calcination at 450 °C, the active Nb₂O₅ catalyst was collected at room temperature.

Pd-Zn/C catalyst was synthesized following procedures previously reported by Klein et al.²⁷ In a typical preparation, 5 wt% Pd/C was placed in a stainless-steel Parr reactor vessel with a glass-shielded stir bar and 15 mL of methanol. A calculated amount of ZnCl₂ (based on the desired molar ratio between Pd vs. Zn) was added to the mixture. The vessel was then sealed and purged with H₂ three times and pressurized to 20 bar at room temperature. The reactor was heated to 150 °C and held at that T for 8 h. Then the mixture was cooled to room temperature and the solid Pd-Zn/C catalyst was filtered and dried under vacuum.

Regeneration of Spent Nb₂O₅. The used Nb₂O₅ showed reduced activity and significant colour change after 4 reactions/recycles. To regenerate the Nb₂O₅, the spent catalyst was washed with water and ethanol twice and isolated by centrifugation. The washed Nb₂O₅ was oven dried at 120 °C over night. The dried catalyst was calcined in a Thermolyne F6020 1200C Muffle furnace. The ramping rate was set to 1 °C/min to 450 °C under air. After 20 min calcination at 450 °C, the regenerated Nb₂O₅ catalyst was cooled to room temperature.

Catalytic reactions

Catalytic depolymerization of lignin (CDL). CDL was carried out in a 75 mL stainless-steel reactor vessel (Parr Instrument Co., 5000 series). In a typical reaction, 0.5 g of lignin substrate was mixed with 10 – 20 wt% Pd-Zn/C catalyst in the vessel followed by adding 30 mL methanol as the solvent. A glass-shielded stirring bar was also placed in the reaction mixture. The reactor vessel was sealed and loaded into a heating jacket equipped with magnetic stirring at 700 rpm. The vessel was purged three times with 5.0 grade hydrogen and pressurized to 35 bar of hydrogen at room temperature. Then the vessel was heated to 225 °C and held at that temperature for 12 h. The heating and temperature maintaining process was controlled by a programmed controller box (Parr Instrument Co., MRS 5000 system). After 12 h at 225 °C, the reaction mixture was cooled to room temperature. The products in the liquid phase were then collected in ethyl acetate and analyzed by GC-FID.

Catalytic Conversion with Nb₂O₅. The lignin monomers collected from the CDL reaction were converted to a catechol (DHEO) and a pyrogallol (DMPPO) by Nb₂O₅. The reaction with Nb₂O₅ was also carried out in a 75 mL stainless-steel reactor vessel (Parr Instrument Company 5000 series). For a typical reaction, 400 mg lignin monomers (from CDL reaction without separation, or 400 mg DMPP isolated from CDL reaction after column) were loaded into the vessel with 200 mg Nb₂O₅. Then 12 mL water and 0.8 mL methanol were added to the mixture as co-solvents. A glass-shielded stir bar was placed in the reaction mixture. The reactor vessel was sealed and loaded to a heating jacket equipped with magnetic stirring at 700 rpm and then purged and pressurized with nitrogen gas to 10 bar. The pressurized reactor vessel was heated to 230 °C and held at temperature for 20 h. The heating and temperature maintaining process was controlled by a programmed controller box from Parr Instrument Inc. After 20 h at 230 °C, the reaction mixture was cooled to room temperature. The products in the liquid phase were extracted into ethyl acetate by centrifuge at 5000 rpm for 5 min, repeated three times. Then the products in ethyl acetate solution were injected to GC-FID for analysis.

Nb₂O₅ Recyclability Test. Recyclability tests were carried out in a 75 mL stainless-steel reactor vessel from Parr Instrument Company with

the same equipment setup as mentioned above. The initial reaction started with 0.5 g DMPP and 0.15 g fresh Nb₂O₅ in 12 mL water and 0.8 mL methanol under 10 bar N₂. The reaction was quenched after 10 h at 230 °C and the products were collected by extraction with EtOAc and centrifugation at 5000 rpm for 5 min. The organic layer was collected while the spent Nb₂O₅ catalyst was retained on the bottom of the centrifuge tube. The products were analysed by GC-FID and HPLC. The spent Nb₂O₅ was first washed and centrifuged by DI water twice followed by additional two washes and centrifugation with ethanol. After that, the recovered Nb₂O₅ was dried in a 120 °C oven over 12 h. The first, second, and third recycle entries in Figure 7 were run with 0.5 g DMPP and dried recycled Nb₂O₅. The reaction conditions of the recycles were the same as the initial reaction.

Synthesis of Tri-epoxide Monomers. A 400 mg mixture of DMPPO (96%) and MeO-DHEO (4%) with 6 g epichlorohydrin was mixed in a 250 mL round bottom flask. A 460 mg tetrabutylammonium bromide (TBAB) was then loaded to the reaction mixture as catalyst. Prior to the reaction, the round bottom flask was purged with N₂. The reaction was carried out at 60 °C with magnetic stirring at 250 rpm. After 3 h heating, 50% (w/w) NaOH solution (600 mg) was added dropwise to the reaction mixture and the temperature increased to 70 °C. After an additional 3 – 6 h, the reaction was quenched by removing it from the heat and adding acetone. The tri-epoxide products were collected in the organic oil phase.

Synthesis of Tri-epoxide Thermoset. DMPPO epoxy mixture was introduced to diethylenetriamine (DETA) with a 1:1 stoichiometric ratio of epoxy vs –NH for curing. The mixture was stirred for 5 min, degassed under vacuum to remove entrapped air, and poured into a mould for curing according to the profile: 45 °C for 1h, 55°C for 2h and 65°C for 2h.

Products analysis

GC-FID analysis was performed by Agilent 6890 N gas chromatograph (GC) equipped with a flame ionization detector (FID). A J&W DB-5 GC column (30 m x 0.25 mm I.D. x 0.25 μm film thickness) was used for analyte separation. The liquid products were pre-dissolved in 50 mL ethyl acetate in a volumetric flask. A 1 mL sample of the liquid was taken and filtered through 0.2-micron PTFE syringe filter to remove any possible solid particles. Then 0.5 mL of the filtrate was mixed with 0.5 mL of 10 mM n-dodecane in ethyl acetate in a 2 mL Agilent chromatography vial and sealed. (The n-dodecane was added as an internal standard.) Then an aliquot of the sample was injected into the GC instrument for analysis by the automated sampler equipped with 10 μL glass syringe. The inlet port temperature was pre-set to 280 °C while the FID detector was equilibrated at 310 °C. The initial oven temperature was set to 40 °C and equilibrated for 3 minutes. A split mode was used in the analysis method with split ratio of 10:1. Helium was used as the carrier gas and set to 14 mL/min flow rate, at which the column pressure reached 11.1 psi. Once the GC analysis method started, the oven was first held at 40 °C for 7 min to separate the ethyl acetate peak from the analyte signals. The oven was heated with a ramping rate of 10 °C/min to 250 °C, where it was held for 5 min to complete the detection. The identification of each analyte peak was according to the characteristic retention time based on that of a commercial standard under the same GC conditions. The quantification was based on a calibration curve which represented the relationship between concentration versus the ratio of peak area between analyte and internal standard. The quantification of the analyte without accessible standards was estimated by the effective

carbon number calculation with n-dodecane as the standard calibration.³³

HPLC analysis was also performed to analyse the products from lignin depolymerization reactions. An Agilent 1260 Infinity Quaternary High-Performance Liquid Chromatography (HPLC) system equipped with Zorbax Eclipse XDB-C18 column (250 x 74.6 mm) and Diode Array detector (DAD, G1315D) was used. The HPLC analytical condition was set to 30 °C column temperature and 0.5 mL/min of mobile phase flow rate. Water acquired from a Milli-Q A10 purification system and HPLC grade acetonitrile were used as mobile phase solvents. The nonlinear gradient of the two solvents was set to 80% A and 20% B from beginning and sequentially changed to 5% A and 95% B at 55 min of detection. The total detection duration was 60 min. For a typical measurement, 600 μL analyte dissolved in HPLC grade methanol was mixed with 400 μL internal standard in a 2 mL Agilent HPLC vial. A 10 mM benzyl phenyl ether solution in HPLC grade methanol was prepared as internal standard solution. Then the vial was loaded to the automatic sampler tray for data acquisition. The results were taken at 270 nm wavelength by the DAD detector with a UV lamp. Identification of analytes was based on the retention time of the HPLC chromatogram while the quantification was according to calibration curves and the ratio of peak areas between analyte and internal standard.

ESI Mass Spectrometry. The DMPPO product and tri-epoxide were identified by ESI mass spectrometry using a Waters LCT Premier ESI TOF instrument. In general, 1 μL of neat analyte was first dissolved in 1 mL standard methanol solvent. Then 1 μL of the solution was obtained and diluted with 1 mL methanol in an Agilent chromatography vial. After that, the vial was loaded on the autosampler for injection into the ESI instrument. DMPPO was detected under ES⁻ (negative) mode while the tri-epoxide was detected under ES⁺ (positive) mode.

¹H NMR Analysis. ¹H NMR spectra were obtained in chloroform-d₁ on a Varian Unity Inova 600 MHz spectrometer. For each analysis, 90 mg of neat analyte was dissolved in 700 μL chloroform-d₁ in a glass NMR tube.

2D HSQC NMR Analysis. The lignin polymer structure and linkages were analysed by 2D HSQC NMR with a Bruker AVANCE500 spectrometer operated at 500.13 MHz. The 2D HSQC spectra were acquired for a 50 mg lignin sample dissolved in 700 μL DMSO-d₆ by an echo-antiecho experiment called HSQCETGP. The quantification of the lignin G and S unit was calculated according to the contours following a literature procedure.²⁹

Dynamic Nuclear Polarization (DNP) Enhanced Solid State NMR (SSNMR) Analysis. The DNP-SSNMR analysis was performed on a 400 MHz (9.4T) Bruker Ascend DNP-NMR spectrometer with a 25 W gyrotron microwave source. A 3.2 mm MAS DNP-NMR triple resonance broadband probe was used and operated at 100 K. The SSNMR sample was spun at 8 kHz during the measurement. In this study, the intact high-S poplar solid (30 mg) was pre-mixed with 70 μL of 10 mM AMUPol in D₂O/H₂O solvent in rotor. The lignin samples (FPL and OPL) were first packed in rotor then added with 25 μL of 10 mM TekPol in TCE. The cellulose residue samples were prepared with 10 mM AMUPol at mass/volume ratio 1:2 (i.e., 20 mg cellulose sample mixed with 40 μL AMUPol) in D₂O/H₂O then packed in rotor. The ¹³C SSNMR signal of each sample was acquired by cross-polarization magic angle spinning (CPMAS) experiment with 328 scans.

Gel Permeation Chromatography (GPC) Analysis. The GPC analysis was done on a Waters Alliance HPLC system (2690 Separation Module) which was equipped with the Tosoh TSKgel Super HM-M column and guard. The detection of lignin polymer was measured by

the Waters 2414 differential refractometer. *N,N*-dimethyl formamide (DMF) with 0.1% LiBr was used as the mobile phase. The instrument was pre-calibrated with polystyrene standards while the number average molecular weight (M_n) and weight average molecular weight (M_w) were acquired based on the calibrations.

Fourier-Transform Infrared (FTIR) Spectroscopy. FTIR spectra of DMPPPO and epoxides were recorded on a Nicolet iS10 FT-IR spectrometer equipped with a diamond Attenuated Total Reflection (ATR) probe. For each measurement, 3 mg of sample was loaded to the probe and scanned over a range of 500–4000 cm^{-1} .

Thermogravimetric (TGA) Analysis. TGA analysis was carried out on a Discovery 5500 Thermo-Gravimetric Analyzer. For each measurement, 5–10 mg sample was loaded into an Al_2O_3 ceramic crucible. The crucible is then placed on a platinum sample pan and transferred to an autosampler. To analyse the Nb_2O_5 samples, the crucible first underwent an isothermal step under 25 mL/min N_2 flow at 50 °C for 5 min to remove moisture. Then the crucible was heated to 550 °C at a ramping rate of 20 °C/min and held for 10 min at 550 °C. TGA analysis of thermoset sample was pre-set to 500 °C with ramping rate 20 °C/min under N_2 flow of 40 mL/min.

Tensile Test. The tensile measurement of thermoset sample was taken on a customized high-strain test machine in the Mechanical Test Lab of the Department of Mechanical Engineering at UC Santa Barbara (UCSB). Prior to the mechanical measurement, the thermoset polymer sample was moulded into a 25 mm length and 0.1 mm thickness dog bone shape.

X-ray Diffraction (XRD) Analysis. The fresh and spent Nb_2O_5 catalyst

Two different approaches were used to produce lignin monomers from high-S poplar biomass (Figure 2). On one hand, the biomass was first treated by various organosolv methods where the lignin was first extracted and concentrated by using organic solvents and acids (see Experimental Section). Several different organosolv lignins were produced in this manner, and their depolymerization reactions were investigated over the Pd-Zn/C catalyst (Figure 2, brown pathway). Alternatively, the high-S poplar biomass was reacted directly with Pd-Zn/C catalyst to convert the intact lignin into its monomers (Figure 2, green approach), leaving behind the carbohydrate components as a solid residue, reductive catalytic fractionation (RCF).

High-S lignin extraction with different organosolv methods

SI Table S-1 summarizes the five methods used to extract lignin biopolymer from high-S poplar biomass into the liquid phase. In each case, lignin solubilization required an elevated temperature (>70 °C). Under certain conditions, the cellulose and hemicellulose components were also partially degraded and removed by the organic solvent as well. After treatment, the liquid phase was collected by vacuum filtration. To recover the isolated lignin from the filtrate, 50% (v/v) of the organic solvent was first removed, then an equivalent amount of water was added to the remaining filtrate to precipitate the lignin. The leftover extractives were mainly cellulose and hemicellulose and remained soluble in the final filtrate.

SI Table S-2 summarizes the yield, molecular weight and composition of lignin obtained from the different organosolv methods compared to the composition of the original high-S

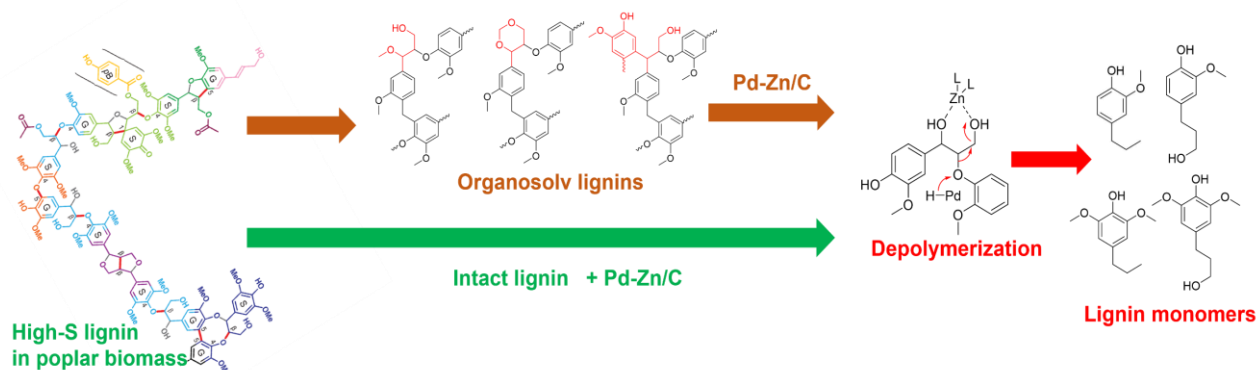


Figure 2. Pd-Zn/C catalysed depolymerization of lignin into lignin monomers. The pathway labelled in green colour indicates using intact poplar biomass directly as feed stock for the reaction with Pd-Zn/C catalyst, reductive catalytic fractionation (RCF). The pathway labelled in brown colour shows the poplar biomass is first treated by organosolv methods to extract organosolv lignin from biomass. Then the organosolv lignin is catalysed by Pd-Zn/C to make lignin monomers.

samples were analysed on a powder diffractometer Scintag X 2 that is equipped with a sealed Cu tube x-ray source and a solid-state point detector.

Scanning Electron Microscopy Analysis. The fresh and used Nb_2O_5 catalysts were observed by FEI Nova Nano 650 FEG SEM. The SEM is equipped with a high stability Schottky field emission gun and ETD election imaging and through-lens detector. The catalyst sample was loaded to the sample holder by a double-sided Cu tape. The voltage was pre-set to 3.00 kV during the measurement.

Results

biomass. Entry 1 refers to lignin content in the intact high-S poplar biomass, which is 22% by weight and used as a reference for calculating lignin isolated yield by each organosolv method. Entries 2–6 indicate the lignin yield by each isolation method. Notably, the lignin yield from the FPL method was 125% (entry 3, Table S-2). The mass gain is partly due to formaldehyde addition in the FPL treatment to the α and γ carbons of the β -O-4 linkage forming dioxane rings. Figure 3 illustrates the aliphatic region of 2D HSQC NMR spectrum of FPL, which indicates the dioxane rings formed upon addition of formaldehyde to give the FPL framework (circled in red). Moreover, the chemical shifts circled in black in Figure 3 indicate the additional presence of diformylxylose in the FPL product which added extra mass.³² The presence of diformylxylose would be

formed by the side reaction between xylose (derived from hemicellulose) and formaldehyde. Thus, the FPL treatment also extracts some of the carbohydrates. The FA/AA and OPL treatments gave the second and third highest yields of lignin at 37% and 25% of the theoretical yield (entries 2 and 4, Table S-2), respectively. The H₂O/H₂SO₄ technique gave the poorest yield (13%, entry 6, Table S-2).

The times required for the various organosolv extraction methods should be taken into consideration in evaluating the

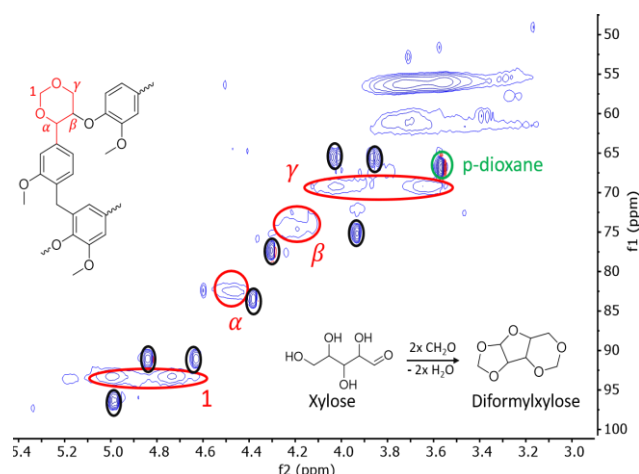


Figure 3. Illustration of dioxane ring and 2D (¹H/¹³C) HSQC NMR aliphatic region of FPL. Peaks circled by red colour indicate the dioxane ring formed by formaldehyde protection on the lignin structure. Peaks circled by the black colour indicate the diformylxylose formed between xylose (derivative from hemicellulose) and formaldehyde. Peak circled by the green colour indicates the p-dioxane solvent residue from the FPL treatment.

efficacy of lignin extraction. The OPL treatment required 336 hours of heating time (entry 2, Table S-2) while the other methods were completed within 5 hours of heating (entries 3-6, Table S-2). Taking the yield of lignin and the extraction efficiency together, the FPL and FA/AA extractions gave the highest lignin yields per hour.

The weight average (*M_w*) and number average (*M_n*) molecular weight of the isolated lignin were analysed by gel permeation chromatography (GPC) in DMF. Entry 2 in Table S-2 shows OPL lignin to have the highest *M_w* of 3.9 kg/mol. The FA/AA lignin gave the second highest *M_w* value (2.5 kg/mol, entry 4, Table S-2) while those obtained from the H₂O/HCl and H₂O/H₂SO₄ extractions had smaller *M_w* values, 1.2 and 1.6 kg/mol, respectively (entries 5 and 6, Table S-2). Therefore, this trend suggests that the lignin extracted using organic solvent generally have higher *M_w* values, although extraction with water co-solvent had faster rates of lignin isolation (less heating duration, entries 4-6, Table S-2), and led to the breakdown of lignin biopolymer into smaller oligomers with relatively smaller *M_w* values.

Table S-2 also lists the contents of S and G units in each organosolv lignin as determined from the aromatic region of the 2D HSQC NMR (SI, Figure S-1) and compares these to the S and G units present in the original high-S poplar lignocellulose biomass. FPL lignin showed the best retention of the S unit (80%), while its G content was 19% (entry 3). The FA/AA lignin had similar S and G contents (79% and 21%), but the OPL and H₂O/H₂SO₄ methods gave lower S-content (62% and 67%, respectively) in the isolated lignin (entries 2 and 6).

Displayed in Figure 4 are the dynamic nuclear polarization (DNP) enhanced solid state NMR (SSNMR) spectra of intact high-S poplar

biomass and the extractives (lignin and cellulose residues) obtained from organosolv OPL and FPL extraction methods. For the spectrum of high-S poplar biomass before organosolv treatments (Figure 4 (a)), the chemical shift of carbohydrate carbons is between 45 and 110 ppm, specifically 82 and 88 ppm represent amorphous and crystalline cellulose, respectively. The chemical shifts between 120-180 ppm are assigned to lignin. Figure 4 (b) illustrates the SSNMR spectrum of the cellulose residue obtained after FPL extraction. One noteworthy observation from Figure 4 (b) was the disappearance of peaks from the lignin region while the pattern of carbohydrate signals remained unchanged from the starting biomass sample (Figure 4 (a)). In contrast, the spectrum of the OPL cellulose residue in Figure 4 (d) showed diminished but observable peaks in the lignin region. This phenomenon suggests that the FPL method achieved nearly complete lignin extraction/removal while the OPL method had some lignin remaining in the cellulose matrix. It also explains the higher lignin isolated yield from the FPL extraction (entry 3, Table S-2) versus OPL (entry 2, Table S-2). Comparing the DNP spectra of isolated lignins in Figure 4 (c), stronger signals for carbohydrates are detected for FPL lignin than OPL lignin. This indicates that the FPL method extracted carbohydrates in addition to the lignin fraction, another reason for the higher mass yield of FPL lignin (entry 3, Table S-2).

Catalytic depolymerization of lignin to monomers over Pd-Zn/C

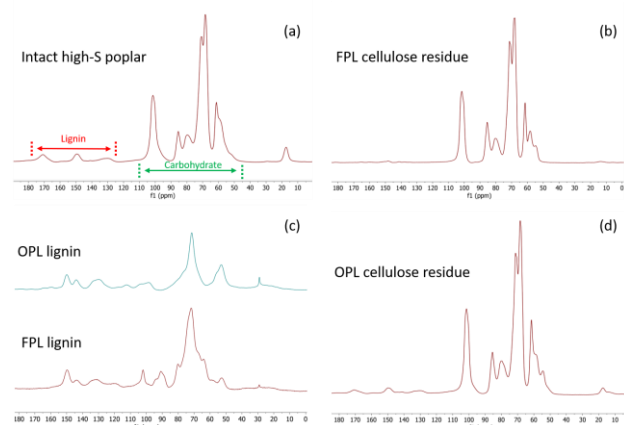


Figure 4. DNP-enhanced ¹³C CPMAS SSNMR spectra of (a) intact high-S poplar biomass, (b) FPL cellulose residue, (c) OPL and FPL lignins, and (d) OPL cellulose residue samples. All the measurements displayed in this figure were acquired with microwave turned on.

To understand the ideal conditions for lignin depolymerization, the catalytic system was investigated with variations of the Pd:Zn ratio (Table S-3). Notably, the product selectivity shifted from making DHE-OH and DMPP-OH to produce more DHE and DMPP with increased loading of Zn. As a result, a synthesized Pd-Zn/C catalyst with Pd:Zn ratio of 1:10 was applied to the lignin depolymerizations, since it gave the highest selectivity of DMPP formation at 71% (entry 4, Table S-3). Subsequent reactions were carried out under 35 bar H₂ with 10 wt% loading of this catalyst in 30 mL methanol solvent and heated to 225 °C for 12 h.

The content of intact lignin in high-S poplar biomass was 22%. Thus, based on 10 g scale feedstock, 2.2 g intact lignin would have been presented to react over the Pd-Zn/C catalyst under these conditions. After reaction, a 1.34 g mixture of lignin monomers was obtained which corresponds to 61% total yield from the intact lignin

(entry 4, Table S-3 and the green path in Figure 5). The same reaction conditions were applied to the various organosolv lignins. However, the total yield of lignin monomers from these substrates was considerably less than that obtained from biomass intact lignin (Table S-4). Of these, the OPL and H₂O/HCl lignin showed the best monomers yield of 32% and 33%, respectively, while FPL lignin and H₂O/H₂SO₄ lignin gave monomer yields of only 22% and 10%, respectively (entries 1-5, Table S-4). The FA/AA lignin gave the smallest yield at 3.6%. Although DMPP selectivity was surprisingly improved to 92% and 93% when using FA/AA and H₂O/H₂SO₄ lignins as feedstocks, the low overall yields suggest that proceeding via these types of organosolv lignin was ineffective for DMPP synthesis. Notably, not only did intact high-S lignin biomass as the feedstock produce the highest overall yield of lignin monomers, the overall procedure was simplified by removing one major step.

It is likely that the suppressed monomer yields from the

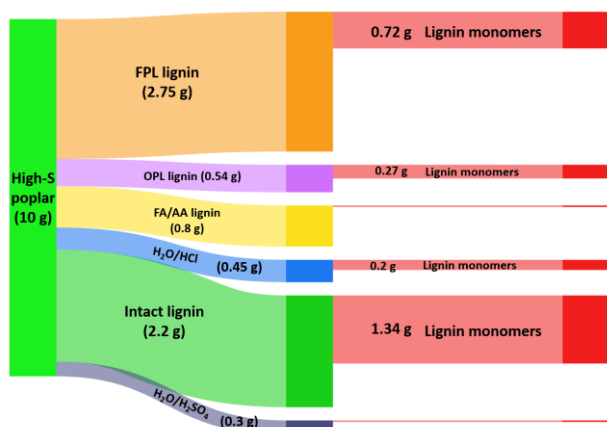


Figure 5. Illustration of organosolv lignin made from 10 g high-S poplar biomass and the further conversion of different types of lignin into lignin monomers. The corresponding reaction conditions are summarized in Tables S-2, S-3, and S-4.

extracted lignins are due to polymer structure alterations during the organosolv treatment. For instance, the methoxy attachments, dioxane structure, and diformylxylose were apparent in the HSQC NMR spectra of OPL and FPL lignins (Figure 3 and Figure S-3). The altered lignins were less reactive than the biomass intact lignin; therefore, higher Pd-Zn/C catalyst loadings (up to 30 wt%), and longer reaction times were applied to improve the yield of monomers from OPL, FPL, and H₂O/HCl lignins (Table S-5 and Table S-6). SI Table S-5 summarizes results from optimal reaction conditions using 30 wt% Pd-Zn/C loading and 12 h reaction time leading to improved overall yields of 50%, 35%, and 45% for OPL, FPL, and H₂O/HCl lignins, respectively (entries 1-3, Table S-5). Taking the yield of OPL, FPL, and H₂O/HCl lignin from the organosolv treatments together, the overall lignin monomers made from 10 g high-S poplar biomass through the organosolv methods were 0.27 g, 0.72 g, and 0.2 g, respectively (purple path (OPL), orange path (FPL), and blue path (H₂O/HCl) in Figure 5). As a result, the FPL lignin gave the second highest yield of lignin monomers after that observed for biomass intact lignin.

Conversion of lignin derived DMPP to the novel molecule DMPPPO

After the lignin depolymerizations, the monomers product mixtures contained many by-products and unidentified species. The GC chromatogram displayed in Figure S-3(a) illustrates detection of DMPP along with other unidentified analytes were derived from high-S lignin. Figure S-3(b) shows the chromatogram after hydrolysis

of this oil directly by our Nb₂O₅ catalyst to give prominently DMPPPO. Although the latter experiments demonstrate that our Nb₂O₅ catalyst is tolerant to the complicated mixture of lignin monomers, the presence of other analytes distracted from further treatment of DMPPPO to prepare the tri-epoxides.

Therefore, an exclusive production of DMPPPO were obtained by isolating and combining DMPP from several runs of lignin depolymerization through chromatography with hexane/ethyl acetate (4:1 v/v) as the mobile phase. This combined product was then used to convert DMPP (400 mg) to DMPPPO over Nb₂O₅. According to our previous finding, the Nb₂O₅ catalyst calcined at 450 °C demonstrated abundant acid sites and effectively catalysed the reaction of DHE to 4-propylcatechol.²² Taking advantage of this Nb₂O₅ catalyst, the conversion of lignin derived DMPP to DMPPPO was accomplished in aqueous solution at 230 °C using the modified conditions described in the Experimental Section and Figure 6. The result was 96% conversion of the lignin derived DMPP with 96% selectivity to DMPPPO (Figure 6). The DMPPPO product was characterized by ¹H NMR and ES- mass spectrometry (SI, Figures S-4 and S-5).

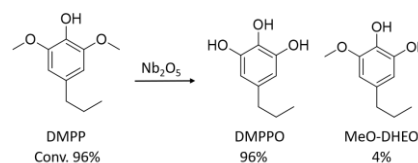


Figure 6. Hydrolysis of DMPP obtained from high-S OPL lignin. Reaction condition: 400 mg DMPP, 200 mg Nb₂O₅, 12 mL H₂O, 0.8 mL methanol, 10 bar N₂, 230 °C, 20 h reaction time.

Compared to the conventional method of *o*-demethylation which requires the use of halogenated and toxic reagents (HBr, HCl or BBr₃), this catalytic system offers a greener and simpler strategy for catechol and pyrogallol production from lignin-derived monomers¹⁶ with water as the only additional reagent and solvent. Furthermore, the Nb₂O₅ catalytic system showed excellent tolerance to impurities in the lignin monomers from native biomass. This tolerance was demonstrated by recycling the Nb₂O₅ in several subsequent runs. The catalyst was recycled twice after the initial run and displayed comparable activity and selectivity for the conversion of DMPP to DMPPPO (Figure 7). The third recycle run showed a decrease in activity and selectivity. By which, the one methoxy product MEO-DHEO became the major product. This could be due to partial degradation of Nb₂O₅. After the third recycling reaction, the colour of the Nb₂O₅ powder changed from white to brown and the material became more crystalline (SI, Figure S-6 (A) and (B) and Figure S-7). This coloration was not removed after washing with organic solvents. Notably, the particle size of Nb₂O₅ after the reaction

was significantly smaller and became more uniform at ~500 – 800 nm (SI, Figure S-8).

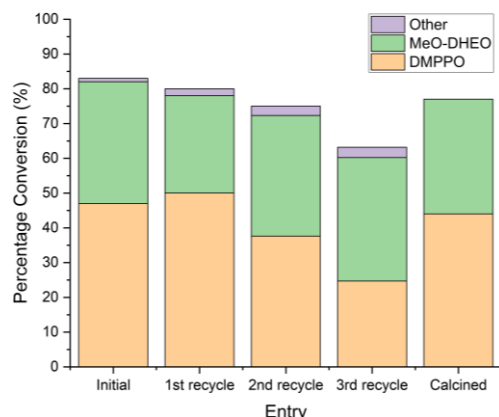


Figure 7. Performance of Nb₂O₅ reusability for DMPP conversion to DMPPO. The catalyst was collected on the bottom layer from reaction mixture by centrifuge. The catalyst was washed twice by 5 mL water in centrifuge at 5000 rpm for 5 min each time. After that, the catalyst was washed again by 10 mL ethanol under sonication for 15 min. Then the recycled catalyst was placed in an oven at 120 °C for 12 h prior to the next run. The height of the coloured bar represents the DMPPO and MeO-DHEO product selectivity and their sum the conversion. Reaction condition: 0.5 g DMPP, 0.15 g Nb₂O₅, 12 mL H₂O, 0.8 mL methanol, under 10 bar N₂, 230 °C, 10 h reaction time.

To regenerate the Nb₂O₅ catalyst, the brown coloured Nb₂O₅ was calcined at 450 °C under the same calcination ramping rate as used to prepare fresh Nb₂O₅.³⁴ After 20 min calcination, the regenerated Nb₂O₅ catalyst was a slightly yellow colour and showed comparable activity and selectivity to that of the fresh catalyst (SI, Figure S-6 (C)). The TGA analysis indicates the weight percentage accompanying the colour change on Nb₂O₅ upon several recycles was around 5 – 7% (SI, Figure S-9). We attribute the appearance of this brown colour to coke or polymer formation on the catalyst surface.

Conversion of novel DMPPO to tri-epoxides and thermoset polymer

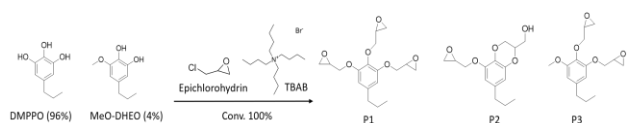


Figure 8. Conversion of DMPPO to epoxides. Reaction condition: 400 mg mixture of DMPPO (96%) and MeO-DHEO (4%), 6 g epichlorohydrin, 400 mg tetrabutylammonium bromide (TBAB), 60 °C, 3 h reaction time. Then dropwise added 50% NaOH aqueous solution with stirring and heated to 70 °C for another 3 h.

One important application of pyrogallol is as a building block for making bio-based thermosetting plastics. Displayed in Figure 8 is the tetrabutylammonium bromide (TBAB) reaction of DMPPO with epichlorohydrin to give the tri-epoxide P1. When the net product mixture of the Nb₂O₅ system (400 mg of 96% DMPPO and 4% MeO-DHEO) reacted with excess epichlorohydrin, three epoxy products (P1, P2, and P3 with P1:P2 nearly 1:1) were obtained as identified by ES+ mass spectrometry (SI, Figure S-10) and FT-IR (SI, Figure S-11). The multi-functionalized epoxy monomers P1 and P3 are suitable building blocks for curing with diamines to produce epoxy

thermosets. P2 is less desirable because it contains only one active epoxy group (Figure 8), and as a result it provides less crosslinking in the resulting epoxy thermosetting polymer. Nonetheless, the conversion of the DMPPO mixture to the epoxy monomers was 100%, thereby confirming that these lignin monomers are upgradable directly toward epoxide building blocks.

To investigate how a DMPPO epoxy would function as a thermoset, a polymer sample was synthesised with the tri-epoxides made from commercial DMPP. The DMPPO epoxy mixture which contained P1, P2 and P3 was introduced to diethylenetriamine (DETA) with a 1:1:1 stoichiometric ratio between the epoxy and amine for curing in a dog bone shape mould. The tensile test of the resulting polymer showed that the thermoset withstood stress up to around 16 MPa with a strain of less than 0.1% (Figure 9). The brittleness of the thermoset sample may be attributed to the rigid aromatic structure and the presence of the benzodioxane side product (P2) which does not crosslink and can occupy certain free volume that negatively affects the cross-linking density of the network. Thermogravimetric analysis (TGA) thermograms show a one-step degradation profile, which is attributed to the decomposition of cross-linked polymer network. The onset degradation temperature T_{d5} (temperature at 5% weight loss) was observed to be 252 °C (SI, Figure S-12). To improve the physical properties of tri-epoxide thermoset, further optimization with different curing agents will be the subject of future studies.

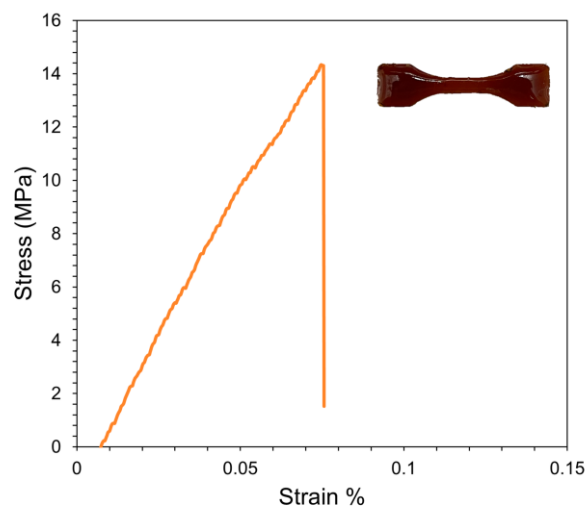


Figure 9. Stress-Strain curve of dog bone shape thermoset polymer made with tri-epoxides derived from DMPPO.

Discussion

This study offers a complete “production chain” from renewable high-S poplar biomass to epoxide polymer precursors. We also show that the most efficient approach is the direct “lignin-first” conversion of the biomass intact high-S lignin via Pd-Zn/C-catalysed hydrogenolysis to give largely the monomer 4-propyl-2,6-dimethoxyphenol (DMPP). The highest selectivity toward DMPP was accomplished with a Pd/Zn ratio optimized at 1/10 in methanol solution at 225 °C. Once the DMPP was separated from the other

monomers by chromatography, this step was followed by nearly quantitative Nb₂O₅-catalysed hydrolysis of the DMPP to the propylpyrogallol DMPPPO. The latter demethoxylation step was accomplished in water and was quite tolerant of impurities in the DMPP. Lastly, reaction of the resulting propylpyrogallol with epichlorohydrin gave epoxide derivatives which may serve as renewable polymer precursors.

We also compared the above approach to one where several organosolv methods were used to separate lignins from the high-S poplar biomass prior to the hydrogenolysis to monomers.^{30, 35-39} However, the drawbacks of these methods are obvious given that they require extra usage of solvents, time, and energy.^{31, 38-41} More importantly, the properties of organosolv lignins are often altered during these fractionation treatments, including re-condensation reactions forming unnatural and recalcitrant C-C bonds.^{30, 31, 40-43}

The extra-step suffers from two problems. With the exception of the FPL method, the efficiency of lignin extraction was relatively low so that considerable material loss was experienced as illustrated in Figure 5. While the FPL method appeared much more efficient, it should be noted that the mass balance may have been affected by the extraction of carbohydrates (see above). The second problem is that hydrogenolysis of the organosolv lignins in each case studied gave lower monomer yields and selectivity than seen from the high-S biomass itself (Table S-5), perhaps as the result of the altered structures of these macromolecules as noted. Even OPL, which was obtained under milder conditions and gave 50% yield of monomers over Pd-Zn/C, proved to be less reactive than the intact high-S lignin biomass.

A third problem found upon extracting the lignin by organosolv methods is that in several cases there were decreases in the relative amounts of S units. The reduction of S units could be due to the solubility difference between S and G lignins in agreement with a recent report by Vermaas et al., suggesting that additional syringyl units generally reduce lignin solubility.⁴³ Notably, the combination of dioxane and formaldehyde showed much more efficient lignin extraction from biomass and the resulting FPL gave nearly the same G and S content as high-S biomass lignin (entries 1 and 3, Table S-2). However, the FPL treatment still affected the further lignin depolymerization reaction. Even with the same G and S content, the distribution and yield of monomers from FPL lignin were lower than that obtained with biomass (lignin).

The DMPP made from biomass always contained impurities resulting in a dark brown coloured oil. The quinone-like by-products, lignin oligomers, inorganic salts and unidentified biomass derivatives are commonly accumulated in the oil.⁴⁴⁻⁴⁸ The conventional *o*-demethylation reaction converts DMPP to DMPPPO with BBr₃ or HBr. Instead, we introduce an alternative approach which uses Nb₂O₅ as catalyst to convert DMPP to DMPPPO in a greener way. Our results indicate the Nb₂O₅ catalyst was able to convert 96% of the biomass derived DMPP into DMPPPO. Although our previous catalyst studies with Nb₂O₅ were performed in an aqueous medium with hydrogen sources such as methanol and H₂ gas,²² for the reactions described here such hydrogen sources are unnecessary, but added water was required and small amount of methanol to improve the solubility of DMPP. Therefore, DMPP undergoes hydrolysis over Nb₂O₅ to DMPPPO. Moreover, this Nb₂O₅ catalyst is recyclable without deactivation over three runs. A quick calcination at 450 °C can remove the coke from catalyst and regenerate the activity of Nb₂O₅ catalyst sufficiently.

In summary, the two catalytic reactions described here provide a direct pathway to a versatile biophenol monomer from high-S biomass lignin. Reductive catalytic fractionation of high S poplar

biomass with Pd/Zn (1:10) affords DMPP in 61% yield. Hydrolysis of DMPP over Nb₂O₅ in water gives a versatile monomer (DMPPPO) in nearly quantitative yields. The resulting lignin based DMPPPO can be converted in high yields to epoxides, and a novel thermosetting plastic based on the DMPPPO-epoxides mixture was successfully synthesized.

To put these results in the context of feasible scalability, 300 kta (kilo ton per annum) of this novel biophenol monomer (DMPPPO) could be produced from approximately 2,300 kta high S poplar biomass (13% overall yield on mass basis). This amount of DMPPPO would displace only 3.75% of the BPA market (8,000 kta in 2016) and would carry a value of ca. \$600 million (based on average BPA price of \$2 per kg in 2016).^{49,50} For poplar wood plantations, yields are estimated to be 7.0 dry ton per acre annually on good agricultural soil at a cost of \$25-\$60 per dry ton of poplar biomass.⁵¹ As a result, 329,000 acres would be required to grow 2.3 million tons of poplar biomass, which corresponds to 1% of the land in the state of Iowa, for example (35.7 million acres). The cost to produce 2.3 million tons of polar biomass would be \$58-138 million (SI, Table S-7). The value of the DMPPPO product is in the range of 10x to 4x the cost of the biomass without adding value from the carbohydrate components.

Author Contributions

Baoyuan Liu: Formal analysis, investigation, methodology, visualization, writing- original draft.

Melissa Sanchez: Formal analysis, investigation, verification, writing- original draft.

Julianne Truong: Formal analysis, investigation.

Peter C. Ford: Conceptualization, methodology, project administration, supervision, visualization, writing- review & editing.

Mahdi M. Abu-Omar: Conceptualization, funding acquisition, methodology, project administration, supervision, visualization, writing- review & editing.

Conflicts of interest

MMAO is founder and part owner of Spero Renewables, LLC, a technology company making biomass-based renewable alternative to petrochemicals.

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Notes and references

- Tran, C. D.; Chen, J. H.; Keum, J. K.; Naskar, A. K., A New Class of Renewable Thermoplastics with Extraordinary Performance from Nanostructured Lignin-Elastomers. *Adv Funct Mater* **2016**, *26* (16), 2677-2685.
- Stewart, D., Lignin as a base material for materials applications: Chemistry, application and economics. *Ind Crop Prod* **2008**, *27* (2), 202-207.

3. Wang, M.; Wang, F., Catalytic Scissoring of Lignin into Aryl Monomers. *Adv Mater* **2019**, *31* (50).
4. Duval, A.; Lawoko, M., A review on lignin-based polymeric, micro- and nano-structured materials. *React Funct Polym* **2014**, *85*, 78-96.
5. Baker, D. A.; Rials, T. G., Recent advances in low-cost carbon fiber manufacture from lignin. *J Appl Polym Sci* **2013**, *130* (2), 713-728.
6. Beckham, G. T.; Johnson, C. W.; Karp, E. M.; Salvachua, D.; Vardon, D. R., Opportunities and challenges in biological lignin valorization. *Curr Opin Biotech* **2016**, *42*, 40-53.
7. Bova, T.; Tran, C. D.; Balakshin, M. Y.; Chen, J.; Capanema, E. A.; Naskar, A. K., An approach towards tailoring interfacial structures and properties of multiphase renewable thermoplastics from lignin-nitrile rubber. *Green Chem* **2016**, *18* (20), 5423-5437.
8. Cheng, C. B.; Shen, D.; Gu, S.; Luo, K. H., State-of-the-art catalytic hydrogenolysis of lignin for the production of aromatic chemicals. *Catal Sci Technol* **2018**, *8* (24), 6275-6296.
9. Deoliveira, W.; Glasser, W. G., Multiphase Materials with Lignin .2. Starlike Copolymers with Caprolactone. *Macromolecules* **1994**, *27* (1), 5-11.
10. Falkehag, S. I.; Braddon, D. V.; Dougherty, W. K., Lignin Polymer Applications. *Abstr Pap Am Chem S* **1975**, (169), 6-7.
11. Funaoka, M., Sequential transformation and utilization of natural network polymer "LIGNIN". *React Funct Polym* **2013**, *73* (2), 396-404.
12. Jawerth, M. E.; Brett, C. J.; Terrier, C.; Larsson, P. T.; Lawoko, M.; Roth, S. V.; Lundmark, S.; Johansson, M., Mechanical and Morphological Properties of Lignin-Based Thermosets. *ACS Appl Polym Mater* **2020**, *2* (2), 668-676.
13. Bajwa, D. S.; Pourhashem, G.; Ullah, A. H.; Bajwa, S. G., A concise review of current lignin production, applications, products and their environmental impact. *Ind Crop Prod* **2019**, *139*.
14. Calvo-Flores, F. G.; Dobado, J. A., Lignin as Renewable Raw Material. *Chemsuschem* **2010**, *3* (11), 1227-1235.
15. Gillet, S.; Aguedo, M.; Petitjean, L.; Morais, A. R. C.; Lopes, A. M. D.; Lukasik, R. M.; Anastas, P. T., Lignin transformations for high value applications: towards targeted modifications using green chemistry. *Green Chem* **2017**, *19* (18), 4200-4233.
16. Fadlallah, S.; Roy, P. S.; Garnier, G.; Saito, K.; Allais, F., Are lignin-derived monomers and polymers truly sustainable? An in-depth green metrics calculations approach. *Green Chem* **2021**, *23* (4), 1495-1535.
17. Luo, H.; Abu-Omar, M. M., Chemicals From Lignin. In *Encyclopedia of Sustainable Technologies*, Abraham, M. A., Ed. Elsevier: Oxford, 2017; pp 573-585.
18. Zhao, S.; Abu-Omar, M. M., Biobased Epoxy Nanocomposites Derived from Lignin-Based Monomers. *Biomacromolecules* **2015**, *16* (7), 2025-2031.
19. Zhao, S.; Abu-Omar, M. M., Renewable Epoxy Networks Derived from Lignin-Based Monomers: Effect of Cross-Linking Density. *ACS Sustain Chem Eng* **2016**, *4* (11), 6082-6089.
20. Zhao, S.; Abu-Omar, M. M., Renewable Thermoplastics Based on Lignin-Derived Polyphenols. *Macromolecules* **2017**, *50* (9), 3573-3581.
21. Zhao, S.; Abu-Omar, M. M., Catechol-Mediated Glycidylation toward Epoxy Vitrimers/Polymers with Tunable Properties. *Macromolecules* **2019**, *52* (10), 3646-3654.
22. Li, S.; Liu, B.; Truong, J.; Luo, Z.; Ford, P. C.; Abu-Omar, M. M., One-pot hydrodeoxygenation (HDO) of lignin monomers to C9 hydrocarbons co-catalysed by Ru/C and Nb2O5. *Green Chem* **2020**, *22* (21), 7406-7416.
23. Arapova, O. V.; Chistyakov, A. V.; Tsodikov, M. V.; Moiseev, I. I., Lignin as a Renewable Resource of Hydrocarbon Products and Energy Carriers (A Review). *Petrol Chem+* **2020**, *60* (3), 227-243.
24. Franke, R.; McMichael, C. M.; Meyer, K.; Shirley, A. M.; Cusumano, J. C.; Chapple, C., Modified lignin in tobacco and poplar plants over-expressing the Arabidopsis gene encoding ferulate 5-hydroxylase. *Plant J* **2000**, *22* (3), 223-234.
25. Gao, F.; Webb, J. D.; Sorek, H.; Wemmer, D. E.; Hartwig, J. F., Fragmentation of Lignin Samples with Commercial Pd/C under Ambient Pressure of Hydrogen. *ACS Catal* **2016**, *6* (11), 7385-7392.
26. Van den Bosch, S.; Schutyser, W.; Koelewijn, S. F.; Renders, T.; Courtin, C. M.; Sels, B. F., Tuning the lignin oil OH-content with Ru and Pd catalysts during lignin hydrogenolysis on birch wood. *Chem Commun* **2015**, *51* (67), 13158-13161.
27. Klein, I.; Marcum, C.; Kenttamaaa, H.; Abu-Omar, M. M., Mechanistic investigation of the Zn/Pd/C catalyzed cleavage and hydrodeoxygenation of lignin. *Green Chem* **2016**, *18* (8), 2399-2405.
28. Patil, D. M.; Phalak, G. A.; Mhaske, S. T., Synthesis of bio-based epoxy resin from gallic acid with various epoxy equivalent weights and its effects on coating properties. *J Coat Technol Res* **2017**, *14* (2), 355-365.
29. Cheng, C. B.; Truong, J.; Barrett, J. A.; Shen, D. K.; Abu-Omar, M. M.; Ford, P. C., Hydrogenolysis of Organosolv Lignin in Ethanol/Isopropanol Media without Added Transition-Metal Catalyst. *ACS Sustain Chem Eng* **2020**, *8* (2), 1023-1030.
30. Luo, H.; Abu-Omar, M. M., Lignin extraction and catalytic upgrading from genetically modified poplar. *Green Chem* **2018**, *20* (3), 745-753.
31. Zijlstra, D. S.; Lahive, C.; Analbers, C. A.; Figueiredo, M. B.; Wang, Z. W.; Lancefield, C.; Deuss, P. J., Mild Organosolv Lignin Extraction with Alcohols: The Importance of Benzylic Alkoxylation. *ACS Sustain Chem Eng* **2020**, *8* (13), 5119-5131.
32. Shuai, L.; Amiri, M. T.; Questell-Santiago, Y. M.; Heroguel, F.; Li, Y. D.; Kim, H.; Meilan, R.; Chapple, C.; Ralph, J.; Luterbacher, J. S., Formaldehyde stabilization facilitates lignin monomer production during biomass depolymerization. *Science* **2016**, *354* (6310), 329-333.
33. Bernt, C. M.; Bottari, G.; Barrett, J. A.; Scott, S. L.; Barta, K.; Ford, P. C., Mapping reactivities of aromatic models with a lignin disassembly catalyst. Steps toward controlling product selectivity. *Catal Sci Technol* **2016**, *6* (9), 2984-2994.
34. Li, S. M.; Liu, B. Y.; Truong, J.; Luo, Z. Y.; Ford, P. C.; Abu-Omar, M. M., One-pot hydrodeoxygenation (HDO) of lignin monomers to C9 hydrocarbons co-catalysed by Ru/C and Nb2O5. *Green Chem* **2020**, *22* (21), 7406-7416.
35. Nishide, R. N.; Truong, J. H.; Abu-Omar, M. M., Organosolv Fractionation of Walnut Shell Biomass to Isolate Lignocellulosic Components for Chemical Upgrading of Lignin to Aromatics. *ACS Omega* **2021**, *6* (12), 8142-8150.
36. Cheng, C.; Li, P.; Yu, W.; Shen, D.; Jiang, X.; Gu, S., Nonprecious Metal/Bimetallic Catalytic Hydrogenolysis of Lignin in a Mixed-Solvent System. *ACS Sustain Chem Eng* **2020**, *8* (43), 16217-16228.
37. Du, X.; Tricker, A. W.; Yang, W.; Katahira, R.; Liu, W.; Kwok, T. T.; Gogoi, P.; Deng, Y., Oxidative Catalytic Fractionation and Depolymerization of Lignin in a One-Pot Single-Catalyst System. *ACS Sustain Chem Eng* **2021**, *9* (23), 7719-7727.
38. Nitsos, C.; Rova, U.; Christakopoulos, P., Organosolv Fractionation of Softwood Biomass for Biofuel and Biorefinery Applications. *Energies* **2018**, *11* (1).
39. Barta, K.; Matson, T. D.; Fettig, M. L.; Scott, S. L.; Iretskii, A. V.; Ford, P. C., Catalytic disassembly of an organosolv lignin via hydrogen transfer from supercritical methanol. *Green Chem* **2010**, *12* (9), 1640-1647.
40. Paulsen Thoresen, P.; Lange, H.; Crestini, C.; Rova, U.; Matsakas, L.; Christakopoulos, P., Characterization of Organosolv

Birch Lignins: Toward Application-Specific Lignin Production. *Acs Omega* **2021**, *6* (6), 4374-4385.

41. Ebrahimi Majdar, R.; Ghasemian, A.; Resalati, H.; Saraeian, A.; Crestini, C.; Lange, H., Case Study in Kraft Lignin Fractionation: "Structurally Purified" Lignin Fractions—The Role of Solvent H-Bonding Affinity. *Acs Sustain Chem Eng* **2020**, *8* (45), 16803-16813.

42. Sadeghifar, H.; Wells, T.; Le, R. K.; Sadeghifar, F.; Yuan, J. S.; Jonas Ragauskas, A., Fractionation of Organosolv Lignin Using Acetone:Water and Properties of the Obtained Fractions. *Acs Sustain Chem Eng* **2017**, *5* (1), 580-587.

43. Vermaas, J. V.; Crowley, M. F.; Beckham, G. T., Molecular Lignin Solubility and Structure in Organic Solvents. *Acs Sustain Chem Eng* **2020**, *8* (48), 17839-17850.

44. Rinaldi, R.; Jastrzebski, R.; Clough, M. T.; Ralph, J.; Kennema, M.; Bruijninx, P. C. A.; Weckhuysen, B. M., Paving the Way for Lignin Valorisation: Recent Advances in Bioengineering, Biorefining and Catalysis. *Angew Chem Int Edit* **2016**, *55* (29), 8164-8215.

45. Ma, Z. Q.; Wang, J. H.; Zhou, H. Z.; Zhang, Y.; Yang, Y. Y.; Liu, X. H.; Ye, J. W.; Chen, D. Y.; Wang, S. R., Relationship of thermal degradation behavior and chemical structure of lignin isolated from palm kernel shell under different process severities. *Fuel Process Technol* **2018**, *181*, 142-156.

46. Zhang, X. H.; Tang, W. W.; Zhang, Q.; Li, Y. P.; Chen, L. G.; Xu, Y.; Wang, C. G.; Ma, L. L., Production of hydrocarbon fuels from heavy fraction of bio-oil through hydrodeoxygenative upgrading with Ru-based catalyst. *Fuel* **2018**, *215*, 825-834.

47. Kong, J. C.; Li, B. L.; Zhao, C., Tuning Ni nanoparticles and the acid sites of silica-alumina for liquefaction and hydrodeoxygenation of lignin to cyclic alkanes. *Rsc Adv* **2016**, *6* (76), 71940-71951.

48. Shuai, L.; Saha, B., Towards high-yield lignin monomer production. *Green Chem* **2017**, *19* (16), 3752-3758.

49. Almeida, S.; Raposo, A.; Almeida-Gonzalez, M.; Carrascosa, C., Bisphenol A: Food Exposure and Impact on Human Health. *Compr Rev Food Sci F* **2018**, *17* (6), 1503-1517.

50. Tao, Y. Q.; Fang, L. X.; Dai, M. L.; Wang, C. Y.; Sun, J.; Fang, Q., Sustainable alternative to bisphenol A epoxy resin: high-performance recyclable epoxy vitrimers derived from protocatechuic acid. *Polym Chem-Uk* **2020**, *11* (27), 4500-4506.

51. M. H. Langholtz, B. J. S., L. M. Eaton, 2016 Billion-Ton Report: Advancing Domestic Resources for a Thriving Bioeconomy. *U.S. Department of Energy. Oak Ridge National Laboratory* **2016**, Volume 1: Economic Availability.