ACS Sustainable Chemistry & Engineering

Research Article

pubs.acs.org/journal/ascecg

Characterization and Catalytic Transfer Hydrogenolysis of Deep Eutectic Solvent Extracted Sorghum Lignin to Phenolic Compounds

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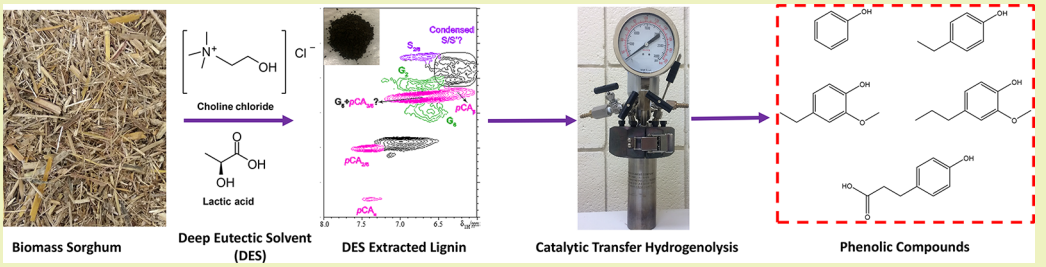
Supporting Information



ABSTRACT: Deep eutectic solvent (DES) is intrinsically cheaper than many ionic liquids (ILs) due to low precursor cost, simple synthesis, and improved recyclability. Meanwhile, DES can be as effective as ILs toward dissolving lignin from plant materials. However, the lignin depolymerization mechanism in DES, the structural and chemical properties of DES-extracted lignin (DES-EL), and the possible valorization pathways of DES-EL toward value-added products were not well understood. This study aims to characterize the lignin streams from DES (1:2 choline chloride:lactic acid) treated sorghum and further upgrade the extracted lignin to phenolic compounds. As revealed by HSQC, ^{13}C, and ^{31}P NMR analysis, DES cleaved nearly all ether linkages in native lignin, resulting in significant size reduction. We further catalytically upgraded DES-EL to phenolic compounds via catalytic transfer hydrogenolysis in the presence of isopropyl alcohol. Among the three tested catalysts (Ru/C, Pd/C, and Pt/C), Ru/C proved the most effective in deconstructing DES-EL, with oil, char, and gas yields of 36.3, 46.4, 17.3 wt %, respectively. Major lignin monomeric products in the oil were phenol, 4-ethylphenol, 4-ethyl-2-methoxyphenol, 2-methoxy-4-propylphenol, and 4-hydroxy-benzenepropanoic acid. This study provides a mechanistic understanding of lignin depolymerization in DES and demonstrates a possible way to catalytic upgrading of DES-EL to low molecular weight phenolic compounds.

KEYWORDS: *Deep eutectic solvents, Hydrogenolysis, Lignin, Catalysis, Sorghum*

INTRODUCTION

Lignin is a phenolic heteropolymer and is the second most abundant natural terrestrial biopolymer. Unlike cellulose, which is a polysaccharide consisting of several linear chains of β-(1−4)-linked glucose units, lignin is an amorphous and randomly branched polymer composed of phenylpropanoid units.[1] Lignin constitutes up to 35% of a typical woody material by mass and 50% by energy, providing strength and rigidity to the plant cell wall.[2] Lignocellulosic biomass has the potential to produce low molecular weight compounds, with lignin being the most promising element due to its unique aromatic backbone, which is transformable to an array of value-added chemicals.[3] For more than a century, pulp and paper industries have been pursuing research for efficient means to upgrade lignin into value-added products. A recent thrust on using lignocellulosic biomass as a feedstock for fuels and chemicals has infused new incentives for lignin valorization.[4] However, challenges exist during lignin fractionation possesses in retaining its native structural properties. Depending on the conversion process, more structural complexity is added to the physical and chemical properties of extracted lignin.[3] These complications have created many obstacles in the large scale

Received: April 19, 2018
Revised: May 28, 2018
Published: June 6, 2018

DOI: 10.1021/acssuschemeng.8b01763
ACS Sustainable Chem. Eng. XXXX, XXX, XXX−XXX

application of lignin; hence, a more effective and economical lignin fractionation process that creates fewer structural complexities will provide a new dimension to the lignin recovery and its consequent valorization.

Recent advances in the application of deep eutectic solvents (DES) for biomass deconstruction and subsequent lignin extraction has given new tangent to the biomass pretreatment process.[5−8] DES is a mixture of two or more hydrogen-bond donors (HBD) and hydrogen-bond acceptors (HBA). Many DESs share similar solvent characteristics of ionic liquids (ILs). In addition, DES can be easily prepared with high purity and low cost compared with ILs.[6,9] Certain DESs are capable of retaining most of the advantages from ILs while at the same time overcoming some of their limitations, which makes DES a promising candidate for multiple applications including biomass deconstruction.[6] For instance, Zhang and co-workers[7] demonstrated that cholinium chloride:lactic acid based DES acted as a mild dual acid−base catalyst that dictates the controlled cleavage of aryl ether linkages in the phenylpropane units, leading to the delignification of biomass. In a more recent study, renewable DESs were synthesized from lignin-derived phenolic compounds for delignification of switchgrass.[10] Although lignocellulosic biomass pretreatment using DES is still in nascent stage, results from several studies indicate that DES may facilitate lignin dissolution from cellulosic biomass thus improving the enzymatic hydrolysis of the resulting biomass.[11−13] A better mechanistic understanding and characterization of DES extracted lignin will pave the way for further lignin conversion.

Catalytic lignin valorization has been widely investigated; among them, catalytic hydrogenolysis has received increasing attention.[14] During hydrogenolysis, reductive bond cleavage takes place within lignin and/or lignin model compounds in the presence of hydrogen as a reducing agent.[15] Heterogeneous catalysts have been extensively investigated to aid the bond cleavage. However, aryl ether cleavage of lignin by hydrogenolysis with H_2 requires high temperature and excessive pressure due to the low solubility of H_2 in many organic solvents,[16−18] posing safety concerns and operational hazards toward application of this technology. As an alternative route, catalytic transfer hydrogenolysis (CTH) has shown great promise.[19] In CTH reaction scheme, an equivalent of H_2 is transferred from a donor molecule to the acceptor molecule. Hydrogen donor molecules are often inexpensive organic alcohols capable of readily generating hydrogen molecules and the same time serving as solvents for lignin.[14] A variety of hydrogen donating agents have been tested including formic acid, methanol, ethanol, tetralin etc., among, which isopropyl alcohol (IPA) remains a popular choice due to its relatively low cost and easy subsequent separation from the reaction mixture.[20]

Lignin depolymerization via CTH in acids, bases and supercritical alcohols have been investigated previously.[21] Depolymerization of lignin into monomeric phenols using formic acid, methanol, or ethanol in the presence of transition metal catalysts have been reported in several studies.[22] An aromatic monomer yield of 6.1 wt % was obtained from CTH of concentrated acid hydrolysis lignin using Ru/C catalyst at 350 °C for 60 min and a 1:3 formic acid-to-lignin mass ratio.[23] In a recent study, selective depolymerization of lignin to alkylphenols via CTH was reported on lignin rich residues recovered from cholinium lysinate IL pretreatment using Ru/C catalyst in IPA at 300 °C.[20] Several nanoparticles (FeB, NiB, and FeNiB) were applied for CTH of organosolv lignin in supercritical ethanol at 320 °C.[14] Results suggest that in the presence of FeNiB alloy, the number-average molecular weight of lignin was reduced from 1800 to 317 Da, producing monomeric phenols with intact deoxygenated aliphatic side chains.[14] CTH of alkaline lignin using Pd/C catalyst combined with metal chlorides at 260 °C was investigated and results suggest that 24% of phenolic monomers was produced using $CrCl_3$ catalyst; however, when combining with Pd/C catalyst the phenolic monomer yield was increased to 28.5%,[24] likely attributed to the interaction of $CrCl_3$ with oxygen electron pair to promote the crack of methoxyl groups. These studies have shed light on using platinum group noble metals and transition metal catalysts in different combinations and on various supports for assisting transfer hydrogenolysis and breakdown of various types of lignins; however, the effectiveness of catalysts and CTH conditions on DES extracted lignin has not been investigated.

Biomass sorghum has received increasing attention from the biofuel research community in the past decade. As an attractive energy crop, sorghum is a promising source of biomass feedstock for biofuels because fewer inputs (e.g., nitrogen) and less water are required for growing sorghum when compared with corn production.[25] Forage sorghum feedstock has the potential of producing 530−700 gallons of ethanol per acre as compared to the typical ethanol yield from switchgrass of 310−350 gallons per acre.[26,27] The lignin fractions in sorghum contain a high abundance of ferulate and *p*-coumarate moieties in addition to the S/G/H lignin structural units, demonstrating a great potential for upgrading sorghum lignin to high value chemicals for various applications.[28,29]

With growing interest in using DES for lignin fractionation and depolymerization, it has been demonstrated that DES can selectively cleave ether linkages and the process can generate lower and narrowly distributed molecular weight lignin.[7] To achieve the long-term goal of developing an efficient and effective process for lignin depolymerization via DES, it is important to further characterize DES-extracted lignin stream (DES-EL) and explore ways to valorize DES-EL. However, to our knowledge, the depolymerization of DES-EL using CTH has not been reported. In this work, we aim to characterize and perform CTH of DES extracted lignin from an attractive energy crop, biomass sorghum, to low molecular weight chemicals. The objectives of this study are to (1) fractionate and characterize the lignin streams from DES treated sorghum; (2) investigate the role of catalysts, catalyst loading, temperature, and reaction time in the CTH of DES extracted lignin; (3) identify and characterize DES-EL and the liquid/gas products and the residual solids after CTH reaction. The results from this study provide a better understanding of the chemical and structural properties of DES-EL and a way to the upgrading of DES-EL via CTH toward formation of phenolic compounds.

MATERIAL AND METHODS

Materials. Biomass sorghum (*Sorghum bicolor*, forage variety ES5200) was provided by the Bioenergy Feedstock Library, Idaho National Laboratory (Idaho Falls, ID). Air-dried sorghum sample was grounded to pass a 2 mm sieve using a model 4 Wiley mill, and stored in Ziploc bags at room temperature for subsequent experiments. Isopropyl alcohol, Ru/C (5 wt % Ru), choline chloride, and lactic acid were purchased from TCI America, whereas acetone, ethanol, Pd/C (5 wt % Pd), and Pt/C (5 wt % Pt) were purchased and used as is from Sigma-Aldrich.

DOI: 10.1021/acssuschemeng.8b01763
ACS Sustainable Chem. Eng. XXXX, XXX, XXX−XXX

Pretreatment and Lignin Recovery. DES was prepared by mixing choline chloride and lactic acid in its solid state in a molar ratio of 1:2, followed by heating the mixture with constant stirring at 65 °C for 2 h in an oil bath as described elsewhere.[6,7] The mixture was stirred until no solids left, leading to a final transparent liquid (DES). The DES was cooled down and kept in a desiccator for further use. Pretreatment of sorghum was performed by mixing 2 g of biomass with 18 g of DES (10 wt % solid loading) in a glass pressure tube reactor. The pressure tubes were then sealed and the contents of the tubes were stirred at 200 rpm at 145 ± 2 °C in a temperature controlled oil bath for 6 h, according to a previous report.[7] The pretreated biomass was washed with 20 mL of ethanol and then manually squeezed through a 0.074 mm nylon filter (200 mesh) to separate the solids from the pretreatment liquid. Lignin was precipitated from the pretreatment liquid by adding water to the liquid until reaching a water:ethanol ratio of 1:2. Precipitated lignin was further purified, namely DES extracted lignin (DES-EL), by washing 3 times with a 9:1 water/ethanol mixture and then freeze-dried for future use.[7] All the experiments were performed in duplicates.

Lignin Depolymerization by Catalytic Transfer Hydrogenolysis. Lignin depolymerization was carried out in a 100 mL Parr reactor (4593 benchtop reactor, Alloy C276, Parr Instruments, IL). In a typical reaction, 0.5 g of lignin and 20 mL of isopropyl alcohol (IPA) were added to the reactor; subsequently, 0.01−0.1 g (2−20 wt %) of Pt/C, Ru/C, or Pd/C catalyst was added to the reactor. After purging the reactor with nitrogen, the reaction was carried out at 270 °C for 1 h at 250 rpm stirring speed. The heat-up time for reactor to reach set reaction temperature was approximately 35 min, which was not included in the reaction time. After reaction, the reactor was removed from the heating mantle and quenched rapidly at first by forced air and then in an ice bath to prevent undesirable secondary reactions. Once the reactor was cooled, gas was collected in a 1 L Tedlar gas sampling bag (CEL Scientific, Cerritos, CA); while liquid and solid residues were transferred to a beaker by washing the reactor content with acetone. Separation of liquid and solid residues were performed by centrifugation at 8000 rpm for 15 min. The acetone and IPA were removed from the liquid fraction in a vacuum oven at 20 °C for 24 h. After drying, the leftover liquid oil was weighed to estimate the oil yield (eq 1). The oil was redissolved in 2-methyltetrahydrofuran (MeTHF) for GC−MS analysis. The residual solid was further washed with 15 mL of acetone for 3 times and then dried at 80 °C for 24 h to determine the solid yield (eq 2).

$$\text{oil yield (wt\%)} = \frac{\text{dry weight of bio-oil (g)}}{\text{dry weight of lignin (g)}} \times 100 \quad (1)$$

$$\text{solid yield (wt\%)} = \frac{\text{dry weight of solid residue (g)} - \text{weight of catalyst (g)}}{\text{dry weight of lignin (g)}} \times 100 \quad (2)$$

$$\text{gas yield (wt\%)} = 100 - \text{oil yield (\%)} - \text{solid yield (\%)} \quad (3)$$

Analytical Methods. Identification of the lignin depolymerization products from the CTH reaction were performed by Agilent 7890B GC coupled 5977B MS with a HP-5MS (60 m × 0.32 mm) capillary column. The temperature program started at 50 °C and increased to 120 °C at 10 °C min^{-1} with a holding time of 5 min; then, it was raised to 280 °C at 10 °C min^{-1} with a holding time of 8 min and to 300 °C at 10 °C min^{-1} with holding time of 2 min. Helium was used as a carrier gas with a flow rate of 1.2 mL min^{-1}. Calibration curves were created using commercially available pure compounds: guaiacol (C_6), vanillin (C_6C_1), syringaldehyde (C_6C_2), and 4-propylphenol (C_6C_3) (Sigma-Aldrich, St. Louis, MO). The effluent gases from hydrogenolysis were analyzed using a Micro GC (HP, Quad series, Refinery Gas analyzer) equipped with a TCD detector. Calibration curves were generated using pure C_1−C_7 olefins, H_2, CH_4, CO, and CO_2.

Lignin Characterization. *Gel Permeation Chromatographic (GPC) Analysis.* The weight-average molecular weight (M_w) and number-average molecular weight (M_n) of the lignin samples were determined by GPC. The samples were first acetylated using acetic acid and acetyl bromide as previously described.[30] An Ultimate 3000 HPLC system (Dionex Corporation, Sunnyvale, CA) equipped with an ultraviolet (UV) detector was used. Separation was accomplished in a mobile phase of THF at a flow rate of 0.5 mL min^{-1}, with a Mixed-D PLgel column (5 μm particle size, 300 mm × 7.5 mm i.d., linear molecular weight range of 200 to 400 000 u, Polymer Laboratories, Amherst, MA) at 50 °C. Elution profile of materials eluting from the column were calibrated using low molecular weight polystyrene standards (Product No. 48937, Sigma-Aldrich) at UV absorbance of 280 nm.

Fourier Transform Infrared (FTIR) Spectroscopic Analysis. FTIR was performed by using a Thermo Nicolet Nexus 870 FT-IR ESP to examine the chemical structure alternations of the lignin samples. Samples were pressed to 12 psi using a spring loaded jack onto the ATR crystal. Sample spectra were obtained using an average of 64 scans between 400 and 4000 cm^{-1} with a spectral resolution of 1.928 cm^{-1}. The raw FTIR spectra were baseline corrected and normalized using Omnic 6.1a software and compared in the range 750−4000 cm^{-1}.

Cellulolytic Enzyme Lignin (CEL) Isolation. Cellulolytic enzyme lignin (CEL) was isolated from the toluene/ethanol (2/1 by volume) extracted sorghum according to the published literature procedure.[31,32] In brief, the extractives-free samples were loaded to 50 mL ZrO_2 grinding jar (including 10 × 10 ball bearings) in Retsch Ball Mill PM 100. The biomass was then ball milled at 550 rpm in a frequency of 5 min with 5 min pauses in-between for 1.5 h total time. The milled fine cell wall powder was then subjected to enzymatic hydrolysis with a mixture (1:1 by volume) of Cellic CTec2 and HTec2 (gifts from Novozymes) in 5 mM citrate buffer (pH 4.8, 50 °C) under continuous agitation at 200 rpm for 48 h. The residue was isolated by centrifugation and was hydrolyzed once more with freshly added enzymes mixture. The residue obtained was rich in lignin and was washed with deionized water, centrifuged, and freeze-dried. The lignin-enriched residue was extracted with dioxane-water (96% v/v, 10.0 mL/g biomass) for 24 h. The extracted mixture was centrifuged, and the supernatant was collected. *p*-Dioxane extraction was repeated once by adding fresh *p*-dioxane−water. The extracts were combined, rotoevaporated to reduce the volume at less than 45 °C, and freeze-dried. The obtained lignin samples, designated as CEL, was used for further analysis.

Nuclear Magnetic Resonance (NMR) Spectroscopic Analysis. NMR spectra of lignin samples and hydrogenolysis products were acquired in a Bruker Avance III HD 500-MHz spectrometer and spectral processing was carried out using a Bruker Topspin 3.5 (Mac) software. CEL (20 mg) and hydrogenolysis product (9 mg) were dissolved in 100 mg DMSO-d_6 in a micro-NMR tube independently. DES lignin (40 mg) was dissolved in 0.5 mL of DMSO-d_6 in a 5 mm NMR tube. Heteronuclear single quantum coherence (HSQC) experiments were carried out with a Bruker pulse sequence (hsqcetgpspsi2.2) on a N_2 cryoprobe (BBO 1H&19F-5 mm) with the following acquisition parameters: spectra width 12 ppm in F2 (^{1}H) dimension with 1024 data points (acquisition time 85.2 ms), 166 ppm in F1 (^{13}C) dimension with 256 increments (acquisition time 6.1 ms), a 1.0 s delay, a $^1J_{C-H}$ of 145 Hz, and 128 scans. The central DMSO-d_6 solvent peak (δ_C/δ_H at 39.5/2.49) was used for chemical shifts calibration. Assignment and the relative abundance of lignin compositional subunits and interunit linkage were estimated using volume integration of contours in HSQC spectra according to published literature.[31,33] For volume integration of monolignol compositions of syringyl (S), guaiacyl (G), *p*-hydroxyphenyl (H), *p*-coumarate (*p*CA), and ferulate (FA), the cross peaks of $S_{2/6}$, G_2, $H_{2/6}$, $pCA_{2/6}$, and FA_2 contours were used with G_2 and FA_2 integrals doubled were integrated. The $T_{2'/6'}$ of tricin (T) was used for quantification of tricin. The C_α signals were used for volume integration for interunit linkages estimation. Detailed assignments of the lignin ^{13}C−^{1}H correlation signals observed in the HSQC spectra

DOI: 10.1021/acssuschemeng.8b01763
ACS Sustainable Chem. Eng. XXXX, XXX, XXX−XXX

Table 1. Effect of Reaction Parameters on the Oil, Char, and Gas Yield from DES-EL

catalyst loading (%)	temperature (°C)	time (min)	oil yield (%)	char yield (%)	gas yield (%)
2% Ru/C	270	30	22.51 ± 1.51	65.01 ± 0.09	12.48 ± 1.42
	270	60	26.42 ± 1.97	60.51 ± 1.69	13.07 ± 3.66
	270	180	19.36 ± 0.85	56.17 ± 1.59	24.47 ± 0.74
5% Ru/C	270	30	22.74 ± 1.59	60.04 ± 1.97	17.21 ± 0.38
	270	60	30.83 ± 0.62	56.47 ± 2.03	12.70 ± 2.64
	270	180	22.13 ± 1.56	54.92 ± 2.46	22.95 ± 4.02
	300	30	18.04 ± 0.83	57.38 ± 1.77	24.57 ± 2.60
	300	60	20.96 ± 0.54	53.73 ± 0.72	25.31 ± 1.26
	300	180	22.18 ± 1.02	52.70 ± 2.04	25.12 ± 1.05
15% Ru/C	270	30	24.72 ± 0.37	56.15 ± 1.32	19.13 ± 0.94
	270	60	36.28 ± 0.45	46.43 ± 1.65	17.29 ± 2.10
	270	180	31.55 ± 1.05	45.26 ± 1.41	23.19 ± 2.41
20% Ru/C	270	60	27.16 ± 0.25	55.57 ± 2.05	17.26 ± 2.30
5% Pd/C	270	60	20.15 ± 1.18	61.10 ± 1.12	18.74 ± 0.8
15% Pd/C	270	60	22.12 ± 0.48	59.46 ± 0.81	18.42 ± 1.29
5% Pt/C	270	60	20.81 ± 1.66	62.65 ± 1.53	16.54 ± 0.13
15% Pt/C	270	60	19.38 ± 1.31	60.94 ± 1.47	19.67 ± 2.78
no catalyst	270	60	20.04 ± 1.36	62.92 ± 1.67	17.04 ± 0.32
	300	60	20.19 ± 2.43	61.40 ± 0.82	18.41 ± 3.25

are listed in Table S1. The abundances of aromatics and side-chain linkages were presented as percentage of total SGH units and total side-chain linkages, respectively. The ^{31}P NMR spectra of lignin and hydrogenolysis products were measured after derivatization with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP).[34] The spectra of phosphitylated compounds were acquired using an inverse-gated decoupling pulse sequence (Waltz-16), 90° pulse, 25-spulse delay with 64 scans. All chemical shifts reported are relative to the product of TMDP with water, which has been observed to give a sharp signal in pyridine/$CDCl_3$ at 132.2 ppm. The ^{13}C NMR acquisition was performed using a 90° pulse with an inverse-gated decoupling pulse sequence, a 2.0 s pulse delay, and 30 000 scans at 27 °C. Approximately 0.01 mg/mL chromium acetylacetonate was added to decrease relaxation time.

RESULTS AND DISCUSSION

Pretreatment and Lignin Recovery. The chemical composition of sorghum was determined following NREL standard protocol,[35] and its compositions (wt %) are glucan 35.2 ± 0.1, xylan 22.1 ± 0.1, lignin 18.3 ± 0.1, extractives 15.6 ± 0.7, and others 8.8 ± 0.4. The glucan, xylan, and lignin contents of sorghum are comparable to other lignocellulosic biomass, such as corn stover and switchgrass.[27] Several studies have reported fractionation of sorghum using different pretreatment methods such as dilute acid and alkaline pretreatments.[27] Under the condition tested in this work, the amount of lignin recovered from the liquid fraction following DES pretreatment was 14.3 g (78%) on the basis of 100 g of initial biomass. It was shown that a simple precipitation and washing method using ethanol−water was effective for obtaining high lignin yield and purity. A composition analysis of the extract DES lignin (DES-EL) demonstrated very high purity (>97%), with only trace amounts of carbohydrates and residual DES (based on lactic acid content), and very low ash content (<1%). These results are comparable to a previous report on choline chloride/lactic acid (ChCl:Lac) based DES pretreatment of woody biomass where lignin yields were 78% for poplar and 58% for Douglas fir, respectively, using 1:2 of ChCl:Lac.[7] Moreover, the extracted lignin has 95% purity with low and narrowly distributed molecular weight.[7] In another study, Kumar et al. 2015 used betaine/lactic acid (B:Lac) and ChCl:Lac at different molar ratios for extraction of lignin from rice straw.[11] A maximum lignin extraction of 60 ± 5% of total lignin was achieved with 1:5 ratio of ChCl:Lac based DES, whereas a lower lignin yield of 52 ± 6% can be extracted with B:Lac at its optimal ratio. In addition, Li et al. isolated lignin from willow (*Salix matsudana* cv. Zhuliu) at high yield (91.8 wt %) and purity (94.5%) using ChCl:Lac molar ratio of 1:10.[13] Results from this work along with previous studies demonstrate that DES pretreatment is capable of fractionating lignin from a variety of biomass feedstocks, including sorghum, with high lignin recovery and purity.

Effect of Reaction Parameters on Yield and Lignin Breakdown Products. Depolymerization of lignin and/or lignin model compounds via catalyst including platinum group noble metals and transition metals has been studied widely.[18,36−40] The lignin depolymerization compounds are mainly retained in the liquid/oil fraction after reaction while the solid fraction contains unreacted lignin and undesirable byproducts from lignin decomposition. The gaseous products can be collected in gas fraction where most of the short chain hydrocarbon and carbon oxides are retained. The mass yields of the lignin depolymerization fractions (solid, oil, and gas) from the CTH reaction are shown in Table 1. As a baseline, the oil yield was 20.0 wt % along with 62.8% solid and 17% gas yields when the reaction was performed at 270 °C for 60 min, in the absence of catalyst. Upon increasing the reaction temperature to 300 °C for 60 min, no significant change was seen on the oil yield (20.2 wt %). To improve the oil yield, we tested a range of temperatures, reaction times and catalyst type combinations, with specific emphasis on Ru/C catalyst. Catalytic applications of Ru have been well documented, including its effectiveness in CTH of lignocellulosic biomass component.[41,42] Two other noble metal catalysts, Pd/C and Pt/C catalysts, were also tested at selected reaction conditions and the performances were compared with Ru/C catalyst.

Reaction Conditions Optimization with Ru/C Catalyst. To evaluate the effectiveness of Ru/C catalyst in response to reaction conditions, different catalyst loading (2, 5, 15, and 20%) combined with varying temperature (270 and 300 °C) and reaction time (30, 60, and 180 min) were tested.

DOI: 10.1021/acssuschemeng.8b01763
ACS Sustainable Chem. Eng. XXXX, XXX, XXX−XXX

Table 2. Composition of Products in the Liquid Phase Determined by GC−MS[a]

peak no.	product	wt% in liquid			
		Ru/C	Pd/C	Pt/C	no catalyst
1	phenol	2.63	0.83	1.88	0.75
2	*p*-cresol	1.74	0.97	1.13	0.82
3	2-methoxy phenol	2.14	0.42	1.31	0.77
4	4-ethyl-phenol	4.16	5.46	4.47	3.94
5	cresol	0.97	0.32	0.51	0.43
6	catechol	0.43	1.90	ND[b]	ND[b]
7	3-(1-methylethyl)-phenol	1.60	ND[b]	ND[b]	0.61
8	3-methoxy-1,2-benzenediol	0.58	ND[b]	ND[b]	ND[b]
9	4-ethyl-2-methoxy phenol	4.38	ND[b]	2.67	2.33
10	2,6-dimethoxyphenol	1.29	0.59	0.76	0.77
11	2-methoxy-4-propyl phenol	1.23	0.90	1.19	0.86
12	4-methoxy-3-(methoxymethyl)-phenol	1.41	0.54	0.53	0.72
13	butylated hydroxytoluene	stabilizer	stabilizer	stabilizer	stabilizer
14	1,2,3-trimethoxy-5-methyl-benzene	1.18	0.72	0.70	0.68
15	3,4-diethyl-, dimethyl ester, (*Z*,*Z*)-2,4-hexadienedioic acid	DNQ	DNQ	DNQ	DNQ
16	4-hydroxy-benzenepropanoic acid	3.64	1.58	1.55	1.50
17	13-methyl-, methyl ester pentadecanoic acid	DNQ	DNQ	DNQ	DNQ
18	isopropyl palmitate	DNQ	DNQ	DNQ	DNQ
	total lignin derivatives	27.39	14.23	16.68	14.17

[a]Reaction conditions: temperature at 270 °C, reaction time of 60 min, and 15% catalyst loading. [b]ND, Not detected; DNQ, did not quantify.

Temperature plays a crucial role in the catalytic depolymerization of lignin. In the presence of 5% Ru/C catalyst, it can be seen that in general the oil yields from reactions at 270 °C and different reaction times were higher when compared with the yields at 300 °C under similar reaction conditions (Table 1). Higher reaction temperature increases the hydrogen production from that hydrogen donor molecules;[14] however, at the same time it may lead to further decomposition of lignin derived compounds to gaseous products or condensation to char and tars. As a result, the oil yields were generally reduced whereas the gas yield was increased while solid yields varied. The optimal temperature for CTH reaction is dependent on the type of lignin employed as well as the catalyst being applied. For instance, Gosselink et al. investigated the depolymerization of organosolv lignins from hardwood and wheat straw in a supercritical fluid consisting of carbon dioxide/acetone/water at 300−370 °C.[43] The results showed a decrease in monomeric phenols at 370 °C and higher char formation compared with the yields obtained at 300 °C. The decrease in oil yield can be attributed to the formation of stable char or tars due to condensation reaction of monomeric phenols. Based on temperature screening results, we selected 270 °C and further tested the effects of catalyst type and loadings.

Catalyst loading is another important factor controlling CTH reaction; an increase in catalyst dosage creates more active sites that facilitate hydrogen evolution from donor molecules and cleavage of lignin linkage and side chains. Various catalyst loading (2, 5, 15, and 20%) were investigated at 270 °C to determine its effect on oil, solid, and gas yields. At 2% catalyst loading, oil yields were in the range of 19.36−26.51 wt %; while with an increase in catalyst loading up to 5% under similar reaction conditions, oil yields increased to 22.13−30.83 wt %. Further increasing the catalyst loading to 15% led to the highest oil yields of 24.72−36.28 wt % depending on reaction times. However, at 20% catalyst loading, oil yield decreased to 27.16 wt % when compared to that of 15% catalyst loading at the same reaction condition of 270 °C and 60 min. Results are in accordance with Kim et al.,[22] that reported decreases in the overall monomeric phenolic yields with an increase of catalyst loading from 10 to 20%. Taking together, results suggest that increase in catalyst dosage improved the oil yield, but excessive catalyst loading may have caused side reactions, hindering the production of monomeric phenolic compounds.[44]

Apart from catalyst loading and temperature, reaction time also plays an important role in lignin depolymerization during CTH reaction. Impact of reaction time, 30, 60, and 180 min on oil yield was investigated at selected reaction temperatures and catalyst loadings. As a general observation, the oil yield increased when reaction time was increased from 30 to 60 min at 270 °C with 2−15% Ru/C catalyst loadings; while further increasing reaction time to 180 min, the oil yield decreased. This trend is in general agreement with a previous study that a 10% increase in oil yield was reported when the reaction time increased from 1 to 3 h at 300 °C with 5% Ru/C catalyst loading.[20] It should be noted that other reaction parameters (temperature and catalyst loading) also play a role in oil yield. In another study, Kristianto et al.[45] explored Ru/C catalyst for hydrogenolysis of acid lignin in ethanol/formic acid media; varying the reaction time from 0 to 30 min led to an increase of oil yield from 30.6% to 41.2%. Taken together, among all the conditions tested for Ru/C catalyst, reaction at 15% catalyst loading, 270 °C, and 60 min gave the highest oil yield of 36.28 wt %. This represents a 16% increase when compared with the baseline oil yield of 20.04 wt % without catalyst. Results also suggest that CTH transformation of DES extracted lignin to phenolic compounds (oil) was facilitated by the presence of Ru catalyst; however, the oil yield was dependent on reaction time, catalyst loading, and temperature.[46]

Comparisons across Different Types of Catalysts. The effectiveness of Pd/C and Pt/C catalysts on the CTH of lignin was compared with Ru/C at 270 °C with reaction time of 60 min and catalyst loading of 5% and 15% (Table 1). When the Pd/C catalyst was used, the yield of lignin hydrogenation products (oil, gas, solids) with catalyst loadings of 5 and 15 wt % at 270 °C for 60 min appeared similar to those without

DOI: 10.1021/acssuschemeng.8b01763
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catalyst and was much lower than that of Ru/C catalyst. Similarly, oil yields obtained for Pt/C at 5% and 15% catalyst loading were 20.81 and 19.38 wt %, respectively, which was significantly lower than that of Ru/C. Several previous studies had suggested that Ru is a highly active metal suitable for hydrogenation and hydrogenolysis of lignin in the presence of alcohols.[22,41,47] It is possible that the Ru/C promoted transfer hydrogenation by releasing hydrogen from donor molecules and meanwhile suppressed recondensation reactions leading to char formation. Knowing that the reaction conditions for Pd/C and Pt/C catalysts were not fully optimized in this study, future work is warranted for optimal conditions that balance the rate of lignin depolymerization and recondensation toward desirable phenolic compounds products. Other noble or transition catalysts may also be explored as suitable catalyst for DES extracted lignin.[48,49]

Chemical Analysis of the Liquid, Solid, and Gas Products. Chemical composition of the oil from the CTH reaction of DES extract lignin was identified by GC−MS, with the compounds listed in Table 2 at representative catalyst types and reaction conditions, and GC chromatogram shown in Figure 1 at a representative reaction condition (270 °C, 60 min, and Ru/C loading of 15%). The oil was composed of primarily phenolic compounds irrespective of the catalyst and reaction parameter. Among the GC detected compounds with peak numbers, 14 out of 18 identified compounds (excluding 13, 15, 17, and 18) had a monomeric phenol structure. Peak 13 in the chromatogram (Figure 1) was assigned to butylated hydroxytoluene, which is a stabilizer for MeTHF. The distribution and total amount of lignin derived phenolic compounds varied among catalyst types as compared to the control without catalyst (Table 2). The main phenolic compounds from Ru/C catalyzed CTH reaction were phenol, 2-methoxyphenol, 4-ethyl-phenol, 4-ethyl-2-methoxy phenol, and 4-hydroxy-benzenepropanoic acid; whereas for Pd/C, 4-ethyl-phenol was the major compound. For Pt/C and no catalyst conditions, 4-ethyl-phenol and 4-ethyl-2-methoxy phenol were the main compounds. At selected reaction condition of 270 °C, 60 min, and 15% catalyst loading, the total yield of detected lignin monomer products (Table 2) for no catalyst, Ru/C, Pd/C, and Pt/C were 14.17, 27.39, 14.23, and 16.68 wt %, respectively. At similar reaction conditions for Ru/C catalyst the mass fraction of identified compounds from the hydrogenolysis oil is 0.05 g/0.5 g of starting lignin. For example, the mass fraction of 4-ethyl-phenol and 4-ethyl-2-methoxy phenol is 0.002 g/0.5 g of DES-EL.

In addition to monomeric phenols, certain long chain fatty acids including 13-methyl-, methyl ester pentadecanoic acid, isopropyl palmitate, and 3,4-diethyl-, dimethyl ester, (Z,Z)-2,4-hexadienedioic acid were also detected. In a previous study, Kim et al. observed long chain fatty acids in hydrogenolysis of Asian lignin samples derived from soda processing of herbaceous crops such as wheat straw and sarkanda grass. The authors attributed those long chain fatty acids to the recondensation reaction between low molecular compounds with reactive C—O or C═O bonds.[22,50] In this study, DES-EL was thoroughly washed with ethanol and water; as a result, the fatty acids in the raw biomass sorghum were likely removed during DES pretreatment and washing steps.[51] We suspect that fatty acids in the hydrogenolysis oil were derived from reductive coupling reaction of lignin rather than from the original lignin source. Taken together, our results suggest that CTH of DES extract lignin led to formation of alkylphenols due to the hydrogenolysis and stabilization of the primary lignin depolymerization products.[52] Ru/C catalyst proved to be effective at producing higher oil yield and total phenolic compounds (27.39 wt %) when compared to no catalyst control and other catalysts (Figure 2).

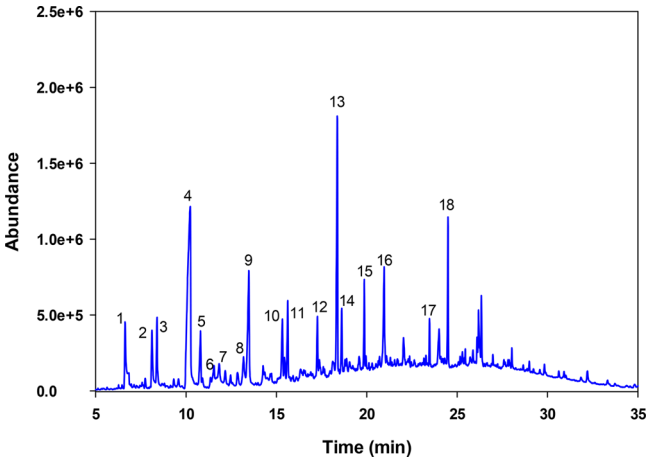

Figure 1. Representative GC−MS profile showing lignin breakdown products in the liquid oil recovered from catalytic transfer hydrogenolysis of DES extracted lignin. Reaction conditions: temperature at 270 °C, reaction time of 60 min, and catalyst (Ru) loading of 15%.

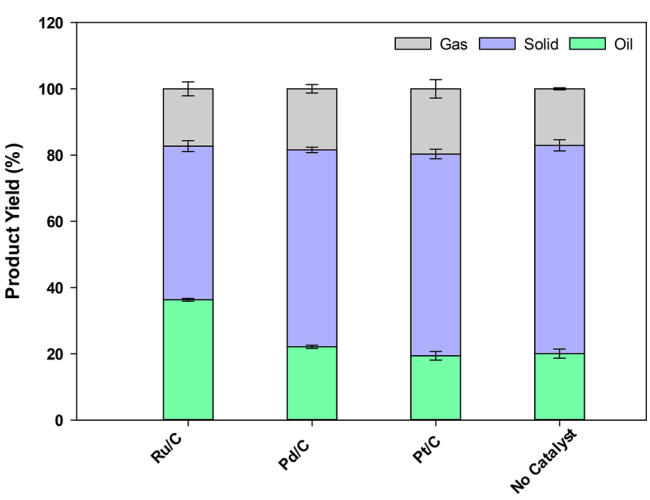

Figure 2. Effect of catalyst on the distribution of reaction products at temperature of 270 °C, reaction time of 60 min, and catalyst loading of 15%.

The insoluble fraction obtained after the CTH reaction was defined as solid residues. Overall, these results (Table 1) suggest that the solid yields decreased with an increase in reaction time and temperature for all the reaction conditions with Ru/C catalyst. The lowest solid yields of 45−46% were obtained at 270 °C for 60−180 min reaction time employing 15% Ru/C, which were significantly lower compared to the solid yield of 62.92% for no catalyst control. Similar results were reported by Kloekhorst et al.,[53] where the solid yield decreased by ∼30% with presence of Ru/C catalyst at 400 °C for 4 h as compared to noncatalyzed reaction. Generally speaking, higher catalyst loading led to lower solid yield for a given reaction temperature and time. Formation of less solid

DOI: 10.1021/acssuschemeng.8b01763
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residues is desirable as the solids contain mostly unreacted lignin and condensation products like char or tar from the repolymerization of low molecular weight phenolic compounds.[54,55] Furthermore, deposition of solid residues on the surface of the catalyst may lead to catalyst deactivation thus impair its activity.[56] The results from this study clearly indicates that the selection of catalyst type and reaction condition can help to reduce solid residue formation.

Table 3 shows the composition of gases collected from the CTH reaction. Hydrogen was the major gas produced,

Table 3. Composition of Gas Products Derived from Hydrogenolysis of DES-EL in Isopropyl Alcohol at 270 °C, Reaction Time of 60 min, and 15% Catalyst Loading

	relative mol (%)		
gas	Ru/C	Pd/C	Pt/C
hydrogen	71.47	57.30	64.15
methane	3.15	5.30	4.93
carbon monoxide	4.60	6.21	5.54
carbon dioxide	6.89	5.29	5.06
n-propane	3.57	6.97	13.99
propylene	9.86	18.24	5.78

indicating that catalysts promoted the release of hydrogen form IPA thus enabling the hydrogenolysis reaction. In the presence of Ru/C catalyst, the gas products consisted of a higher (71.47) relative mol % of hydrogen gas as compared to 57.30 mol % and 64.15 mol % for Pt/C and Pd/C, respectively, which corroborates the higher oil yield obtained with Ru/C catalyst. In addition to hydrogen, other gaseous products included methane, carbon monoxide, carbon dioxide, *n*-propane, and propylene. These gaseous products may be derived from cracking of the side chain of the lignin.[20] In general, gas product yields increased with increase in reaction time irrespective of the catalyst loading and reaction temperature, with the highest hydrogen release was observed in the presence of Ru/C catalyst, which is consistent with a previous study on CTH of organosolv lignin.[57]

GPC and FTIR Characterization of Lignin Streams. Large molecular weight (MW) phenolics, which were undetectable in the GC−MS analysis due to their low volatility, can be captured via GPC. Hence, GPC analysis was performed to investigate the molecular weight distribution of the unreacted DES-EL, the solid residues and the liquid fraction after CTH. Figure 3 shows the GPC chromatograms of acetylated solid residues and liquid fractions after CTH reaction catalyzed by Ru/C, Pd/C, and Pt/C in comparison with the unreacted DES-EL. Molecular weight distribution (MWD) of the solid residues from all the three catalysts shifted to the right (i.e., lower MW) than the unreacted DES-EL (Figure 3a). The average M_W of the DES-EL was 3037.1 g/mol; whereas the average M_W values of Ru/C, Pd/C, and Pt/C catalyzed lignin residues were 2593.4, 2363.1, and 2182.7 g/mol, respectively (Table 4). The decrease in average MW of solid residues indicates lignin depolymerization caused by CTH reaction. The polydispersity index (PDI = 2.73) of DES-EL was, however, lower than the PDIs (in the range of 3.02−3.23) of solid residues for all three catalysts. The increase in PDI for the residual solids demonstrated a wider span of MW after CTH reaction, suggesting that lignin depolymerization and recondensation may occur at the same time. The liquid fractions had much lower MW than the unreacted DES-EL,

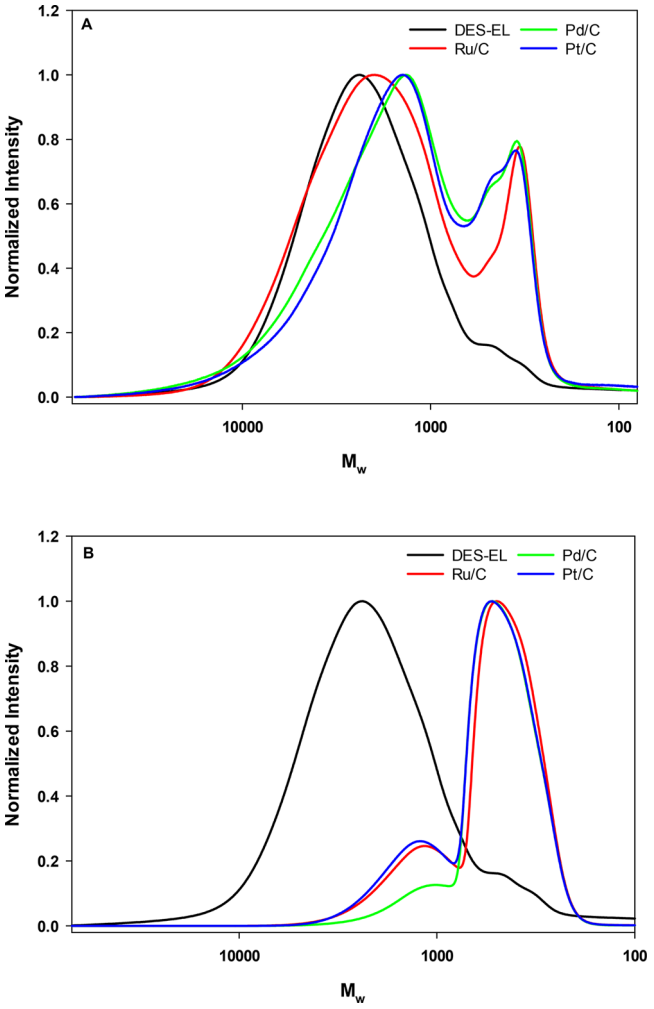

Figure 3. Molecular weight distribution of unreacted DES-EL and (a) residual solids and (b) liquid fractions from the catalytic transfer hydrogenolysis reaction; Reaction conditions: temperature at 270 °C, reaction time of 60 min, and catalyst loading of 15%.

Table 4. Molecular Weight Distribution of Residual Solid and Liquid Fractions Derived from Hydrogenolysis of DES-EL at 270 °C, 60 min Reaction Time, and 15% Catalyst Loading

Source	M_w (g/mol)	M_n (g/mol)	polydispersity index (PDI)
DES lignin	3037.05	1114.18	2.73
residual lignin (Ru/C)	2539.44	841.33	3.02
residual lignin (Pd/C)	2363.14	752.80	3.14
residual lignin (Pt/C)	2182.73	669.68	3.23
lignin in liquid stream (Ru/C)	681.62	478.08	1.43
lignin in liquid stream (Pd/C)	570.15	455.45	1.25
lignin in liquid stream (Pt/C)	704.97	497.46	1.42

with an overall M_W between 570.2 and 705.0 g/mol (Figure 3b). The MWD curves of the liquid fractions for all the catalysts showed very similar peak shapes, with PDI ranging from 1.25 to 1.43. The reductions in MW for both acetylated solid residues and liquid fractions in the presence of catalysts indicate the depolymerization of DES-EL due to CTH reaction. Combining the GPC profiles and GC/MS results, it

DOI: 10.1021/acssuschemeng.8b01763
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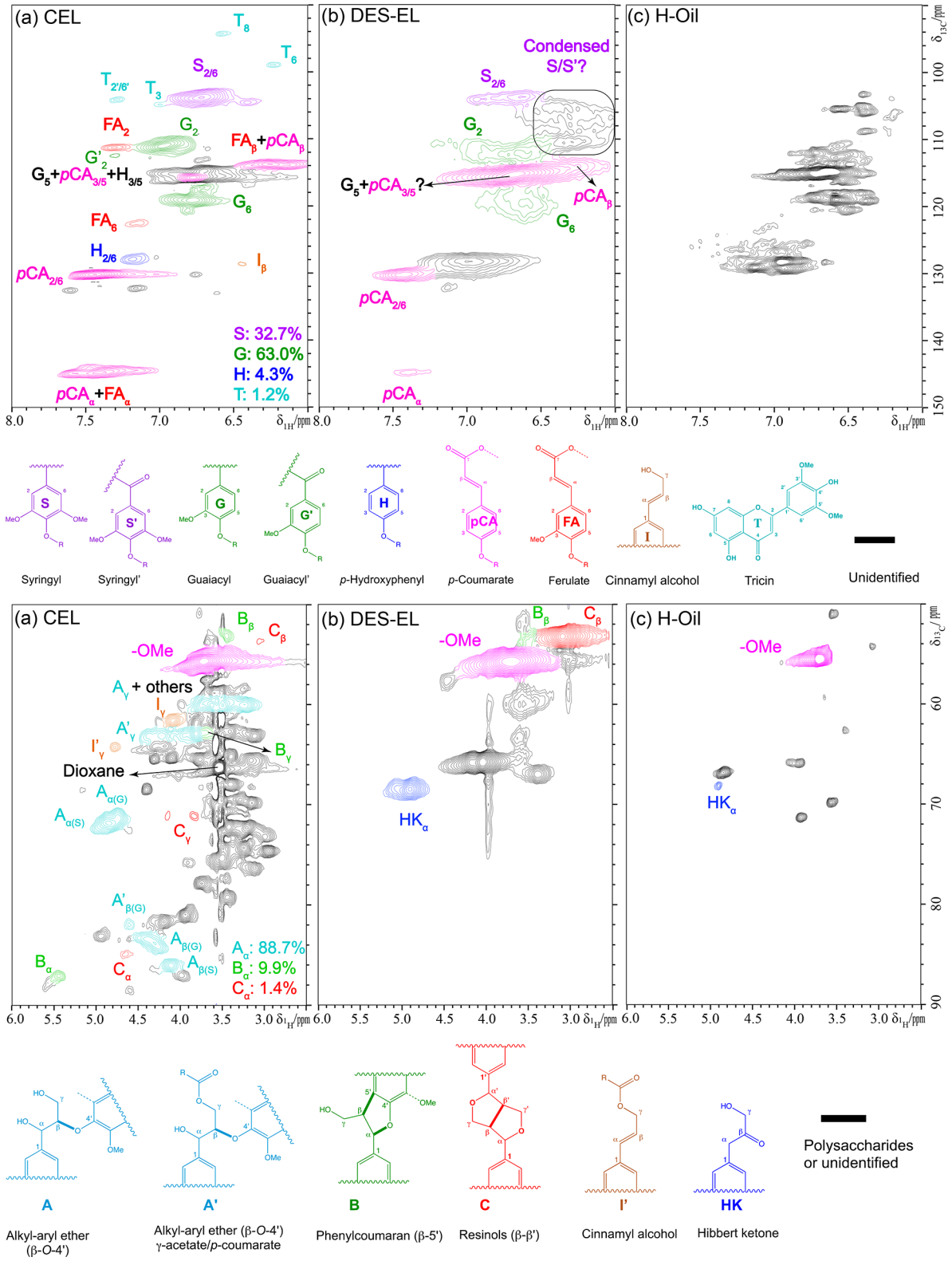

Figure 4. $^{13}C-^{1}H$ (HSQC) spectra of aromatic (top) and alkyl regions (bottom) of (a) sorghum cellulolytic enzyme lignin (CEL), (b) DES extracted lignin (DES-EL), and (c) hydrogenolysis oil (H-Oil).

can be inferred that CTH was effective in breaking down DES-EL to lower MW phenolic compounds.

The ATR-IR spectra of the unreacted DES-EL and the solid residues after hydrogenolysis are shown in Figure S1. Generally speaking, the IR spectra of the solid residues were significantly different from the IR spectrum of the unreacted DES lignin. The peaks at 3400 and 2920 cm^{-1} represent the stretching of O—H and CH_n bonds, respectively.[58] The decrease in absorbance in the 3400 cm^{-1} region for the solid residues can be attributed to the reduction of hydroxyl groups during hydrogenolysis. The aromatic skeletal vibrations[59] were represented by signals between 1400 and 1700 cm^{-1} while

DOI: 10.1021/acssuschemeng.8b01763
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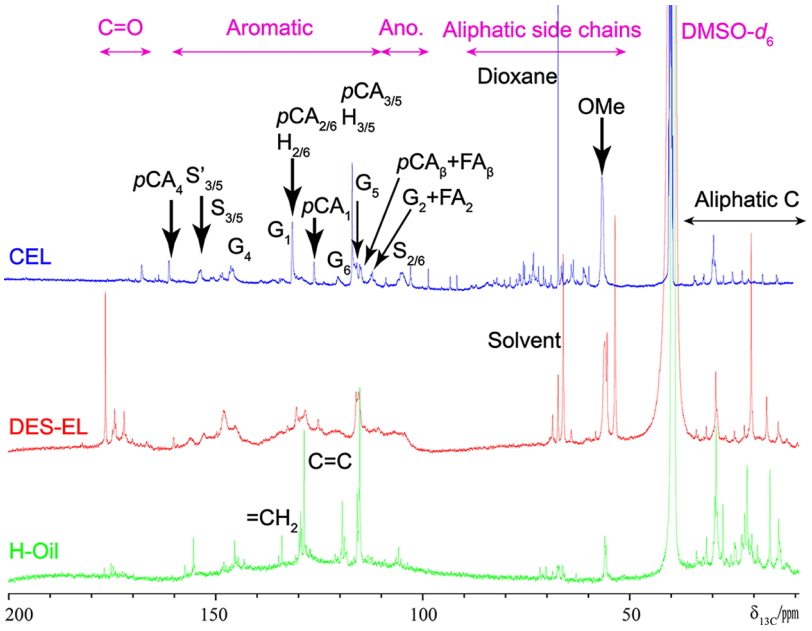

Figure 5. ^{13}C NMR spectra of CEL, DES-EL, and H-Oil from sorghum.

the bands at 1510 and 1595 cm^{-1} can be assigned to C=C of aromatic skeletal vibrations.[60] It appeared that the bands around 1595 cm^{-1} were retained for all the solid residues derived from hydrogenolysis, suggesting that the aromatic ring was not saturated by the hydrogenolysis. The peaks at 1420 and 1460 cm^{-1} can be attributed to the C—H aromatic ring vibrations and C—H deformation in CH_n groups,[61] respectively; while the hydrogenolysis solid residue showed notable decrease or no absorbance for these peaks when compared to untreated DES-EL. Additionally, the spectra at 1030, 1110, and 1220 cm^{-1} correspond to guaiacyl (G) and syringyl (S) units of lignin;[62] all solid residues showed significant reduction in absorbance in this range as compared with unreacted DES lignin. Collectively, the FTIR results on the residual solids illustrate that during CTH reaction, a portion of the DES-EL lost its original structure and was most likely condensed to char-like materials; while the other portion depolymerized to lower molecular weight products as shown by GPC and GC/MS results.

NMR Characterization of Lignin Streams. 2D $^{13}C-^{1}H$ HSQC NMR was used to characterize the structural changes of lignin through DES treatment and hydrogenolysis reaction. The spectra of sorghum CEL, DES-EL, and the H-Oils are compared in terms of two regions: aromatic region between 6.0 and 8.0/90–150 ppm revealing lignin subunits, and aliphatic region between 2.5 and 6.0/50–90 ppm, which examines the nature of lignin side chain linkages (Figure 4). The aromatic region of CEL revealed that sorghum lignin is comprised of SGH type lignin with hydroxycinnamates (ferulate (FA), *p*-coumarate (*p*CA), and tricin (T)).[63] On a basis of total SGH amount, the abundance of S:G:H was 33:63:4% and tricin of 1.2%, which is comparable with the results presented by other researchers.[64] In addition, the sorghum lignin had 51% *p*CA and 7% FA in the isolated CEL. Lignin in herbaceous plants seems to have high *p*-coumarate level. For example, del Río et al. reported that *p*-coumarate accounts for 68% and 48% of bagasse aromatic molecules revealed from whole cell and MWL lignin HSQC spectra[65] while Samuel et al. found that *p*-coumarate accounts for ~32% of switchgrass lignin aromatics.[30]

After DES treatment, the lignin underwent significant structural changes. For instance, the aromatic spectra of DES-EL (Figure 4b) showed that the tricin units completely disappeared while the signal intensity of hydroxycinnamates was significantly reduced. In addition, the contours of S and G units moved slightly downfield (~2–3 ppm) in ^{13}C axis in comparison to their chemical shifts in CEL. Previous studies suggested that transformation of these structures accompanying with chemical shifts changes are likely due to the condensed/oxidized subunits.[66] After hydrogenolysis reaction, the original S, G, or H subunits in CEL were almost completely transformed, which was indicated by the loss or shift of their signals in the spectra of the hydrogenolysis oil, supporting the GC–MS results of the oil composed mostly of phenolic compounds. These structural transformations may be associated with demethoxylation or interactions of other functional groups in the hydrogenolysis reaction.[67]

The HSQC spectra of the aliphatic region in Figure 4 (bottom) denoted the changes of lignin linkages among CEL, DES-EL, and H-Oil. Consistent with a previous study, sorghum lignin contains side chains *β*–*O*–4′, *β*–5′ and *β*–*β*′linkages.[68] In the case of DES-EL, methoxyl groups were retained while *β*–*O*–4′ aryl ether linkages were completely depleted. The HSQC spectrum of the DES-EL also illustrated that *β*–*β*′ linkages were the major interunit linkages with the presence of a small amount of *β*–5′, while the signals from their ether linkages (i.e., C*α*/H*α*) were not observed likely due to its cleavage during DES treatment. This is in line with the previous study on DES extracted lignin from Douglas fir.[7] In addition, the presence of Hibbert's ketone (HK) (68.6/4.93 ppm) in DES lignin corroborates the cleavage of *β*–*O*–4′ linkages by DES.[7] The spectrum for H-Oil in Figure 4c (bottom) revealed that the major interunit linkages in lignin were not detected, and only the methoxyl groups were retained. These contours in the aromatic region appeared to be phenolic compounds after hydrogenolysis. The presence of methoxyl groups is in agreement with the identified

DOI: 10.1021/acssuschemeng.8b01763
ACS Sustainable Chem. Eng. XXXX, XXX, XXX–XXX

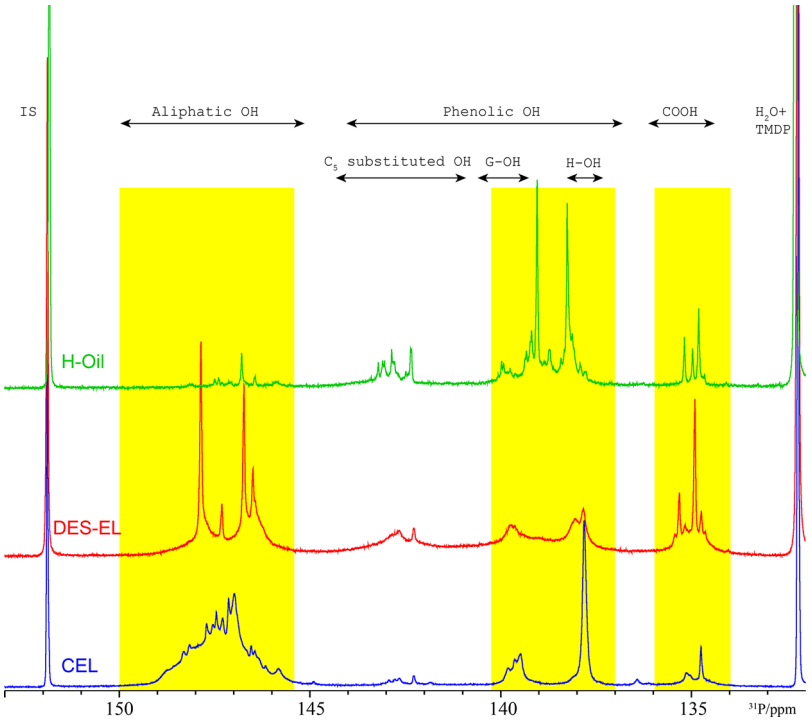

Figure 6. ^{31}P NMR spectra of sorghum CEL, DES-EL, and H-Oil after phosphitylation.

alkylphenols via GC−MS such as 4-ethylphenol, 4-ethyl-2-methoxyphenol, and 2-methoxy-4-propylphenol.

^{13}C NMR was also performed to provide supportive data to HSQC-NMR. The lack of prominent signals between 72 and 90 ppm in the DES-EL compared with CEL confirms the depletion of ether linkages (Figure 5). In comparison to CEL, the DES-EL had a substantially increased carbonyl groups (C═O); after hydrogenolysis, these C═O signals in DES-EL were decreased significantly in hydrogenolysis products. This suggested that lignin has been oxidized through DES treatment and the resulting carboxylate groups were readily subject to hydrogenolysis in the following catalytic reaction, in accordance with previous literature, which shows that Ru greatly improved the rate of hydrogenation of carbonyl groups.[69,70] The ^{13}C spectra also showed that the major lignin structural units were retained in the DES-EL, but were not detected in the oil due to hydrogenolysis of these macromolecules to phenolic monomers, suggesting a substantial depolymerization of DES-EL through catalytic hydrogenolysis. In addition, aromatic signals from phenolic compounds at 105−145 ppm along with a high level of saturated aliphatic peaks at 15−40 ppm were observed in the ^{13}C spectrum of H-Oil sample, which is in agreement with the previous HSQC results.

To further examine the structural characteristics of sorghum CEL, DES-EL, and H-Oil, ^{31}P NMR was conducted on phosphitylated samples to investigate the change of hydroxyl groups in these samples (Figure 6 and Figure S2). The results demonstrated that hydroxyl groups underwent a significant change during DES treatment and hydrogenolysis reaction. For example, the aliphatic OHs decreased remarkably from CEL to DES-EL. The aliphatic OHs further decreased significantly in H-Oils, which indicates there is negligible side chain hydroxyl groups left in the hydrogenolysis products, which could be a result of lignin degradation or cleavage of side chains in this reaction. This is in line with the ^{13}C spectra showing that an increase of alkylated compounds in the H-Oils after catalytic hydrogenolysis. In addition, the phenolic OHs (Ar−OH) increased strikingly in hydrogenolysis oil compared with DES-EL indicating a breakdown of lignin into alkylphenolic products in hydrogenolysis oil, in support of previous GC−MS results. These results together suggest that DES treatment depolymerized sorghum lignin by cleaving the ether bonds and oxidized some lignin into carboxylate groups; the Ru/C catalyst facilitated the hydrogenolysis reaction forming ketone groups as well as a breakdown to alkylphenolic compounds.

CONCLUSIONS

Deep eutectic solvent was used to extract lignin from sorghum and subsequently catalytic transfer hydrogenolysis (CTH) was performed on the extracted lignin using platinum group noble metals for production of lower molecular weight phenolic compounds. Among tested catalysts, Ru/C proved to be most effective as compared to Pd/C and Pt/C in the presence of isopropyl alcohol. Results illustrate that temperature, catalyst loading, and reaction time played roles in the depolymerization of DES-EL during CTH. The highest lignin oil yield (36.3 wt %) was achieved under a reaction condition at 270 °C, reaction time of 60 min, and Ru/C catalyst loading of 15%, with the main lignin degradation products identified as phenol, 4-ethylphenol, 4-ethyl-2-methoxyphenol, 2-methoxy-4-propylphenol, and 4-hydroxy-benzenepropanoic acid. Molecular weights of the solid residues and the hydrogenolysis oils were lower than the unreacted DES-EL, demonstrating depolymerization of DES-EL to lower molecular weight products. NMR analysis of the DES-EL revealed a significant structural alteration such as a considerable cleavage of the side chain alkyl-aryl ether linkages of sorghum lignin, while retaining methoxyl groups in the hydrogenolysis oil. The hydrogenolysis oil has shown a further transformed structure consisting of alkylated products, which indicates the breakdown of lignin into phenolics and alkylated compounds. The

DOI: 10.1021/acssuschemeng.8b01763
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results from this study provide a deep understanding of the DES-EL and the hydrogenolysis of DES-EL to valuable products that can be potentially upgraded to ~~the~~ fuel molecules and platform chemicals.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.8b01763.

FTIR spectra of DES-EL and solid residues collected after hydrogenolysis reaction; lignin functional groups determined by ^{31}P NMR; quantitative results of lignin hydroxyl groups (mmol/g lignin); assignments of the lignin ^{13}C−^{1}H correlation signals observed in the HSQC spectra of the sorghum lignins (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We acknowledge the National Science Foundation under Cooperative Agreements 1355438 and 1632854 for partially supporting this research. The information reported in this paper is part of a project of the Kentucky Agricultural Experiment Station and is published with the approval of the Director. Oak Ridge National Laboratory is managed by UT-Battelle, LLC under Contract DE-AC05-00OR22725 with the U.S. Department of Energy (DOE). This work was partially supported by the BioEnergy Science Center (BESC) and the Center for Bioenergy Innovation (CBI). The BESC and CBI are U.S. DOE Bioenergy Research Centers supported by the Office of Biological and Environmental Research in the DOE Office of Science. The views and opinions of the authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. We acknowledge Idaho National Laboratory for providing sorghum ~~biomass~~ samples and Dr. Muthu Gnanamani for assistance ~~on~~ gas composition analysis.

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