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Hydrogenolysis of organosolv lignin in ethanol/iso-propanol media without added transition metal catalyst

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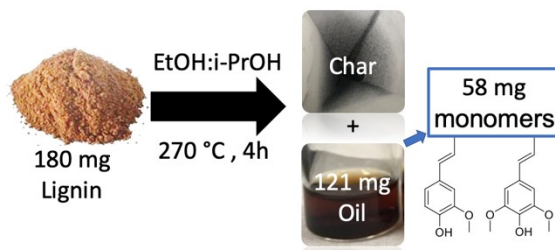
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ABSTRACT: Lignin is the largest renewable source of aromatic chemical building blocks on the planet and has great potential for the production of value-added chemicals. Herein, we describe lignin hydrogenolysis/depolymerization of organosolv poplar lignin (OPL) in ethanol/iso-propanol solvent in the absence of added catalysts. Different EtOH/*i*-PrOH ratios as well as various reaction conditions were evaluated. OPL depolymerization was more effective in the mixed media than in ethanol or iso-propanol alone. Heating OPL at 270 °C for 4 h in 50:50 (v:v) EtOH/*i*-PrOH in a closed pressure vessel gave an overall oil yield of 70 wt% of which about 48% consisted of the monomers (E)-4-propenyl syringol and iso-eugenol. Notably, these catalyst-free reactions in ethanol/iso-propanol media show monomer yields comparable to those reported for lignin depolymerization using precious metal catalysts and dihydrogen, which suggests unexpectedly favorable H-donor ability of this mixed alcohol medium.



KEYWORDS: Lignin, Phenols, Hydrogenolysis, Catalyst-free, supercritical, Mixed solvent, Depolymerization

INTRODUCTION

With the increasing consumption of fossil-carbon resources and the impact of the resulting CO₂ release on the global climate, there has been a growing interest in utilizing biomass as a sustainable feedstock for producing fuels and chemicals.¹⁻³ Lignocellulose, the main non-food component of biomass, which consists of cellulose, hemicellulose and lignin, represents the best candidate to provide sustainable chemicals and fuels.⁴⁻⁶ The chemical conversion of cellulose and hemicellulose to higher value products has seen substantial progress;⁷ however, lignins, which are major byproducts of biorefineries and of the paper pulping industry, are poorly utilized.^{8,9} Lignin, the second most plentiful

biopolymer after cellulose, has the potential to serve as a renewable feedstock in the production of aromatic chemicals.¹⁰⁻¹² The challenge in such utilization lies in lignin's amorphous structure and propensity to cross link into a recalcitrant refractory material under hydrolytic conditions. These properties, make efficient and economic chemical conversion of lignin into useful aromatic products problematic.¹³⁻¹⁶

Thermochemical methods proposed for converting lignin into fuels and chemicals include pyrolysis¹⁷⁻¹⁹, acid and base-catalyzed depolymerization,²⁰ oxidation,^{21,22} and hydrogenolysis²³⁻²⁷ hydrogenolysis being an especially effective strategy. For example, Xiao et

al.²⁸ reported the hydrogenolysis of poplar lignin over a heterogeneous MoO_x/CNT (carbon nanotube) catalyst at 260 °C under 3 MPa H₂ giving a 28 wt% overall yield of monomeric phenols. In other examples, Zhai et al.²⁹ achieved 23 wt% yield of propylguaiacol and propylsyringol upon hydrogenolysis of organosolv birch lignin over a Ni-Fe/activated carbon (AC) catalyst at 225 °C under 2 MPa H₂. For these and most other examples of lignin hydrogenolysis, metal catalysts are required for lignin depolymerization. However, catalyzed hydrogenolysis in some cases also leads to undesired hydrogenation of aromatic rings of the phenolic products.^{27,30}

Another approach is catalytic hydrogen transfer hydrogenolysis (HTH) from reductive organic compounds such as alcohols, formic acid and formates.³¹⁻³³ Alcohols that readily dissolve lignin and are potential hydrogen donors, such as methanol,^{27,34} ethanol³⁵ and iso-propanol,³⁶ have been the most widely used solvents in this regard. Toledano et al.³⁷ reported HTH of lignin over a (Ni/Al)SBA-15 catalyst in various hydrogen donor solvents (tetralin, isopropanol, glycerol, and formic acid). No char was generated and the highest bio-oil yield was obtained in formic acid solvent. Song et al.³⁸ investigated HTH of birch lignin over a Ni/AC catalyst in different solvents (methanol, iso-propanol, 1,4-dioxane, glycerol, cyclohexane). Methanol gave the highest monomer yield among these solvents. Ethanol with formic acid proved to be a more reactive hydrogen source than added H₂ for lignin hydrogenolysis.³⁹

Mixed solvents may have synergistic capability by suppressing the formation of solid residues and promoting the liquefaction conversion of lignocellulose.⁴⁰ Kloekhorst et al.⁴¹ investigated the depolymerization of Alcell lignin over a Ru/C catalyst in three mixed solvents (iso-propanol/formic acid, ethanol/formic acid, methanol/formic acid). The highest yield of bio-oil was obtained in iso-propanol/formic acid solvent. Formic acid (FA) acted as a protecting group to inhibit the repolymerization reaction. Wu et al.⁴² reported the depolymerization of industrial lignin in a mixture solvent of ethanol/1,4-dioxane/formic acid. Their results showed that depolymerization of lignin carried out in the mixed media was more effective than the reaction in ethanol alone. In this case FA also acted as an acid catalyst. Each of these systems used a transition metal catalyst.

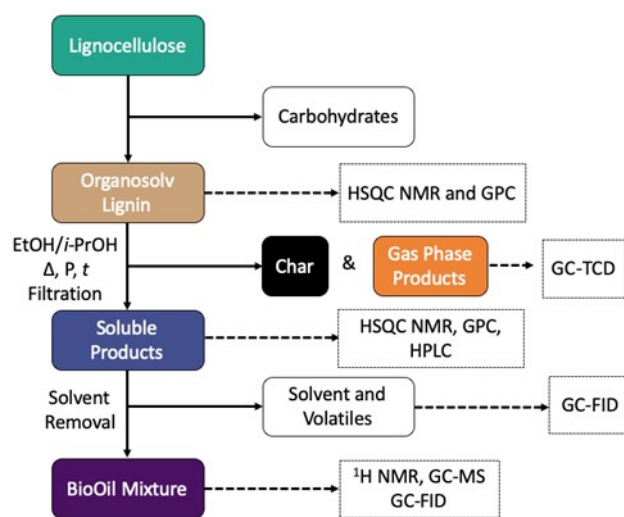
Inspired by the possibility that mixed solvents may exhibit synergistic capabilities in hydrogen transfer hydrogenolysis, we describe herein an investigation of lignin disassembly by catalyst-free ethanol/iso-propanol mixtures in a closed pressure reactor at elevated temperature.

Notably, this mixed solvent system is surprisingly effective at the hydrogenolysis/depolymerization of organosolv poplar lignin (OPL) to generate phenolic lignin monomers. Moreover, the catalyst-free EtOH/*i*-PrOH system shows phenolic monomer yields that rival several reported methods using transition metal catalysts and added H₂.

EXPERIMENTAL

Two methods were used to extract lignin from Poplar wood. Biomass substrates were milled to 40 mesh by a Mini Wiley Mill (Thomas Scientific, Swedesboro, NJ) before use. Organosolv poplar lignin (OPL) was isolated from poplar shavings obtained from ACE Hardware lumberyard, Santa Barbara. 2-Phenoxy-1-phenylethanol was synthesized and characterized according to previously reported methods.⁴³ Ethanol (200 proof), isopropanol (HPLC grade), methanol (ACS Reagent Grade), glacial acetic acid, formic acid (88wt%), sulfuric acid (98 wt%), formaldehyde (37 wt%), and dichloromethane were purchased from Fischer Chemical and used as received.

Scheme 1. Lignin processing sequence and analysis used.



Isolation and Depolymerization of Lignin from Poplar

Scheme 1 provides a graphical roadmap of the isolation and characterization of the organosolv lignins and of the procedures used to analyze the products from the reaction with the EtOH/*i*-PrOH mixed solvent.

Lignin Extraction and Isolation. Poplar wood substrates were treated in methanol/water mixtures to separate lignin.⁴⁴ A 2 g sample of 40

mesh raw biomass was added to a mixture containing 0.045 N H₂SO₄ (25 mL), MeOH (25 mL), and 37 wt % aqueous formaldehyde (4 mL) in a Parr pressure vessel. The reaction was purged with N₂ gas five times and stirred at 700 rpm. The N₂ gas pressure was increased to 10 bar, and the contents were allowed to react at 160 °C for 0.5 h. After cooling to room temperature, the contents were filtered to separate the solid residue, mainly carbohydrates, from the filtrate. The filtrate was concentrated by rotary evaporation to remove the MeOH. Nanopure water (150 mL) was added to the remaining acidic aqueous solution to precipitate the lignin. The extracted lignin was then collected by filtration and washed three times with Nanopure water. The solid lignin was dried overnight and then characterized by heteronuclear Single Quantum Coherence NMR (HSQC) and Gel Permeation Chromatography (GPC). This lignin is referred to in this study as MPL. Elemental analysis of MPL: C, 60.8%; H 6.6%; N, 0.34%.

In the other method,⁴⁵ poplar wood shavings were treated with 1:1 ethanol:toluene, filtered, and dried overnight. In a 10 L round bottom flask, 4.5 L of methanol, 600 g of treated poplar wood shavings and 12 mL of concentrated HCl were added. The suspension was heated to 110 °C and stirred for 12 days. The deep brown solution was separated from residual solids, mainly carbohydrates, by filtration and the volume reduced to half in vacuo. One liter of ice was added to precipitate the lignin as a beige solid. The solid was collected by filtration and washed with cold water until the pH of the filtrate was 7. The resulting organosolv poplar lignin was then dried in vacuo overnight, yielding 21.6 g of material. This lignin is referred to in this study as OPL. Elemental analysis of OPL: C, 59.8%; H 6.6%.

Lignin depolymerization in mini-autoclave reactors. Stainless-steel mini-reactors consisting of a 3/4 inch Swagelok® union with 3/4 inch Swagelok plugs were used for small scale reactions (<5 mL solvent).⁴⁶ The internal volume of these reactors is 10 ml. A typical run contained 30-150 mg lignin, 5 mL 50:50 (v:v) ethanol:isopropanol mixture, and 20 µL of n-decane as an internal standard. The reactors were sealed and placed in an aluminum heating block in a preheated oven set at a specified temperature. The contents of the reactor after cooling to ambient temperature were filtered using a 10 mL syringe fitted with a 0.22 µm Acrodisc nylon membrane filter. Both types of lignin were tested under these conditions. Since the results were comparable, OPL was used as the main focus in this paper.

OPL depolymerization in a Parr® reactor.

The depolymerization of lignin was also performed in a stainless-steel 75 mL 6-series pressure vessel (Parr Instrument Company). The lignin was dried at 60 °C overnight before use. For a typical experiment, 180 mg of lignin and 30 mL volume of the 50:50 (v:v) ethanol:isopropanol mixture were loaded into the vessel, and the sealed reactor was purged with N₂ five times. The reaction system was then pressurized with 10 bar N₂ at room temperature and heated to 270 °C at a stirring speed of 700 rpm. The desired reaction temperature was typically established within 30 min. After reaching 270 °C for 4 h, the reactor was removed from the heating mantle and cooled to room temperature using a water bath. All experiments were reproduced in triplicates and in different high-pressure reactors to ascertain that these observations are not artifacts of a specific reactor.

After cooling the reactor, the gas phase products were collected and analyzed by gas chromatography using thermal conductivity detection (GC-TCD). The liquid sample was filtered, and the solid residue was further washed with 5 mL of ethanol twice. The solid residue was dried in a desiccator under vacuum prior to determining its mass by weighing. All liquid fractions were combined and diluted to a total of 50 mL. From the 50 mL sample, 100 µL of the sample was added to 500 µL of MeOH and 400 µL benzyl phenol (Internal Standard) to give a total volume of 1 mL. This sample was then analyzed by High Performance Liquid Chromatography (HPLC). Afterward, the ethanol and isopropanol in the 50 mL sample were removed by rotary evaporation in order to measure the actual weight of the oil product. This oil was analyzed by ¹H NMR and GPC in triplicate.

Instrumental Analysis Methodology

GC analysis. Gas chromatography with mass spectrometric detection (GC-MS) was used to identify volatile liquid products using a Shimadzu model 2010 QP2010 GC-MS, equipped with a 60 x 0.25 mm x 0.25 µm Agilent DB-5 Column (0.25 µm (5%-phenyl)-methylpolysiloxane lining). The injector temperature was set at 250 °C. Samples were diluted in methanol. The temperature was held at 40 °C for 10 min. and increased at 10 °C/min to 270 °C. The MS detector was kept at 285 °C with a solvent cutoff of 2.25 min. to avoid oversaturation by the solvents.

Gas chromatography with flame ionization detection (GC-FID) was used to quantify the components of the liquid products using the previously described effective carbon number (ECN) methodology.⁴⁷ An Agilent 6890N (G1530N) gas chromatograph equipped a 30 m x 0.25 mm

Agilent DB-5 Column (0.25 μm (5%- phenyl)-methylpolysiloxane lining) and with flame ionization detector was used. The inlet temperature was 200 $^{\circ}\text{C}$ with a split ratio of 80:1 and helium carrier gas at 27 mL/min flow rate. One μL of the filtered liquid mixture was injected. The column temperature was held at 70 $^{\circ}\text{C}$ for 2 min, then ramped to 250 $^{\circ}\text{C}$ at 12 $^{\circ}\text{C}/\text{min}$ where it was held for 2 min. The FID was set at 250 $^{\circ}\text{C}$ with a 30 mL/min H_2 flow rate and 350 mL/min air flow rate.

GC-TCD was used to identify gas phase products. The same Agilent 6890N (G1530N) gas chromatograph was also equipped with a thermal conductivity detector and 30 m \times 0.53 mm Fused Silica Carboxen 1010 capillary column. Samples were collected using a gas tight sampling bag and injected into the inlet at 230 $^{\circ}\text{C}$ using a gas-tight Hamilton syringe. The carrier gas, helium, was set at a constant flow rate of 1 mL/min. The column temperature was held at 35 $^{\circ}\text{C}$ for 14 min., then ramped to 245 $^{\circ}\text{C}$ at 10 $^{\circ}\text{C}/\text{min}$ where it was held for 60 min. The detector was set at 250 $^{\circ}\text{C}$ with a 7 mL/min He flow rate and 8 mL/min air flow rate.

HPLC analysis. The liquid phase from lignin depolymerization was filtered using a 0.22 μm Acrodisc nylon membrane syringe filter and analyzed with an Agilent 1260 Infinity Quaternary High-Performance Liquid Chromatography system, using a Zorbax Eclipse XDB-C18 column (250 \times 74.6 mm) set at 30 $^{\circ}\text{C}$. The HPLC instrument was equipped with a G1315D Diode Array Detector (DAD). The mobile phase was a mixture of H_2O (A) and acetonitrile (B) at a flow rate of 0.5 mL/min and a nonlinear gradient from 80% A and 20% B and to 5% A and 95 % B at 55.0 min. A fixed amount (400 μL) of a 10 mM internal standard solution (benzyl phenyl ether) was added into each sample for quantification purposes. Standard curves for all the aromatic products were made by comparison of the products to the internal standard. All results were analyzed and quantified according to standard curves.

GPC analysis. Gel permeation chromatography was carried out on a Waters (Millford, MA) chromatograph equipped with a Waters Alliance HPLC pump (2695 Separation Module) and two Tosoh TSKgel Super HM-M columns with N,N-dimethyl formamide (DMF) A Waters 2414 differential refractometer was used as the detector. Number average molecular weights (M_n) and weight average molecular weights (M_w) were calculated relative to linear polystyrene standards.

NMR analysis. ^1H -NMR spectra were recorded on a Varian Unity Inova 400 MHz. Eight

spectra were collected with a 5s relaxation delay. A Bruker AVANCE500 spectrometer was used for HSQC which has a narrow AS600 magnet that is charged to 500 MHz. The spectrometer operates at 500.13 and 125.77 MHz for ^1H and ^{13}C nuclei, respectively. For 2D-HSQC, we used an echo-antiecho experiment called HSQCETGP. Spectra of isolated lignin (40 mg) was acquired in 700 μL 5:1 v:v DMSO- d_6 :pyridine- d_5 solvent.

RESULTS

Lignin Substrates. The choice of lignin feedstock greatly influences the outcome of conversion studies. It is understood that lignin substrates with abundant ether linkages, resembling native lignin in plants, are more amenable to depolymerization and upgrading than lignin substrates containing C-C bond cross-linkages that are formed during extraction processes. Organosolv Poplar Lignin (OPL) was selected for this study and compared to Methanol-extracted Poplar Lignin (MPL), which has been shown to retain significant native ether linkages.

The HSQC-NMR spectra of OPL (Figure 1) are divided into two regions. Chemical shift assignments are presented as $^{13}\text{C}/^1\text{H}$ ppm'. An aromatic region between 126 - 100 / 7.5 - 6.1 ppm and a side chain region between 90 - 50 / 5.6 - 2.2 ppm are evident in Figure 1. In the side chain region, several peaks can be assigned to the methoxy group and interunit linkages of β -O-4, β - β , and β -5 motifs. The proportions of β -O-4, β - β , and β -5 in OPL can be calculated by integrating the contour signals and compared to MPL (Table 1).⁴⁸ Based on integration of β -aryl ether (A_a), phenylcoumaran (B_a) and resinol (C_a) contour signals, the linkage percentages of these three linkages in OPL are 82% β -O-4, 16% β - β , and a small amount of β -5 (see Table 1). The analogous analysis of MPL gave nearly the same result (Table 1). The aromatic region of the HSQC spectra also show the distribution of H:G:S (see Figure 1 caption). Similarly, the integration of $(S_{2/6}+S'_{2/6})/(G_2+G_5+G_6)$ contour signals shows that OPL and MPL contain substantial amounts of syringyl units- as well as guaiacyl units (see Table 1). These results agree with a previous report by Luo et al.²⁶ where the native lignin connectivity was not altered significantly by the extraction and isolation methods.

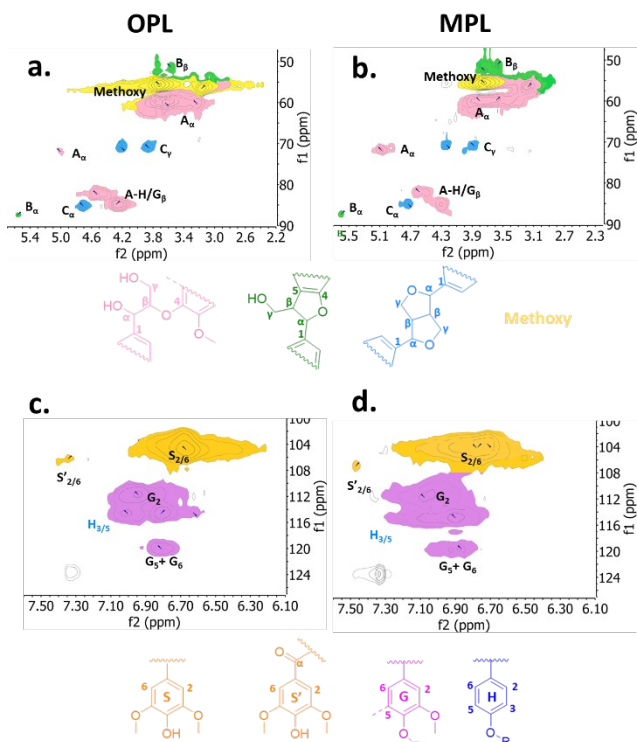


Figure 1. Shown above is a 2D ^1H - ^{13}C HSQC NMR spectra ran in DMSO-d_6 : pyridine-d_5 solvent showing characteristics of the organosolv poplar lignin (OPL) in comparison to methanol organosolv poplar lignin (MPL). The interunit linkages are color coded in order to depict which linkages are shown in the Chemical shift assignments are presented as $^1\text{H}/^{13}\text{C}$ ppm. β -O-4 linkage (pink), β -5 linkage (green), β - β (light blue) in the aliphatic region. S and S' (orange), G (purple), and H (indigo) in the aromatic region. The top spectrum is depicting the aliphatic region (a. and b.: $\delta_{\text{C}}/\delta_{\text{H}}$ of 50–90/2–5.5 ppm). The spectra, a. and b., show similarities where the β -O-4 is consistently shown in the 3.1–4.2/55–65 ppm region for threo and erythro diastereomers. The β -5 linkage is present in the 3.0–4.0/50–55 ppm region. β - β appears also in the 3.8–4.6/70–75 ppm region. The bottom spectrum is depicting the aromatic region (c. and d.: $\delta_{\text{C}}/\delta_{\text{H}}$ of 100–130/6.1–7.5 ppm). S region is shown from 6.2–7/100–110 ppm. G region is shown from 6.5–7.3/110–120 ppm. Assignments in linkages were determined based on literature.⁴⁸

GPC analysis gives a M_n 1939 g mol^{-1} and a dispersity of 2.84 for OPL which is typical for organosolv lignin. Semi-quantitative evaluation of inter-unit bonds in lignins can be expressed as the numbers of specific inter-unit bonds per 100 lignin monomers or C9 units. In order to perform a semi-quantitative evaluation of the inter-unit bonds in OPL and MPL, it was necessary to use as an internal standard with a cluster of signals that are representative of all C9 units present in the

sample. According to the research by Sette et al.,⁴⁸ the overall number of C9 units present in hardwood can be quantified by the sum of half the syringyl signal plus the G signal ($0.5(\text{S}+\text{S}')+\text{G}$). Thus, the total linkages (β -O-4, β -5, β - β) in every 100 basic lignin units can be calculated by the signal of $(\text{A}_\alpha+\text{B}_\alpha+\text{C}_\alpha)/[0.5(\text{S}+\text{S}')+\text{G}]$. Accordingly, OPL contains 71 linkages (58 β -O-4, 11 β - β , and 2 β -5) in every 100 units compared to 75 linkages in MPL.

Table 1. Characteristics of the organosolv poplar lignin. [S: syringyl units, G: guaiacyl units, H: *p*-hydroxyphenyl units]

Type	S	G	H	β -O-4	β - β	β -5
OPL	62	38	a.	82	16	~2
MPL	59	41	a.	79	18	~3

a. Too small to ascertain

$\%X = X / (\text{S}_{2/6} + \text{S}'_{2/6} + \text{G}_2 + \text{G}_5 + \text{G}_6)$, $X = \text{S}_{2/6} + \text{S}'_{2/6}$, $\text{G}_2 + \text{G}_5 + \text{G}_6$

$\%Y = Y / (\text{A}_\alpha + \text{B}_\alpha + \text{C}_\alpha)$, $Y = \text{A}_\alpha, \text{B}_\alpha, \text{C}_\alpha$

Reactions in Different Solvent Mixtures.

All the reactions described in this section were carried out without any added metal-based catalyst. A sample of OPL (180 mg) was heated at 270 °C in a 75 mL Parr reactor with pure ethanol (30 mL) for 4 h and then the solution was filtered to recover the char formed (20–30 mg). The remaining solution was concentrated by rotary evaporation to give a soluble oil (115–120 mg, ~64–67 WT% based on the original OPL). GC-MS and GC-FID analysis demonstrated that this soluble oil contains the monomers. 4-propenyl-syringol ((2,5-dimethoxy-4-propenylphenol or i-DMPP) and isoeugenol (2-methoxy-4-propenylphenol), but the total yield of these was small (12 mg, ~10 wt% of the soluble oil).

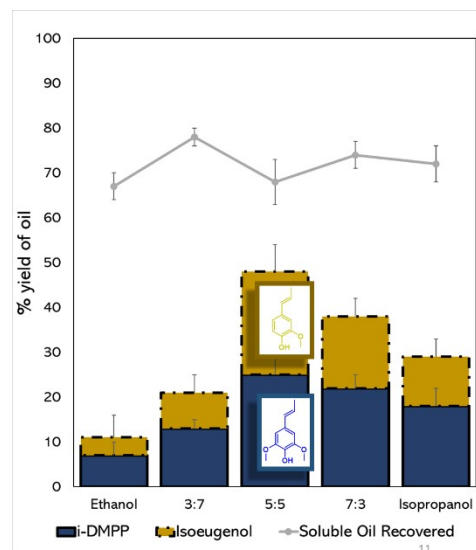


Figure 2. Specific product percent yield of oil as a function of ethanol/isopropanol determined by

using quantitative HPLC analysis. Conditions: 10 bar N₂, 270 °C, 4 h reaction time, stirred at 700 rpm in a Parr reactor.

When the analogous reaction was conducted in pure iso-propanol as the solvent, the yield of the soluble oil was slightly higher at ~ 70% (126 mg) but more significantly, the soluble oil contained a much higher amount (~30 wt%) of the monomers, isoeugenol and i-DMPP (Figure 2). This result led us to explore the effect of using different ethanol/iso-propanol mixtures as the solvent. Notably, the yield of oil from the reaction in these solvent mixtures under supercritical solvent conditions (270 °C) was consistent (65-75% in each case), but the fractions of these oils that are identifiable monomeric products varied with the solvent composition. The 50:50 (v:v) EtOH/*i*-PrOH ratio gave optimal selectivity toward monomer yield. Thus, there appears to be a distinct synergy of such mixtures in the depolymerization pathway.

HPLC analysis of the recovered oil shows that the principal monomeric products are *i*-DMPP and isoeugenol. The remaining material in the oil is apparently a mixture of dimers, trimers and other cross-coupled products that we did not identify.

Figure 3 displays the aromatic region HSQC spectra for the OPL solution before and after reaction in 50:50 (v:v) EtOH/*i*-PrOH. A key feature is that the reaction product displays the same S:G ratio as seen in OPL indicating the process does not disrupt the aromatic methoxy groups. However, in the aliphatic region, approximately 14% of the inter-lignol linkages remain, with the apparent composition being 4% β-O-4, 9% β-β, and 2% β-5 linkages. This result indicates that the supercritical solvent conditions readily cleave the predominant β-O-4 linkages (apparently by hydrogen transfer hydrogenolysis) accompanied by deoxygenation of aliphatic sites. However, the β-β and β-5 C-C bond cross-links remain intact under these conditions.

GPC Analysis. This was conducted in order to confirm that OPL was depolymerized. Table 2 summarizes the number-average (M_n), weight-average (M_w) molecular weight, and polydispersity (M_w/M_n) of the residual lignin (relative to polystyrene standards) obtained after lignin depolymerization by the EtOH/*i*-PrOH solvent system. Compared to untreated OPL (entry #1), entries 2-4 show that the molecular weight and dispersity have decreased; therefore, depolymerization has occurred. The recovered lignin when re-dissolved for GPC analysis dissolved into the solution with no signs of repolymerization/condensation.

Table 2. GPC analyses. Entry #1 is OPL before the reaction is performed. Entries #2 and #3 are for the soluble oils isolated after reaction. Entry #4 is OPL with a Ni/C catalyst under H₂. Conditions: 50:50 EtOH:*i*-PrOH (30 mL), 4 h reaction at 270 °C in a 75 mL Parr reactor stirred at 700 rpm.

#	Sample	M _n /g mol ⁻¹	M _w /g mol ⁻¹	PDI
1 ^a	OPL	1939	5515	2.8 4
2 ^b	OPL + 10 bar N ₂	523	1056	2.0 2
3 ^b	OPL + 10 bar H ₂	583	1075	1.8 4
4 ^b	OPL+ 10 bar H ₂ Ni/C	591	1153	1.9 5

^a before the reaction. ^b from soluble oil collected after reaction.

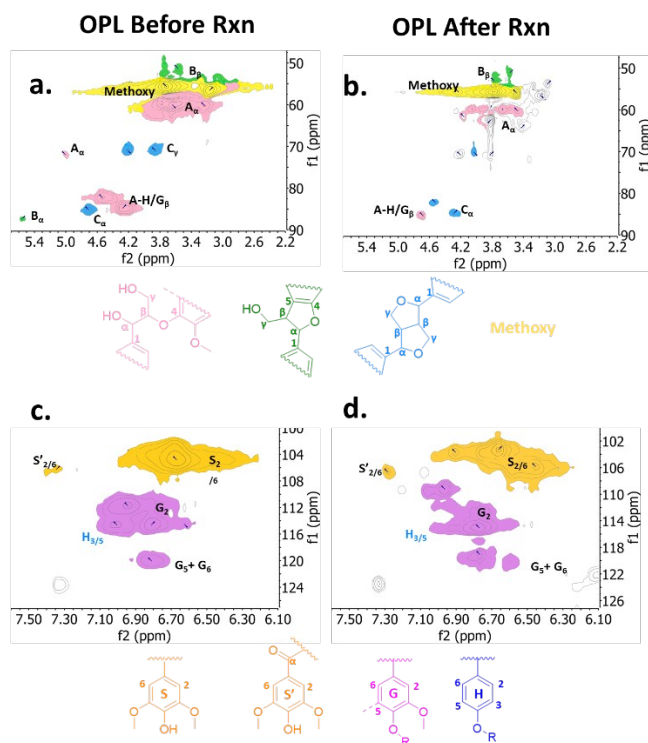


Figure 3. 2D ¹H-¹³C HSQC NMR spectra showing characteristics of OPL before reaction vs. OPL after reaction using 50:50 EtOH/*i*-PrOH. Conditions: 180 mg OPL, 50:50 EtOH/*i*-PrOH (30 mL), 270 °C, 10 bar N₂, 4 h stirring at 700 rpm in Parr vessel. The top spectrum is the aliphatic side chain region (a. and b.: δ_C/δ_H of 50-90/2-5.5 ppm). The spectra, a. show the β-O-4 in the 3.1-4.2/55-65 ppm region, but a decrease in spectrum b. suggesting cleavage of the linkage. The β-5 linkage is present in the 3.0-4.0/50-55

ppm region for spectrum a. but decreased in b. β - β appears also in a. 3.8-4.6/70-75 ppm region, but not as prevalent in b. The bottom spectrum is depicting the aromatic region (c. and d.: δ_C/δ_H of 100-130/6.1-7.5 ppm). S region is shown from 6.2-7/100-110 ppm. G region is shown from 6.5-7.3/110-120 ppm. Assignments in linkages were determined based on literature.⁴⁸

Temperature effect. The reactivity of OPL in 50:50 EtOH:*i*-PrOH was investigated at 215 °C, 235 °C, 255 °C, and 270 °C (Swagelok). Notably, the supercritical temperature of iso-propanol is 235.6 °C (5.4 MPa) while that for EtOH is 241 °C (6.3 MPa), and we assume that the mixtures enclosed in the reactors are supercritical above 240 °C. Not surprisingly, the reaction proved to be quite sensitive to temperature, a significant drop in monomer yields being observed at temperatures below 255 °C (Figure 4). At 215 °C and 235 °C, the yields of *i*-DMPP and isoeugenol were negligible, while the HPLC analysis indicated the presence of a large number of side products (unidentified). Temperatures at or above 255 °C result in more complete hydrogenolysis of OPL. However, again it was found that the yields of recovered oil (ca. 70%) and char (ca. 30%) remain roughly the same.

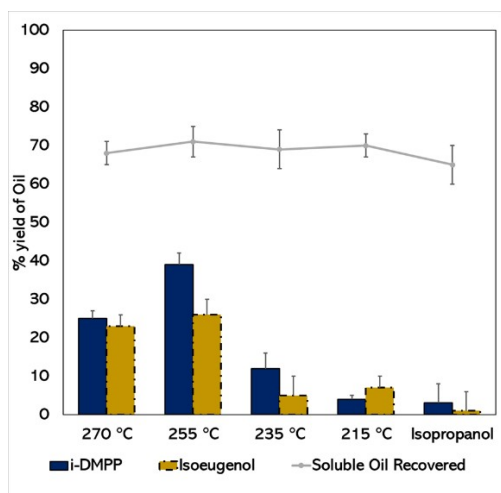


Figure 4. Temperature effects on yields of monomeric products from the conversion of OPL in 50:50 (v:v) EtOH/*i*-PrOH as determined by HPLC analysis. All reactions were for 4 h in a Parr reactor stirred at 700 rpm and pressurized to 10 bar (N₂) with no added metal-based catalyst. The data of the 5th column was derived from an analogous run at 235 °C in iso-propanol only.

Pressure effect. Table 3 summarizes results for reactions carried out in the Parr reactor while pressurizing the system with an added gas (N₂ or H₂) at 1-35 bar (starting pressure at room temperature). The yields of recovered oil and char do not show major differences. However, the yield of monomers *i*-DMPP and isoeugenol did

improve at higher pressure, with an increase for H₂ versus N₂ at 35 bar.

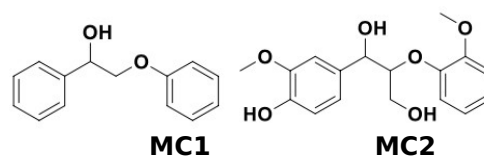
Table 3. The effects of added gasses and pressure in 50:50 (v:v) EtOH/*i*-PrOH solvent system. Conditions: 180 mg OPL, 270 °C, 10 bar N₂, 4 h, in Parr reactor stirred at 700 rpm.

Pressure (Bar)	Char (mg)	Soluble Oil (mg)	Monomers from Oil (mg)	Wt% Yield of monomers ^a
1 (N ₂)	62	98	40	22
10 (N ₂)	57	120	59	33
35 (N ₂)	71	103	52	29
10 (H ₂)	62	120	65	36
35 (H ₂)	45	130	83	46

^a = (monomers from soluble oil/180 mg) x 100

Mass Balance. For a 180 mg OPL reaction in 50:50 EtOH:*i*-PrOH solvent under 10 bar N₂ gas, 275 °C, and 4 h, complete mass balance was taken for this reaction. Filtered char was weighed and dried to give 57 mg of solid. The recovered oil was 120 mg; thus the sum of the recovered solid and soluble oil corresponds to 98% of the original weight of OPL. Analysis of the soluble oil indicated the presence of 32 mg and 27 mg of *i*-DMPP and isoeugenol, respectively, corresponding to a 33 wt% yield of identifiable monomers yield of 33% from the starting 180 mg OPL. Similar mass balance and monomer yields were obtained with other applied pressures of N₂ or H₂ (Table 3)

Reactivity studies with model compounds: In order to gain greater insight into the depolymerization pathways, two β -O-4 model compounds 2-phenoxy-1-phenylethanol (MC1) and 1-(4-hydroxy-3-methoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol (MC2) were subjected to the same conditions as shown above for OPL substrate. Remarkably, MC1 proved to be refractory when heated at 270 °C for 4 h in 50:50 (v:v) EtOH/*i*-PrOH as analyzed by HPLC (Supporting information Figure S1). When a small amount of OPL (5 wt% relative to the MC1 substrate) was added to the reaction mixture, some products were observed, but these may have largely originated with the OPL. Within experimental uncertainty none of the MC1 was consumed.



In contrast, the substrate MC2 is more reactive under the standard conditions in 50:50 EtOH/*i*PrOH (270 °C), although after 4 h, conversion was only 48%. (see SI Figure S2 and Table S1). Neither isoeugenol nor guaiacol was formed in significant quantities, although some other unidentified species are seen in the HPLC chromatogram. However, when the same reaction was carried out in the presence of small amount of added OPL (5 wt%, relative to the substrate), the conversion increased to 100% under otherwise identical conditions (SI Figure S2). Furthermore, the product distribution as analyzed by HPLC was significantly different with substantial generation of both guaiacol (~62% of theoretical) and isoeugenol (~40% of theoretical), which are not formed in the absence of OPL. Thus, OPL appears to contain a component that clearly affects substrate reactivity and product distribution.

The question remains regarding what OPL component may be responsible for this activity. A previous study from this laboratory⁴⁹ found that OPL prepared by an HCl extraction method as described here contains significant chloride impurities. Thus, the organosolv extraction method may lead to HCl impurities that could be acting as a catalyst for the depolymerization of lignin. In this context, SI Figure S2 illustrates the HPLC results for different 4 h reactions of MC2 at 270 °C in 50:50 EtOH/*i*PrOH to which additives relevant to potential OPL impurities have been added. The quantitative data are summarized in SI Table S1. Notably, these data show that addition of HCl or NaCl (1000 ppm in the solution) leads to complete consumption of MC2 coupled with substantial yields of guaiacol (83% and 55%) and isoeugenol (59% and 41%, respectively). The analogous reaction with added KOH also led to complete consumption of the substrate but the only major identified product was guaiacol (~90%), which can be formed by simple hydrolysis of the β -O-4 bond. There was very little or no isoeugenol formation.

When the analogous of MC2 was carried out with added MPL (5 wt% to the substrate), ~90% of the substrate was consumed with guaiacol (~55%) and isoeugenol (40%) being among the products. Sulfuric acid is used in the extraction of MPL, so the 4 h reaction of MC2 at 270 °C in 50:50 EtOH/*i*-PrOH containing H₂SO₄ (1000 ppm to the solution) was also examined. Notably, while nearly complete consumption of MC2 was observed, the HPLC product chromatogram proved to be different from the other systems studied (SI Figure S2), although both guaiacol (~88%) and isoeugenol (19%) were among the products.

GC analysis of solvent based products.

The principal monomeric products, especially isoeugenol, are qualitatively the result of the hydrogenolysis of phenolic ether linkages in OPL. Given the absence of added H₂ the likely source of the necessary hydrogen equivalents would be the solvent itself-most likely *i*-PrOH. In this context, we analyzed both the solvent and gas phase collected after the reaction for 180 mg OPL in 50:50 EtOH/*i*-PrOH (30 mL), 10 bar of N₂, 270 °C, in a 75 mL stainless steel Parr reactor stirred at 700 rpm. GC-FID analysis of the solvent showed, in addition to EtOH and *i*-PrOH, a strong peak at a retention time (2 min) corresponding to acetone (SI Figure S3). The amount of acetone is ~5 mmol in the after-reaction solvent calculated by ECN method.⁴⁹ Expanding the vertical axis of this chromatogram also demonstrated the presence of at least 7 very minor species in quantities very much smaller (<1%) than that for acetone. GC-TCD analysis of the corresponding gas phase (SI Figure S4) showed only N₂ and that no H₂ was evident. In this context, it appears that direct hydrogen transfer from *i*-PrOH is the principal source of the reducing equivalents leading to the HTH of OPL ether linkages under these conditions. Given that the reaction does occur in neat EtOH, albeit with lower efficiency, it is likely that ethanol is a lesser source of reducing equivalents in the mixed solvent system.

DISCUSSION

Reported is the thermochemical reaction of organosolv poplar lignin in catalyst-free ethanol/iso-propanol solvent mixtures. The depolymerization of OPL in EtOH/*i*-PrOH gave solid char and liquid oil fractions with yields of the phenolic monomers within the soluble oil product dependent on the solvent ratios (Figure 2). Although the yields of soluble oil were comparable for different EtOH/*i*-PrOH ratios, yields of the monomers *i*-DMPP and isoeugenol proved to be optimal in the 50:50 solvent mixture. With ethanol or iso-propanol alone, the selectivity toward these monomers decreased, although pure *i*-PrOH did perform better than pure ethanol. Thus, it appears that the mixed EtOH/*i*-PrOH medium shows synergistic effects for the hydrogen transfer hydrogenolysis of OPL.

To our knowledge, there are no previous reports of using EtOH/*i*-PrOH mixtures alone for lignin depolymerization and HTH, although there have been reports for using supercritical ethanol or iso-propanol as sources of hydrogen equivalents for metal catalyzed HTH.⁵⁰⁻⁵⁷ It has also been shown potassium isopropoxide aids in transfer hydrogenation from iso-propanol to coal in the formation of acetone and the equivalent of H₂ transfer to substrate.⁵⁸ In our work, the observation of acetone in the liquid phase after

reaction with OPL (Figure S3) clearly indicates that *i*-PrOH is the major source of hydrogen reducing equivalents needed for HTH of OPL. Hydrogen donor solvents such as *i*-PrOH have also been used to suppress reactions of radical intermediates produced in the high temperature pyrolysis of lignins.⁵⁹

The catalytic effect of OPL was much more evident with MC2. There are clear differences in the two model compounds where MC2 contains electron-donating methoxy substituents on the aryl rings, and thus would be a better model of lignin. For MC2, there was a low conversion in 50:50 EtOH/*i*-PrOH, but when 5 wt% OPL was added, there was markedly increased selectivity towards the generation of guaiacol and isoeugenol. One known OPL impurity is chloride, given the procedure used in the organosolv extraction process. Sulfur is another possible impurity in organosolv lignins. Addition of NaCl, HCl, or H₂SO₄ to the reaction medium changed the product distribution to favor hydrogenolysis. These results imply that such impurities in the OPL assist in hydrogenolysis cleavage of the β -O-4 bonds of both MC2 and OPL into guaiacol as well as polyols that are subsequently hydrodeoxygenated to isoeugenol.

Although guaiacol can be formed from MC2 by simple hydrolysis or hydrogenolysis of the β -O-4 linkage, the formation of isoeugenol requires a much more complex series of steps. SI Scheme S1 illustrates a possible reaction sequence including hydrogenolysis, dehydration and hydrogenation. Regardless the exact sequence, which remains to be determined, the formation of this product requires two H₂ equivalents, the primary source presumably being *i*-PrOH give the observed acetone formation. Li and coworkers concluded that the disassembly of a model substrate very similar to MC2 using a Re/activated carbon catalyst and *i*-PrOH as the hydrogen source proceeded initially by β -O-4 hydrogenolysis followed by additional reductions as shown in this Scheme. However, how the cleavage of the β -O-4 linkage in MC2 (and presumably in lignin) is activated by OPL or the impurities included remains an open question.

In summary, our findings show a new process for lignin depolymerization and hydrogenolysis in which EtOH/*i*-PrOH solvent mixture provides the reducing equivalents through a hydrogen transfer pathway. The identity of the active hydrogen transfer species is not known, but acid or ions introduced along with the lignin substrate act as a catalyst in this unique depolymerization/hydrogenolysis system. The reaction does not require the addition of a transition-metal catalyst and affords monomer phenols in yields (~33% based on the mass of

starting lignin substrate) that are competitive with those obtained with most transition metal catalysts.

ASSOCIATED CONTENT

Supporting Information:
HPLC, GPC, Elemental Analysis, Proposed mechanisms. This material is available free of charge via the Internet at <http://pubs.acs.org>

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TOC:

Synopsis: Depolymerization of lignin into monomers can be accomplished by hydrogen transfer from EtOH:*i*-PrOH in the absence of added transition metal catalyst.

